

Assessment of Ground Water Quality to Identify the Hydrogeochemical Processes in the Marakkanam Region of Tamilnadu, India

Abiya Lukose¹, M. Suresh Gandhi^{1*}, Selvin Shyam Paul¹ and Gowtham. B²

¹Department of Geology, University of Madras, Guindy Campus, Chennai

²Department of Geology, Presidency College, Chennai

*Corresponding author: msureshgandhi@gmail.com

Abstract: This study was carried out with the aim of providing an overview of regional aquifer systems long-term geological and anthropogenic impacts on groundwater geochemistry and drinking water quality. The study area is Marakkanam, which is situated in the coastal panchayat of the Tindivanam Taluk in northern Tamil Nadu, in the Vilupuram District. A detailed hydrogeochemical analysis and interpretation of groundwater samples have revealed several factors worthy of our attention. The quality of water existing in the aquifer system is moderately alkaline and acidic in the spring of 2017 (April). The range of EC values is from 445.31 to 1304.68 $\mu\text{S}/\text{cm}$. Most of the samples have shown predominance of ions Na^+ and Cl^- . The statistical studies show that, the hydrogeochemical processes in this region are controlled by anthropogenic and inverse ion exchange factors. Groundwater is unsuitable for domestic use according to the heavy metal pollution index, heavy metal rating index, health hazard index, and pollution level.

Keywords: Hydrogeochemistry, Water quality, Statistical analysis, Health Risk Assessment, Marakkanam.

Introduction

Groundwater quality and chemical composition vary based on various factors like climate, soil, geology, hydrogeology, and the anthropogenic activities at a given place. Several geochemical processes alter the quality of water from the time it condenses in the atmosphere until the time it is discharged into an aquifer (Gupta et al., 2004). According to Todd (2007), the most practiced technique for keeping track of seawater incursion into littoral zones is periodic groundwater chemistry studies. Super saturation of soil zones with sodium and chloride ions results from the salinization process. The salt pans that have grown up in this region are continuously vulnerable to seawater evaporation and have a tendency to get blocked in certain shallow square segments when sunlight is deployed. In the study area, groundwater is the source for coastal areas. Hence these studies advocate the hydrogeochemical processes, water chemistry, and its spatial valuation.

Study Area

The study area, Marakkanam, is located in the Vilupuram District of northern Tamil Nadu, in the coastal panchayat of Tindivanam Taluk. By way of the Buckingham Canal, which runs north and south, it is well connected to Kakinada (Andhra Pradesh) and Pondicherry. The area is situated 107 km south of Chennai on the East Coast Road, close to the Union Territory of Pondicherry. The Karaveli River flows through the north of the Marakkanam region, covering an area of 27 km². The region has a tropical climate with average temperatures between 26° and 41°C, usually rising during the summer, and receives southwest (June-September) and northeast monsoons (October-December) with an average annual rainfall of 1119.8 mm to 1200 mm towards the coast. The soils in the area consist of forest soils, redsoils, some patches of alluvium, and some terisand deposits exposed by aeolian activity in the area. Clay sand and alluvial deposits are found near the eastern and northern parts of the study area.

Materials and Methods

Field and laboratory methods

In April 2017, 31 water samples were collected from boreholes in and around Marakkanam region (Fig. 1). One litre water sample was collected at each site using high density polyethylene bottles. Prior to sampling, all bottles were washed with 1:10 diluted HCl and rinsed repeatedly with distilled water. After pumping for 5 minutes, water was collected from the well and transported to the laboratory (4°C). In the sample site, pH, EC and TDS were determined using a multi-parameter (OaktonWD-35425-10PCSTester 25). Samples were analysed for major cations, anions, and heavy metals using standard methods (APHA 1995). Calcium (Ca^{2+}) and magnesium (Mg^{2+}) were analyzed by the titration method. Sodium (Na^+) and Potassium (K^+) ions were analyzed by Flame photometry (Model CL 378 Elico Limited, Hyderabad, India). Alkalinity is measured by the titration method. The bicarbonate content of water is calculated based on the alkalinity value. Mohr titration determines inorganic anion (Cl^-) of chloride. Sulfate (SO_4^{2-}) was determined by turbidity. Nitrate (NO_3^-) was measured using a UV

Spectrophotometer model SPECTRONIC200 Phosphate (PO_4^-) was measured using the ascorbic acid method. Trace elements were analyzed using flame atomic absorption spectroscopy (AAS). Geochemical maps were produced using AQUACHEM (4.0), and EXCEL (2010) software. The results were processed by the WATEQ4F program to calculate the saturation index. Spatial distributions were performed using the Karteninfo software (V8.5) in combination with the Vertical Mapper. Correlation matrices were constructed by Pearson correlation, and factor analysis between ion pairs was done using software (SPSS) 16.0.

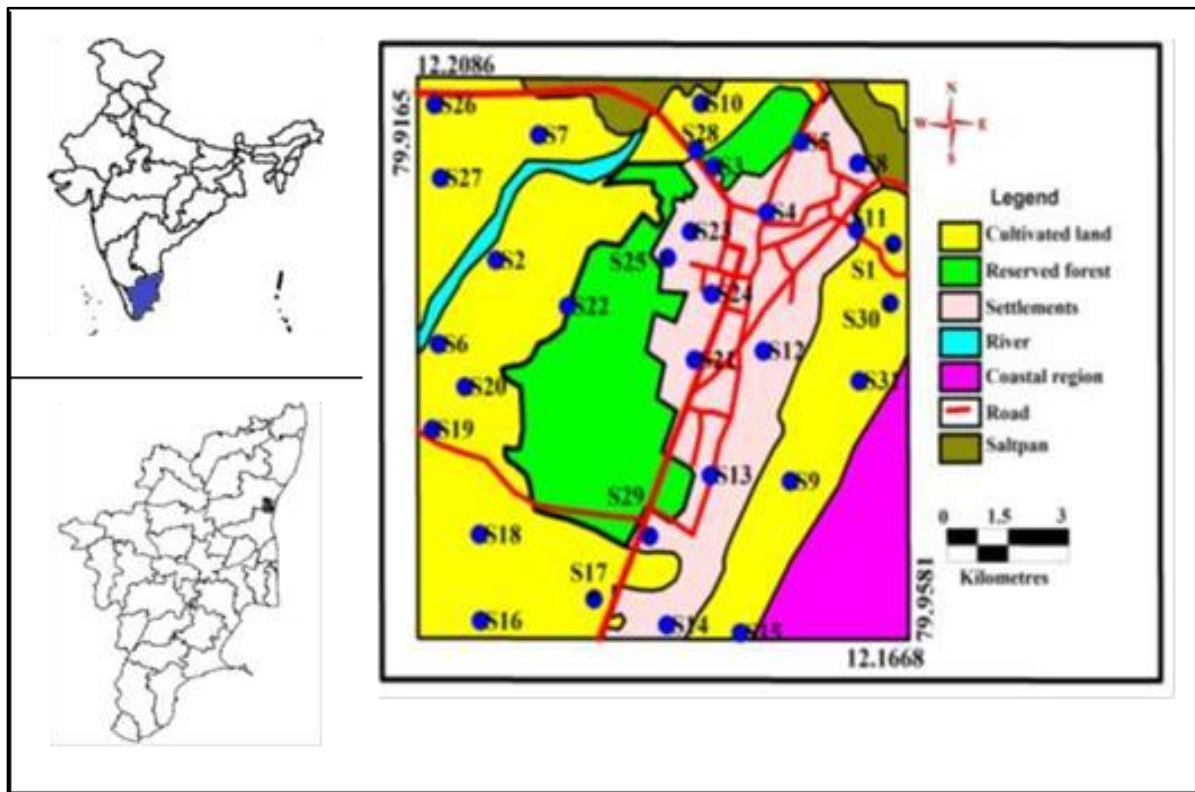


Fig. 1. Location map of the study area.

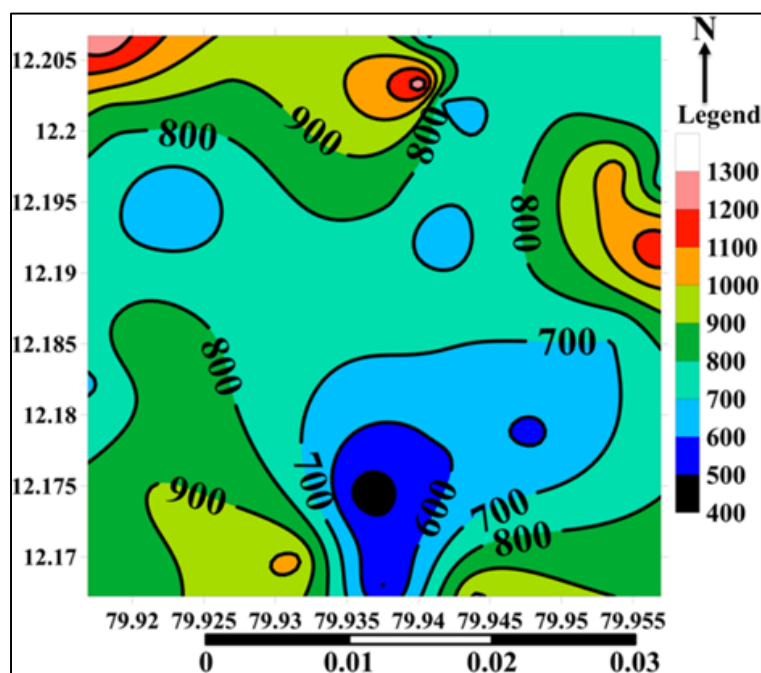


Fig. 2. Spatial distribution of electrical conductivity ($\mu\text{S}/\text{cm}$).

Results and Discussion

Groundwater Geochemistry

In the study area the pH ranges from 4.6 to 8.3 with an average of 6.5, which indicates the water samples were acidic to alkaline in nature. The EC values range from 445.31 to 1304.68 $\mu\text{S}/\text{cm}$ with an average of 811.20 $\mu\text{S}/\text{cm}$ (Fig. 2). The spatial distribution map shows that the northern part of the study area shows higher EC, whereas the southern area denotes less electrical conductivity; this represent the influence of salt pans and saline water intrusion. The total dissolved solids (TDS) of groundwater range from 285 ppm to 835 ppm with an average of 519.17ppm. An increase in TDS may be due to dissolution of minerals and rocks. According to Raju et al. (2009), the variation in the TDS, EC, and ionic concentrations in the groundwater may be due to the variation in geochemical process. The permissible limit of TDS is 2000mg/l (BIS 2012). The groundwater levels in Marakkanam region are within the desirable limit. The results of the chemical constituents of groundwater are shown in Table 1.

Table 1. Results of the chemical constituents of groundwater (All values in mg/l except EC in $\mu\text{S}/\text{cm}$ and pH).

Parameters	Maximum	Minimum	Average	BIS standards (2012) permissible limits
Ca	112	10	41.58	200
Mg	27.6	2.4	8.81	100
Na	138.5	11.7	60.97	200*
K	77.3	0.6	8.1	20*
Cl	345.64	27.48	119.5	1000
CO ₃	18	BDL	5.61	600
HCO ₃	42.7	5.1	19.85	400
PO ₄	5.09	BDL	0.25	6.5-8.5
SO ₄	81.85	0.8	34.54	400
NO ₃	77.47	66.84	72.62	45
H ₄ SiO ₄	100	6.7	44.8	100
TDS	835	285	516.53	2000
EC	1304.69	445.31	807.08	1500\$
pH	8.39	4.61	6.58	6.5-8.5
Cu	0.49	BDL	0.07	1.5
Zn	3.63	0.01	0.18	15
Co	0.74	0.05	0.11	0.05#
Cr	0.2	0.07	0.14	0.05*
Cd	0.04	BDL	0.03	0.005*
Pb	0.4	0.01	0.06	0.05@
Ni	0.53	BDL	0.23	0.02#
Fe	32.9	BDL	4.36	0.3@
Mn	6.96	BDL	0.59	0.3

*WHO (2004); #WHO (2003); @WHO (2008); \$ BIS 2012

From the results of the statistical analysis, it is found that the most dominant is chloride, ranging from 345.64 to 27.48 mg/l, and the least dominant is phosphate, ranging from 5.09 mg/l to BDL among the major ions (Table.1). In the case of trace elements, the most dominant element is iron, ranging from 32.90 mg/l to BDL. This extremely high iron concentration may be derived from laterite and ferruginous sandstone. This was also supported by Tiwari and Dubey (2012). As a whole, it is identified that the majority of the samples in the study area are within the permissible limits (BIS 2012) whereas some elements exceed the limits, suggesting a particular impact of any external factor as well as the endogenic process like rock-water interaction, leaching of Cl from topsoil or weathered zone, and base exchange reactions (Freeze and Cherry, 1979). The high concentration of NO₃ can cause blue baby syndrome,

gastric cancer, goiter, birth malformations, and hypertension (Spalding and Exner, 1993; Chakraborti et al., 2010). In the study area, nitrate concentration ranges from 66.84 ppm to 77.47 ppm, with an average concentration of 72.62 ppm. The permissible limit of nitrate is 45mg/l (BIS, 2012), implying that all the samples exceeded the safe limits, which has harmful effects on human health.

Table 2. Correlation analysis of groundwater samples.

	Ca	Mg	Na	K	Cl	CO ₃	HCO ₃	PO ₄	SO ₄	NO ₃	H ₄ SiO ₄	Cu	Zn	Co	Cr	Cd	Pb	Ni	Fe	Mn	TDS	EC	pH	
Ca	1																							
Mg	0.51	1																						
Na	0.27	0.22	1																					
K	-0.15	0.26	0.07	1																				
Cl	0.46	0.30	0.84	-0.10	1																			
CO ₃	-0.04	0.05	-0.09	0.25	-0.28	1																		
HCO ₃	-0.02	-0.04	-0.17	0.06	-0.10	-0.70	1																	
PO ₄	-0.10	-0.14	-0.18	-0.07	-0.14	-0.15	0.13	1																
SO ₄	0.39	0.46	0.33	0.47	0.11	0.13	-0.02	-0.03	1															
NO ₃	-0.07	0.09	0.13	0.13	0.03	-0.17	0.35	-0.04	0.26	1														
H ₄ SiO ₄	0.30	-0.05	-0.04	-0.31	0.10	-0.21	0.04	0.26	-0.04	-0.35	1													
Cu	0.18	0.21	0.11	-0.10	0.06	-0.20	0.28	-0.14	0.03	0.17	0.03	1												
Zn	0.01	-0.21	-0.10	-0.05	-0.02	-0.18	0.36	-0.06	-0.03	0.17	0.00	-0.07	1											
Co	0.14	0.24	0.05	-0.04	-0.03	-0.13	0.26	-0.10	0.04	0.18	-0.01	0.96	-0.05	1										
Cr	0.25	0.11	0.20	-0.34	0.20	-0.08	-0.18	-0.11	0.00	-0.05	0.09	0.30	-0.36	0.14	1									
Cd	0.22	0.15	0.13	-0.45	0.19	-0.13	-0.09	-0.12	-0.18	-0.14	0.13	0.32	-0.26	0.19	0.91	1								
Pb	0.18	-0.08	0.02	0.00	-0.08	-0.15	0.34	-0.08	0.16	0.27	0.05	0.00	-0.03	-0.09	0.30	0.23	1							
Ni	0.57	0.46	0.30	-0.11	0.23	-0.05	-0.12	-0.24	0.40	0.19	0.11	0.37	-0.24	0.33	0.59	0.43	0.20	1						
Fe	0.59	0.54	0.35	0.04	0.42	-0.23	0.16	-0.09	0.38	0.01	0.08	0.46	-0.04	0.41	0.13	0.09	-0.06	0.49	1					
Mn	0.25	0.34	0.01	-0.02	0.01	-0.17	0.30	-0.10	0.07	0.11	0.06	0.92	-0.02	0.96	0.12	0.20	-0.12	0.35	0.52	1				
TDS	0.54	0.52	0.81	0.12	0.81	-0.21	0.07	-0.17	0.43	0.21	0.14	0.20	-0.05	0.13	0.21	0.15	0.24	0.41	0.49	0.14	1			
EC	0.54	0.52	0.81	0.12	0.81	-0.21	0.07	-0.17	0.43	0.21	0.14	0.20	-0.05	0.13	0.21	0.15	0.24	0.41	0.49	0.14	1.00	1		
pH	-0.20	-0.15	-0.18	0.02	-0.13	0.48	-0.28	0.13	-0.20	-0.16	0.00	-0.49	0.17	-0.45	-0.42	-0.37	-0.04	-0.52	-0.45	-0.48	-0.17	-0.17	1	

Multivariate Statistical Analysis

Factor Analysis

To determine the relative importance of the chemical variables responsible for the variations in the geochemistry of groundwater, a multivariate statistical analysis has been carried out using the hydrogeochemical data (SPSS package 16.0). The variables used for factor analysis were pH, EC, TDS, Ca, Mg, Na, K, HCO₃, Cl, SO₄, NO₃, PO₄, Cu, Co, Cr, Zn, Pb, Fe, Mn, and Ni. The correlation matrix for 20 variables is shown in Table 2. R-mode factor analysis is useful in the interpretation of an aquifer by combining groundwater quality and specific hydrogeological processes along the coastal alluvium in the salt-pan region of Marakkanam. The correlation matrix is used for the inter-correlations among the given set of variables. The eigen value has been computed for all the principal ions. With a minimum acceptable Eigen value >1, the factor extraction has been done. The correlation coefficient value of <0.5 denotes poor correlation, while >0.5 is considered good correlation. Because of the association of Na⁺ and Cl⁻, defined as the salinity component in reference to the salt NaCl, the excellent correlation with Na and Cl suggests highly positive loading. The factor analysis studies revealed a strong correlation between Sodium and Chloride, as well as EC and TDS, confirming saline water intrusion in the Marakkanam area. It also reflects the influence of anthropogenic sources (Thivya et al., 2014). It may also be reverse ion exchange processes, and secondary salt leaching from the salt pan (Subramani et al., 2009). Chidambaram et al. (2011) discovered that feldspar weathering causes Na concentrations in groundwater. Inorganic fertilizer, irrigation drainage, and percolation from saline soil into ground water may be possible reasons for high chloride content.

The correlation between Ca with Mg, Ni, Fe, TDS and EC suggests that the aquifers in this region undergo multiple reverse ion exchange processes, carbonate, and silicate weathering saline water intrusion, leaching, evapotranspiration, and agricultural activities (Subramani et al., 2009). Mg has a good correlation with Fe, TDS, and EC. The Mg²⁺ in groundwater is primarily liberated by Mg-rich minerals (enstatite and hypersthene) (Chidambaram, 2000; Chan et al., 2013). Cu is highly correlated with Co and Mn, and Cr exhibits strong correlation with Cd and Ni, which reveal the sources in the groundwater due to the release of industrial effluents, and anthropogenic activities. Cadmium

concentrations may be high due to industrial waste discharge or leaching from sewage-laden landfills (Singh, 2003). A good correlation of Fe with Mn implies a reduction in pH value. The dominance of Fe in water, and reduced oxygen condition, help in the dissolution of naturally occurring salts in the soil, minerals, and rocks. This may also be due to ions, which play a key role in controlling water chemistry processes in this region.

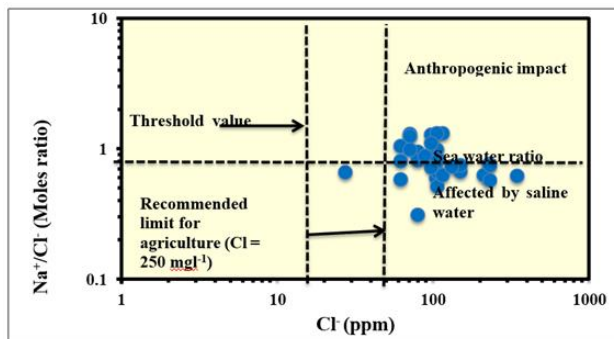


Fig. 3. Molar ratio of Na⁺/Cl⁻ versus Cl⁻ (mg/l) concentrations.

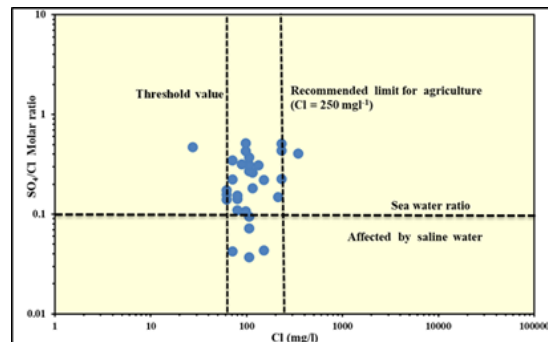


Fig. 4. Molar ratios of SO₄/Cl versus Cl (mg/l) concentrations.

Hydrochemical processes

Na⁺/Cl⁻ Vs. Cl⁻ ion ratio

The effect of seawater intrusion was evaluated by interpreting the range of ion ratio. The plot was used to determine the molar ratio of Na⁺/Cl⁻ concentration to Cl⁻ concentration (mg/l). A linear increase in Na⁺ and Cl⁻ is expected in conservative seawater-freshwater mixtures (Sanchez Martos et al., 1999). As a result, the groundwater decreased around the seawater ratio (0.86), suggesting that the fresh groundwater was contaminated. From feldspar weathering, the amount of Na⁺ released into solution is relatively small compared to the larger contribution from coastal precipitation, but enrichment is observed in dilute ground waters with Na⁺/Cl⁻ > 1. The Na⁺/Cl⁻ ratios ranged from 0.30 to 1.2 mg/L, indicating that most samples were within the contamination range in the study area. The Cl⁻ to Na⁺ and Mg²⁺ ratios indicate that these ions are the primary source of evaporated water. Figure 3 shows that the Na⁺/Cl⁻ to Cl⁻ values exceed the seawater ratio values, indicating that a large proportion of the groundwater in this region is affected by seawater intrusion.

Molar ratio of SO₄/Cl vs. Cl

Changes in the SO₄/Cl molar ratio were evaluated in relation to the Cl concentration distribution. SO₄/Cl ratios ranged from 0.22 to 0.39 mg/l, with most samples located near contaminated areas (Fig. 4). The molar ratio shows that 30% are below seawater levels (0.1), indicating a noteworthy level of seawater pollution. They generally decrease as the concentration of Cl increases.

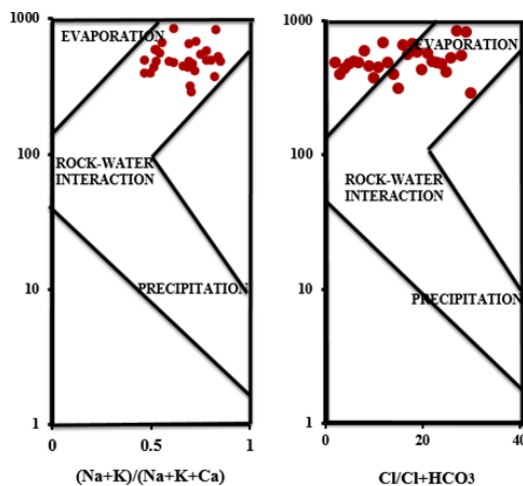


Fig. 5. Gibbs Plot showing water-rock interaction (Gibbs, 1970).

Gibbs plot

Hydrogeochemical processes are determinants of water chemistry. According to Gibbs (1970), the most important natural processes that are controlling surface and groundwater chemistry are (i) atmospheric precipitation, (ii) rock weathering, and (iii) evaporation and fractional crystallization (Fig. 5). Most groundwater samples fall within the evaporation zone due to the dry climatic conditions prevailing in the study area during the sampling period. The basic concept of the chart is based on TDS and a few ion ratios, but there are still very few samples outlie the boomerang chart, and this high TDS sample in the evaporation zone are the result of both anthropogenic and natural resources.

Piper plot

Piper plots display the concentrations of the main cations (Ca, Mg, Na, and K), and anions ($\text{CO}_3 + \text{HCO}_3$, Cl, and SO_4) in two separate triangle plots, and their combined information in squares (Fig. 6), limited to 3 types. Most samples are Na-Cl types with high sodium and chlorine content due to processes that remove other ions from the system by adsorption or precipitation. Some samples were classified as Ca-Cl types, indicating prevalent anthropogenic influence. Few of the samples fell under the Ca-Mg-Cl mixed types, again indicating an artifact, and the samples reflected a mixed cation and anion type that could be attributed to the additional leachate (Chidambaram et al., 2012). The figure shows that alkalis (Na and K) outperform the alkaline earths (Ca and Mg), and the strong acids Cl and SO_4 outperform the weak acids (HCO_3).

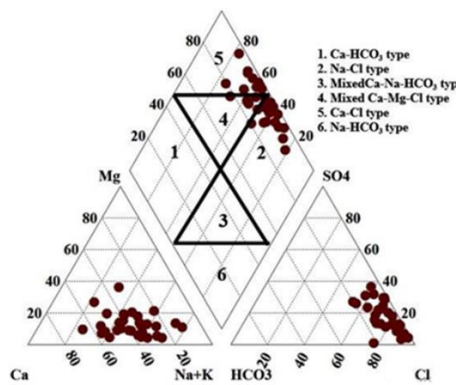


Fig. 6. Piper plot exhibiting the hydrogeochemical facies of groundwater samples.

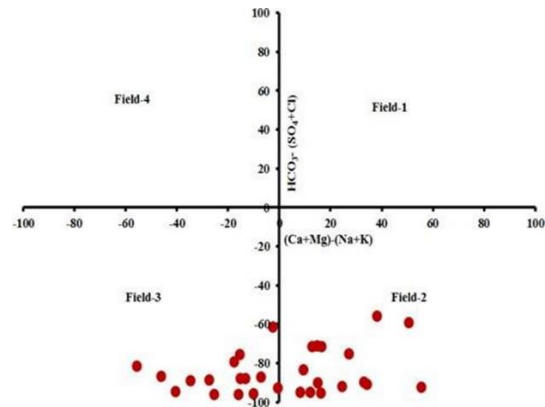


Fig. 7. Chadha's geochemical evolution process plot.

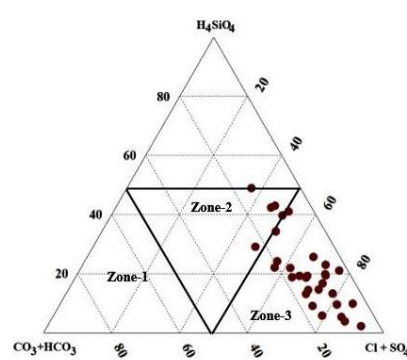
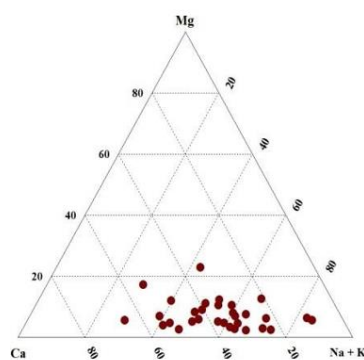


Fig. 8. Ternary plots for cations (a) and anions (b) The cations with more samples in (Na + K) region, the anions are dominated by Cl + SO_4 (Thilgavathi et al., 2014).

Ternary plots

Ternary diagrams were created to characterize ions in groundwater and to understand the proportions of bicarbonates, silicates, chlorides, and sulfates derived from anthropogenic processes. Zones I and II are classified by weathering processes, while Zone III is classified as areas dominated by anthropogenic processes (Fig. 8). Few samples are transferred to anthropogenic processes since the

majority of the samples fall into Zone 3, where Na-Cl and Ca-Cl types are predominant. Na concentrations in groundwater exceed the increasing trend of Ca on the Na+K side due to alkali mineral weathering or cation exchange, saline disturbance, or the addition of NPK fertilizers to agricultural lands infiltrated by surface runoff. Most samples show a trend towards Cl+SO₄, suggesting that Cl- may come from common sources such as saline backwaters and evaporation from unsaturated zones. Cl- can leach from clay beds and SO₄²⁻ can leach from industrial fertilizers (Handa, 1975). Ternary diagrams were created to characterize ions in groundwater and to understand the proportions of bicarbonates, silicates, chlorides and sulfates derived from anthropogenic processes. Zones I and II are classified by weathering processes, whereas Zone III is classified as areas dominated by anthropogenic processes. Most of the samples fall into Zone 3, where Na-Cl, Ca-Cl types are dominant, so few samples are transferred to processes.

Relationship of Log pCO₂ and ionic strength

Figure 9 depicts the calculated ionic strength and pCO₂ values. The log pCO₂ of each sample is determined to examine its relationship to recharge. The log pCO₂ values range from -0.26 to - 4.20. High ionic intensities up to 0.016 were detected in the study area. From this result, it can be concluded that the majority of the samples have low ionic strength, indicating high freshwater influx and charging. The majority of the samples reflect a mixed water type, with log pCO₂ tending to decrease to atmospheric pressure, leading to an increase in saturation, suggesting that the mixing zone is an open system. Few samples fall within the higher logarithmic pCO₂ results around -1.5. This may be due to deep groundwater circulation with less interaction with the atmosphere, or to high saturation of carbonate resulting from the interaction of carbonate flowing material with host rocks (Chidambaram et al., 2011).

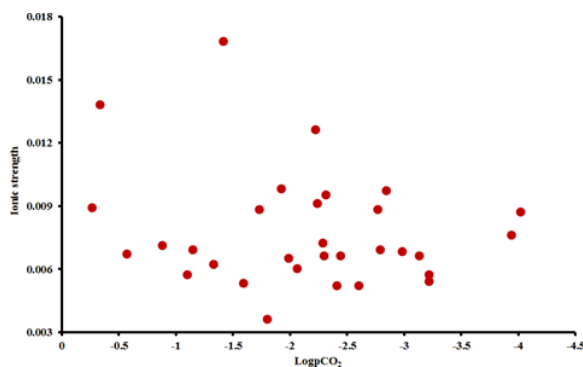


Fig. 9. Bivariate plot between log pCO₂ vs. ionic strength.

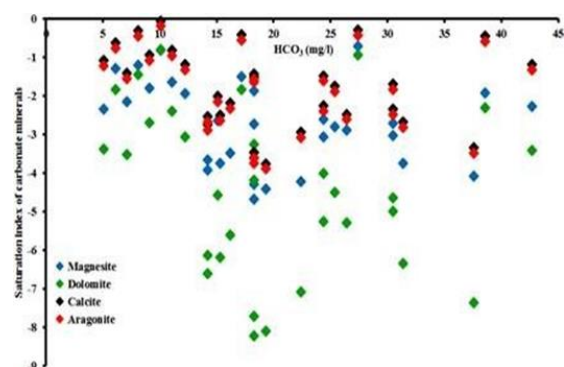


Fig. 10. Variation of Saturation index of different Carbonate minerals with dissolved HCO₃.

Saturation index

The saturation index (SI) was calculated for groundwater samples using the WATEQ4F geochemical computer program to predict subsurface reaction mineralogy from groundwater sample data without collecting solid phase samples, which can be defined as:

$$SI = \log (IAP/k)$$

where IAP is the ion activity product and K is the equilibrium constant.

Saturation index of carbonate minerals

The groundwater saturation indices of minerals such as magnesite (MgCO₃), aragonite (CaCO₃), calcite (CaCO₃), and dolomite (CaMg(CO₃)₂) were plotted against the concentration of HCO₃ (mg/l) (Fig. 10). The SI of carbonate minerals from groundwater samples has been found to drop to super saturation at high HCO₃. This is due to groundwater recharge and dilution of groundwater chemicals associated with these minerals (calcite and aragonite) during subsequent monsoon seasons or when Ca is not available (Gomez et al., 2006). These samples can represent the sedimentary aquifers in the study area, as it can be concluded that the groundwater in all aquifers is unsaturated calcite and aragonite with high concentrations of bicarbonates.

Saturation index of silicate minerals

The saturation indices of these minerals in the samples are observed to follow the trend Cristobalite (SICr) > Chalcedony (SIch) > Silica gel (SIsg). SICr and SICr are supersaturated, and SIsg is unsaturated to saturated. It is also observed that the saturation indices of these minerals increase linearly with increasing dissolved silica concentrations in the study area. However, since these aquifers are semi-constrained by finite conditions, precipitation of silica by evaporation is unlikely. SICr and SICr are observed to reach equilibrium at about 26 mg/l for H₄SiO₄ and 90 mg/l for silica gel (Fig. 11).

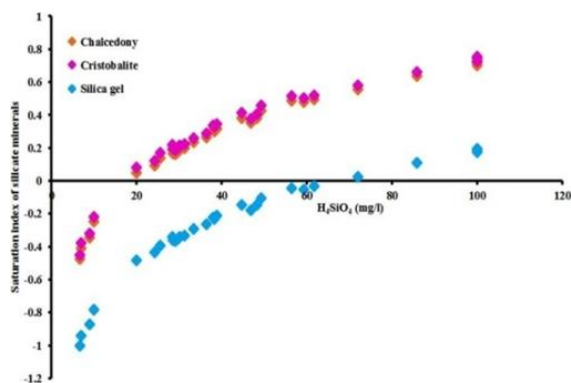


Fig. 11. Variation of Saturation index of different Silicate minerals with dissolved H₄SiO₄ for ground water samples.

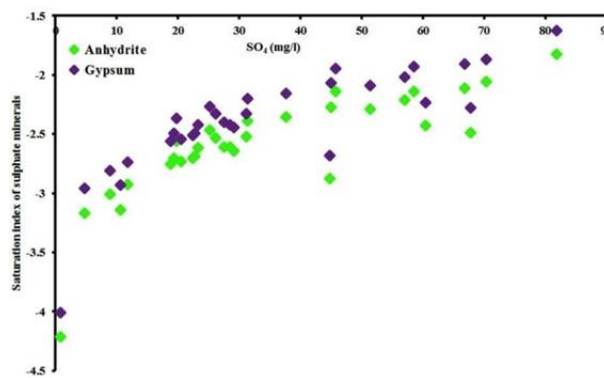


Fig. 12. Variation of Saturation index of different Sulphate minerals with dissolved SO₄.

Saturation index of sulphate minerals

The saturations of sulphate minerals, gypsum (SIGy) and anhydrite (SIAn) were recalculated for the groundwater samples shown in Figure 12. It has been observed that the saturation indices of these minerals tend to be SIGy>SIAn. The SI of both minerals is in an unsaturated state. It has also been discovered that as sulphate concentration increases, the saturation index of these minerals increases linearly. This may be due to bound ion effects or Na interference in the formation of these minerals that seasonally change the chemistry of groundwater. The study area shows a sharp increase in SI, an initial low SO₄ concentration with a sharp increase, a further increase in SO₄ concentration, and a gradual increase as the SI decreases. This could be due to pollutant runoff from nearby industrial areas, or exposure to fertilizers from agricultural lands or the fertilizer industry, which could result in higher concentrations of these ions in local groundwater.

Heavy Metal Pollution Indices

Heavy metal contamination indices were calculated according to ISI standards and presented by HPI. The HPL method assigns a score (any value between 0 and 1) or weight (W_i) to each selected parameter to assess the relative importance of each quality, and the index's underlying contamination parameter is developed by selecting. In this study, the concentration limits (that is, the maximum acceptable value (S_i) for drinking water and the maximum desirable value (I_i) for each parameter) were taken from the ISI standard. HPI values were determined using the following formula (Mohan et al., 1996).

$$HPI = \frac{\sum_{i=1}^n W_i Q_i}{\sum_{i=1}^n W_i}$$

The sub-index (Q_i) is calculated by

$$Q_i = \sum_{i=1}^n \frac{\{M_i(-)I_i\}}{(S_i - I_i)} \times 100$$

where M_i, I_i and S_i are the monitored heavy metal's ideal and standard values of the ith parameter, respectively. The sign (-) indicates the numerical difference of the two values, ignoring the algebraic sign.

Water quality was classified into three categories based on the heavy metal load index: low heavy metal load (HPI<100), threshold risk heavy metal load (HPI = 100), and high heavy metal load (HPI >100) (Mohan et al., 1996). The results show that HPI values range from 6.09 to 7158.09. Twenty-

five percent of the samples exhibited low levels of heavy metals, and 74% of the samples exhibited non- potable high levels of heavy metals (Prasad and Kumari, 2008; Prasad and Mondal, 2008). This indicates that groundwater samples are severely contaminated with heavy metals.

Table 3. Calculated indices for groundwater of the study area.

Sample no.	HP I	Mean Deviation	% Deviation	Cd	Mean Deviation	% Deviation	HEI	Mean Deviation	% Deviation
S1	87.73	-857.78	-90.72	1.37	-27.48	-95.25	10.37	-27.48	-6532.69
S2	188.81	188.81	19.97	0.81	-0.81	-2.80	8.19	8.19	-2965.78
S3	299.50	299.50	31.68	5.75	5.75	19.93	14.75	14.75	-2309.85
S4	63.63	63.63	6.73	9.88	9.88	34.24	18.88	18.88	-1897.15
S5	86.69	86.69	9.17	6.82	6.82	23.64	15.82	15.82	-2203.08
S6	142.17	142.17	15.04	0.41	0.41	1.41	9.41	9.41	-2844.27
S7	1290.13	1290.13	136.45	25.33	25.33	87.81	34.33	34.33	-351.58
S8	162.75	162.75	17.21	3.04	3.04	10.52	12.04	12.04	-2581.34
S9	81.57	81.57	8.63	2.68	2.68	9.30	11.68	11.68	-2616.71
S10	702.94	702.94	74.35	17.41	17.41	60.33	26.41	26.41	-1144.38
S11	154.64	154.64	16.36	8.11	8.11	28.11	17.11	17.11	-2073.98
S12	52.49	52.49	5.55	10.79	10.79	37.42	19.79	19.79	-1805.49
S13	163.86	163.86	17.33	18.60	18.60	64.47	27.60	27.60	-1025.16
S14	170.91	170.91	18.08	15.21	15.21	52.72	24.21	24.21	-1363.90
S15	231.97	231.97	24.53	28.10	28.10	97.39	37.10	37.10	-75.26
S16	6.09	6.09	0.64	9.17	9.17	31.79	18.17	18.17	-1967.68
S17	289.80	289.80	30.65	20.04	20.04	69.45	29.04	29.04	-881.21
S18	4298.79	4298.79	454.65	82.09	82.09	284.54	91.09	91.09	5323.87
S19	47.99	47.99	5.08	11.28	11.28	39.09	20.28	20.28	-1757.23
S20	5194.74	5194.74	549.41	123.2	123.23	427.14	132.23	132.23	9437.78
S21	202.34	202.34	21.40	24.11	24.11	83.58	33.11	33.11	-473.68
S22	87.32	87.32	9.23	19.33	19.33	66.99	28.33	28.33	-952.18
S23	332.12	332.12	35.13	37.96	37.96	131.57	46.96	46.96	910.74
S24	118.33	118.33	12.51	21.35	21.35	74.02	30.35	30.35	-749.52
S25	207.08	207.08	21.90	21.07	21.07	73.05	30.07	30.07	-777.57
S26	135.64	135.64	14.35	18.97	18.97	65.76	27.97	27.97	-987.72
S27	363.14	363.14	38.41	28.69	28.69	99.45	37.69	37.69	-15.97
S28	7158.19	7158.19	757.07	146.16	146.16	506.63	155.16	155.16	11731.06
S29	1617.83	1617.83	171.11	41.74	41.74	144.68	50.74	50.74	1288.92
S30	4427.24	4427.24	468.24	97.22	97.22	337.01	106.22	106.22	6837.49
S31	944.26	944.26	99.87	39.23	39.23	136.00	48.23	48.23	1038.54
Minimum	6.09			0.81			8.19		
Maximum	7158.2			146.16			155.16		
Mean	945.51			28.85			37.85		

Degree of Contamination

Contamination degree (Cd) was used as a criterion to estimate metal contamination degree. The Contamination Index (Cd) summarizes the combined effects of several quality parameters considered detrimental to domestic use and is calculated as

$$C_d = \sum_{i=1}^{i=n} CF$$

The range and mean values of Cd were 0.81 to 146. Cd may be classified into three categories (Edet and Offiong, 2002; Backman et al., 1997) as follows: low (Cd<1), medium (Cd = 1–3), and high (Cd>3). Two samples are classified as low or medium contamination, while the remaining samples are classified as high contamination. Thus, Cd indicates that all the samples are highly polluted.

Mean and Standard Deviation Plot

The means and percent deviations of all indices were calculated for each sample point (Table.3). As observed by Prasad and Bose (2001), and Edet and Offiong (2002), HPI and Cd values are below their respective means, indicating relatively good negative percentage deviations.

$$HEI = \sum_{i=1}^n \frac{H_c}{H_{mac}}$$

Heavy metal evaluation index (HEI)

The heavy metal evaluation index is a method of assessing water quality that focuses on heavy metals in water samples (Edet et al., 2003). The water quality index is classified into three categories: low pollution (HEI < 40), moderate (HEI = 40-80) and high pollution (HEI > 80) (Bhuiyan et al., 2010). The heavy metal evaluation index is a way of estimating the water quality with a focus on heavy metals in The exponent is calculated from the following formula.

$$HEI = \sum_{i=1}^n \frac{H_c}{H_{mac}}$$

where Hc: Measured value for the ith parameter, Hmac: Standard allowed value for ith parameter.

HEI scores range from 8.19 to 155.16, with an average of 37.85. Of the total samples, 24 fall into the low contamination category, 3 into the medium contamination category, and 4 into the heavy contamination category. Samples with a low metal index are suitable for drinking, but low concentrations of metals can accumulate at various stages, and over time, the amount can cause many problems for humans, so long-term use is not recommended. In general, groundwater chemistry in mineralized areas with frequent wet-to-dry precipitation patterns shows a high variation in solute concentrations. The variability is due to the seasonality of groundwater flow, with high recharge and runoff due to dilution during rainfall, and little or no further groundwater runoff in the middle of the dry season (Heyden and New, 2004). This type of hydrological reaction is expected to be the main reason for the higher metal concentrations observed during the dry season (Tiwari et al., 2016).

Human health risk assessment

According to the US Environmental Protection Agency (USEPA) the human health risk assessment considered four methods such as, hazard identification, dose response assessment, exposure assessment, and risk characterization. Trace metals in the groundwater through human exposure could occur through different pathways, such as potential exposure through ingestion and dermal pathways, which were calculated using equations (1) and (2) as shown below. Risk assessment of trace elements through oral ingestion and dermal exposure concentrations was carried out based on the USEPA (2000), ICMR (2009) and UNDESA (2013) guidelines. According to the United States Environmental Protection Agency (USEPA), human health risk assessment considers four methods: hazard identification, dose-response assessment, exposure assessment, and risk characterization. Trace metals in groundwater from human exposure can occur in a variety of ways, including Potential exposure by ingestion and dermal routes was calculated using equations (1) and (2) shown below. A risk assessment for trace elements by ingestion and dermal exposure concentrations was performed based on USEPA (2000), ICMR (2009) and UNDESA (2013) guidelines.

$$CDI_{Ingestion} = \frac{C_w \times IR \times ABS_g \times EF \times ED}{BW \times AT} \quad (1)$$

$$CDI_{Dermal} = \frac{C_w \times SA \times K_p \times ABS_d \times ET \times EF \times ED \times F}{BW \times AT} \quad (2)$$

whereas C_w concentration of trace elements in groundwater (mg/L); IR (Ingestion Rate (L/day)); SA (Skin surface Area (cm²); Kp(skin adherence factor (cm/h); ET (Exposure Time (h/day); ABSg(gastrointestinal absorption factor); ABSd(dermal absorption factor EF(Exposure Frequency (day/year); ED (Exposure Duration (years); CF (conversion factor (L/cm³); BW (Bodyweight (kg); AT (Averaging Time (days). The human health risk assessment was calculated using the Hazard quotients (USEPA, 1989) for metals, which is shown in equation (3).

$$Hazard\ quotient\ (HQ) = \frac{CDI}{RFD} \quad (3)$$

Table 4. Estimation of element wise reference dose (RfD), exposure dose (CDI) and hazard quotients (HQ) through oral and dermal pathways in the groundwater.

Element	RfD Ingestion (ug/kg/day)	RfD Dermal (ug/kg/day)	CDI Ingestion (ug/kg/day)		CDI Dermal (ug/kg/day)		HQ Ingestion		HQ Dermal	
			Min	Max	Min	Max	Min	Max	Min	Max
Fe	300	45	0	2169.791	0	1.029	0	7.226	0	0.022
Mn	20	0.8	0	72.77	0	0.128	0	12.628	0	0.149
Cu	40	12	1.67	17.78	0	0.0008	0	0.444	0	7.03
Cr	3	0.015	2.613	7.40	0.002	0.007	0.871	0.963	0.165	0.468
Pb	1.4	0.42	0.362	14.52	1.722	0.0006	0.259	2.468	0.0004	0.0016
Ni	20	5.4	0.073	19.27	0.002	6.87	0.004	10.369	0.1287	0.0003
Zn	300	60	0.435	155.33	0.0001	0.044	0.001	0.517	0.0002	0.00007

A human health risk assessment was performed on the collected groundwater samples in order to determine the impact of each chemical element on the human body through continuous consumption and use. Through continuous exposure, these elements will gradually accumulate in the human body, which gradually reacts to form a toxic component that develops adverse diseases. The studies were carried out using Fe, Mn, Cu, Co, Ni, Cr, Pb, and Zn. The data obtained show that the values are varying in higher ranges, implying that the toxicity of the pollutant is increasing. The samples with HQI>1 is considered hazardous, and the results indicate that the majority of the aquifers are unbearably polluted with Fe (5% of the samples), Mn (9% of the samples), Cr (27% of the samples), and Pb (19% of the samples) (Figure 13). Most of these elements emerge from industrial effluents and, to an extent from ion exchange or mineralisation processes as geogenic components. Higher concentrations of iron cause bad taste, discoloration, staining, turbidity, aesthetic, and operational problems in water supply systems (Vigneshwaran and Viswanathan, 1995). The desirable limit for iron concentration in drinking water is 0.1 mg/L, and the permissible limit is 0.3 mg/L (WHO, 2008).

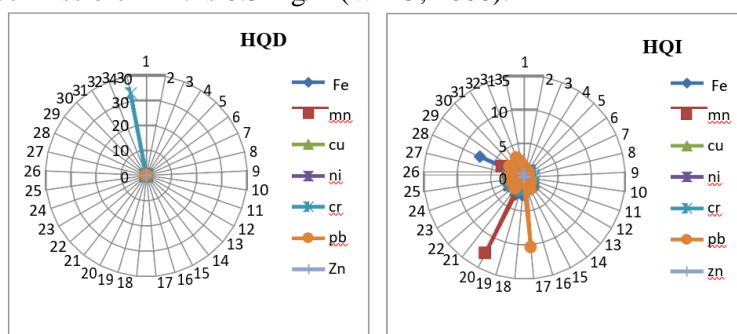


Fig. 13. Risk assessment of trace elements using HQI and HQD.

Besides natural sources, the corrosive nature of the casing pipe used for water supply in bore wells might contribute to the elevated iron concentration. Manganese is one of the more abundant metals in the earth’s crust, and usually occurs together with Fe, and is widely distributed in soil, sedimentary rocks, and water. On exposure to oxygen, Mn can form insoluble oxides that may result in undesirable deposits and color problems in distribution systems (Tiwari et al., 2013). Manganese is considered one of the least toxic elements, but too much of it can cause growth retardation, fever, fatigue, blindness, and reproductive problems.

Conclusions

This study shows that the groundwater in the Marakkanam area of Tamil Nadu is not generally suitable for drinking water purposes but is suitable for agricultural purposes. The main geochemical processes that determine groundwater chemistry in the study area are a) ion exchange processes, b) anthropogenic activities, and c) saltwater intrusion. Heavy metal concentrations are high in certain locations, indicating the impact of geological and anthropogenic activities. Iron is the main pollutant in the study area and also arises from the corrosiveness of pipes due to oxidation processes. Primary ion interpretations show the interplay of salt fields, anthropogenic processes, temperature-dependent reactions, and the effects of ion-exchange processes.

Acknowledgement

The authors thank the Professor and Head, Department of Geology, University of Madras, for granting permission to carry out this work in the Geology Department Lab. Authors also thank Dr. L.Elango, former Head of the Department, Department of Geology, Anna University for granting permission to use the lab facilities. We are also thankful to the anonymous referees for valuable suggestions for improving the manuscript.

Authors Contribution

The first author Ms. A.L has carried out sample collection, laboratory analysis and prepared the manuscript. The second and fourth authors Dr.M.SG and Dr. B. G have participated in the field work and interpretation of the analysed data. The third author Mr. SSP assisted in the field visits and laboratory analyses.

References

- Backman, B., Bodis, D., Lahermo, P., Rapant, S. and Tarvainen, T. (1997) Application of a groundwater contamination index in Finland and Slovakia. *Environ Geol.*, v.36, pp.55–64.
- Bhuiyan, M.A.H., Islam, M.A., Dampare, S.B., Parvez, L. and Suzuki, S. (2010) Evaluation of hazardous metal pollution in irrigation and drinking water systems in the vicinity of a coal mine area of northwestern Bangladesh. *Jour. Hazardous Mat.*, v.179, pp.1065–1077.
- BIS (Bureau of Indian Standards) (2012) Indian standard for drinking water—specification, second edition, IS 10500: 2012, Drinking Water Sectional Committee, FAD 25. New Delhi, India.
- CGWB (2009) District groundwater brochure Perambalur district. Tamil Nadu, pp.1-22.
- Chakraborti, D., Rahman, M.M., Das, B., Murrill, M., Dey, S., Mukherjee, S.C., Dhar, R.K., Biswas, B.K., Chowdhury, U.K., Roy, S. and Sorif, S. (2010) Status of groundwater arsenic contamination in Bangladesh: a 14-year study report. *Water Research*, v.44, pp.5789–5802.
- Chen, S., Fu, X. F., Gui, H. R. and Sun L. H. (2013) Multivariate statistical analysis of the hydro-geochemical characteristics for Mining groundwater: a case study from Baishan mining, northern Anhui Province, China. *Water Practice Technology*, v.8, pp.131-141.
- Chidambaram, S. (2000) Hydrogeochemical studies of groundwater in Periyar district, Tamilnadu, India, unpublished Ph.D thesis, Department of Geology, Annamalai University, Tamilnadu. p.121.
- Chidambaram, S., Karmegam, U., Prasanna, M.V., Sasidhar, P. and Vasanthavigar, M (2011) A study on hydrochemical elucidation of coastal groundwater in and around Kalpakkam region, Southern India. *Environ Earth Sci.*, v.64(5), pp.1419–1431.
- Chidambaram, S., Bala Krishna Prasad, M., Manivannan, R., Karmegam, U., Singaraja, C., Anandhan, P., Prasanna, M.V. and Manikandan, S. (2012) Environmental hydrogeochemistry and genesis of fluoride in groundwaters of Dindigul district, Tamilnadu (India). *Environmental Earth Science*, v.68, pp.333–342.
- Edet, A. E., Merkel, B. J. and Offiong, O. E. (2003) Trace element hydrochemical assessment of the Calabar Coastal Plain Aquifer, southeastern Nigeria using statistical methods. *Environ. Geol.*, v.44, pp.137-149.
- Edet, A.E. and Offiong O. E. (2002) Evaluation of water quality pollution indices for heavy metal contamination monitoring. A study case from Akpabuyo-Odukpani area, Lower Cross River Basin (southeastern Nigeria). *Geo Journal*, v.57, pp.295–304.
- Gibbs, J.R. (1970) Mechanisms controlling world water chemistry. *Science*, v.170, pp.1088–1090.
- Gomez, P., Garralón, A., Buil, B., Turrero, M.J., Sánchez, L. and De la Cruz, B. (2006) Modeling of geochemical processes related to uranium mobilization in the groundwater of a Uranium mine. *Science of the Total Environment*, v.366, pp.295-309.
- Handa B.K. (1975) Geochemistry and genesis of fluoride containing ground waters in India. *Groundwater*, v.25, pp.255-264.

- Heyden, C.J. and New, M.G. (2004) Groundwater pollution on the Zambian Copper belt: deciphering the source and the risk. *Sci. Total Environ.*, v.327, pp.17–30.
- ICMR (Indian Council of Medical Research) (2009) Nutrient requirements and recommended dietary allowances for Indians. A report of the expert group of the ICMR, Hyderabad, India, p.334.
- Javdi, A. A., Abd-Elhaid, H. F. and Farmani, R. (2011) A simulation–optimization model to control seawater intrusion in coastal aquifers using abstraction/recharge wells. *Int. Jour. Numer. Anal Meth Geomech.*, v.36, pp.1757–1779.
- Krishnakumar, S., Rammohan, V., Sahayam, J.D. and Jeevanandam, M. (2009) Assessment of groundwater quality and hydrogeochemistry of Manimuktha River basin, Tamil Nadu, India. *Environ Monit. Assess.*, v.159, pp.341–351.
- Mohan, S.V., Nithila, P. and Reddy, S. J. (1996) Estimation of heavy metal in drinking water and development of heavy metal pollution index. *Jour. Environ. Sci. Health A*, v.31, pp.283–289.
- Prasad, B. and Bose, J. M. (2001) Evaluation of the heavy metal pollution index for surface and spring water near a limestone mining area of the lower Himalayas. *Environ. Geol.* v.41, pp.183–188.
- Prasad, B. and Kumari, S. (2008) Heavy Metal Pollution Index of Ground Water of an Abandoned Open Cast Mine Filled with Fly Ash: a Case Study. *Mine Water and the Environ.*, v.27, pp.265–267
- Prasad, R. K., Mondal, N.C., Banerjee, P., Nandakumar, M.V. and Singh, V.S. (2008) Deciphering potential groundwater zone in hard rock through the application of GIS. *Environ. Geol.* v.55, pp.467–475.
- Raju, N. J., Ram, P. and Dey, S. (2009) Groundwater quality in the lower Varuna River basin, Varanasi district, Uttar Pradesh, India. *Jour. Geol. Soc. India*, v.73, pp.178–192.
- Sanchez Martos, F., Pulido-Bosch, A., Molina-Sánchez, L. and Vallejos-Izquierdo, A. (2002) Identification of the origin of salinization in groundwater using minor ions (Lower Andarax, Southeast Spain). *Sci. Total Environ.*, v.297, pp.43–58.
- Singh, R.K. (2003) Assessment of Pollution level of Aadaigaha estuary in coastal region of Maharashtra in relation to aquaculture. *Jour. Ecotoxicology and Environ. Monit.*, v.13, pp.133-240.
- Spalding, R. F., Exner, M. E. (1993) Occurrence of Nitrate in Groundwater-A Review. *Jour. Environmental Quality*, v.22, pp.392-402.
- Subramani, T., Rajmohan, N. and Elango, L. (2009) Groundwater geochemistry and identification of hydrogeochemical processes in a hard rock region, Southern India *Environ. Monit. Assess.*, v.162, pp.123-137.
- Thilagavathi, R., Thivya, C. and Chidambaram, S. (2014) Evaluation of Drinking water quality index (DWQI) and its seasonal variations in hard rock aquifers of Madurai district, Tamilnadu. *Int. Jour. Adv. Geosci.*, v.2, pp.48 -52.
- Tiwari, A.K., De Maio, M., Singh, P.K. and Mahato, M. K. (2016) Estimation of Heavy Metal Contamination in Groundwater and Development of a Heavy Metal Pollution Index by using GIS Technique. *Bull. Environ. Contam. Toxicol.*, v.96, pp.508-515.
- Tiwari, R. N. and Dubey, D. P. (2012) A study of Bauxite deposit of Tikar Plateau Rewa district, M.P. *Gond. Geol. Soc. (Special Issue)*, v.13, pp.111-118.
- Tiwari, R. N., Mishra, S. and Pandey, P. (2013) Study of major and trace elements in groundwater of Birsinghpur Area, Satna District Madhya Pradesh, India. *Int. Jour. Water Resour. Environ. Eng.*, v.5, pp.380- 386.
- Todd, D. K (2007) *Groundwater hydrology*, 3rd edn. Wiley, New York, p 347.
- UNDESA (United Nations Department of Economic and Social Affairs) (2013) *World Population Prospects. Population Division Database. Detailed indicators 2012 Revision.*
- USEP A (2000) *Supplementary Guidance for Conducting Health Risk Assessment of Chemical Mixtures.* United States Environmental Protection Agency, Washington DC.
- USEPA (1989) *Risk Assessment Guidance for Superfund, Human Health Evaluation Manual Part A, Interim Final, I,* United States Environmental Protection Agency, Washington DC (1989).
- Vigneswaran, S. and Viswanathan, C. (1995). *Water treatment process: Simple options*, New York: CRC 11 p.224.
- WHO (2003) International year of fresh water. General Assembly Resolution A/RES/55/196.
- WHO (2004) *Guidelines for drinking water quality, vol.1 Recommendations*, 3rd edn. WHO, Geneva, 515.
- WHO (2008) *Guidelines for drinking water quality 3rd edn. Incorporating the first and second agenda volume recommendations* (World Health Organizations, Geneva).
- WHO (2011) *Water and sanitation. Guidelines for drinking-water quality Wilcox LV (1955) Classification and use of irrigation waters.* USDA, circular 969, Washington, DC, USA.

Manuscript received: 25-11-2022

Manuscript accepted: 14-12-2022