

Hydrogeochemical study of shallow carbonate aquifers, Rameswaram Island, India

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Abstract Groundwater quality assessment has been carried out based on physicochemical parameters (pH, EC, TDS, CO₃, HCO₃, Cl, SO₄, PO₄, NO₂, Ca⁺², Mg⁺², Na⁺ and K⁺) and metal concentration in the Rameswaram Island from 25 bore wells. The Langelier Saturation Index of the groundwater shows positive values (63% samples) with a tendency to deposit the CaCO₃ in the majority of water samples. Scatter plot (Ca+Mg/HCO₃) suggests carbonate weathering pro-

cess, which is the main contributor of Ca²⁺, Mg²⁺ and HCO₃ ions to the water. Gibbs diagram suggests rock–water interaction dominance and evaporation dominance which are responsible for the change in the quality of water in the study area. NaCl and mixed CaNaHCO₃ facies are two main hydrogeochemical facies of groundwater. Mathematical calculations and graphical plots of geochemical data reveal that the groundwater of Rameswaram Island is influenced by natural weathering of rocks, anthropogenic activities and seawater intrusion due to over exploitation. Weathering and dissolution of carbonate and gypsum minerals also control the concentration of major ions (Ca⁺², Mg⁺², Na⁺ and K⁺) in the groundwater. The nutrient concentration of groundwater is controlled to a large extent by the fertilizers used in agricultural lands and aquaforms. Comparison of geochemical data shows that majority of the groundwater samples are suitable for drinking water and irrigation purposes.

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Introduction

Groundwater forms the common source of drinking, irrigation, and industrial purposes. However, its quality is getting deteriorated due to low rainfall and high evapotranspiration. Most of the important fresh-

water bodies are getting polluted by anthropogenic activities and natural processes thus decrease the potability of water (Dixit et al. 2005). The chemistry of groundwater depends on the number of factors which includes the nature of recharge, hydrologic gradient, residence time of groundwater in the aquifer, pollution by anthropogenic activities and rock–water interactions beneath the surface. The geochemical processes are responsible for the seasonal and spatial variation in groundwater chemistry. In addition, poor quality of water may lead to leaching of nutrient and release of metals from soil. Leached metals and nutrients are one of the major environmental concerns as high concentration of some ions in the drinking water is harmful for human health. According to Ballukraya and Ravi (1999), the raising of water table in the post-monsoon period dissolves more saline matter from the soil and increases the salinity of water after monsoon. In small islands, seawater intrusion into the aquifers is mainly due to overexploitation of groundwater. To protect the coastal aquifers from seawater intrusion, the source of saline water and mobility mechanism need to be identified for sustainable development of groundwater sources and more recharge practices along the coastal areas. The rapid recycling and repeated circulation of groundwater increase the salinity of groundwater in addition to evaporation and evapotranspiration (Nativ and Smith 1987; Rajmohan and Elango 2004). Moreover, the cations and silica are released from weathering of primary and secondary minerals (Jacks 1973; Rajmohan et al. 2000). Various authors have reported the portability of groundwater in various parts of the world (Suresh Babu et al. 2002; Samuel Obiri 2007; Malini et al. 2003; Rajmohan et al. 2000; Tyagi et al. 2009; Krishna Kumar et al. 2009; Venugopal et al. 2009). Consumption of contaminated groundwater causes health problems and diseases (Reddy and Subbarao 2001). It is necessary to assess the groundwater quality before human consumption, irrigation, and industrial purposes. The present study focuses on the groundwater quality of Rameswaram Island, Tamil Nadu, India.

Study area

The Rameswaram Island is located between the latitude from 9°15' to 9°20' N and 79°15' to 79°25' E, with an average elevation of about 10 m above

mean sea level. It covers an area of 51.8 km² (Fig. 1). It is bounded by Palk Bay in the north, Gulf of Mannar in the south, Indian main land in the west, and Bay of Bengal in the east. This region received much attention from different agencies for development activities such as tourism, fisheries, placer mineral mining and shipping. The growth of such activities requires a simultaneous strategy for the use and development of water resources. A major part of the Rameswaram Island is manifested with coral carbonate rocks which is overlain by quaternary sediments of fluvio-marine, marine facies and aeolian sand dunes. This quaternary alluvium is loose, not cemented and so acts as good groundwater reservoir. The Rameswaram Island with several ridges slope gently from west to east and is characterized by coral growth or with coral cliff/terraces along the northeast and northwest shoreline. The central part of the island consists of undulatory sand bodies. A sheet of sand covers the southwest zone of the island, while north central part of the island has a lagoon with coral growth. The island lies in semi arid belt where sporadic rainfall may occur from time to time. Sometimes, an extensive drought or with scanty rainfall may continue for several years. The island experiences tropical climatic condition with temperature ranging from 30 to 38°C. During the monsoon season, the average annual rainfall of the island is about 500 mm. Beachrocks consisting of carbonate minerals, quartz, feldspar, gypsum and heavy minerals are found on the northeastern part of the island. Tidal creeks, beaches, lagoons, beach ridges, sand dunes, mud flats and coral terraces are important geomorphological features of the study area. Agricultural activities include chilies, coconuts, groundnut, etc. Water for agricultural and drinking purposes are drawn from tanks, open wells and tube wells. The depth of the bore holes ranges from 5 to 15 m below the ground level.

Methodology

Groundwater samples were collected from 25 representative wells, which are based on the local stratigraphic units and availability of boreholes. The water samples were collected in pre-cleaned (with 1 N HCl) polyethylene bottles which are stored at 10°C for further laboratory analysis. In addition, 1 litre of water sample was collected

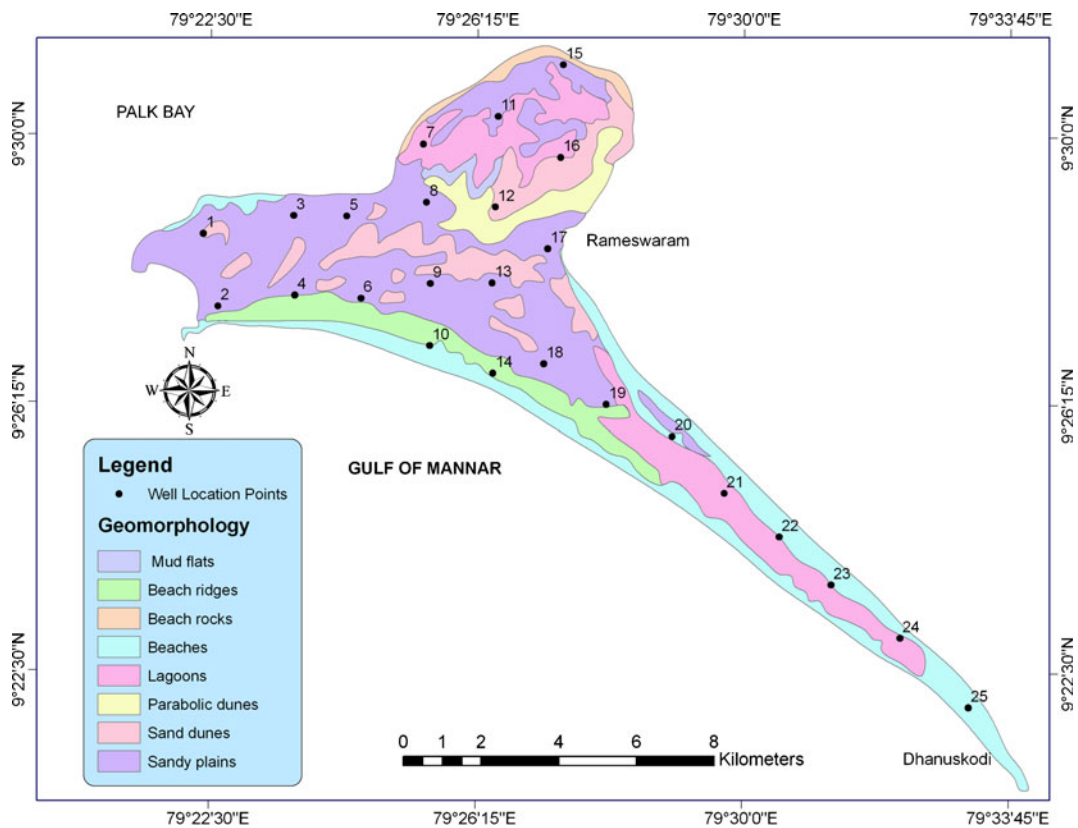


Fig. 1 Well location and geomorphology map of Rameswaram Island, Tamil Nadu, India

separately to measure pH, temperature and inorganic constituents. Trace elements concentrations were determined from separately collected, filtered and HNO₃-acidified groundwater samples. pH and temperature were measured from non-acidified water samples in the field itself using portable field analytical kits. Bicarbonate analysis was carried out using acid titration method; chloride concentration was measured by AgNO₃ titration method; sulphate by BaCl₃ method using spectrophotometer. Orthophosphate analysis was carried out using spectrophotometer-ascorbic acid method; nitrate was analyzed using cadmium column reduction method; sodium and potassium were analyzed using flame photometer; calcium and magnesium by titration method. The analytical procedures are as suggested by American Public Health Association (APHA 1995). The trace element analysis (As, Pb, Zn, Cu, Cr, Ni and Fe) were performed by IRIS INTREPID II XSP-Thermo Electron Corporation

model induced coupled plasma atomic emission spectrophotometer. The limits of detection of trace elements were 0.01 ppm for Fe, Ni, Cu, Cr, Zn, 0.02 ppm for As and 0.05 ppm for Pb.

Results and discussion

Physicochemical characteristics of groundwater

The physical parameters, major anions, cations, heavy metal concentration and coordinates are shown in Table 1. Temperature varies from 29 to 32°C, while pH values show slightly acidic to basic nature (6.7–7.3; Fig. 2a, b). The acidic nature of groundwater is probably due to the dissolution of carbonates and also the application of lime products in agriculture fields and aquaforms. The EC values range from 262 to 8,600 µS/cm with an average value of 2,033.4 µS/cm (Fig. 2c).

Table 1 Drinking water standard specifications given by WHO (1971), USEPA (2002) and ISI (1983) and statistical information of ion concentrations

Parameters	This study			WHO standard (WHO 1971)	U.S Environmental Protection Agency Secondary drinking water standard (2002)	Indian Drinking water standards (ISI, 1983)
	Minimum	Maximum	Mean			
PH	6.8	7.3	7.2	6.5–8.5 on scale	6.5–8.5 on scale	6.5–8.5 on scale
EC ($\mu\text{S}/\text{cm}$)	262	8,600	2,033.4			
CO_3^- (mg/l)	ND	ND	ND	–	–	–
HCO_3^- (mg/l)	134.2	518.5	305	–	–	–
Cl^- (mg/l)	124.1	3,341.2	670.6	200	250	250
F^- (mg/l)	BDL	2.4	0.51	0.82–1.78	2	1.5
SO_4^- (mg/l)	0.15	7.04	2.28	200	250	150
PO_4^- (mg/l)	0.08	14.05	4.61	–	0.1	–
NO_2^- (as N) (mg/l)	0.77	37.51	7.35	45	10	45
Ca^+ (mg/l)	34	436	113.07	75	–	75
Mg^+ (mg/l)	6	174	36.08	<30 if SO_4 is 250 mg/l, up to 150 mg/l if SO_4 is less than 250 mg/l	–	30
Na^+ (mg/l)	53	16,788	1,796.87	200	–	–
K^+ (mg/l)	4	141	36.07	12	–	–
Cr (mg/l)	BDL	0.05	–	0.05		
Cu (mg/l)	BDL	0.02	0.02	1.5	1.0	1.5
Fe (mg/l)	0.18	2.44	0.87	1.5	0.3	1.0
Ni (mg/l)	BDL	–	–	–		
Sr (mg/l)	1.12	42.40	8.09	–	–	–
Zn (mg/l)	0.03	0.13	0.05	15	5	15
As (mg/l)	BDL	0.05	–	0.05		
Pb (mg/l)	BDL	0.1	–	0.1		

ND Not detected, below detection limit, WHO World Health Organization, USEPA United States Environmental Protection Agency

Major cations geochemistry

The concentration of calcium and magnesium ranges from 34 to 436 mg/l and 6 to 174 mg/l respectively, with mean concentration of 113.07 and 36.08 mg/l (Fig. 3a, b). The calcium and magnesium ions in the groundwater are probably derived from limestone, dolomite and anhydrides. The lower concentration of Ca^{2+} in the study area, in comparison to Na^{2+} is due to cations exchange process that occurs naturally when seawater intrudes into the coastal aquifer system (Ahmad Zaharin et al. 2006). The sodium and potassium concentration ranges from 53 to 16,788 mg/l and 4 to 141 mg/l, with mean concentration of 1,796.87 and 36.07 mg/l, respectively (Fig. 3c, d). The large variation of Na/Cl and K/Cl ratio of the groundwater along the study area reveals that they are probably due to the seawater percolation into freshwater aquifers.

Major anions geochemistry

The bicarbonate concentration ranges from 134.2 to 518.5 mg/l with mean concentration of 305 mg/l (Fig. 4a), while chloride ranges from 124.1 to 3,341.2 mg/l with mean concentration of 670.60 mg/l (Fig. 4b). The high concentration of chloride in the study area is due to the mixture of seawater with groundwater. The low ratio of Cl/HCO_3 in the shallow well reveals that the mixing of meteoric water into groundwater, which is supported by the high ratios of Cl/HCO_3 in the coastal vicinity wells (0.5 to 10.9). The concentration of sulphate ranges from 0.15 to 7.04 mg/l with mean concentration of 2.28 mg/l (Fig. 4c). Sulphate ion concentrations are derived from gypsum bearing sedimentary rocks and from saltpan (Jeevanandam et al. 2006; Krishna Kumar et al. 2009). However, sulphate ion concentration in the present study area

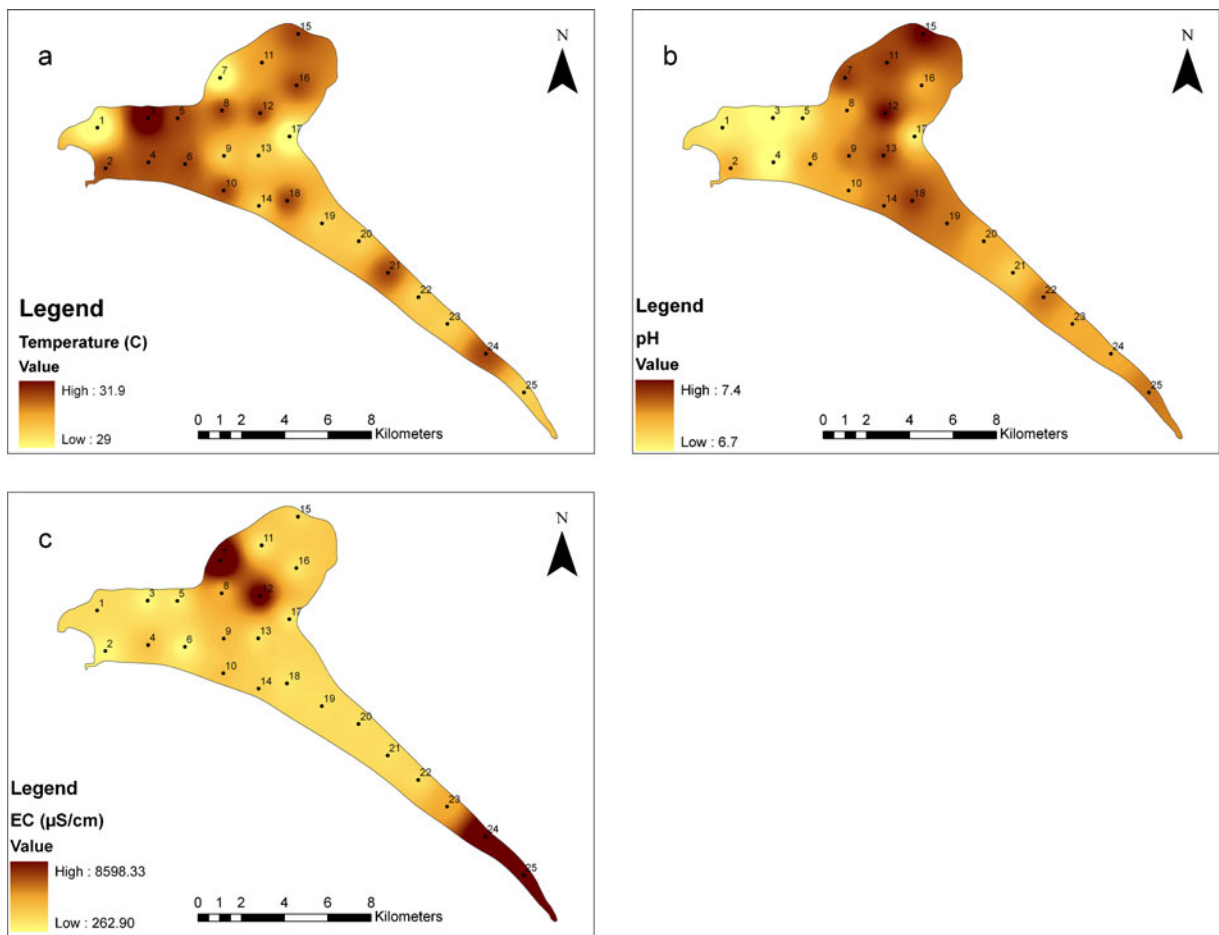


Fig. 2 a Spatial distribution of temperature in the study area. b Spatial distribution of pH values in the study area. c Spatial distribution of EC values in the study area

is lower than the suggested standards by WHO and Indian Standards Institution (ISI). The concentration of nitrate ranges from 0.77 to 37.51 mg/l with mean concentration of 7.35 mg/l (Fig. 4d). Nitrate is observed in majority of the groundwater samples of the study area. Domestic wastes, buried organic matters and wastes from aquaforms in the study area have contributed nitrate to groundwater. The concentration of phosphate ranges from 0.08 to 14.05 mg/l with mean concentration of 4.61 mg/l (Fig. 4e). Phosphate ions are present in the few samples which are collected in the vicinity of urbanization and aquaforms. The concentration of fluoride contamination ranges from below detection limit (BDL) to 2.4 mg/l. The fluoride contamination in the groundwater indicates the presence of fluoride-bearing minerals along the coastal area (Ramachandramoorthy et al. 2009; Kulasekaran and Balakrishnan 2002). Con-

sumption of fluoride-contaminated groundwater (>1.50 mg/l) causes dental fluorosis (Billings et al. 2004).

Hydrogeochemical processes

In groundwater, dissolved major cations and anions can be reconstituted by weathering of minerals associated with rock formations. In general, carbonate and silicate weathering processes are the main contributors to the major ions into the groundwater. The scatter plots of $Ca^{2+}+Mg^{2+}$ and HCO_3^- shows that majority of the sampling points fall above the $Ca+Mg=HCO_3^-$ trend line (Fig. 5). The relationship between the $Ca^{2+}+Mg^{2+}$ and HCO_3^- ions points to carbonate weathering process which forms the main contributor of Ca^{2+} , Mg^{2+} and HCO_3^- ions to the groundwater. The predominant

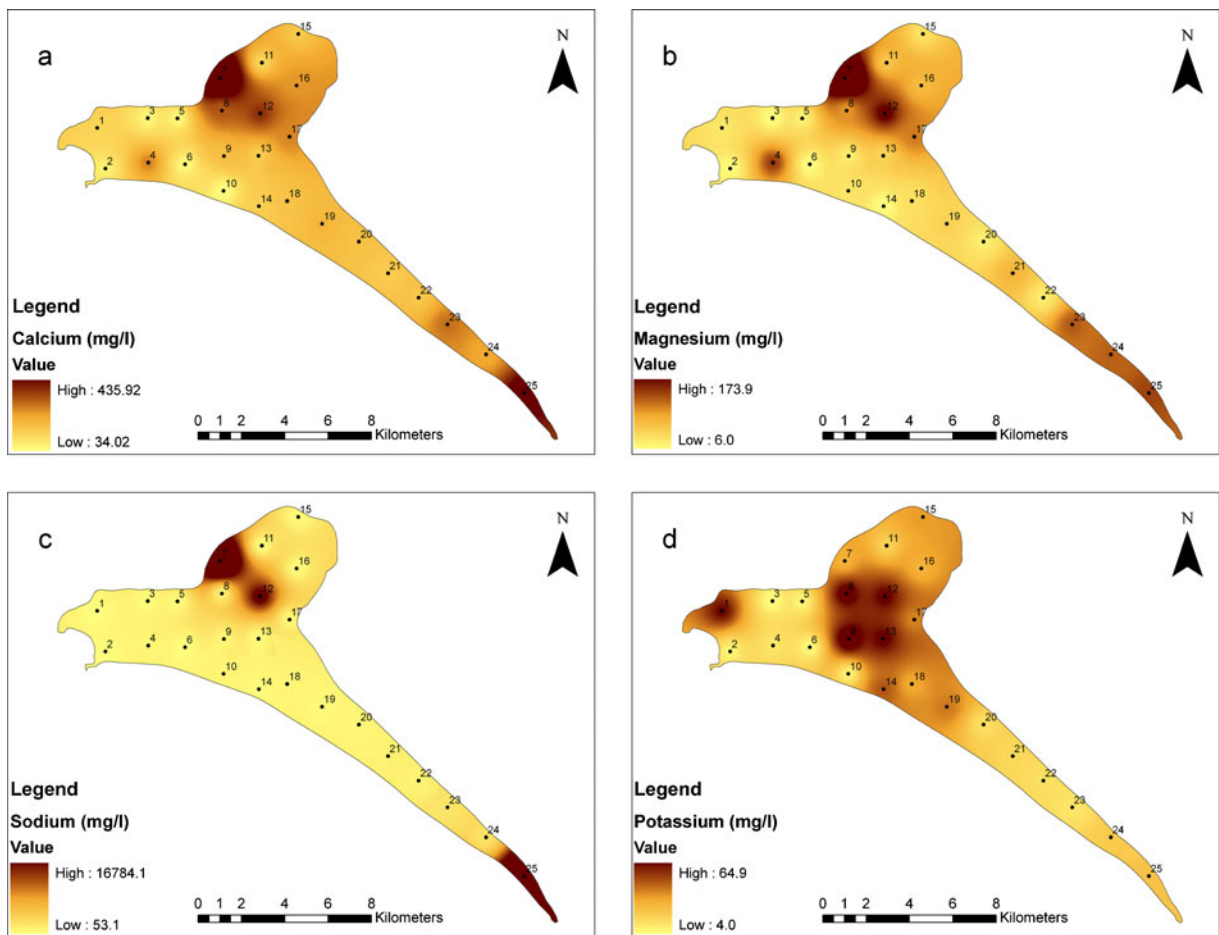


Fig. 3 a Spatial distribution of calcium ion concentration of the study area. b Spatial distribution of magnesium ion concentration of the study area. c Spatial distribution of sodium

ion concentration of the study area d Spatial distribution of potassium ion concentration of the study area

ions in the study area are $\text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{SO}_4^-$. The variations of dominant ions are due to the rate of infiltration, geological structures, and leaching processes. The dominance of magnesium and sulphate ions is due to the impact of the dissolution of epsom and gypsum from salt pans.

Langelier saturation index

Langelier Saturation Index (LSI) is a system for estimating the degree of problem with lime scale (Eq. 1). The LSI calculation is suggested by Langelier (1946). The LSI value usually lies between -3 and $+3$. If the LSI value is zero, then the water is chemically in a balance state. The positive and negative values of LSI suggest the

deposition of CaCO_3 and dissolution of CaCO_3 in water. The corrosive action of water is principally due to an excess of free CO_2 and its interaction with calcium and magnesium carbonates. The presence of carbon dioxide in the water is normally in the form of bicarbonate. The corresponding concentration of calcium, magnesium, and carbon dioxide in the groundwater prevents conversion of bicarbonate to carbonate. Low pH values suggest the presence of low alkalinity and high free carbon dioxide in the water. According to LSI equation, majority of the groundwater shows positive values, and 63% of samples have a tendency to deposit CaCO_3 during the period of sample collection. This is proved by the least concentration of Ca^{+2} and Mg^{2+} ions in the studied groundwater. The remaining groundwater samples show negative LSI values. The value

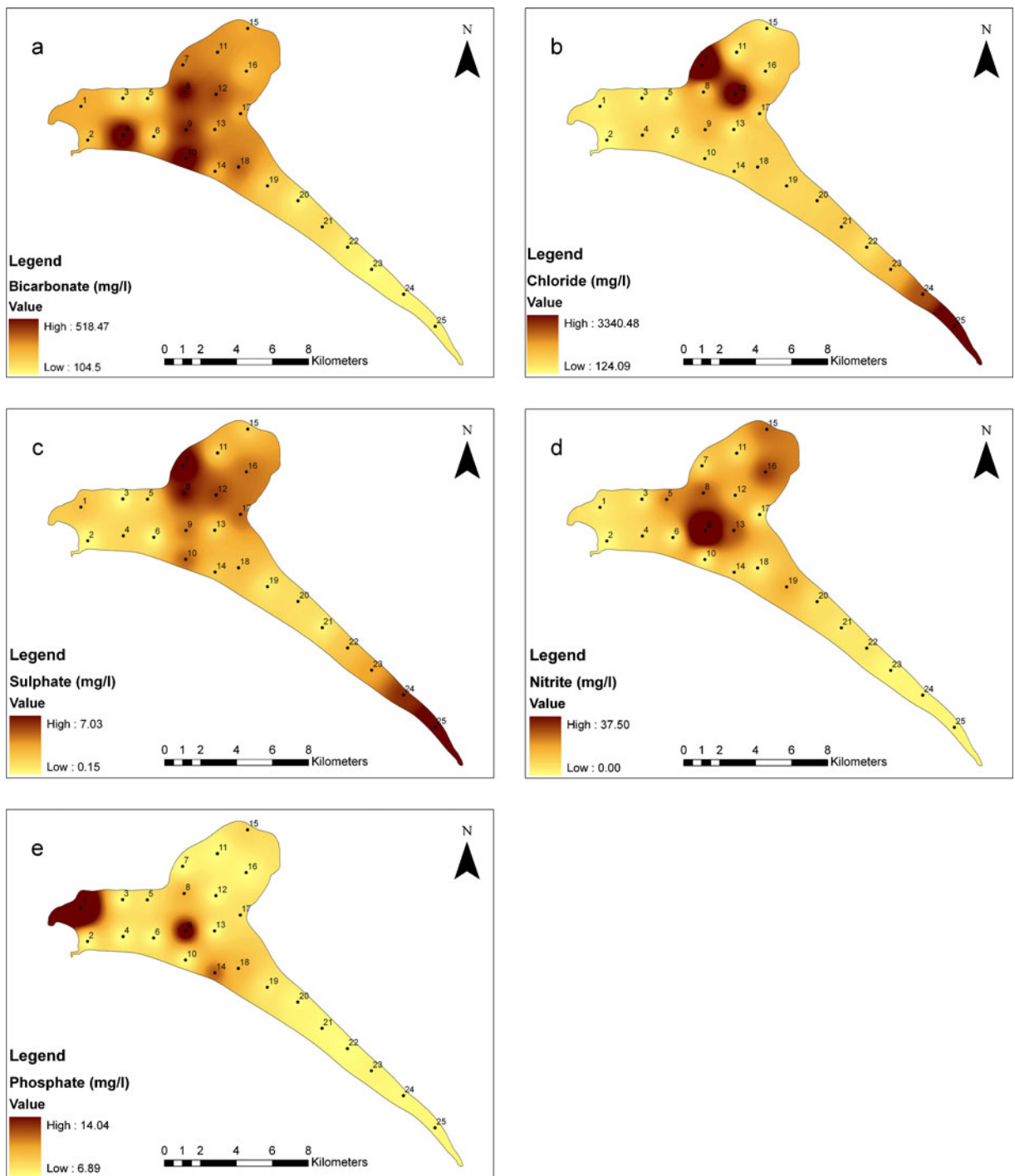


Fig. 4 a Spatial distribution of bicarbonate ion concentration of the study area. b Spatial distribution of chloride ion concentration of the study area. c Spatial distribution of sulphate ion

concentration of the study area d Spatial distribution of nitrate ion concentration of the study area. e Spatial distribution of phosphate ion concentration of the study area

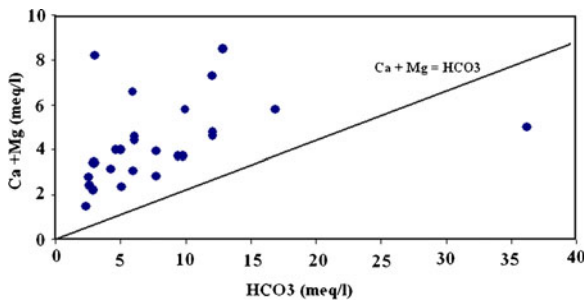


Fig. 5 Scatter diagram of (Ca^{2+}, Mg^{2+}) and HCO_3 for groundwater of Rameswaram Island, attributing carbonate weathering

accounts from slight to strong corrosive nature with a tendency to dissolve the calcium carbonate as a result of high free CO_2 content.

$$LSI = pH - pH_{(s)} \tag{1}$$

Where $pH = -\log[H^+]$,

$$pH_{(s)} = (9.3 + a + b) - (c + d),$$

$$a = \log_{10}(TDS) - 1/10,$$

$$b = -13.12 \times \log_{10}(^{\circ}C + 273) + 34.55,$$

$$c = \log_{10}(Ca^{+2} \text{ as } CaCO_3 \text{ mg/l}) - 0.4,$$

$$d = \log_{10}(\text{alkalinity as } CaCO_3 \text{ mg/l}).$$

Trace metals in groundwater

Selected trace metals (As, Pb, Zn, Cu, Cr, Ni and Fe) were studied from groundwater samples of the study area. The maximum concentration of Zn and Cu in the groundwater is 0.13 and 0.02 ppm respectively. The level of Sr in the water ranges from 1.12 to 42.4 ppm. The Indian Standards Institution (ISI 1983) has specified the iron concentration at 0.3 mg/l as desirable limits and the maximum permissible limit in the absence of an alternate source at 1.0 mg/l. Fe is detected in most of the groundwater samples and it ranges from 0.18 to 2.44 ppm. The presence of iron in the water samples is attributed to weathering of iron carbonate minerals in the aquifers and redox environment in groundwater, which may create the problem to human health. As, Pb, Cr and Ni values are below the detection limit. The accumulation of metals concentration in the groundwater aquifers of the study area is more than crustal average (Dajkumar 2005).

Except few samples, the metal concentrations in the groundwater samples below the detection limits and is probably due to low intensity of weathering processes or less residence time of water in the aquifers.

Groundwater quality classification

Groundwater quality for irrigation and drinking purposes is assessed through Gibbs equation, Wilcox, and United States Salinity Laboratory (USSL) diagrams. In general, the quality of the drinking water may change due to weathering process and anthropogenic activities.

United States Salinity Laboratory Diagram and Wilcox diagram

The classification of irrigation waters is determined by plotting the value of electrical conductivity (EC) and Sodium Absorption Ratio (SAR) on the USSL diagram (1954; Fig. 6). The salinity (with respect to the total dissolved solids) of groundwater affects the

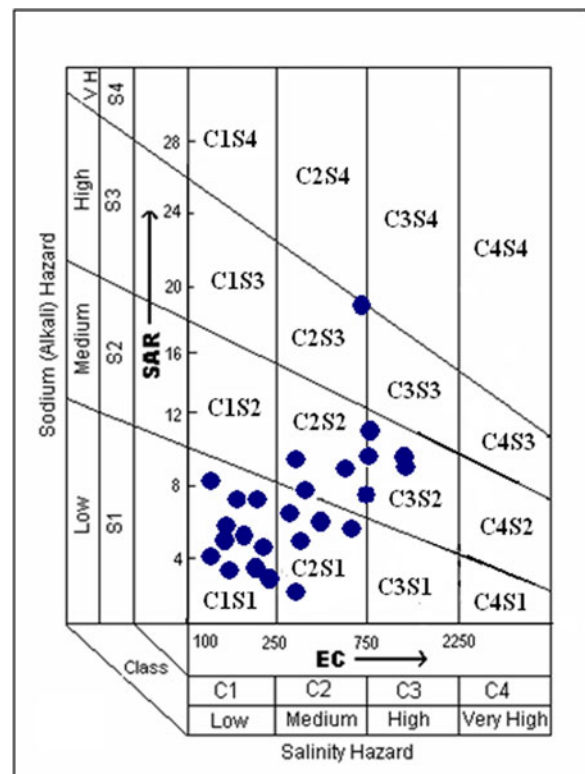


Fig. 6 Water quality ratings in relation to salinity and sodium hazard relationship plot (USSL Diagram 1954)

growth of plants directly and also affects the soil structure, permeability and aeration (Mohan et al. 2000; Jeevanandam et al. 2006). In the USSL diagram, S1, S2, S3, S4 types indicate sodium hazards and C1, C2, C3, C4 types indicate the salinity hazards. Based on this classification, majority of the samples belongs to C1S1 (low salinity with low sodium), C2S1 (medium salinity with low sodium), C2S2 (medium salinity with medium sodium), and C3S2 (high salinity with medium sodium) types. Few samples do fall under these categories due to mixing of sea water with freshwater aquifers. Wilcox (1955) proposed a method for rating irrigation waters to be used, based on electrical conductivity (EC) and sodium percentage (Na%; Fig. 7). The diagram consists of five distinct fields such as excellent to good, good to permissible, permissible to doubtful, doubtful to unsuitable and unsuitable. Majority of the samples belong to excellent to good and good to permissible limit type. Few samples fall away from

Wilcox specified fields due to the percolation of seawater into freshwater aquifers.

Gibbs and piper diagram

Gibbs diagram is relatively used to find out the relationship between water composition and aquifer lithological characteristics (Gibbs 1970; Eq. 2). The precipitation dominance, evaporation dominance and rock–water interaction dominance are the three distinct field of the Gibbs plot (Fig. 8). The rock–water interaction dominance field indicates the interaction between rock chemistry and the chemistry of the percolation waters under the subsurface.

$$\text{Gibbs ratio I (for anion)} = \frac{\text{Cl}^-}{(\text{Cl}^- + \text{HCO}_3^-)} \quad (2)$$

$$\text{Gibbs ratio II (for cation)} = \frac{\text{Na}^+ + \text{K}^{2+}}{(\text{Na}^+ + \text{K}^{2+} + \text{Ca}^{2+})}$$

Fig. 7 Specific conductance and sodium percentage (Na%) relationship for rating of irrigation water quality (Wilcox 1955)

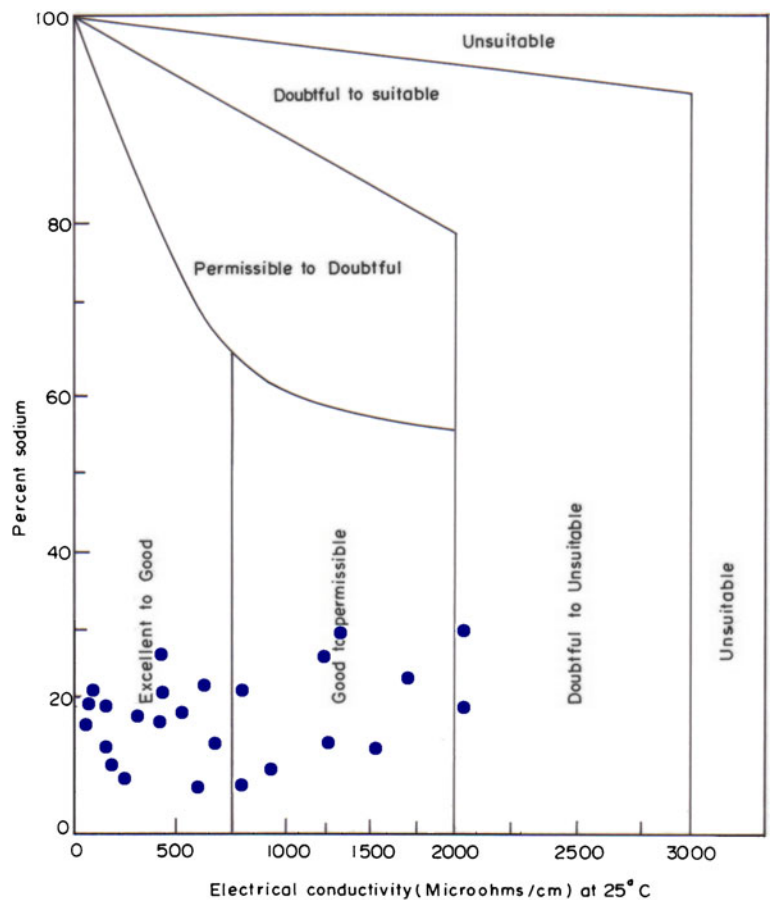
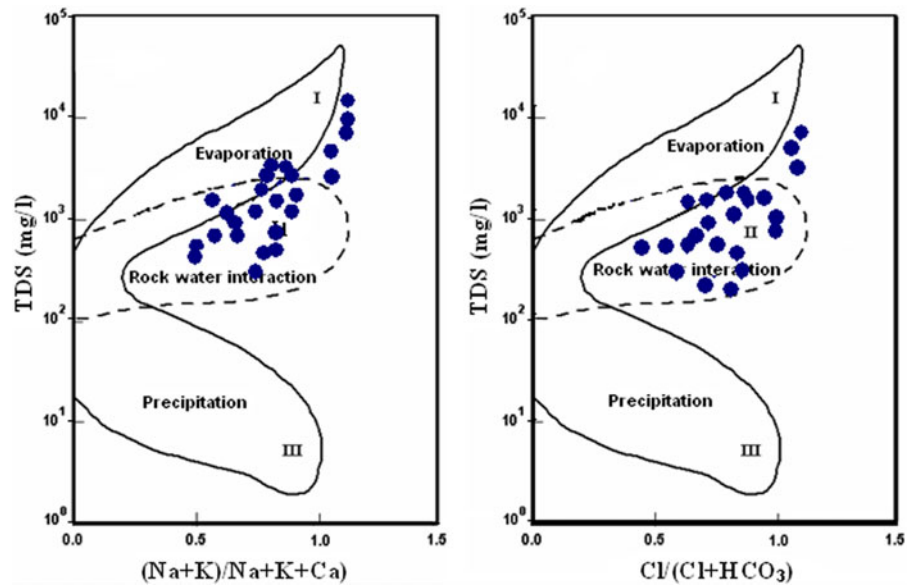


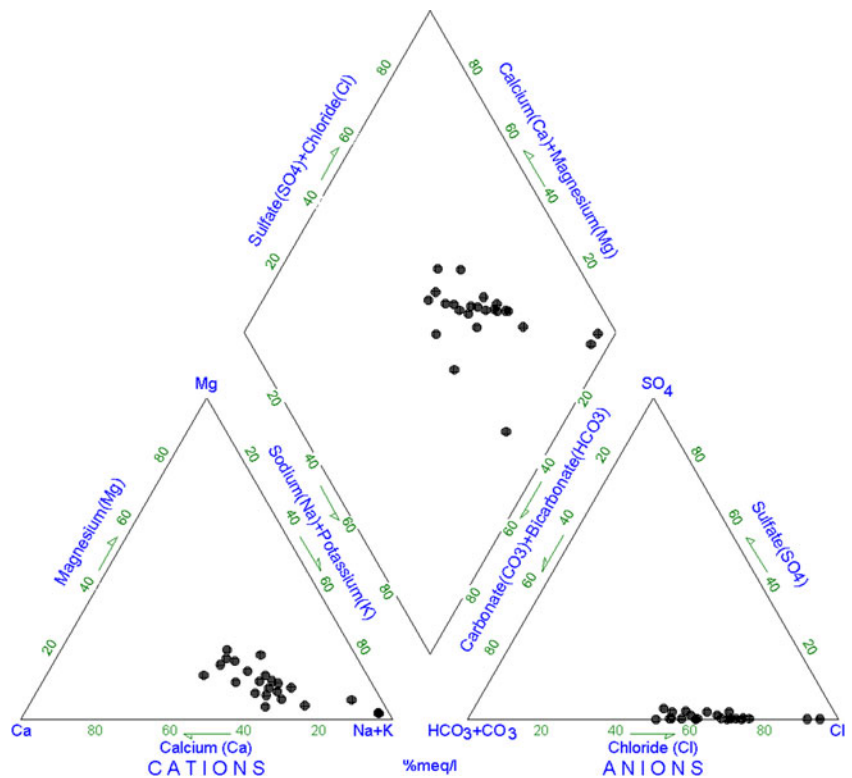
Fig. 8 Controlling mechanism diagram of groundwater chemistry (Gibbs 1970)



Whereas all the ionic concentration is expressed in milliequivalent per liter. Majority of the samples belong to rock–water interaction dominance and evaporation dominance in the field of Gibbs diagram. The geochemical evaluation in groundwater flow systems are

graphically represented by Piper diagram (Piper 1944; Fig. 9). The salt combinations of quaternary aquifer in carbonate platform are predominantly NaCl and mixed CaNaHCO₃ facies type due to leaching and dissolution process of weathered rocks and seawater intrusion.

Fig. 9 Piper trilinear diagram showing hydrogeochemical facies of groundwater



Sodium absorption ratio

Sodium concentration is an important factor in classifying the water for irrigation purposes because sodium concentration can reduce the soil permeability and soil structure (Todd 1980; Domenico and Schwartz 1990). The high soluble salt content in the water (high EC) leads to formation of saline soil and high sodium content (sodium absorption ratio, SAR) leads to formation of an alkaline soil. According to SAR calculations, majority of samples are excellent for irrigation purposes except few samples. The SAR results also suggest that the most of the water samples are satisfactory for irrigation purpose.

Permeability index

The soil permeability is affected by long-term usage of water for irrigation and other purposes. Sodium, calcium, magnesium and bicarbonate content of the groundwater are important contributor which affects the soil permeability (Mohan et al. 2000). Doneen (1964) presented water suitability classification for irrigation purpose based on the permeability index (PI) (Eq. 3).

$$PI = Na + \sqrt{(HCO_3^- / (Ca^{2+} + Mg^{2+} + Na^+))} \times 100 \quad (3)$$

Where, all the ions are represented in milliequivalent per liter. The PI values of the groundwater varying from 58.8 to 99.3 (class II) suggest that most of the samples are suitable for irrigation purposes with maximum permeability.

Residual sodium bicarbonate

The residual sodium bicarbonate (RSBC) values are calculated to determine the water quality for irrigation purposes (Eq. 4). The positive RSBC value indicates the dissolved calcium and magnesium ions which is less than that of carbonate and bicarbonate contents.

$$RSBC = HCO_3^- - Ca^{2+} \quad (4)$$

The RSBC value of the water samples were found to be below <5 meq/l, which indicates that all the samples of the study area are good for irrigation purpose based on the RSBC classification proposed by Gupta and Gupta (1987).

Conclusion

Groundwater in the study area is slightly basic in nature except a few samples. Cl, HCO₃⁻, Na and Ca are the dominant ions in the groundwater. The scatter plot diagram reveals that the carbonate weathering is the main contributor to the supply of Ca²⁺, Mg²⁺ and HCO₃⁻ ions to the groundwater. According to LSI equation, majority of the groundwater samples show positive values, and 63% of samples have a tendency to deposit CaCO₃ during the sample collection. According to ISI (1983), the trace elements concentration is below the detection limit except iron. The concentration of iron may be due to dissolution of iron-bearing minerals in the aquifers. Based on the Gibbs diagram, rock–water interaction dominance and evaporation dominance are the two main contributors to change the water quality of the study area. Wilcox diagram shows that majority of the samples fall under excellent to good category, while the remaining samples are good to permissible category. USSL graphical geochemical representation of irrigation water quality suggests that majority of the samples falls under low-to-high salinity with low-to-medium alkali hazards. According to SAR, majority of the samples are good for irrigation purposes except few. The RSBC values suggest that all the water samples are suitable for irrigation purpose. PI reveals that all the samples are good for irrigation purposes with maximum permeability. In general, the groundwater chemistry of this area is principally controlled by the mixing of seawater, precipitation, dissolution and anthropogenic activities. Reduce the over exploitation of groundwater, construction and proper maintenance of rainwater harvesting structures for recharge are helpful to preserve and improve the groundwater quality along the coastal freshwater aquifers of the study region.

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References

- APHA. (1995). *Standard methods for the examination of water and waste water (19th edn.)*. Washington D.C: American Public Health Association.
- Ahmad Zaharin, A., Abdullah, M. H., & Woog, K. K. (2006). Hydrogeochemistry of groundwater in Manukan Island Malaysia. *The Malaysian Journal of Analytical Sciences*, 11(2), 407–413.
- Ballukraya, P. N., & Ravi, R. (1999). Characterisation of groundwater in the unconfined aquifer of Chennai city, India. *Journal of the Geological Society of India*, 54, 1–11.
- Billings, R. J., Berkowitz, R. J., & Watson, G. (2004). Teeth. *Pediatrics*, 113, 1120–1127.
- Dajkumar, J.D. (2005). Genesis of beachrock formation along the southeastern coast of Tamil Nadu and its significance to sea level variations, Unpublished Ph.D thesis, Tamil University, Thanjavur.
- Dixit, S., Gupta, S. K., & Tiwari, S. (2005). Nutrients overloading of a freshwater lake in Bhopal, India. *Electronic Green Journal*, 21, 2–6.
- Domenico, P. A., & Schwartz, F. W. (1990). *Physical and chemical hydrogeology*. New York: Wiley.
- Doneen, L.D. (1964). Notes on water quality in agriculture. Published in Water Science and Engineering, Univ. California, Davis.
- Gibbs, R. J. (1970). Mechanism controlling world water chemistry. *Sciences*, 170, 795–840.
- Gupta, S. K., & Gupta, I. C. (1987). *Management of saline soils and water* (p. 399). New Delhi India: Oxford and IBH Publication. Co.
- ISI. (1983). Drinking water standard-substances or characteristic affecting the acceptability of water for domestic use. *IS, 10500*, 1–22.
- Jacks, G. (1973). Chemistry of groundwater in a district in Southern India. *Journal of Hydrology*, 18, 185–200.
- Jeevanandam, M., Kannan, R., Srinivasalu, S., & Rammohan, V. (2006). Hydrogeochemistry and groundwater quality assessment of lower part of the Ponnaiyar River Basin, Cuddalore District, South India. *Environmental Monitoring and Assessment*, 132(1), 263–274.
- Krishna Kumar, S., Ram Mohan, V., Dajkumar Sahayam, J., & Jeevanandam, M. (2009). Assessment of groundwater quality and hydrogeochemistry of Manimuktha River basin, Tamil Nadu, India. *Environmental Monitoring and Assessment*, 159(1–4), 341–351.
- Kulasekaran, A. & Balakrishnan, P. (2002). Status of fluoride in groundwater in Tamil Nadu, Chennai. Tamil Nadu Water Administrative Department.
- Langelier, W. F. (1946). Chemical equilibria in water treatment. *Journal of American Water Works Association*, 38, 169.
- Malini, S., Nagaiah, N., Paramesh, L., Venkataramaiah, P., & Balasubramanian, A. (2003). Groundwater quality around Mysore, Karnataka, India. *International Journal of Environmental Studies*, 60, 87–98.
- Mohan, R., Singh, A. K., Tripathi, J. K., & Choudhry, G. C. (2000). Hydrochemistry and quality assessment of groundwater in Naini industrial area Allahabad District, Uttar Pradesh. *Journal of the Geological Society of India*, 55, 77–89.
- Nativ, R., & Smith, A. (1987). Hydrogeology and geochemistry of the Ogallala aquifer Southern High Plains. *Journal of Hydrology*, 91, 217–253.
- Obiri, S. (2007). Determination of heavy metals in water from boreholes in Dumasi in the Wassa West District of western region of Republic of Ghana. *Environmental Monitoring and Assessment*, 130, 455–463.
- Piper, A. M. (1944). A graphical interpretation of water—analysis. *Transactions of the American Geophysical Union*, 25, 914–928.
- Rajmohan, N., & Elango, L. (2004). Identification and evolution of hydrogeochemical processes in the groundwater environment in an area of the Palar and Cheyyar River Basins, Southern India. *Environmental Geology*, 46, 47–61.
- Rajmohan, N., Elango, L., Ramachandran, S., & Natarajan, M. (2000). Major ion correlation in groundwater of Kancheepuram region, South India. *Indian Journal of Environmental Protection*, 20(3), 188–193.
- Ramachandramoorthy, T., Sivakumar, V., & Subramanian, V. (2009). A seasonal quality assessment on portability of fresh shallow aquifers along the Rameswaram-Dhanuskodi coastal tract, India. *Environmental Monitoring and Assessment*, 159(1–4), 511–520.
- Reddy, P. M., & Subbarao. (2001). Effect of industrial effluents on the groundwater regime in Vishakhapatnam. *Pollution Research*, 20(3), 383–386.
- Suresh Babu, D. S., Hindi, E. C., Da Rosa Filho, E. F., & Bittencourt, A. V. L. (2002). Characteristics of Valadares Island aquifer, Paranagua coastal Plain, Brazil. *Environmental Geology*, 41, 954–959.
- Todd, D. K. (1980). *Groundwater hydrology* (2nd ed., p. 535). New York: Wiley.
- Tyagi, S. K., Datta, P. S., & Pruthi, N. K. (2009). Hydrochemical appraisal of groundwater and its suitability in the intensive agricultural area of Muzaffarnagar district, Uttar Pradesh, India. *Environmental Geology*, 56, 901–912.
- USEPA (2002). National water quality inventory-2000 Report to Congress, U. E. P. Agency, EPA 841-R-02-001.
- USSL (1954). Diagnosis and improvement of salinity and alkaline soil. USDA Hand Book no. 60, Washington.
- Venugopal, T., Giridharan, L., Jayaprakash, M., & Periakali, P. (2009). Environmental impact assessment and seasonal variation study of the groundwater in the vicinity of River Adyar, Chennai, India. *Environmental Monitoring and Assessment*, 149, 81–97.
- WHO (1971). Guidelines for drinking- water quality, VOL. 1 Recommendations, Geneva, p130.
- Wilcox, L.V. (1955). Classification and use of irrigation waters, USDA Circular No. 969, pp19.