

A study on groundwater geochemistry and water quality in layered aquifers system of Pondicherry region, southeast India

R. Thilagavathi · S. Chidambaram ·
M. V. Prasanna · C. Thivya · C. Singaraja

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Abstract Geochemical signatures of groundwater in the Pondicherry region, south India, were determined. The coastal aquifers are fragile and this situation becomes more intense in layered aquifer systems like that of the Pondicherry region. In this region, groundwater occurs in alluvium, Lower Cuddalore, Upper Cuddalore, Tertiary, Cretaceous and mixed aquifers. The geochemical signature of groundwater in these formations was studied by collecting 93 groundwater samples. The collected samples from specific formations were analysed for physical parameters, such as electrical conductivity (EC), pH and major ion concentrations, such as Ca, Mg, Na, K, Cl, HCO_3 , PO_4 and SO_4 . The results of the analysis were interpreted with geology; the ionic concentrations in the groundwater vary spatially and temporally. The abundance of these ions are in the following order: $\text{Na} > \text{Ca} > \text{Mg} > \text{K} = \text{Cl} > \text{HCO}_3 > \text{SO}_4$. Interpretation of analytical data shows that Ca–Na and Cl– SO_4 – HCO_3 is the dominant facies in all the formations. Groundwater in the area is generally hard and fresh-brackish in most of the formations and brackish in nature in alluvium formation. The sodium absorption ratio shows that most of the samples are grouped under excellent category to good category in all the formations. The residual sodium carbonate also are in good category in all the formations. Chloro-alkaline indices reveal that the majority of samples show negative values in

all the litho units indicating the exchange of Na and K in groundwater with Mg or Ca in rock. Scholler classification of water indicates that longer residence time of water with more prominent base exchange. High EC and TDS values in certain locations of alluvial, Upper Cuddalore and Cretaceous formations prove to be unsuitable for drinking and irrigation purposes.

Keywords Groundwater · Aquifers · Geochemistry · Water quality · Pondicherry

Introduction

The emerging global freshwater crisis in terms of water quality and quantity is already felt in India. The over-drafting of groundwater in India due to the lack of surface waters during summer season has urged the need to undertake a detailed study on the quality and quantity of groundwater in different parts of India. Water quality gets modified along the course of movement of water through the hydrological cycle and through the operation of the following processes: evaporation, transpiration, selective uptake by vegetation, oxidation/reduction, cation exchange, dissociation of minerals, precipitation of secondary minerals, mixing of waters, leaching of fertilizers and manure, pollution and biological processes (Appelo and Postma 1999). The quality of water is of vital concern for mankind, since it is directly linked with human welfare. Poor quality of water adversely affects the plant growth and human health (Wilcox 1984; Thorne and Peterson 1954; US Salinity Laboratory Staff 1954; Holden 1971; Todd 1980; ISI 1983; WHO 1984; Hem 1991; Karanth 1997). Groundwater quality data give important clues to the geologic history of rocks and indications of

R. Thilagavathi · S. Chidambaram · C. Thivya · C. Singaraja
Department of Earth Sciences, Annamalai University,
Annamalai Nagar, Chidambaram 608002, India

M. V. Prasanna (✉)
Department of Applied Geology, School of Engineering and
Science, Curtin University, Sarawak Campus, CDT 250,
98009 Miri, Sarawak, Malaysia
e-mail: geoprasanna@gmail.com

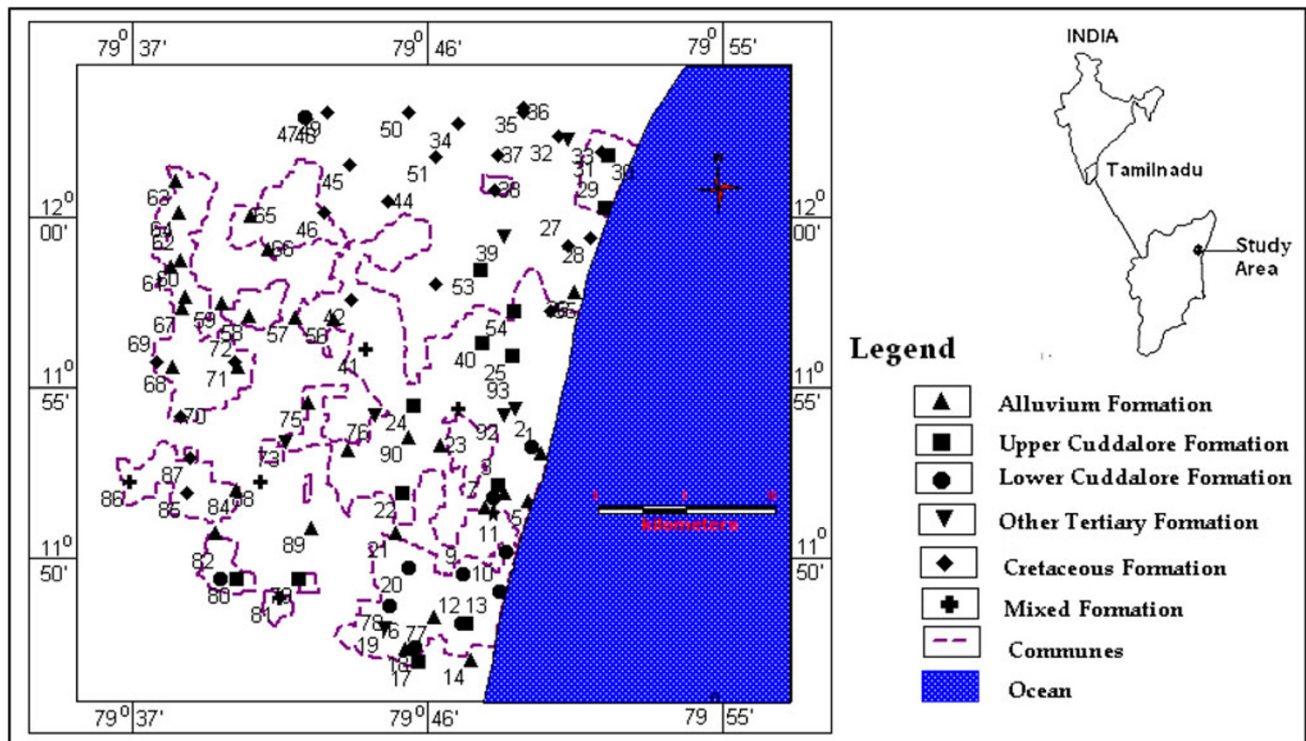


Fig. 1 Location map of the study area along with the water sampling points

groundwater recharge, movement and storage (Walton 1970). The knowledge of hydrochemistry is essential to determine the origin of chemical composition of groundwater (Zaporozec 1972). The hydrology and geochemistry of waters have been further discussed in the classic works of Stumm and Morgan (1996), Hem (1991), Drever (1988) and Domenico and Schwartz (1998). Determination of physical, chemical and bacteriological quality of water is essential for assessing its suitability for various purposes like drinking, domestic, agricultural and industrial uses. A number of studies on groundwater quality with respect to drinking and irrigation purposes have been carried out in different parts of India (Durvey et al. 1997; Agarwal and Jagetia 1997; Niranjana Babu et al. 1997; Subba Rao et al. 1999; Majumdar and Gupta 2000; Dasgupta and Purohit 2001; Khurshid et al. 2002; Sujatha and Reddy 2003; Pulle et al. 2005; Hussain et al. 2005; Sunitha et al. 2005; Subba Rao 2006). The study area is predominantly an agricultural zone with dense agricultural activities and also located near the coastal region. The majority of the people in this region depend on agriculture (i.e. cultivators and agricultural labourers). Both for drinking and irrigation purposes, substantial amount of groundwater is used in this area. Hence, this study forms the baseline attempt on the geochemistry of sub-surface water, impact of salt water intrusion and suitability for drinking and agricultural purposes in the study area.

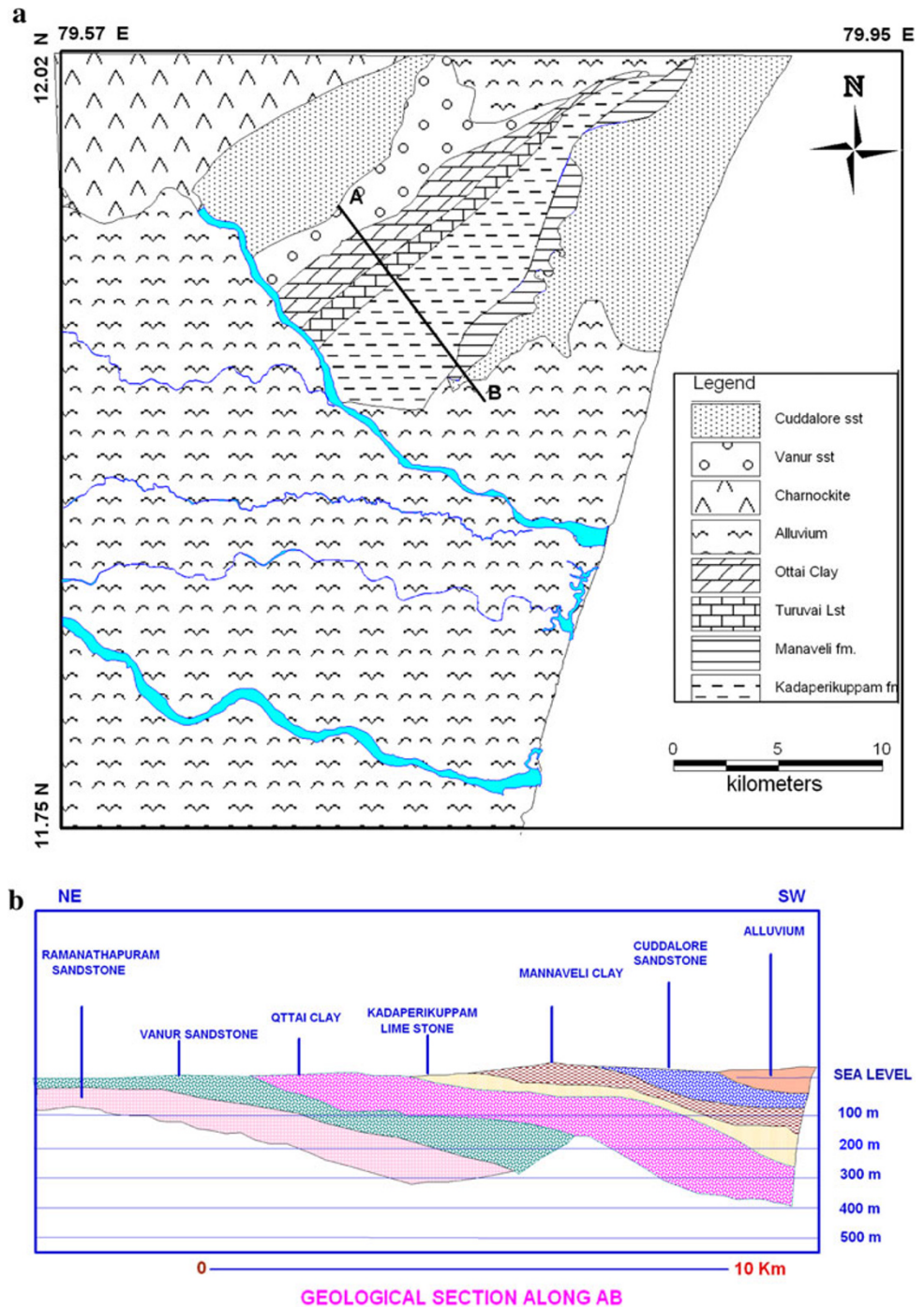
Physiography and geomorphology of the study area

Pondicherry region is located on the east coast of India, forming enclaves within the Cuddalore District of Tamilnadu. It is surrounded by northern latitudes $11^{\circ}45'$ – $12^{\circ}03'$ and eastern longitudes $79^{\circ}37'$ – $79^{\circ}53'$ (Fig. 1). The region is bounded on the east by the Bay of Bengal and on the remaining sides by Cuddalore District. The Pondicherry region is a flat peneplain with an average elevation of about 15 m above MSL. The terrain becomes a little undulating with prominent high grounds varying from 30 to 45 m above mean sea level (MSL) towards interior northwest and northeastern parts of the region. Three major physiographic units are generally observed, namely (1) coastal plain, (2) alluvial plain and (3) uplands. There are two major rivers draining the Pondicherry region, namely the Gingee River in the north and Ponnaiyar River in the south. The Gingee River runs for 34 km in the region before joining the Bay of Bengal. The mean monthly temperature ranges between 22 and 33 °C. The average annual rainfall at Pondicherry is 1,254.4 mm (CGWB 1993).

Geology of the study area

The entire area is covered by sedimentary formations ranging in age from Cretaceous to recent (Fig. 2a, b). The geological succession of the region is given in Table 1.

Fig. 2 **a** Geology map of the study area (after Pethaperumal 2010). **b** Cross section along the line AB in **a** (after Pethaperumal 2010)



Cretaceous aquifers

a) Ramanathapuram and Vanur aquifers

They occur in the northwestern part of the Pondicherry region and are encountered in boreholes drilled in the major part of the region. The aquifers of this formation include sands and calcareous sandstones. They are coarse grained in the western part and graded into finer facies towards east and northeast. The thickness of these aquifers ranges between 38 and 92 m.

Groundwater occurs under confined conditions, and the piezometric head at present is about 20 to 60 m bgl. The depth of the tube wells tapping these aquifers ranges between 65 m in the NW and 300 m in the NE of Pondicherry region. The yield of the tube wells tapping these aquifers ranges between 120 and 700 lpm. The investigation carried out reveals that the transmissivity value of these aquifers ranges between 92 and 1,925 m²/day. The storage coefficient value ranges between 2.93×10^{-5} and 1.36×10^{-4} .

Table 1 Geological succession of the study area (CGWB 1993)

Era	Period	Formation	Lithology
Quarternary	Recent	Alluvium	Sands, clays, silts, kankar, and gravels
Tertiary	Mio-Pliocene	Cuddalore	Sandstone, pebbly and gravelly and coarse grained with minor clays and silt stones and thin seams of lignite
Unconformity			
Tertiary	Palaeocene	Manaveli	Yellow and yellowish brown, gray calcareous siltstone and claystone, and shale with thin bands of limestone
Tertiary	Palaeocene	Kadapeperikuppam	Yellowish white to dirty white, sandy, hard fossiliferous limestone, calcareous sandstone and clay
Unconformity			
Mesozoic	Upper Cretaceous	Turuvai limestone	Highly fossiliferous limestone, conglomeritic at places, calcareous sandstone, and clays
Mesozoic	Upper Cretaceous	Ottai claystone	Greyish to greyish green claystones, siltstone with thin bands of sandy limestone and fine-grained calcareous sandstone.
Mesozoic	Upper Cretaceous	Vanur sandstone	Quartzose sandstone, hard coarse grained, occasionally felspathic or calcareous with minor clays
Mesozoic	Lower Cretaceous	Ramanathapuram (unexposed)	Black carbonaceous, silty clays and fine- to medium-grained sands with bands of lignite and sandstone, medium to coarse grained
Unconformity			
Archaean		Eastern Ghats complex	Charnockite and biotite hornblende gneisses

b) Ottai aquifers

The Upper Cretaceous Ottai Formations are constituted mainly by clay stone. The water-bearing property of Ottai aquifers is chiefly dependent on the few bands of fine-grained sandstone and limestone occurring locally at deeper depths and, as a result, yields meagre to moderate quantity of water. The thickness of this aquifer varies from 42 to 56 m and the yield of the wells ranges between 120 and 600 lpm with drawdown varying from 6.6 to 25 m.

Tertiary aquifers

a) The Manaveli Formation of Palaeocene is mainly an aquitard and the localized granular zones do not provide any appreciable yield. Another unit of this group, namely the Kadapperikuppam Formation, contains some productive aquifers. The thickness of this aquifer shows wide lateral and vertical variations. Amongst Tertiary aquifers, the Cuddalore sandstones of Mio-Pliocene age constitute the most potential aquifers.

b) Kadapperikuppam Aquifers

The aquifers of this group are constituted by fine-grained sandstones and give moderate to good yield as seen around Sedarapet, Pillaiyarkuppam and further northeast. The thickness of aquifer ranges between 52 and 90 m in the areas south of Gingee River, whereas in the areas the north of Gingee River, it is between 13 and 37 m. Groundwater occurs under un-confined condition. The investigation

carried out reveals a field permeability of 3 m/day in the areas to the south of Gingee River, whereas towards north of Gingee River it is around 0.8 m/day.

c) Cuddalore sandstone aquifers

The Cuddalore Sandstones (Upper Tertiary), comprising sandstones and gravels, occupy an extensive area in the region. The thickness of this aquifer in Ozhukarai that communes with the north of Gingee River ranges between 20 and 66 m, and the maximum thickness of 245 m is encountered in Bahour commune in the southern part of the region. The yield of the tube wells tapping this aquifer ranges between 200 and 3,000 lpm with drawdown varying from 5 to 10 m. The piezometric level in this aquifer ranges between 10 and 25 m bgl. The investigation carried out reveals that the average transmissivity values of these aquifers are around 2,000 m²/day. The storage coefficient value ranges between 9.583×10^{-5} and 8.9×10^{-4} .

Alluvial aquifer

Sands and gravels constitute the alluvial aquifer. Alluvial deposits occupy nearly three-fourths of the study area. These aquifers form the most potential shallow aquifer system of the study area, with thickness ranging between 5 and 34 m. Thick alluvial aquifers occur in the area bordered by Thirukanji, Odiyampet, Thavalakuppam, Villianur, Mangalam and Sathamangalam. Groundwater occurs

in this aquifer under un-confined to semi-confined condition. The depth of the tube wells tapping this aquifer ranges between 25 and 50 m bgl. The average annual fluctuation is around 7.50 m. The studies (CGWB 1993) indicate that the transmissivity values of the aquifers in the west are 275.4 m²/day at Madukarai and 770 m²/day at Thirukanji in the east.

Hydrogeology

As mentioned earlier, the sedimentary formations occur in almost the entire region and are represented by Cretaceous, Palaeocene, Mio-Pliocene and Quaternary formations. Groundwater occurs in these formations both under water table as well as under confined conditions and is developed by means of dug wells, dug cum borewells and tube wells.

Methodology

From borewells, 93 groundwater samples were collected in order to cover different litho units in the study area [alluvium (31), Tertiary (Upper Cuddalore sandstone) (15), Tertiary (Lower Cuddalore sandstone) (15), Other Tertiary (7), Cretaceous (25) and mixed (5)] (Fig. 1). The samples were analysed using standard procedures (APHA 1998). Major cations such as Ca and Mg were analysed by titrimetry, Na and K by flame photometer (Elico CL 378), major anions Cl and HCO₃ by titrimetry, and SO₄, PO₄ and H₄SiO₄ by spectrophotometer (SL 171 minispec). EC and pH were determined in the field itself using electrode (Thermo). The total cation (Tz⁺) and total anion (Tz⁻)

balance (Domenico and Schwartz 1998; Freeze and Cherry, 1979) is considered to show the ionic balance error percentage. The error percentage in the samples ranged from ±1 to ±10 %.

Results and discussion

Maximum and minimum values for the chemical composition of groundwater is given in Table 2, compared with WHO standards. The abundance of ions is in the following order: Na > Ca > Mg > K = Cl > HCO₃ > SO₄.

Hydrochemical facies

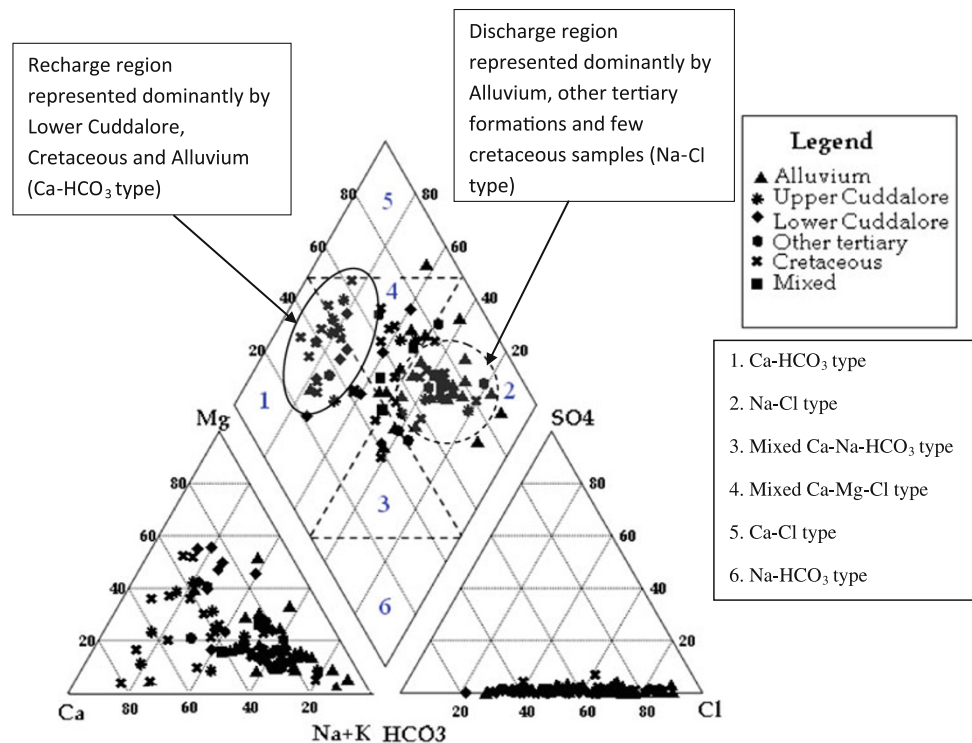
Piper diagrams (Piper 1953) are drawn by plotting the proportions (in equivalents) of the major cations (Ca²⁺, Mg²⁺, Na⁺+K⁺) on one triangular diagram, the proportions of the major anions (CO₃⁻ + HCO₃⁻, Cl⁻, SO₄²⁻) on another, and combining the information from the two triangles on a quadrilateral. The position of this plotting indicates the relative composition of groundwater in terms of the cation–anion pairs that correspond to four vertices of the field. The geochemical evolution can be understood from the Piper plot (Fig. 3), which has been divided into six sub-fields, viz. 1 (Ca–HCO₃ type); 2 (Na–Cl type); 3 (mixed Ca–Na–HCO₃ type); 4 (mixed Ca–Mg–Cl type); 5 (Ca–Cl type) and 6 (Na–HCO₃ type). The groundwater samples were collected from different formations like, Cretaceous, Tertiary and alluvium. Hence, it is presumed that the samples reveal the characters of the same term ‘hydrosome’ which is analogous to the stratigraphic concept ‘lithosome’ (Krumbein and Sloss 1963). Within a given hydrosome, the

Table 2 Maximum and minimum values of the chemical composition of groundwater samples

Parameters	Alluvium (n = 31)	Tertiary			Cretaceous (n = 25)	Mixed (n = 5)	WHO 2004
		Lower Cuddalore (n = 13)	Upper Cuddalore (n = 13)	Other Tertiary (n = 7)			
EC	334–3,310 (19)	321–3,250 (1)	270–1,432 (2)	562–1,571 (1)	340–3,127 (7)	810–2,795(1)	1,400
pH	6.6–7.8	6.6–7.82	6.22–7.65	6.77–7.71	6.24–7.84	7.02–7.65	6.5–8.5
TDS	241–2,250 (18)	205–2,190 (3)	211–993	444–1,054 (1)	234–2,376 (4)	518–1,905 (3)	500–1,000
Ca	12–104 (1)	28–88	16–112 (1)	32–72	20–172 (3)	28–64	100
Mg	7.2–62.4 (1)	0–33	7.2–48	12–28.8	2.4–45	14–26	50
Na	20–517 (12)	7–567 (1)	12–146	27–389 (1)	6.8–550 (3)	67–176	200
K	0.1–47 (2)	0–18	0–8	0.2–4.8	0.1–16.9	0–11	20
HCO ₃	73.2–1,475.8 (4)	73–402.6 (1)	85.4–268.4	109–305	73–366	170–268	125–350
SO ₄	0–28	0–11	0–4	0.04–9.2	0.4–44	2.4–13.6	250
Cl	35–797 (23)	53–744 (3)	26–389 (2)	70–602 (2)	53–904 (7)	88–390 (2)	250

All the values are in mg/L except pH and EC in µs/cm; numbers within the bracket represent the number of samples beyond the WHO limit

Fig. 3 Piper facies diagram for groundwater samples



chemical composition of water varies in time and space due to changes in recharge composition and flow patterns, and due to chemical processes between the water and the porous medium. Such variations in chemical character are used to subdivide a hydrosome into characteristic zones, or 'hydrochemical facies', a term introduced by Back (1960).

In alluvium formation, samples are clustered in the fields of 2, 3 and 4, and the majority of the samples are concentrated in the Na–Cl type (Fig. 3), indicating the saline nature in the groundwater (Prasanna et al. 2010). Strong quality fluctuations are induced mainly by cyclic atmospheric and biological changes, to a very stable water quality and by longitudinal and transversal dispersion (Stuyfzand 1993). Equilibrium between the exchange complex of the porous medium and its interstitial water to ion exchange and site reactions was noted during and after displacement by another hydrosome (Versluys 1931; Stuyfzand 1992). A similar process happens when fresh dune water intrudes into a coastal aquifer containing salt water. In Tertiary and Lower Cuddalore Formation, the dominant fields are 1, 2 and 4, and the majority of the samples are concentrated in Ca–HCO₃ facies indicating the dominance of freshwater recharge into the aquifers. In Upper Cuddalore Formation, samples mainly fall in the fields of 1, 2 and 4. The same trend was followed in the Cretaceous formation (Fig. 2), and most of the samples fall in the Ca–HCO₃ facies indicating the dominance of freshwater recharge. In mixed aquifer, the samples are of Ca–HCO₃ and Na–Cl types. Stuyfzand (1999) points out that fresh to brackish or

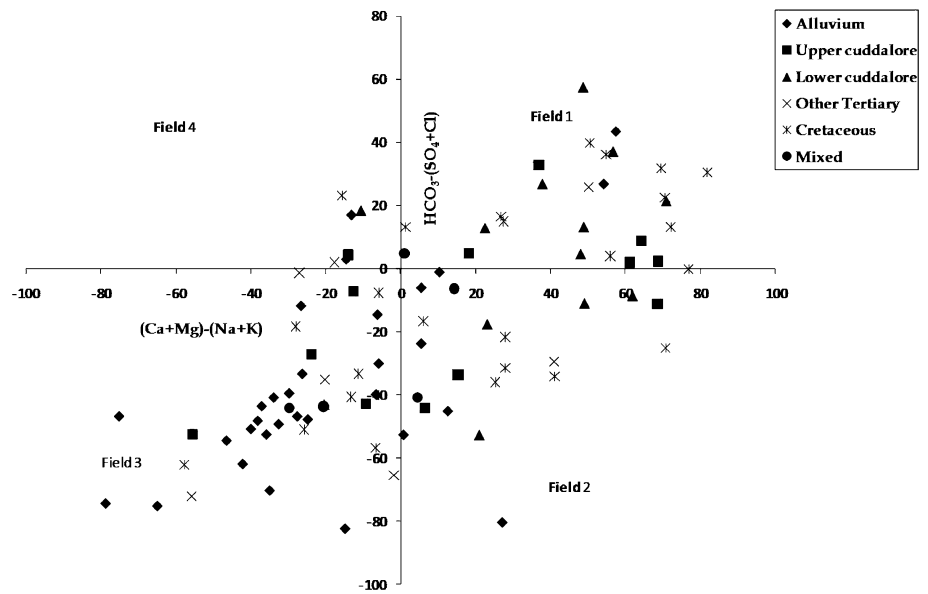
saline water occurs by hydrodynamic dispersion across the boundaries of adjacent hydrosomes or by continued evapotranspiration. The latter may lead to evolution lines described by Hardie and Eugster (1978) and Jankowski and Jacobson (1989).

Shipovalov (1984) recognizes three types of hydrochemical zones on a global scale: (1) horizontal or latitudinal zonation (2) vertical zonation and (3) altitudinal zonation. The study area is dominantly coastal alluvium with lesser variation in the topography; more over, the samples are collected with respect to formations. Hence, the horizontal zonation of geochemical facies with respect to formation will provide us the information about the variation in the geochemistry along its flow path. In general, a gradual increase of the mineralization of groundwater and shift from the dominant anion HCO₃ via SO₄ to Cl are observed in waters moving from shallow to greater depth, due to decreasing groundwater circulation and increasing water–rock interaction. The decreasing flushing rate of the aquifer system with meteoric water probably is the most dominant factor, because of its major impact on each of Shipovalov's zones.

Hydrogeochemical process evaluation

A hydrochemical diagram proposed by (Chadha 1999) has been applied in this study to interpret the hydrochemical processes occurring in the study area. The same procedure was successfully applied by (Karmegam et al. 2010;

Fig. 4 Chadda's geochemical process evolution plot



Vandenbohede et al. 2010) in a coastal aquifer to determine the evolution of two different hydrogeochemical processes. Data were converted to percentage reaction values (milli-equivalent percentages) and expressed as the difference between alkaline earths (Ca + Mg) and alkali metals (Na + K) for cations, and the difference between weak acidic anions ($HCO_3^- + CO_3^{2-}$) and strong acidic anions ($Cl^- + SO_4^{2-}$). The hydrochemical processes suggested by Chadha (1999) are indicated in each of the four quadrants of the graph. These are broadly summarized as:

- Field 1: Ca– HCO_3^- type of recharging waters
- Field 2: Ca–Mg–Cl type of reverse ion-exchange waters
- Field 3: Na–Cl type of end-member waters (seawater)
- Field 4: Na– HCO_3^- type of base ion-exchange waters

The resultant diagram is shown in Fig. 4 and the majority of alluvium samples fall in Field 3 (Na–Cl) suggesting that the waters show typical seawater mixing and are mostly constrained to the coastal areas. Most of the

Upper and Lower Cuddalore and Cretaceous samples are in Field 1 (recharging water). When water enters into the ground from the surface, it carries dissolved carbonate in the form of HCO_3^- and the geochemically mobile Ca. Few samples in all the formations fall in Field 2 (reverse ion exchange), revealing that the waters are less easily defined and less common, but represent groundwater where Ca + Mg is in excess to Na + K either due to the preferential release of Ca and Mg from mineral weathering of exposed bedrock or possibly reverse base cation-exchange reactions of Ca + Mg into solution and subsequent adsorption of Na into mineral surfaces (Karmegam et al. 2010). Field 4 (Na– HCO_3^-) waters, which is less prominent in the study area.

Seawater has distinct ionic ratios, as presented in Table 3 (Vengosh et al. 2002; Vengosh and Rosenthal 1994). Relatively, 29 % of alluvium and Other Tertiary samples show the high Na^+/Cl^- and $Ca^{2+}/(HCO_3^- + SO_4^{2-})$ ratios (greater than unity) (Vengosh

Table 3 Comparative ionic ratio of potential salinization sources with present groundwater compositions

Parameter	Seawater intrusion	Alluvium (n = 31) (%)	Tertiary Upper Cuddalore (n = 13) (%)	Tertiary Lower Cuddalore (n = 13) (%)	Other Tertiary (n = 7) (%)	Cretaceous (n = 25) (%)	Mixed (n = 5) (%)
Na^+/Cl^-	0.86–1 ^a	29	7.6	7.6	28.5	20	20
SO_4^{2-}/Cl^-	0.05 ^{a,c}	–	–	–	–	8	–
K^+/Cl^-	0.019	–	–	–	–	–	–
Mg^{2+}/Ca^{2+}	>5 ^b	–	–	–	–	–	–
$Ca^{2+}/(HCO_3^- + SO_4^{2-})$	0.35–1	35.4	69.2	30.7	42.8	68	60

^a Vengosh and Rosenthal (1994)

^b Vengosh and Ben-Zvi (1994)

^c Vengosh et al. (1994)

et al. 2002). Each probable source of salinization is characterized by a distinguishable chemistry and well-known ionic ratios. For example, if seawater intrusion is expected to be the only source of salinization, then the Mg^{2+}/Ca^{2+} ionic ratio will be greater than 5. The Mg^{2+}/Ca^{2+} ionic ratio greater than 5 is a direct indicator of seawater contamination (Metcafe and Eddy 2000). Likewise, seawater and seawater diluted with freshwater have distinguished geochemical characteristics (Metcafe and Eddy 2000). The value of these ratios in the study area is greater than unity and may be due to deep saline upconing or ion-exchange process.

Modification of the geochemical characteristics of these saline waters is caused by water–rock interaction in which three possible mechanisms may be involved: (1) base-exchange reactions with clay minerals (Vengosh et al. 1994); (2) adsorption onto clay minerals; and (3) carbonate dissolution–precipitation (Vengosh et al. 1994; Ghabayen et al. 2006).

The improper treatment and disposal of domestic wastewater could be one of the major sources of salinization in the coastal aquifers (Metcafe and Eddy 2000). The chemical character of polluted water with urban wastewater or from the reuse of treated wastewater is very distinguishable. Sewage effluent has a relatively high Na^+/Cl^- ratio (greater than unity) and comparatively high SO_4^{2-}/Cl^- ratio (0.09) (Ghabayen et al. 2006). These ratios are attributed to applications of Na–Cl salts and domestic wastewater characteristics. Agriculture return flows have a distinctive chemical composition relative to other salinization sources. This water is characterized by high SO_4^{2-}/Cl^- ratios, and 8 % in Cretaceous shows much greater than 0.05 (Vengosh et al. 2002). A high SO_4^{2-}/Cl^- ratio is attributed to the application of gypsum fertilizers (Vengosh et al. 2002). Lesser values of K/Cl and SO_4/Cl^- are noted in the deeper aquifers, indicating relatively lesser anthropogenic impact.

The comparison of the Na^+/Cl^- ratio shows that freshwater mixing with seawater is responsible for high salinity in the area (Table 3). Migration of anthropogenic impact or dissolution and leaching of precipitated salts is also evident by the high SO_4^{2-}/Cl^- ratio in Cretaceous aquifers, which substantiate that there is some impact from agriculture return flows. It is also true in the background that salt patches can be easily observed in the area at the time of high evapotranspiration. Nevertheless, this temporary phase has been released and once again inland salinity seems to be the governing factor. K^+ seems to be contributed from anthropogenic sources; this finding gets strengthened by the comparison of K^+/Cl^- ratio that was found to be quite higher and equivalent to wastewater infiltration. $Ca^{2+}/(HCO_3^- + SO_4^{2-})$ ratio depicts that the seawater intrusion process is mostly responsible (Kumar et al. 2006).

Figure 5 shows the relationship of pH to $(Ca^{2+} + Mg^{2+})/HCO_3^-$ ratio. pH determines the nature of carbonate

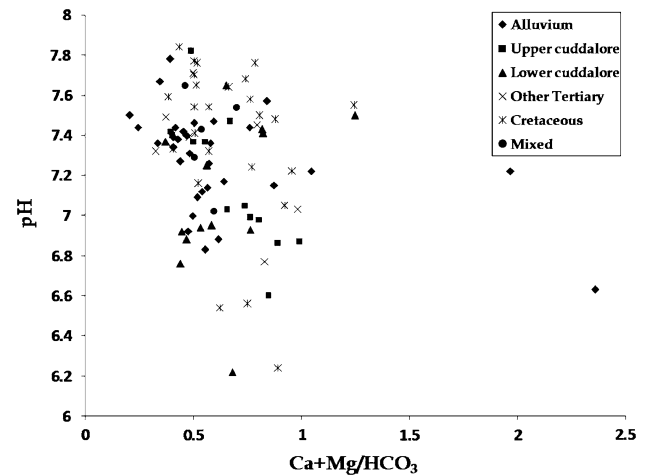
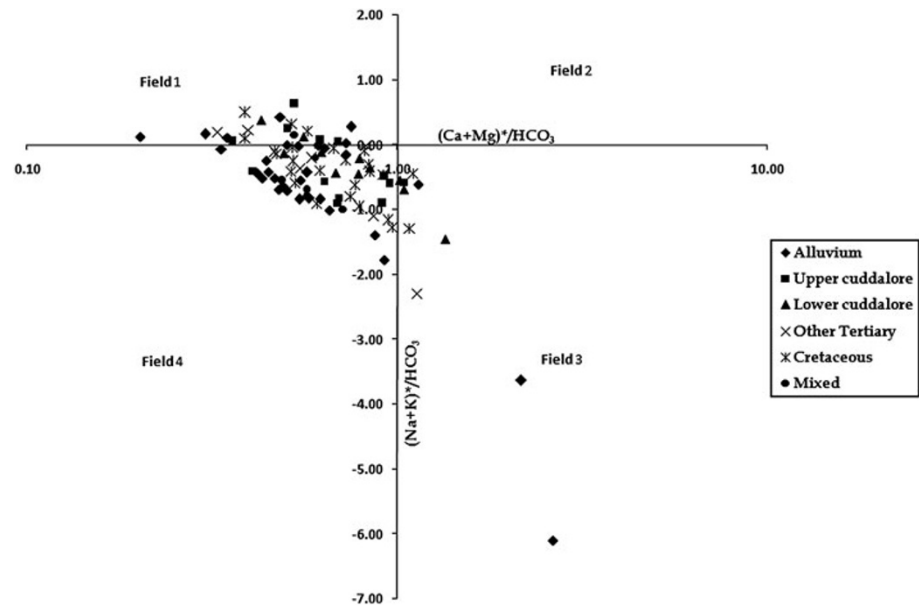


Fig. 5 Relationship of $(Ca + Mg)/HCO_3$ ratio to pH

present in water as $H_2CO_3^-$, HCO_3^- , and CO_3^- , in acidic to alkaline pH conditions. The pH of the study area ranges from acidic to alkaline condition. The gradual increase of pH might be due to the higher amount of H^+ availability in all the aquifers. This may be due to nonavailability of neutralizing ions or strong ion-exchange complex by cation with clay minerals. This process also helps us to evaluate the H^+ ions circulation in the groundwater. Higher concentration of H^+ ions available in alluvial aquifers is neutralized by the process of weathering and dissolution. Further, in Lower Cuddalore, the pH decreases due to the exchange of cations in clay/rock matrix with H^+ ions in groundwater or the availability of neutralizing ions. The groundwater from the study area mostly show the $[Ca^{2+} + Mg^{2+}]/[HCO_3^-]$ ratios below 1 in all the formations, and only few samples in alluvium show ratios above 1. Samples with lower ratios indicate additional HCO_3^- input from albite mineral weathering, rather than from Ca^{2+} and Mg^{2+} production reactions alone.

The $(mCa^{2+} + mMg^{2+} - mSO_4^{2-})$ versus $(mNa^+ + mK^+ - mCl^-)$ relationship provides information on the geological sources of Ca^{2+} and Mg^{2+} in the aquifer. To account for meteoric Ca^{2+} from the dissolution of evaporate gypsum ($CaSO_4^-$), an amount of Ca^{2+} equal to the concentration of SO_4^{2-} is subtracted from the sum of Ca^{2+} and Mg^{2+} ions. Calculation of Na^+ values depletion caused by cation exchange was done by assuming that all meteoric Na^+ inputs are from Na^+Cl^- . Since all Cl^- ions are meteoric in origin, subtracting Cl^- from the total Na^+ determines the meteoric Na^+ contribution. There are four fields demarcated in Fig. 6. It is to be noted that the 'Y' axis crosses the 'X' axis at 1, i.e. the line along which $(Ca + Mg)^*/HCO_3$ is equal to unity. Field 1 has higher ratio of $(Na + K)^*/HCO_3$ and $(Ca + Mg)^*/HCO_3$, with $Na^+ + K^+ - Ca^{2+} + Mg^{2+} - HCO_3^-$ water type. Field 2 shows the dominance of excess $(Ca^{2+} + Mg^{2+})^*$ and higher

Fig. 6 The ratio between the $(Ca + Mg)^*/HCO_3$ and $(Na + K)^*/HCO_3$



$(Na^+ + K)^*$. This shows that the field has dominance of excess $(Ca^{2+} + Mg^{2+})^*$ and $(Na^+ + K)^*$, with no significant indications of influencing anions due to contamination. Field 3 has the dominance of excess anion Cl^- over $Na + K$ and higher $(Ca^{2+} + Mg^{2+})^*$, which may be due to ion exchange with $Ca-Mg-Cl$ water type. Field 4 represents the $Ca-Mg-HCO_3-Cl$ water type. Most of the groundwater samples in the study area are in Field 4, representing $Ca-Mg-HCO_3-Cl$ water type, and few of them are represented in Field 1 (Fig. 6). This suggests that weathering of silicate minerals or saline intrusions are the significant contributors to the water chemistry of this region.

Ionic strength

Ionic strength is a measure of total concentration of ions, which emphasizes increased contribution of species with charges greater than one to solution non-ideality (Domenico and Schwartz 1998).

$$I = 0.5 \sum m_1 z_1^2$$

where m_1 is the atomic/molecular weight and z_1 is the valance of the respective ion. Ionic strength of freshwater is less than 0.005 (Hem 1959). In the study area, higher ionic strength was noted in alluvium and Tertiary formations, indicating lesser inflow of freshwater into the system. Low ionic strength was noted in Cretaceous formation indicating higher inflow of freshwater/recharge (Prasanna et al. 2006).

Partial pressure of carbon dioxide (pCO_2)

The partial pressure of CO_2 (pCO_2) in rivers is commonly out of equilibrium with the atmosphere. The $\log pCO_2$ for

each sample is determined to study its relation to recharge. The atmospheric $\log pCO_2$ value is around -3.75 (Raymahashay 1986). Water with high pCO_2 of around -1.5 results due to deep circulation of groundwaters, with lesser atmospheric interaction or due to higher saturation of carbonates, resulting from the interaction with the host rock of the material through which it flows (Chidambaram et al. 2011).

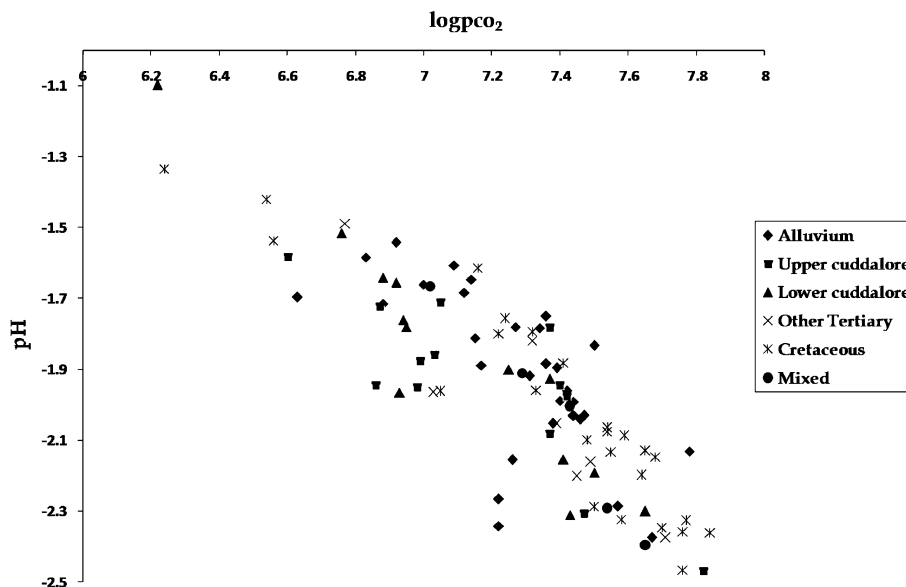
In mixed water, pCO_2 tends to decrease to the atmospheric value and this causes increase in saturation, suggesting that the mixing zone is an open system (Raymahashay 1986). The composition of freshwater is controlled by dissolution and precipitation processes and by degassing of CO_2 . The $\log pCO_2$ values range from -2.5 to -1 . The samples from Tertiary, Lower and Upper Cuddalore Formations and few samples of alluvium show nearly the same value (Fig. 7). Lower values of pCO_2 were noted in the alluvial and Cretaceous aquifers and also in few Lower Cuddalore sandstone samples, indicating recharge effect. Some samples from Cretaceous formation show higher pCO_2 value, suggesting that the additional CO_2 has been acquired from the soils during the process of infiltration towards the zone of saturation (Prasanna et al. 2006).

Water quality

Domestic water quality

The physicochemical properties related to the salinity of water can be appreciated by the measurements of the following parameters: chloride concentration, electric

Fig. 7 The ratio between pH and $\log p\text{CO}_2$



conductivity, and total dissolved solids. Desjardin (Desjardins 1988) classified the typology of water according to the TDS content. Table 4 clearly reveals that the higher representations of the samples in alluvium, Tertiary, Cretaceous, and mixed aquifers are noted in moderately fresh-brackish and in slightly brackish water types. The suitability of groundwater for irrigation purpose is mainly based upon the estimation of parameters such as sodium absorption ratio (SAR), Na% and residual sodium carbonate (RSC).

Sodium absorption ratio (SAR)

Salinity of groundwater and SAR determines its utility for agricultural purposes. Salinity originates in groundwater due to weathering of rocks and leaching from topsoil, anthropogenic sources along with minor influence on climate (Prasanna et al. 2011). The level of Na and HCO_3 in irrigation groundwater affects permeability of soil and drainage of the area (Kelly 1976; Tijani 1994). SAR is an estimate of the extent to which sodium ion present in the water would be absorbed by the soil and is expressed as follows: $\text{SAR} = \text{Na} / (\sqrt{\text{Ca} + \text{Mg}/2})$, where the concentrations are expressed in equivalent per million (epm). The distribution of SAR was

plotted using Richard (1954) classification. It was found that 90 % of samples in alluvium formation fall under excellent categories, 7 % fall in good class and the remaining 3 % fall under the permissible category (Table 5). The samples from mixed and Lower Cuddalore Formations fall in excellent category; 92 % of samples in Upper Cuddalore Formation are in excellent category and 8 % are in good category. In Tertiary formation, 86 % of samples fall in excellent category and 14 % under good category. In Cretaceous, 96 % of the samples fall under excellent category and 4 in good category.

Sodium percentage (Na%)

Na is an important cation, which in excess deteriorates the soil structure and reduces crop yield (Srinivasamoorthy et al. 2005). Na concentration is important in classifying water for irrigation purposes (Wilcox 1955). As much as 45 % of samples in alluvial formation are in the doubtful range of about (60–80) of Na %, and 10 % of samples are unsuitable (>80) for irrigation purpose (Table 5). In Lower Cuddalore, 15 % of the samples are in excellent and 69 % of the samples under good category. In Upper Cuddalore,

Table 4 Typology of water according to their content of TDS (Desjardins 1988)

Water type	Range (ppm)	Alluvium (n = 31) (%)	Tertiary			Cretaceous (n = 25) (%)	Mixed (n = 5) (%)
			Upper Cuddalore (n = 13) (%)	Lower Cuddalore (n = 13) (%)	Other Tertiary (n = 7) (%)		
Freshwater	<500	12.90	69.20	84.60	42.80	40	20
Moderately fresh-brackish water	500–1,000	58	23	15.30	42.80	44	60
Slightly brackish water	1,000–5,000	29	7.60	–	14.20	16	20

Table 5 Summary of geochemical classification by WATCLAST program

Category	Grade	Mi	Cr	OT	LC	UC	AI	Category	Grade	Mi	Cr	OT	LC	UC	AI
Na% (Wilcox 1955) in %															
Excellent	0–20	0.0	24.0	0.0	15.4	30.8	0.0	SAR (Richards 1954) in %	0–10	100.0	96.0	85.7	100.0	92.3	90.3
Good	20–40	0.0	36.0	28.6	69.2	7.7	9.7	Excellent	10–18	–	4.0	14.3	–	7.7	6.5
Permissible	40–60	60.0	28.0	28.6	7.7	46.2	35.5	Good	18–26	–	–	–	–	–	3.2
Doubtful	60–80	40.0	12.0	42.9	7.7	15.4	45.2	EC (Wilcox 1955) in %	<250	–	4.00	–	–	7.69	–
Unsuitable	>80	–	–	–	–	–	9.7	Excellent	250–750	20.00	36.00	28.57	84.62	46.15	16.13
RSC (Richards 1954)															
Good	<1.25	100	100	85.71	100.00	100.00	90.32	Permissible	750–2,250	80.00	60.00	71.43	15.38	38.46	74.19
Medium	1.25–2.5	–	–	14.29	–	–	6.45	Doubtful	2,250–5,000	–	–	–	–	7.69	9.68
Bad	>2.5	–	–	–	–	–	3.23	Indices of base exchange (IBE) Scholler (1965) in %							
USGS hardness (Handa 1964)															
Slightly hard	75–150	20.0	16.0	14.3	30.8	38.5	9.7	(Na + K)rock → (Ca/Mg) g.w	20.0	16.0	16.0	28.6	23.1	38.5	19.4
Moderately hard	150–300	80.0	52.0	85.7	61.5	53.8	67.7	(Na + K)g.w. → (Ca/Mg) rock	80.0	84.0	84.0	71.4	76.9	61.5	80.6
Very hard	>300	–	32.0	–	7.7	7.7	22.6	Corrosivity ratio (Rangarajan and Balasubramanian 1990) in %							
Chloride classification (Stuyfzand 1989) in %															
Very fresh	0.14–0.84	–	–	–	7.7	–	–	Corrosivity ratio >1	60.0	48.0	48.0	57.1	30.8	46.2	80.6
Fresh	0.84–4.23	40.0	56.0	28.6	76.9	61.5	19.4	Corrosivity ratio <1	40.0	52.0	52.0	42.9	69.2	53.8	19.4
Fresh brackish	4.23–8.46	20.0	24.0	42.9	–	30.8	16.1								
Brackish	8.46–28.20	40.0	20.0	28.6	15.4	7.7	64.5								

Mi mixed, Cr Cretaceous, OT Other Tertiary, LC Lower Cuddalore, UC Upper Cuddalore, AI alluvium

31 % of the samples are in excellent, 8 % in good category, 46 % in permissible and 15 % in the doubtful range. In Other Tertiary formations, 43 % of samples are in the doubtful range and 60 % of the samples in the permissible range. In mixed formation, 60 % of the samples fall under permissible range and 40 % are grouped in the doubtful range. In Cretaceous, 24 % of the samples are in excellent and 36 % are under good category, while 12 % of samples are in the doubtful category. Sodium percentage is calculated against major cations and expressed in terms of SAR. SAR values in all the major litho units range from excellent to good category and the majority of samples fall in the excellent category.

In Wilcox (1955) classification of electrical conductivity, 16 % of samples in alluvium fall in good category, 74 % are in the permissible range and a minor representation of 9.6 % in the doubtful category (Table 5). About 46.2 % of samples in Upper Cuddalore fall in the good category, 38.4 % in permissible limit and only 7.6 % in excellent category. Most of the samples fall in good to permissible range in Other Tertiary, Lower Cuddalore, Cretaceous and mixed formation.

Hardness

Hardness is defined as the sum of concentration of their ions expressed in mg/L of CaCO_3 . Hardness increases from metallic ions dissolved in water. Hardness is used as an indicator of the rate of scale formation in hot water heaters in low-pressure boilers. USGS hardness (Handa 1964) shows four categories of hardness: soft, slightly hard, moderately hard and very hard. Scaling and deposition problems in air-conditioning plants are associated with the total hardness of water. Total hardness of more than 180 mg CaCO_3/L can be treated as very hard water and can lead to scaling problems in air-conditioning plants (Hem 1970).

The moderately hard water is represented in 68 % of the samples and 22 % of very hard category in alluvium formation (Table 5). In Upper Cuddalore, 39 % of samples are slightly hard, 54 % fall under moderately hard and 7 % are in the very hard category. The same trend was followed in Lower Cuddalore. In Other Tertiary formations, 86 % of samples are slightly hard and 14 % in the moderately hard range. In Cretaceous, 16 % of the samples are in the slightly hard category, 52 % in the moderately hard and 32 % in the very hard category. In mixed formation, 20 % of samples fall under the slightly hard category and 80 % in the moderately hard category.

Residual sodium carbonate

Water having excess of carbonate and bicarbonate cover the alkaline earth; mainly Ca and Mg in excess of the

allowable limits affect agriculture unfavourably (Richards 1954).

$$\text{RSC} = (\text{CO}_3 + \text{HCO}_3) - (\text{Ca} + \text{Mg})$$

All values expressed in epm.

The tendency of alkaline earth influences the suitability of water for irrigation purposes. Water with Ca and Mg gets more precipitated and as a result Na in water gets increased in the form of sodium carbonate. The variation in RSC was drawn using (Richards 1954) good, medium and bad categories; 90 % of the samples in alluvium fall in the good category, 6.4 % in the medium category and 3.2 % in the bad category (Table 5). Good category is found in all other formations except in Other Tertiary, where 86 % are in good and 14 % in medium category.

Index of base exchange (IBE)

Scholler (1965) proposed a measure called “index of base exchange” (IBE) to describe the geochemical reactions taking place in groundwater. There are substances which absorb and exchange their cations with cations present in groundwater. Those substances are called permutolites, e.g. clay minerals like kaolinite, illite, chlorite, halloysite, glauconite, zeolites and organic substances. Kaolinite, illite, chlorite and halloysite are the clay minerals in which ions are held at edges and their ionic exchange capacity is low. This case is reverse in montmorillonite and vermiculite; the exchange capacity is higher when the number of ions held on the surface is more. Chloro-alkaline indices, CAI1 and CAI2, are used to measure the extent of base exchange during rock–water interaction. Where there is an exchange of Na^+ and K^+ in groundwater with Mg^{2+} or Ca^{2+} in rock/alluvium, both the indices are positive and vice versa. All ionic concentration is expressed in epm. The indices to base exchange indicate that there is a significant exchange of Na + K in groundwater into the Ca + Mg in rock from the matrix, whereas the reverse is more prominent and the exchange of Na + K in rock to the Ca + Mg in groundwater is less notable (Chidambaram 2000). More than 60 % of samples fall in (Na + K) groundwater \rightarrow Mg/Ca rock and few of the samples are in (Na + K) rock \rightarrow Mg/Ca. The Styfzands classification of chloride shows that 19 % of samples are in the fresh range, 16 % are under the fresh-brackish range and 65 % are brackish in nature in alluvium (Table 5). In Lower Cuddalore, 61 % of samples are fresh in nature, 31 % fresh-brackish and 8 % brackish. In Other Tertiary, 28.6 % of the samples are under fresh and 43 % of the samples are under the fresh-brackish categories, while 29 % of the samples are brackish in nature. In Cretaceous, 56 % of the samples are in the fresh category, 24 % in the fresh-brackish range and 20 % in brackish nature. In mixed formation, 40 % of

samples are under fresh category, 20 % in fresh-brackish and 40 % under brackish category.

Corrosivity ratio

Corrosivity ratio is >1 in most of the samples in all formations (Table 5). In alluvium, 19 % of samples fall under corrosivity ratio <1, 54 % in Upper Cuddalore, 70 % in Lower Cuddalore, 43 % in Other Tertiary, 52 % in Cretaceous and 40 % in mixed formation having the ratio <1.

Permeability index

Permeability index is an important factor, which influences quality of irrigation water in relation to soil for development in agriculture. Based on permeability index, (Table 6) Doneen (1948) classified the groundwater as Class I, Class II and Class III to find out the suitability of groundwater for irrigation purposes. The majority of samples in all the formations fall in Class I and Class II, indicating that the water is moderate to good for irrigation purposes with minor indication in poor irrigation quality.

Correlation

Correlation coefficient is commonly used to measure the relationship between two variables. It is simply a measure to exhibit how well one variable predicts the behaviour of the other. Correlation analysis was performed individually in all the formations (Table 7).

Alluvium

In alluvium, good correlation exists between Cl–Na, HCO₃–Ca, HCO₃–Na, HCO₃–Cl, SO₄–Ca, Ca–NO₃, Mg–Na, Mg–Ca, Mg–Cl and Mg–SO₄. Poor correlation exists between SO₄, PO₄ and H₄SiO₄ with all other ions. Cl shows good correlation with Na indicating leaching of secondary salts; a significant correlation of HCO₃ with Ca, Na and Cl indicates chemical weathering (Table 7). Poor positive correlation of SO₄, PO₄ and H₄SiO₄ shows the lesser possibility of anthropogenic influence into the system.

Tertiary Lower Cuddalore

Good correlation exhibits between Na–Ca, Cl–Ca, Cl–Na, HCO₃–Na, Na–SO₄, NO₃–Ca, NO₃–Na, NO₃–Cl, NO₃–HCO₃, SO₄–Ca, SO₄–Cl, SO₄–HCO₃ and SO₄–NO₃, indicating the leaching of secondary salts along with anthropogenic impact. Poor correlation exists between Mg and PO₄ with other ions indicating lesser influence of magnesium during this season. SO₄ shows good positive correlation with Na, indicating the leaching of marcasite present in this region (Sivalingam 2006). Good correlation between HCO₃, Na and H₄SiO₄ indicates albite weathering. H₄SiO₄ is well correlated with Ca and Mg, indicating intensive weathering reaction that enhances H₄SiO₄. Cl shows good correlation with Ca and Na, indicating leaching of salts.

Tertiary Upper Cuddalore

Good correlation exists between Na–Ca, Na–Mg, K–Ca, K–Mg, K–Na, Cl–Ca, Cl–Mg, Cl–Na, Cl–K, SO₄–Ca SO₄–Mg, SO₄–Na, SO₄–K, SO₄–Cl, NO₃–PO₄ and SO₄–Mg, indicating the leaching of secondary salts along with anthropogenic activities. Cl shows good correlation with Ca, Mg, Na and K, indicating secondary leaching of salts. HCO₃ is well correlated with Na, indicating weathering of sodic feldspar from the source rock. Good to poor positive correlation of HCO₃, Na, K and H₄SiO₄ indicates albite weathering from the source rock. Cl shows good correlation with Ca, Na and K, indicating secondary leaching of salts.

Other Tertiary formations

Good correlation exists between Cl–Na, NO₃–Na, NO₃–Cl, SO₄–Cl and SO₄–NO₃, indicating the leaching of secondary salts along with anthropogenic impact. Poor correlation exists between Mg and PO₄ with other ions indicating the influence of agriculture input into the aquifers. Cl shows good correlation with Ca and Na, indicating leaching of salts.

Cretaceous and mixed

Good correlation exists between Cl–Na, HCO₃–Ca, HCO₃–Na, HCO₃–Cl and SO₄–Ca indicating the leaching of

Table 6 The permeability index of the samples

Permeability index range	Alluvium (n = 31) (%)	Tertiary			Cretaceous (n = 25) (%)	Mixed (n = 5) (%)
		Upper Cuddalore (n = 13) (%)	Lower Cuddalore (n = 13) (%)	Other Tertiary (n = 7) (%)		
40–60	6.45	23.08	38.46	28.57	44	0
60–80	48.39	53.85	53.85	28.57	44	80
80–100	45.16	23.08	7.69	42.86	12	20

Table 7 Correlation analysis for groundwater samples

	Ca	Mg	Na	K	Cl	HCO ₃	NO ₃	PO ₄	SO ₄	SiO ₂	pH	EC
Al												
Ca	1.00											
Mg	-0.05	1.00										
Na	0.18	-0.12	1.00									
K	0.41	0.24	0.12	1.00								
Cl	0.33	0.06	0.92	0.19	1.00							
HCO ₃	0.30	-0.12	0.37	0.36	0.29	1.00						
NO ₃	-0.05	-0.17	0.08	-0.13	0.04	0.34	1.00					
PO ₄	0.24	0.24	-0.06	0.43	-0.01	0.32	0.32	1.00				
SO ₄	0.50	0.14	0.16	0.43	0.17	0.07	-0.03	0.39	1.00			
SiO ₂	0.22	-0.10	-0.04	-0.19	-0.01	0.07	0.26	-0.30	-0.03	1.00		
pH	-0.11	0.12	0.35	0.24	0.26	0.51	0.13	0.11	0.13	0.04	1.00	
EC	0.62	0.09	0.75	0.53	0.81	0.50	0.06	0.29	0.45	0.07	0.41	1.00
LC												
Ca	1.00											
Mg	0.36	1.00										
Na	0.78	0.10	1.00									
K	-0.03	0.31	-0.05	1.00								
Cl	0.93	0.26	0.89	-0.02	1.00							
HCO ₃	0.45	0.34	0.73	0.05	0.49	1.00						
NO ₃	0.78	0.30	0.90	-0.08	0.78	0.77	1.00					
PO ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00				
SO ₄	0.65	0.12	0.86	-0.03	0.79	0.71	0.77	0.00	1.00			
SiO ₂	0.75	0.04	0.98	-0.12	0.86	0.72	0.86	0.00	0.82	1.00		
pH	0.51	0.55	0.51	-0.09	0.49	0.57	0.65	0.00	0.50	0.40	1.00	
EC	0.75	0.25	0.95	-0.02	0.80	0.85	0.94	0.00	0.79	0.94	0.59	1.00
Cr												
Ca	1.00											
Mg	0.31	1.00										
Na	0.36	0.14	1.00									
K	0.37	0.03	-0.01	1.00								
Cl	0.45	0.30	0.95	0.06	1.00							
HCO ₃	0.54	0.47	0.55	0.02	0.53	1.00						
NO ₃	0.30	0.44	0.26	-0.07	0.30	0.43	1.00					
PO ₄	0.39	0.29	0.16	0.36	0.31	0.14	-0.25	1.00				
SO ₄	0.74	0.18	0.23	0.40	0.26	0.30	0.28	0.08	1.00			
SiO ₂	0.29	0.00	0.48	-0.04	0.44	0.37	0.53	-0.31	0.27	1.00		
pH	0.41	0.06	0.04	-0.08	-0.03	0.59	0.09	0.00	0.24	0.27	1.00	
EC	0.58	0.45	0.84	0.01	0.86	0.65	0.52	0.18	0.46	0.51	0.14	1.00
	Ca	Mg	Na	K	Cl	HCO ₃	NO ₃	PO ₄	SO ₄	SiO ₂	pH	EC
UC												
Ca	1.00											
Mg	0.13	1.00										
Na	0.69	0.59	1.00									
K	0.74	0.52	0.71	1.00								
Cl	0.78	0.53	0.97	0.80	1.00							
HCO ₃	0.77	0.36	0.85	0.49	0.84	1.00						
NO ₃	0.01	-0.18	-0.16	-0.08	-0.14	-0.01	1.00					

Table 7 continued

	Ca	Mg	Na	K	Cl	HCO ₃	NO ₃	PO ₄	SO ₄	SiO ₂	pH	EC
PO ₄	0.27	0.33	0.55	0.28	0.47	0.35	−0.36	1.00				
SO ₄	0.75	0.55	0.64	0.78	0.70	0.59	−0.18	0.14	1.00			
SiO ₂	0.03	−0.27	0.06	−0.33	0.05	0.40	0.36	−0.15	−0.31	1.00		
pH	0.26	0.07	0.34	−0.18	0.24	0.60	0.01	0.34	0.22	0.32	1.00	
EC	0.80	0.55	0.97	0.78	0.98	0.86	−0.21	0.55	0.73	−0.03	0.34	1.00
OT												
Ca	1.00											
Mg	−0.16	1.00										
Na	0.32	−0.02	1.00									
K	0.10	0.05	−0.68	1.00								
Cl	0.41	0.24	0.93	−0.69	1.00							
HCO ₃	0.03	−0.66	−0.08	0.31	−0.36	1.00						
NO ₃	0.29	−0.41	0.76	−0.81	0.67	0.17	1.00					
PO ₄	−0.28	0.39	−0.38	0.76	−0.43	0.08	−0.83	1.00				
SO ₄	0.07	−0.09	0.87	−0.81	0.81	−0.05	0.80	−0.54	1.00			
SiO ₂	−0.03	−0.29	0.81	−0.83	0.65	−0.04	0.81	−0.53	0.73	1.00		
pH	−0.58	−0.04	0.18	0.07	−0.10	0.31	−0.14	0.57	0.08	0.30	1.00	
EC	0.30	0.17	0.90	−0.71	0.91	−0.10	0.78	−0.46	0.79	0.71	0.02	1.00
Mi												
Ca	1.00											
Mg	−0.11	1.00										
Na	0.38	0.41	1.00									
K	0.30	0.89	0.53	1.00								
Cl	0.55	0.42	0.95	0.57	1.00							
HCO ₃	0.59	0.46	0.83	0.75	0.79	1.00						
NO ₃	0.45	0.72	0.22	0.80	0.44	0.40	1.00					
PO ₄	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00				
SO ₄	0.44	0.04	0.93	0.20	0.87	0.69	−0.06	0.00	1.00			
SiO ₂	−0.37	0.70	0.52	0.40	0.51	0.13	0.30	0.00	0.31	1.00		
pH	−0.67	0.45	−0.08	0.01	−0.04	−0.46	0.15	0.00	−0.23	0.80	1.00	
EC	0.28	0.86	0.77	0.94	0.78	0.82	0.68	0.00	0.49	0.59	0.09	1.00

Al alluvium, *UC* Upper Cuddalore, *LC* Lower Cuddalore, *OT* Other Tertiary, *Cr* Cretaceous, *Mi* mixed

secondary salts. Poor correlation exists between Na with other ions. The same trend was found in mixed formations.

Conclusions

The cation dominance is in the following order: $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and that of anions is $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$. The study area forms a part of the coastal aquifer, and the higher EC extends from the southeastern part influenced by salt water intrusion. Higher EC is also observed in the central and western parts due to the leaching of ions. Most of the groundwater samples range from soft to moderately hard category. The Styfzands classification shows that all the samples fall in fresh to

fresh-brackish category in all the aquifers. The Piper diagram shows that Na–Cl is the dominant facies in all the aquifers with few representations of Ca–HCO₃ showing the recharge. Chadda's plot shows that saltwater intrusion and ion exchange are more common in alluvium, which has more representations of saltwater contaminated samples. The ionic strength for few of the samples is almost equivalent to freshwater. In general, the dilution effect is evident from the low ionic strength. Lower values of $p\text{CO}_2$ were noted in the alluvial and Cretaceous aquifers and also in few Lower Cuddalore sandstone samples, indicating recharge effect. TDS is higher and exceeds the standard limits for drinking water in all the aquifers except in Upper Cuddalore. Few groundwater samples of the study area are unsuitable for domestic and drinking purposes.

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