MAJOR AND TRACE ELEMENTS CHARACTERISATION OF GROUNDWATER IN COASTAL REGION FROM TAMIRABARANI RIVER TO THIRUCHENDUR, THOOTHUKUDI DISTRICT, TAMIL NADU, INDIA

Jeyavel Raja Kumar, T*, Dushiyanthan, C., Thiruneelakandan, B., Suresh, R., Vasanth Raja, S., Senthilkumar, M and Karthikeyan. K

Department of Earth Sciences, Annamalai University, Annamalai Nagar – 608002 1. Department of Civil Engineering, Annamalai University, Annamalai Nagar – 608002 *Corresponding author E-mail: <u>tjeyavel@rediffmail.com</u>

ABSTRACT

The chemical characterization of groundwater in coastal region from Tamirabarani River to Thiruchendur of Thoothukudi District was studied to demarcate potable groundwater zones and ionic source. Geologically, the region consists of Archaean age gneisses, charnockites, and quartzites in the inland and calcareous grits sandstone, shell limestone and alluvium along the coast. The area is covered with black, red, and alluvial sandy soils. In total, 16 groundwater samples were collected from open wells. Groundwater samples were analyzed for pH, Electrical conductivity (EC), Total Dissolved Solids (TDS), major cations Ca²⁺, Mg²⁺, Na⁺, K⁺ and anions HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- and F^- . The value of pH, EC and TDS are varied from 7.1 to 8.2, 320 to 14980 micromhos/cm, and 215 to 10200 mg/l. The concentration of Ca²⁺, Mg²⁺, Na⁺, K⁺, and HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- and F^- were varied from 30 to 608 mg/l, 9 to 181 mg/l, 32 to 690 mg/l, 2 to 94 mg/l and 80 to 781 mg/l, 12 to 4590 mg/l, 13 to 1012 mg/l, 5 to 85 mg/l and 0.2 to 0.8 mg/l, respectively. The analyzed chemistry data of groundwater samples were interpreted in the WATCLAST software. Most of the groundwater samples represented moderate to very hard. Hydrochemical facies of the groundwater samples are found $Ca^{2+}>Na^+>Cl^>SO_4^{-2}$ and Stufzand chloride classification indicates both fresh and brackish category. The Na⁺/Cl⁻ ratio varied from 0.10 to 3.3 and favors saline water in nature at few locations. A few trace elements (i.e., Zn, Pb, Cr, Fe, Cd, Cu and Mn) were also analyzed and compared to WHO standards for drinking purpose. It reveals that except few locations, other groundwater samples are suitable for the drinking. The study found that apart from anthropogenic, precipitation and infiltration factors, host rock is the main source for ionic the concentration, nevertheless, saline water intrusion also supported in few locations.

Keywords: Groundwater chemistry, Major and trace elements, Groundwater quality, Coastal aquifer, Tamil Nadu.

INTRODUCTION

Groundwater is one of the most important, widely distributed natural resources and is considered as supplemental resource to surface water to meet the domestic, agricultural and industrial requirements. As population grows, need for water also increases in many fold and it put pressure on groundwater resources which lead to over exploitation and decline of water level. The other side, contamination is a major threat to groundwater resources in many areas (Mondal and Singh, 2011), particularly in the coastal region (Mondal *et al.*, 2017). Generally, groundwater system in any terrain is being polluted from influence of the physicochemical changes in the surrounding groundwater. The character of groundwater in different aquifers over space and time proved to be an important technique in solving different geochemical problems (Chebotarev, 1955, Hem,1959; Back *et al.*, 1956; Singh *et al.*, 2009).

Groundwater resources in coastal areas are always in danger of contamination by sea natural water intrusion due to and anthropogenic sources (Mondal et al., 2011). The major contamination sources of coast aquifers are diverse, including natural saline groundwater, halite dissolution, seawater intrusion, oil and gas-field brine, domestic, agricultural and industrial effluents, and road salts. Seawater intrusion is one of the most common problems in almost all coastal aquifers around the globe (Park et al., 2005; Batayneh 2006; Sherif et al., 2006; Mondal et al., 2010a). It takes place when saline water displaces or mixes with freshwater in aquifers (Todd ,1953).

In this scenario, studying groundwater chemistry and its quality characteristics is necessary for sustainable development in the coastal region. Keeping this in mind, an attempt has been made to understand major elements characterization of and trace groundwater in coastal region between Tamirabarani River and Thiruchendur of Thoothukudi District, East coast of Tamil Nadu. Globally many researchers have carried out study on groundwater quality and pollution sources and the sources are from geogenic(Balasubramanian, 1986), anthropogen ic (Metcalfe et al., 2011, Prasanna et al., 2011), industrial (Selvam, 2015) and sea water intrusion by tidal action (Singaraja, 2016).

STUDY AREA

The selected study area, Tamirabarani River to Thiruchendur is a part of coastal zone of Thoothukudi District, East coast of Tamil Nadu. It is located between the North latitude of 8°30' to 8°50' and the East Longitude of 77 °50' to 78°10'. The Archaean groups of formations exist in the inland and recent to sub-recent sand occupies coastal areas (Fig. 1). Gneisses, charnockites, and quartzites are important Archaean formations. the Calcareous grits sandstone, shell limestone and alluvium are the sedimentary formations. The major geomorphologic units are beach terrace, coastal and alluvial plan (Fig. 2). The types of soil are clay and sandy soil. The maximum soil thickness of the region is about 3m (Sankul Techno, 2002; Singh et al., 2006; Rangarajan, et al., 2009). Hydro- geologically, the area consisting of porous sedimentary formation at top and followed by fractured rock type. The normal annual rainfall over the district varied from 570 to 740 mm and the average annual rainfall of the district is 672 mm (PWD, 2005). The water level varied from 3 to 7m below ground level (bgl). Porous sedimentary formations, particularly the sandy zones are the main aquifer system in tertiary and alluvial areas. The normal well yields in the sedimentary formation are varied from 566-886 lpm and the permeability varied from 19.13 – 30.92 m/d.





Fig. 2. Geomorphology Map



Fig.3. Groundwater samples Location Map

MATERIALS AND METHODS

For evaluation of groundwater chemistry and quality of the study area, 16 groundwater samples were collected during June 2011 from dug wells and bore wells (Fig. 3). The samples were collected in clean polythene bottles as prescribed by Brown et al., 1974 and APHA (1996). Samples were collected in one litre capacity polythene bottles. Prior to collection, the bottles were thoroughly washed with diluted HNO₃ acid, and then with distilled water in the laboratory before filling bottles with samples. The analysis for major ions was carried out in the Department of Earth Sciences, Annamalai University for pH, Electrical Conductivity (EC), Total Dissolved Solids (TDS), major cations Ca²⁺, Mg²⁺, Na⁺, K⁺ and anions HCO₃⁻, Cl⁻, SO₄⁻²⁻, NO₃⁻ and F⁻.

In the present study, the pH was measured using the instrument model Systronic-335. The TDS was measured using Weight balance Schimedge T4231 muffle furnace technique, and the EC was measured using the model Systronic-304. The Ca²⁺, Mg²⁺ and HCO₃⁻, Cl⁻ were measured by the volumetric method whereas the Na⁺ and K⁺ were measured using flame photo meter model CL 378. The SO₄ ²⁻ was measured using spectrophotometer model SL -171 minispec. NO₃⁻ was measured by cadmium reduction column method and F⁻ was determined by Orion fluoride ion electrode model (94-09).

Except pH, other parameters are expressed in Mg/L whereas the EC value is expressed in mohs/cm at 25°C. The selected trace elements of Zn, Pb, Cr, Fe, Cd, Cu and Mn were analysed using ICP-MS Perkin Elmer Sciex ELAN DRC II model at National Geophysical Research Institute, Hyderabad. The data of major ions had analyzed and interpreted using

software WATCLAST (Chidambaram *et al.*, 2004). The groundwater sample analysis data of the study area is presented in Table -1. **RESULTS AND DISCUSSION**

General hydrogeochemistry

pH is one of the parameters to classify groundwater chemistry where it is generally acidic to alkaline in summer season and alkaline during winter season (Vasanthavigar et al., 2009). The variation in pH is due to the release of ions from various process and provides information geochemical of equilibrium or solubility calculations (Hem. 1985). pH of groundwater in the study area is 7.1(Kulasekaranatham) between to 8.2 (Valavallan) and indicating transient of acidic to alkaline condition. The pH values of all the samples were within the permissible limit of 6.5 to 8.5 for drinking and domestic purposes (WHO, 2006).

The electrical conductivity of the groundwater depends upon temperature, concentration and types of ions present (Hem, 1985). The concentrations in chloride Groundwater normally attribute to high conduction (Davis and Dewiest, 1966) which could be mostly from geogeinc and anthropogenic processes. The electrical conductivity of the groundwater in the study area is varied from 320 (Valasubramaniyapuram) to 14980 microsimens/cm at 25°C (Pudur Colony) and observed above the maximum limit of 1500 microsimens/cm (WHO,2006) for drinking in the eight sample locations. The spatial map of EC is shown in Fig. 4. The spatial variation EC represents that 1000-2000 microsimens/cm range was in western part and >3000 microsimens/cm in eastern part.

The TDS of groundwater is varied from 215 mg/L (Valasubramaniyapuram) to 10200 mg/L (Pudur Colony). According to ICMR

(1975), about 19% of samples were falling desirable for drinking of < 500 mg/L and 31% of samples were within permissible for drinking of 500 mg/L - 1000 mg/L. 25% of samples were falling useable for irrigation category of 1000 mg/L - 3000 mg/L and another 25% were falling >3000. The principal ions contributing to TDS are bicarbonate, carbonate, chloride, sulphate, nitrate, sodium, potassium, calcium and magnesium (EPA, 1976). However, the higher degree of salt concentration is due to groundwater movement and long residence time along the flow path (Norris et al., 1992). In the study area chloride, sodium and sulphate were contributed for the higher level of TDS in groundwater. The spatial map of TDS is shown in Figure 5 and it shows that 1000-2000 mg/L was represented major part whereas <1000 mg/L was noticed as small isolated patches and a patch of >3000 mg/L was noticed in the eastern part.

Total Hardness (TH)

Hardness results from the presence of divalent cations of which Ca2+ and Mg2+ are most abundant in groundwater. Hardness in water also derived from the solution of carbon-dioxide released in bacterial action in soil, in percolating water (Sawyer and McCarty, 1967). The water hardness is primarily due to the result of interaction between water and geological formations (Angino, 1983). In the study area groundwater samples, Total Hardness is varied from 111 mg/l to 2262 mg/l. The permissible limit of TH for drinking water is specified as 500 mg/l (WHO, 2006) and the present study area about 44% of the groundwater samples were above the permissible limit.

According to Handa (1965), the study area samples found with both temporary (A1, A2 & A3) and permanent (B1, B2 & B3) hardness. It is observed that about 10 samples were characterised by temporary hardness and remaining by permanent hardness. The spatial map of TH is shown in Figure 6 and it represents that <300 was noticed as small isolated patches whereas 600-1000 was noticed in eastern and western part. 300-600 range was noticed in northern part.

Cations

The concentration of Ca^{2+} are varied from 30 mg/L (Valasubramaniyapuram) to 608mg/L (Sembur) where 44% of the samples were found below the permissible limit of 75 mg/L (WHO, 2006). 25% of samples were found above the permissible limit and 31% of samples were found above the maximum permissible limit of 200 mg/L for drinking (WHO, 2006). The Mg^{2+} concentration varies from 9 mg/L to 181 mg/L and the permissible limit of Mg²⁺ for drinking water is 30 mg/L (WHO,2006),) and 44% of samples were noted above the permissible limit. The high concentration of Mg²⁺ was observed in Senthamangalam Sembur and locations whereas, low concentration was observed in Valasubramaniyapuram sample location. The Na⁺ concentration varied from 32 mg/L to 2645 mg/L. The permissible limit of Na^+ for drinking water is specified as 200 mg/L (WHO, 2006), and 38% of samples were found above the permissible limit. The higher value was observed in Sembur location and noticed low value was in location Valasubramaniyapuram. The K⁺ concentration varied from 2 mg/L to 94 mg/L. The permissible limit of K⁺ for drinking water is specified as 50 mg/L (WHO, 2006) and only 6% samples were found above the permissible limit. The higher value of 94 mg/L was observed in location Muthukrishnapuram and low value of 2 mg/L was noticed in location Valasubramaniyapuram. The spatial map of

 Ca^{2+} and Na^{+} is shown in Fig. 7(a,b) and they represent that higher concentration was notices in the western part.

In this area, Ca²⁺, Na⁺ and Mg²⁺ ions present relatively higher concentrations in groundwater. The Ca^{2+} concentration could be from dissolution of precipitates of CaCO₃ and $CaMg(CO_3)_2$ during recharge (Datta and Tyagi, 1996, Lakshmanan et al., 2003). The Na^+ silicate derived from minerals, atmospheric precipitation and halite deposits and Mg²⁺ might have been derived from dissolution of magnesium calcite, gypsum and/or dolomite from source rock (Garrels, 1976). Apart from geogeinc, sewage, industrial effluents and water softening process have also contributed to Na⁺ concentration in groundwater of the study area.

Anions

The Bicarbonate concentration is varied from 80 mg/L to 781 mg/L. The $HCO_3^$ concentration was high in location Pudur Colony, and it was observed low in location Valasubramaniyapuram. The Cl^{-} concentration varied from 8 mg/L to 4590mg/L. The permissible limit of Cl⁻ concentration for drinking water is specified as 250 mg/L and excessive limit of 1000 mg/L (WHO, 2006). About 56% of samples were within the permissible limit. Whereas about 25% of samples were found above the permissible limit and 19% of samples were found above the excessive limit. High concentration of Cl⁻ is noticed in location Pudur Colony whereas low concentration was found in sample location Mangalakurichi. The SO_4^{2-} concentration is varied from 13 mg/L to 1012 mg/L. The permissible limit for drinking water is specified as 200 mg/L (WHO, 2006) and about 44% of samples were found above the permissible limit. The NO₃⁻ concentration is varied from 5 to 85 mg/L. The limit for nitrate concentration for drinking water is specified as 50 mg/l (WHO, 2006). In the study area, NO_3^- was found above the limit at 4 locations. The Fluoride concentration is varied from 0.2 mg/L to 0.8 mg/L. The permissible limit for drinking water is specified as 1.5 mg/L (WHO, 2006) and all the samples were within the permissible limit. The spatial map of Cl⁻ and SO₄ ²⁻ is shown in Fig. 8 (a,b) and they were found higher in the eastern part.

In this area, Cl^- and SO_4^{2-} and NO_3^- ions present higher concentrations in groundwater. The Cl⁻ concentration noticed relatively high which could be contributed from leaching from upper soil layers, anthropogenic and saline water intrusion (Srinivasamoorthy, 2008; Mondal et al., 2011; R. J. Kumar et al., 2013). Sulfate ion concentrations are probably derived from application of sulphatic soil conditioners, dissolution of gypsum, leaching of the evaporate sediments rich in gypsum anhydrite and sodium sulfate, sulphur gases and from industries and utilities (Karanth, 1987, Mala,1997, Saxena, 2004). NO₃⁻ may be due to leaching from plant nutrient, irrigation water return flow and nitrate fertilizers (Freeze and Cherry, 1979;Madison and Brunett, 1984; Mondal et al., 2008).

QUALITY OF GROUNDWATER BASED ON CHLORIDE

The quality of groundwater can be assessed using the procedure given by Stuyfzand (1989). According to the classification, the quality of water is classified into 8 main types based on chloride. Classification based on Chloride of groundwater in the study area samples is given below Table 2.

	Cl Range	Number of					
Chloride Type	(mg/l)	Samples					
Very							
Oligohaline	< 5	Nil					
Oligohaline	5 - 30	3					
Fresh	30 - 150	4					
Fresh -							
Brackish	150 - 300	2					
Brackish	300 - 1000	4					
	1000 –						
Brackish – Salt	10000	3					
	10000 –						
Salt	20000	Nil					
Hypersaline	> 20000	Nil					

Table 2. Stuyfzand Chloride Classification

The classification based on chloride concentration shows that about 19% and 25% of the samples were identified with the Oligohaline and fresh water types. Besides, Fresh-Brackish was noted in 13% and Brackish category was observed in 25% locations. About 19% of groundwater found with Brackish - Salt water category. In general, the degree of brackishness of water appears to be controlled by the differing hydrogeological situations. Munn (1936) has found that the black cotton soils contain considerable quantity of ingredients, while the chlorides being more soluble are transported down in solution to groundwater. The brackish-salt category noted in the study area could be attributed from mixing of saline water.

CHEMICAL RELATIONSHIP

Piper (1944) is used to delineate variability and trends in water quality have contributed extensively to understand groundwater flow and geochemical evolution of Groundwater (Dalton and Upchurch, 1978, Karanth, 1987). With the help of the hydrogeochemical relations, it could be used to understand the different facies of the groundwater. The geochemical evolution can be understood from the Piper diagram, which has been divided into six sub categories such as Ca-HCO₃ type; Na-Cl type; Mixed Ca-Na-HCO₃ type; Mixed Ca-Mg-Cl₂ type; Ca-Cl₂ type and Na-HCO₃ type. In the study area, groundwater samples were plotted using Aquachem software and it is shown in Fig. 9. The diagram reveals that majority of the samples fall in the mixed Ca⁺Mg-Na and HCO₃⁻Cl⁺SO₄ category whereas samples 3 &5 fallen in the Na-Cl and sample 6 fallen in the Ca-Cl categories.

Na⁺/Cl⁻ RATIO

Evaluating the ionic ratio is an effective technique to identify the saline water intrusion. Since, the dissolved ions in groundwater are derived from various sources and compositional relations; they can reveal the origin of solutes and processes that generated the observed water composition. Seawater and seawater diluted with freshwater have distinguished geochemical characteristics (M&E,2000).In this study. Na⁺/Cl⁻ relationship was studied to confirm salinity and origin of groundwater, and it has frequently been used to identify saline water intrusion (Sami,1992). The lower Na⁺/Cl⁻ ratio might be due to reaction with clay minerals exchanging Na^+ for Ca^{2+} and Mg^{2+} ions (Mercado, 1985). In the study area samples, Na^{+}/Cl^{-} ratio >1.0 was observed in many locations and ratio <1.0 was noted in few locations. The ratio >1.0 is due to silicate weathering reaction (Meyback, 1987) and ratio <1.0, particularly, 0.35 to 0.515 due to saline water mixing (Jeevanandam et al., 2007). The saline water mixing could be the possible source of Cl₂ in the coastal area in sample locations 4,5,12 & 15 whereas in the

inland area, the Cl_2 is derived from irrigation return flow, particularly in sample locations 1,2,3,6,9,10,13&16 and rock water interaction where intensive agriculture is practiced.

TRACE ELEMENTS

Trace element distribution may help to assess the level of heavy metal concentration in groundwater of the study area and possible source. Selected trace elements of Fe, Pb, Cr, Mn, Cu, Zn and Cd were studied in groundwater samples of the study area (Table-1).

In the study area, Fe concentration varied from 0.018 to 0.062 mg/L. The standard for the drinking is 0.3 mg/L WHO (2006) and all were found below the permissible limit. The Pb concentration varied from 0.001 to 0.003mg/L and all the samples were found with below the permissible limit of 0.05 mg/L WHO (2006) standard for drinking. The concentration of Chromium and Manganese were ranged from 0.011 - 0.037mg/L and 0.001 - 0.144 mg/L, respectively, where chromium found below the permissible limit of 0.05 mg/L whereas Manganese found above the permissible limit of 0.05 mg/L at two locations (2&8). The concentration of the Copper is ranged from 0.001 - 0.147 mg/L. The groundwater quality standard of Copper desirable limit (WHO) is 0.05 mg/L and maximum permissible limit (excessive) is 1.5 mg/L. In the study area, one sample location (11) was found above permissible limit and all other samples were below the permissible limit.

The concentration of the Zinc was ranged from 0.009– 0.211 mg/L. The ground water quality standard of Zinc desirable limit (WHO) is 5.0 mg/L and the maximum permissible limit is 15.0 mg/L. In the study area, all sampling locations are within the desirable limit of WHO. The concentration of the Cadmium was ranged from 0.001 to 0.003 mg/L. The groundwater quality standard of Cadmium desirable and maximum permissible limit (WHO) is 0.01 mg/L.

In the study area, all the analysed trace elements were well below the permissible limit of WHO for drinking water, nevertheless, Cu was found above the permissible limit in one location (11) and Mn was found above the permissible limit in two locations (2&8). The observed level of concentration of Cu and Mn in the groundwater is not objectionable for drinking, however, excess concentrations of manganese make water distasteful to drinking with no specific toxic effects (Longe and Enekwechi, 2007). The anthropogenic activities particularly domestic and industrial waste main sources were for the higher concentration of Cu and Mn in groundwater of the study area.

S.	С	Mg ²	Na⁺	K⁺	CI-	HC	SO4	Ν	F	pН	EC	TDS	TH	Zn	Pb	Cr	Fe	Cd	Cu	Mn
N	a ²	+				O ₃ -	2-	O ₃												
0	+																			
1	15										227	149		0.02			0.05	0.000	0.00	
	8	45	64	31	398	421	180	25	0.3	7.4	0	5	579	5	0.002	0.017	4	2	3	0.001
2											126			0.08			0.03	0.000	0.00	
	80	22	145	2	107	610	157	12	0.4	7.3	0	830	290	2	0.002	0.016	9	1	2	0.144
3											250	167		0.00			0.02	0.000	0.00	
	95	29	521	31	418	659	225	20	0.6	7.7	0	5	356	9	0.003	0.012	1	1	1	0.001
4	40		264		459						149	102	150	0.01			0.03	0.000	0.00	
	6	120	5	31	0	781	900	85	0.8	7.7	80	00	7	1	0.001	0.011	0	1	1	0.001
5																				
	42				204						787	525	155	0.01			0.02	0.000	0.00	
	2	122	690	39	0	232	900	55	0.6	7.7	0	0	5	7	0.001	0.012	7	1	2	0.005
6	32						101				452	300	120							
	5	96	570	31	408	598	2	42	0.6	8.2	0	0	6	0.14	0.002	0.011	0.02	0.000	0.00	0.001

Table1. Analyzed Hydrogeochemical parameters of groundwater of the study area

														2			0	1	6	
7	44	12	71	10	12	283	76	5	0.3	7.6	695	460	159	0.07 7	0.002	0.017	0.03 9	0.000 3	0.00 5	0.031
8	56	12	32	4	102	244	63	10	0.2	7.6	860	575	189	0.16 4	0.002	0.016	0.04 0	0.000 1	0.00 2	0.093
9	60 8	181	690	39	173	232	945	65	0.4	7.1	756 0	518 0	226 2	0.02 4	0.001	0.012	0.02 1	0.000 1	0.00 2	0.001
10	56	15	64	31	171	421	90	10	0.2	7.4	925	610	201	0.15 4	0.002	0.017	0.05 5	0.000 3	0.00 5	0.004
11	30	9	32	2	15	80	13	5	0.2	7.5	320	215	111	0.02 2	0.001	0.037	0.06 2	0.000 1	0.14 7	0.002
12	38 0	111	920	31	170 8	543	900	55	0.2	7.6	725 0	485 0	140 5	0.01 9	0.002	0.012	0.03 1	0.000 1	0.02 7	0.000 1
13	38	10	117	5	86	293	108	10	0.2	7.9	860	575	136	0.07 9	0.001	0.017	0.03 7	0.000 1	0.02 6	0.001
14	43	13	58	31	8	242	27	5	0.2	7.9	625	425	160	0.21 1	0.001	0.017	0.05 3	0.000 1	0.04 9	0.002
15	16 0	44	39	94	581	244	270	25	0.3	7.7	262 0	172 5	580	0.03 8	0.001	0.012	0.01 8	0.000 1	0.03 6	0.001
16	60	15	108	7	47	232	108	10	0.4	7.4	865	575	211	0.09 7	0.001	0.017	0.04 1	0.000 1	0.03 6	0.002

*Except pH, EC, and SAR others are expressed in mg/L. EC is in microsiemens/cm at 25°C





Fig.7a. Showing of Ca²⁺ Spatial Map



Fig. 7b. Showing of Na+ Spatial Map



Fig.8a. Showing of Cl⁻ Spatial Map



Fig. 8b. Showing of SO_4^{2-} Spatial Map



CONCLUSIONS

The study helped to understand major and trace elements characterization and groundwater quality in the study area. The concentrations of cations and anions were under the permissible limit of WHO for drinking in most of the sample locations. Hence, it can be used for the drinking and domestic purposes. Nevertheless, some elements such as Ca^{2+} , Na^+ , Mg^{2+} , Cl^- and SO_4^- concentration were noticed higher at few locations. The TDS values are found higher and permanent hardness also noticed at few locations which indicate the influence of Cl⁻ and SO_4^{2-} . The Cl- and SO_4^{2-} were contributed from dissolution of gypsum and anthropogenic The saline intrusion, activities. water industrial and fertilizers are also contributed significant level to Cl_2 and SO_4 . The Na⁺/Cl⁻ ratio and brackish-salt category of Stuyfzand classification favours the saline water sources. The saline water could have entered due to

over pumping of freshwater or poor freshwater recharge, low rainfall etc. Besides, the major ions concentration also derived from weathering and dissolution of rock formations, which contain feldspar, pyroxene and biotite minerals. The trace element concentration has not shown significant higher values in the Groundwater samples, nevertheless Cu and Mn were observed above the permissible limit in one or two groundwater samples. That also derived from anthropogenic activities particularly domestic. automobile and industrial waste.

Thus, the study helped us to understand the hydrogeochemical characters of groundwater and its suitability for drinking and domestic purposes in the study area. Further it emphasizes that frequent monitoring and suitable groundwater recharge method is needed to control further increase of ionic concentration in the study area, particularly saline water encountered zone.

ACKNOWLEDGEMENTS

This work is a part of sponsored research project funded by EMR-II Scheme of Council of Scientific and Industrial Research (Government of India), New Delhi and the No. is 23(0013)/09/EMR-II; sanction dt.05.03.2009. The authors would also like to extend thanks to two anonymous reviewers whose suggestions have played an important role in improving the quality and writing of the article.

REFERENCES

- Angino, E.E. 1983. Geochemistry and water Quality, Applied Environmental Geochemistry (Ed.Thmton,I.), *Academic press*,London,pp.171-199.
- APHA.1996. Standard methods for the examination of water and waste water,19th ed., *American Public Health Association*, AWWA, AIHA Washington, D.C.
- Back, W. Cherry, R. and Hanshaw, B., 1956. Chemical equilibrium between water and the minerals of a carbonate aquifer. *Int. Speleo. Spc. Bull.*, **28**: 119-126.
- Balasubramanian, A. 1986. Hydrogeological investigations of Tambaraparni River Basin, Tamil Nadu, unpublished Ph.D. Thesis, University of Mysore. 349p.
- Batayneh, A. 2006. Use of Electrical Resistivity Methods for Detecting Subsurface Fresh and Saline Water and Delineating Their Interfacial Configuration: A Case Study of the Eastern Dead Sea Coastal Aquifers, Jordan. *Hydrogeology Journal*, **14**: 1277-1283. <u>http://dx.doi.org/10.</u> <u>1007/s10040-006-0034-3</u>.
- Brown,W, Skougstad,N.W and Fishman,M.J., 1974. *Methods for collection and*

analysis of water samples for dissolved minerals and gases. U.S. Department of Interior Book 5,160p.

- Cheboterev, I. I. 1955. Metamorphism of natural water in the crust of weathering-I. *Geochim. Cosmochim. Acta*, **8**: 22-48.
- Chidambaram. S. Ramanathan. Α L. Srinivasamoorthy. K and Ananthan.P., 2004. WATCLAST - A computer for hydrogeochemical program studies, Recent trends in hydrogeochemistry (case studies from surface and subsurface waters of selected countries), Published by Capital publishing company, New Delhi, pp.203-207.
- Chris, D. Metcalfe, Patricia A. Beddows, Gerardo Gold Bouchot, Tracy L. Metcalfe, Hongxia Li and Hanneke Van Lavieren., 2011. Contaminants in the coastal karst aquifer system along the Caribbean coast of the Yucatan Peninsula, Mexico, *Environmental Pollution*, **159**: 991-997.
- Dalton, M.G. and Upchurch, S.B., 1978. Interpretations of hydrogeochemical facies by factor analysis. *Ground Water*, **10**: 228-233.
- Davis, S.N., De Wiest, R.J., 1966. *Hydrogeology*. New York: Wiley & sons, Inc., New York, 463p.
- Environmental Protection Agency (EPA), 1976. Quality Criteria for Water, Washington D.C, USA.
- Freeze, R.A. and Cherry, J.A. 1979. *Groundwater*. Englewood Cliffs, New Jersey: Prentice-Hall Inc.
- Garrels, R.M. Lerman. A. and Mackenzie, F.T., 1976. Controls of atmospheric O2 andCO2: past, present and feture: AM. *Scientist*, **63**: 306-315.

- Handa, B.K. 1965. Modified Hill-Piper diagram for presentation of water analysis data, *Current science*, **34**: 131-314.
- Hem, J.D. 1985. Study and Interpretation of the chemical characteristics of Natural water, U.S. Geol. Surv, Water supply paper – pp.2254, 264
- Hem, J.D. 1959. Study and interpretation of the chemical characteristic of natural. USGS water supply, 269.
- ICMR. 1975. New dimensions to fluorosis in Andhra Pradesh. *ICMR Bulletin* **5**:1-5.
- Jeevanandam, P., Mulukutla, R.S., Yang, Z.H. Kwen, and Klabunde, K. J., 2007. Nanocrystals to Nanorods: A Precursor Approach for the Synthesis of Magnesium Hydroxide Nanorods from Magnesium Oxychloride Nanorods Starting from Nanocrystalline Magnesium Oxide, *Chem. Mater.* **19**: 5395-5403.
- Jeyavel, Raja Kumar, T., Dushiyanthan, C., Thiruneelakandan, B., Suresh, R., Karthikeyan, K and Davidraju, D., 2013. Study on sea water intrusion using electrical resistivity scanning near Thiruchendur area of Thoothukudi district, Tamilnadu, *Jl. of Applied Geochemistry*, **15**(1):78-87.
- Karanth, K.R. 1987. Groundwater Assessment Development and Management, Tata Mc Grawc- Hill Company Limited, New Delhi, 720 p.
- Lakshmanan, E., Kannan, R., Kumar, M.S., 2003. Major ion chemistry and identification of hydrogeochemical processes of ground water in a part of Kancheepuram district, Tamil Nadu, *India. Environ. Geosci.* **10**(4):157-166.
- Longe, E.O. and Enekwechi, L.O., 2007. Investigation on potential groundwater

impacts and influence of local hydrogeology on natural attenuation of leachate at a municipal landfill. *International Journal of Environmental Science and Technology*, **4**(1): 133-140.

- Madison, R. J. and Brunett, J. D., 1984.
 Overview of the occurrence if nitrate in ground water of the United States, Water Supply Paper 2275. Jn U.S.
 Geological Survey. National Water Summary 1984 Hydrologic Events.
 Selected Water Quality Trends and Ground Water Resources. U.S.
 Geological Survey, Reston, VA.
- Mala,V. 1997. Study of the environmental hydrogeochemical and sedimentological aspects between Puduchatram to Chidambaram area, Cuddalore district, East coast of India,. M.Phil Dissertation, Annamalai University,pp.146.
- Mercado, A. 1985. The use of hydro geochemical patterns in carbonate sand and sandstone aquifers to identify intrusion and using of saline water. *Ground Water*.**23**:635-645.
- Metcalf and EddyInc.(M&E). 2000. Integrated Aquifer Management Plan: Final Report. Gaza Coastal Aquifer Management Program, USAID Contract No.294-C-00-99-00038-00.
- Metcalfe, C.D., P.A. Beddows, G.G. Bouchot, T.L. Metcalfe, H.X. Li, and H. Van Lavieren. 2011. Contaminants in the coastal karst aquifer system along the Caribbean coast of the Yucatan Peninsula, Mexico. Environmental Pollution **159**: 991–997.
- Meybeck, M. 1987. Global Chemical weathering of surficial rocks estimated from river dissolved rock, *American Jour. Sci.*, pp.401-428.

- Mondal, N.C., Singh, V.S., Saxena, V.K., Prasad, R.K., (2008). Improvement of groundwater quality due to fresh water ingress in Potharlanka Island, Krishna delta, India. Environ. Geol. **55** (3): 595–603.
- Mondal, N. C., Singh, V. P., Singh, V. S. and Saxena, V. K., 2010a. Determining the interaction between groundwater and saline water through groundwater major ions chemistry. *Journal of Hydrology*, **388**(1–2):100–111.
- Mondal, N.C., Singh, V.P., Singh, S and Singh, V.S., 2011. Hydrochemical characteristic of coastal aquifer from Tuticorin, Tamil Nadu, India, *Environmental monitoring and* assessment, **175:**1-4, 531-550.
- Mondal, N.C and Singh, V.P., 2011. Hydrochemical analysis of salinization for a tannery belt in Southern India, *Journal of Hydrology* **405** (3-4): 235-247.
- Mondal, N.C., Singh, V.P., Singh, S., and Ahmed., 2017. Hydrochemical investigation of interaction between groundwater and seawater using major ions chemistry in east coast of India, *Groundwater*, **1**: 1-21.
- Munn,L. 1936. A note on the salinity in relation to soil and geology in Raichur district, Jour.Hyderabad *Geol.Surv.*, 3(1):83-90.
- Norris, FH. 1992. Epidemiology of trauma: Frequency and impact of different potentially traumatic events on different demographic groups. *Journal of Consulting and Clinical Psychology* **60:** 409–418.
- Park, S.C., Yun, S.T., Chae, G.T., Yoo I.S., Shin, K.S., Heo, C.H. and Lee, S.K., 2005. Regional hydrochemical study on salinization of coastal aquifers,

western coastal area of South Korea. *Journal of Hydrology*, **313:**182-194.

- Piper, A.M. 1944. A Graphical Procedure in the chemical Interpretation of Groundwater Analyses. *Trans. Amer.Geophy. Union.***25:** 914 – 923.
- Prasanna, M. V. Chidambaram, S. Shahul Hameed, A. and Srinivasamoorthy, K., 2011. Hydrogeochemical analysis and evaluation of groundwater quality in the Gadilam river basin, Tamil Nadu, India, J. Earth Syst. Sci. 120, 1: 85– 98.
- P. S., Datta and S. K. Tyagi "Major ion chemistry of groundwater in Delhi area: chemical weathering processes and groundwater flow regime," Journal of Geological Society of India, Vol. 47, 1996, pp.179–188
- PWD. 2005 Groundwater perspectives: A profile of Thoothukudi District, Tamilnadu
- Rangarajan, R., N.C Mondal, V.S Singh, and S.V Singh, 2009.Estimation of natural recharge and its relation with aquifer parameters in and around Tuticorn tow,Tamil Nadu, India. *Curr*.Sci. 97: 1996, pp. 179-188
- Sami, K. 1992. Recharge mechanisms and geochemical processes in a semi-arid sedimentary basin, Eastern Cape, South Africa, Journal of Hydrology.139: 27–48.
- Sankul Techno. 2002. Geological study and core log test (p.27).Report.
- Sawyer, C. N. and Mc Carty, P. L., 1967. Chemistry for Sanitary Engineers, and classification of naturally soft and naturally hard waters to sources and hardness of their water supplies. *J. Hydrology*.

- Saxena, V. K. Sanjeev Kumar and Singh, V. S. 2004. Occurrence, behaviour and speciation of arsenic in groundwater. *Current Science*, 86: (2). 281-284.
- Selvam, S. Venkatramanan, S. Singaraja C., 2015. A GIS-based assessment of water quality pollution indices for contamination heavy metal in Tuticorin Corporation, Tamilnadu. Arab Geosci, India. J DOI 10.1007/s12517-015-1968-3.
- Sherif, M. El Mahmoudi, A. Garamoon, H. Kacimov, A. Akram, S. Ebraheem, A. and Shetty, A., 2006. Geoeletrical and hydrogeochemical studies for delineating seawater intrusion in the outlet of Wadi Ham, UAE. *Environmental Geology*, **49**: 536-551.
- Singaraja, C. Chidambaram, S. Noble Jacob, Selvam, S. Prasanna M. V., 2016. Tidal effects on groundwater dynamics in shallow coastal aquiferssoutheast coast of Tamilnadu, India, *Arabian Journal of Geosciences*, 9:467.
- Singh,V.S. Mondal,N.C. Singh,S. And Negi,B.C., 2006. Hydrogeological and geophysical investigations to delineate aquifer zone around SIIL, Tuticorin, Tamilnadu (p.24). Tech. Rept. No. NGRI- 2006-GW-564.
- Singh, R.K., Datta, M. and Nema, A.K., 2009. A new system for groundwater contamination hazard rating of landfills, *Journal of Environmental Management*, **91**(2):344-357.

- Srinivasamoorthy, K. Chidambaram, M. Prasanna, M.V. Vasanthavigar, M. John Peter, A. and Anandhan, P., 2008. Identification of major sources controlling Groundwater Chemistry from a hard rock terrain A case study from Mettur taluk, Salem district, Tamilnadu, India. J. Earth Syst. Sci. 117(1): .49-58.
- Stuyfzand, P.T. 1989. A new hydrochemical classification of water types with examples of application, AHS. **184**: 89-98.
- Todd, D.K. 1953. *Seawater intrusion in costal aquifers*. Transactions American Geophysical Union pp. 749–754.
- Vasanthavigar, M., Srinivasamoorthy, K., Vijayaragavan, K., Rajiv Ganthi,R., Chidambaram, S., Sarama, V. S., Anandhan, P., Manivannan, R. and Vasudevan,S.,2009.Hydrogeochemistr y of Thirumanimuttar Basin: An Indication of Weathering and Anthropogenic Impact, *Int. J. Environ. Res., (Autumn)* **3**(4):617-628.
- WHO. 2006. Guidelines for drinking water quality,V.1, Recommendations, World Health Organisation, Gene