

A Study on Hydrochemical characteristics of Surface and Sub-surface water in and around Perumal Lake, Cuddalore District, Tamilnadu, South India.

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Abstract

Hydrogeochemical investigations are carried out in and around Perumal Lake, Cuddalore district, South India in order to assess its suitability in relation to domestic and agricultural uses. The water samples (surface water=16; groundwater=12) were analyzed for various physico-chemical attributes like pH, Electrical Conductivity (EC), Sodium (Na⁺), Potassium (K⁺), Calcium (Ca²⁺), Magnesium (Mg²⁺), Chloride (Cl⁻), Bicarbonate (HCO₃⁻), Sulphate (SO₄²⁻), Phosphate (PO₄), Silica (H₄SiO₄), Total Dissolved Solids (TDS). Major hydrochemical facies were identified using Piper trilinear diagram. Hydrogeochemical processes controlling the water chemistry are water-rock interaction rather than evaporation and precipitation. Interpretation of isotopic signatures reveals that groundwater samples recharged from meteoric water with few water-rock interactions. A comparison of water quality in relation to drinking water quality standard proves that the surface water samples are suitable for drinking purpose, whereas groundwater in some areas exceeds the permissible limit. Various determinants such as Sodium Absorption Ratio (SAR), Percent Sodium (Na%), Residual Sodium Carbonate (RSC) and Permeability Index (PI) revealed that most of the samples are suitable for irrigation.

Key words: Hydrogeochemistry, Groundwater quality, Chemical weathering, Stable isotope, Perumal Lake.

Introduction

The emerging global fresh water crisis in terms of water quality and quantity is already felt in India. The over drafting of ground water 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 ground water 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 lake/sea, biological process (Appelo and Postma 1993). 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 1948; Thorne and Peterson 1954; US Salinity Laboratory Staff 1954; Holden 1971; Todd

1980; ISI 1983; WHO 1984; Hem 1991; Karanth 1997). Groundwater quality data gives important clues to the geologic history of rocks and indications of groundwater recharge, movement and storage (Walton 1970). The knowledge of hydrochemistry is essential to determine the origin of chemical composition of groundwater (Zaparozeć 1972). The hydrology and geochemistry of waters have been further discussed in the classic works of Stumm and Morgan (1981), Hem (1991), Drever (1988), Domenico and Schwartz (1990). Adverse conditions increase investment in irrigations and health and decrease agricultural production, which in turn, reduce agrarian economy and retard improvement in living conditions of rural people. 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 the different parts of India (Durvey et al. 1991; Agrawal and Jagetia 1997; Niranjana Babu et al. 1997; Subba Rao et al. 1999; Majumder and Gupta 2000; Dasgupta and Purohit 2001; Khurshid et al. 2002; Sujatha and Reddy 2003; Sreedevi 2004; 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. Majority of the people in this region depend on agriculture (i.e. cultivators and agricultural labourers). Both for drinking as well as irrigation purposes substantial amount of groundwater is being used in this area. This study forms the baseline attempt on the geochemistry of surface and sub-surface water and its suitability for drinking and agricultural purpose in the study area. The purpose of the present study is to determine the geochemistry of surface and sub-surface water in and around Perumal Lake and to classify the water in order to evaluate its suitability for domestic and agricultural uses.

Study area

Perumal Lake is situated in Kurinjipadi taluk of Cuddalore district, Tamilnadu. It is located at 24.9 km east of Neyveli and 16.7 km south of Cuddalore. The length of lake is 13.05 km and it's having total perimeter 31.31km. The total area of lake is 5.037sq.km. The lake is located in between the geographical coordinates, latitude of 11°10'-11°76' and longitude of 79°37'-79°42' (Fig. 1). The source of water for the lake is from the Gadilam river and Walaja tank and it also get water from Neyveli aquifers. The area is drained by Gadilam and Ponnaiyar rivers in the north, Vellar and Coleroon rivers in the south. All these rivers are ephemeral and carry floods during monsoon period. They generally flow from west towards east and the pattern is mainly sub parallel.

Climate

The mean maximum temperature ranges between 27.9 and 36.9°C and the mean minimum temperature ranges between 20.8 and 27.1°C at Cuddalore, whereas at Lekkur the western part of the district, the average maximum temperature ranges between 29.05 and 39.19°C and the average minimum temperature ranges between 19.81 and 29.97°C. The higher temperature are recorded during the month of April and May, where as the lowest

temperature are recorded during the month of December and January. The relative humidity recorded in the eastern part of the district i.e. at Cuddalore ranged between 60 and 83 percent, whereas at Lekkur ranged between 46.73 and 71.12 percent. Higher rates of relative humidity are observed during the month of North-East monsoon period i.e. from October-November-December, whereas lower rates are observed during the summer months of April and May. The study area is benefited by the influence of south-west monsoon stretching from June to September and north-east monsoon from October to December. The winter and hot seasons from January to May form the transition period and the rainfall is scanty. The long term average annual rainfall of the district is 1162.35mm.

General Geology

The study area is underlined by the various geological formations ranging in age from Mio-pliocene to Recent sediments (Fig. 2). The general geological succession of the formations encounter in the region is presented in Table 1. The lithology of the study area has two stratigraphic units as follows: (1) *Tertiary Unit*, Argillaceous sandstone, pebble bearing grits, clays (variegated) with lignite seams and pebble beds, (2) *Quarternary Unit*, soils, alluvium and coastal sands and laterite. Prasanna et al. (2008) conducted electrical sounding in some of the locations in the study area. The maximum depth of investigation is 60 m. The nature and distribution of different lithologic layers as represented by depthwise resistivity values are correlated with geoelectrical logging data to show the existing hydrogeological environment in the region (Fig. 3).

i. Tertiray Formation

The Gopurapuram formations of Lower Eocene to Palacocene age are essentially argillaceous, comprising silts, claystone, calcareous sand stone, siliceous lime stone and algal lime stone. They are also considered essentially as a transitional formation from Cretaceous to Tertiary and placed equivalent to Ninniyur stage of Trichinopoly, Cretaceous group. The exposures of these formations are seen as a narrow belt and sometimes also as inliers in Cuddalore sand stone.

The Cuddalore sand stone formations of Miocene age are exposed in major part of the study area and are characterized by laterite cover at exposures. The alluvial cover of Gadilam river in the north and Vellar river alluvium in the south has presented these formations as two detached out crops in the district. The Cuddalore sand stone are often ferruginous and consist of pebble beds, sands and clays with seams of lignite. The sand stones are variegated in colour and friable. Pebble bearing sand stones is seen near Palakollai, Kallamedu and Kadarnbuliyur. The lenticular beds of white or mottled clay are observed occasionally in association with sand stones. Lignite has been found to occur in association with Cuddalore sand stone at Neyveli and north of Cuddalore near Bahur.

ii. Quarternary Formation

The Quarternary formation includes various types of soils, fine to coarse grained sands, silts, clays, laterite and lateritic gravels. The fluvial sediments occupy the flood plains of the Ponnaiyar, Gadilam, Manimuktha, Vellar

and Coleroon rivers. It consists of mainly sands, sandy loams or clayey loams. Laterite and lateritic gravels occur in major regions covering the Cuddalore sand stones. Laterites are dark brown, yellowish, hard and assume metallic luster. Along the coast in the district, windblown sands of 1.5-3 kms width are common occurring in the form of low and flat topped sand dunes excepting at the confluence of the rivers with sea. Irregular mounds of 10-15 m height are the prominent features due to the wind action near Cuddalore district.

Methodology

12 groundwater samples were collected at different parts of study area and 16 water samples from surface reservoir (Perumal Lake) during December 2007. One litre of water samples was collected in polyethylene bottle. Then it was sealed and brought to laboratory for analysis and stored properly (4°C) before analysis. The samples collected were analyzed for major cations like, Ca and Mg by Titrimetry, Na and K by Flame photometer (CL 378); anions, Cl and HCO₃ by Titrimetry, SO₄, PO₄, and H₄SiO₄ by Spectrophotometer (SL 171 minispec). EC and pH were determined in the field using electrode (Eutech). The analyses were done by adopting standard procedures (APHA 1998). The results of the analysis were checked by the cation-anion balance, which was within ±8%. A computer programme WATCLAST in C++ was used for calculation and graphical representations (Chidambaram et al. 2003)

Stable isotopic studies ($\delta^{18}\text{O}$ and δD) were carried out for 14 samples from different locations of the study area following standard procedures (IAEA) for both groundwater and surface water samples. Oxygen ($\delta^{18}\text{O}$) and Deuterium (δD) in samples were analyzed by using Isotopic Ratio Mass Spectrophotometer (Finnigan Delta^{plus} Xp, Thermo Electron Corporation, Bermen, Germany, the standard deviation of our measurements is ±1.72‰ for Oxygen and ±0.8‰ for Hydrogen). All the measurements were carried out against laboratory substandard that were periodically calibrated against the international isotope water standards recommended by the IAEA (V-SMOW). Deuterium and Oxygen isotopes are expressed as per mill difference of the isotope ratios of sample (sp) and standard (std), which is usually referred to as SMOW (Standard Mean Ocean Water). They are defined as follows,

$$\delta^{18}\text{O}(\delta\text{D}) = (R_{\text{sp}} - R_{\text{std}} / R_{\text{std}}) \times 10^3$$

Where R is the ratio of the heavy to the light isotope, that is, R= (¹⁸O/¹⁶O) or (D/H).

Results and Discussion

A summary of the physic-chemical analysis of the groundwater samples is presented in Table 2.

Hydrochemistry (isotope geochemistry) and its controlling factors

Understanding the groundwater quality is important as it is the main factor determining its suitability for drinking, domestic, agricultural and industrial purposes (Subramani et al. 2005). The pH value of groundwater samples ranges from 6.13 to 8.46 (average 7.22) and from 6.81 to 8.09 (average 7.26) in surface water samples, indicating an alkaline type of water. EC ranges from 409 to 4490 $\mu\text{S}/\text{cm}$ (average 1878.75 $\mu\text{S}/\text{cm}$) in groundwater and from 268 to 859 $\mu\text{S}/\text{cm}$ (average 549.13 $\mu\text{S}/\text{cm}$) in surface water. TDS values ranges from 286 to 2790 mg/L (average 1164.50 mg/L) in groundwater and from 160 to 527 mg/L (average 340.63 mg/L) in surface water.

Major ions chemistry

With Na^+ being the dominant cation, it ranges from 36.70 to 505.75 mg/L (average 159.55 mg/L) in groundwater and from 13.20 to 91.95 mg/L (average 46.21 mg/L) in surface water. Ca^{2+} ranges from 20 to 140 mg/L (average 63.67 mg/L) in groundwater and from 16 to 44 mg/L (average 29 mg/L) in surface water. The coastal groundwater of this region shows higher concentrations of Na^+ followed by Ca^{2+} (Chidambaram et al. 2005). Mg^{2+} ranges from 4.80 to 45.60 mg/L (average 18.20 mg/L) in groundwater and from 2.40 to 26.40 mg/L (average 8.25 mg/L) in surface water. K^+ ranges from 5.80 to 92 mg/L (average 23.48 mg/L) in groundwater and from 6.10 to 16.30 mg/L (average 7.99 mg/L) in surface water.

Cl^- concentration in groundwater varies between 88.62 to 478.58 mg/L (average 230.43 mg/L) and from 53.18 to 124.10 mg/L (average 76.44 mg/L) in surface water, indicating longer residence of the groundwater in the shallow aquifers. Main source of chloride in groundwater may be due to saline intrusion or due to leaching of chlorides that have accumulated in soil/sediment layer in dry climate (Chidambaram et al. 2005).

HCO_3^- concentration in groundwater varies from 36.60 to 549 mg/L (average 200.28 mg/L) and from 73.20 to 170.80 mg/L (average 93.03 mg/L) in surface water. SO_4^{2-} ranges from 0.68 to 248.33 mg/L (average 78.13 mg/L) in groundwater and from 3.56 to 89.61 mg/L (average 27.24 mg/L) in surface water.

Silica concentration in groundwater varies from 14.14 to 198.07 (average 79.71) and from 14.14 to 109.69 mg/L (average 44.20 mg/L) in surface water. Phosphate concentration ranged from 0.14 to 5.13 mg/L (average 3.69 mg/L) in groundwater and from 0.04 to 6.04 mg/L (average 1.92 mg/L) in surface water.

Among the major cations, Na^+ and Ca^{2+} played a dominant role in both surface and groundwater. The concentration of Mg^{2+} and K^+ are relatively low when compared to other major cations. Among the major anions, Cl^- is dominant in groundwater, but in the surface water HCO_3^- was dominant indicating significant weathering process. Dissolution of carbonates and neutralization of the carbonate alkalinity by carbonic acid of atmospheric origin make bicarbonate the dominant anion (Afifi and Bricker 1983). The abundance of the cations and anions are $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$ in groundwater; $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ in surface water.

Spatial distribution

The spatial distribution of electrical conductivity gives a general trend of the anions and cations present in water. Spatial distribution of EC of surface water samples (Fig. 4) shows that higher concentration was noted in the southern part of the Perumal Lake. This region coincides with the river water inlet region of the lake. Lower concentration of EC is noted in the northern part of the lake. Similarly spatial distribution of pH was carried out for the surface water. Higher pH was noted around the inlet of the lake, which is located in the southern part (Fig. 5).

Hydrogeochemical Facies

The hydrochemical evolution of groundwater can be understood by plotting the major cations and anions in the Piper trilinear diagram (Piper, 1944). This diagram reveals similarities and differences among water samples because those with similar qualities will tend to plot together as groups (Todd 2001). This diagram useful in bringing out chemical relationships among water in more definite terms (Walton 1970). The plot shows that the majority of surface water samples fall in mixed CaMgCl facies with minor representation in NaCl facies. The groundwater samples fall in the transition zone between mixed CaMgCl to NaCl facies (Fig. 6). This indicates that an increase in Na and Cl in the system, which has eventually helped in the migration of these samples towards the sea water composition. These observations indicate the longer residence time of groundwater in the shallow aquifers.

The changes in hydrogeochemical phases of water in the study area can be interpreted from Johnson (1975) modified diagram. The comparison of the Trilinear plot of hydrochemical facies with Johnson plot reveals that most of the surface and groundwater samples fall in zone of water contaminated with gypsum and also in static and dis-coordinated regimes indicating intensive ion exchange and weathering of bed rocks processes in this region (Fig. 7).

Isotope Geochemistry

Two stable isotopes, deuterium (δD) and oxygen ($\delta^{18}O$) were measured for 9 groundwater samples and 5 surface water samples by IRMS (Isotope Ratio Mass Spectrometry).

Criag (1961) established a relation between ^{18}O and 2H in worldwide fresh surface waters as “Global meteoric water line” (GMWL). Criag’s line is only global in application, and is actually an average of many local or regional meteoric water lines which differ from the global line due to varying climatic and geographic parameters. Local lines will differ from the global line in both slope and deuterium intercepts, but this GMWL provides a referencing for interpreting the provenance of ground waters. An important observation made by him was that isotopically depleted waters are associated with cold regions and enriched waters are found in warm regions. The partitioning helps in characterizing the recharge environments.

The local meteoric water line (LMWL) for the study area was obtained from rain water samples collected in this region during the period of 2005 – 2007 (Prasanna 2008). It is witnessed that there is a clear demarcation of isotopic signatures in ground water of different terrains in the study area.

Stable isotopes, Deuterium (δD) and Oxygen ($\delta^{18}O$) were estimated in ground and surface water samples to identify the source and are expressed as reference to LMWL. In general $\delta^{18}O$ and δD values showed decrease from coast to the inland. As moist air originating from the ocean, condenses near the coast, the first condensate have heavy isotopic content similar to that of ocean water. As air moves further inland the vapor gets depleted in the heavy isotopes (Navada et al. 1986). Figure 8 shows, that δD and $\delta^{18}O$ values of the groundwater samples in Alluvium formation (Zone 1) fall parallel to the LMWL line indicating recharged by the local precipitation. Groundwater samples in Tertiary formation and surface water samples (Zone 2) fall away from the LMWL line indicating few water-rock interaction mechanisms are noted in this region. In Zone 2, it is clear that recharge by surface water via bank infiltration to the adjacent groundwater (Bhattacharya et al. 1985; Gupta and Deshpande 2005; Prasanna et al. 2009).

Mechanisms controlling groundwater chemistry

Reactions between groundwater and aquifer minerals have a significant role on water quality, which are also useful to understand the genesis of groundwater (Cederstorm 1946; Gupta et al. 2008; Subramani et al. 2009). The water chemistry in the study area is regulated by diverse processes and mechanisms. Hence, Gibbs plot is employed in this study area to understand and differentiate the influences of water-rock interaction, evaporation and precipitation in water chemistry (Gibbs 1970). Gibbs diagrams, representing the ratios of Na^+ : ($Na^+ + Ca^{2+}$) and Cl^- : ($Cl^- + HCO_3^-$) as a function of TDS are widely employed to assess the functional sources of dissolved chemical constituents, such as precipitation-dominance, rock-dominance and evaporation dominance. The chemical data of surface and groundwater samples are plotted in Gibbs diagram (Fig. 9). Majority of samples suggest that the chemical weathering of rock-forming minerals are influencing the groundwater quality, with minor representations of groundwater samples fall in evaporation zone. Evaporation increases salinity by increasing Na^+ and Cl^- with relation to increase of TDS. This is also supported by Piper plot, having significant increase of Na^+ and Cl^- in the groundwater. Anthropogenic activities (agricultural fertilizers and irrigation-return flows) also influence the evaporation by increasing Na^+ and Cl^- and thus TDS (Gupta et al. 2008).

Ion-exchange processes

Control on the dissolution of undesirable constituents in water is impossible during the subsurface runoff but it is essential to know the various changes undergone by waters during their trend (Johnson 1979; Sastri 1994). According to Schoeller (1965, 1967), ion exchange between the groundwater and its host environment during residence or travel can be understood by studying the chloro-alkaline indices, i.e. CA-I ($(Cl-Na+K)/Cl$) and CA-II ($(Cl-Na+K)/(SO_4+HCO_3+CO_3+NO_3)$). All the ionic concentration is expressed in meq/L. Na and K ions in water are

exchanged with Mg and Ca ions, if the indices value is positive, which indicates base-exchange reaction whereas negative indicates chloro-alkaline disequilibrium. The reaction is known as cation-anion exchange reaction. During this process the host rocks are the primary sources of dissolved solids in the water. In Schoeller (1965) classification, surface and groundwater samples show equally in both positive and negative values (Table 3). In Scholler (1967) classification of water types, majority of samples in both surface and groundwater falls in Type I with minor representation in Type III, indicating longer residence time of water with more prominent base-exchange reaction.

Water quality and utilization

The physical and chemical parameters of the analytical results of surface and groundwater were compared with the standard guideline values recommended by the World Health Organization (WHO 2004) for drinking and public health standards. The results of the chemical analyses indicate that the surface water in the study area is chemically potable and suitable for domestic purposes (Table 4). The cation concentrations in groundwater indicate that 25%, 42% and 42% of the Ca^{2+} , Na^+ and K^+ concentrations exceed the WHO limit. The anion concentrations show that 42% of the Cl^- concentrations exceed the permissible limit and HCO_3^- and SO_4^{2-} concentrations are within the limit.

Water is valuable only when its quality is suitable for a variety of purposes. Water for irrigation should satisfy the needs of soil and the crop as the liquid phase in soil water plant growth and crop production. EC and Na^+ play a vital role in the suitability of water for irrigation. The high salt content in irrigation water causes an increase in soil solution osmotic pressure. The salts, besides affecting the growth of plants directly, also affect the soil structure, permeability and aeration, which directly affect plant growth. The suitability of water for irrigation can be estimated by means of many determinants through Sodium Adsorption Ratio (SAR), percent Sodium ($\text{Na}\%$), Permeability Index (PI) and Residual Sodium Carbonate (RSC).

Sodium Adsorption Ratio (SAR)

Excess Na^+ in water produces the undesirable effects of changing soil properties and reducing soil permeability (Kelley 1946). Hence, for considering the suitability for irrigation, the assessment of Na^+ concentration is essential. The degree to which irrigation water enters into cation exchange reactions in soil can be indicated by SAR. The Na^+ replacing adsorbed Ca^{2+} and Mg^{2+} is a hazard as it causes damage to the soil structure, making it compact and impervious. SAR is defined:

$$\text{SAR} = \frac{\text{Na}^+}{\sqrt{(\text{Ca}^{2+} + \text{Mg}^{2+})/2}}$$

Where the concentrations are reported in meq/L.

Irrigation water classified based on SAR (Richards 1954) has indicated that both surface and groundwater samples fall in excellent category. US Salinity Laboratory (USSL) also suggested a diagram for rating irrigation water, wherein SAR is plotted against specific conductance. Na^+ and salinity hazard are the two important parameters, which can indicate suitability of water for irrigation purposes. Majority of groundwater samples fall in C3S1 zone indicating high salinity and low sodium hazard (Fig. 10). These waters can be used to irrigate salt tolerant and semi-tolerant crops under favourable drainage conditions. Most of the surface water samples fall in C2S1 category indicates medium salinity and low sodium hazard. These waters can be used for irrigation with little danger of harmful levels of exchangeable Na^+ .

Permeability Index (PI)

The Permeability index also indicates whether groundwater is suitable for irrigation. Doneen (1964) classified irrigation water based on the Permeability index:

$$PI = \frac{\text{Na}^+ + \sqrt{\text{HCO}_3^-}}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+} * 100$$

Where the concentrations are reported in meq/L.

Accordingly, water can be classified as Class I, II and III. Class I and II water are categorized as good for irrigation with 75% or more of maximum permeability. Class III water is unsuitable with 25% of maximum permeability. About 99% of surface and groundwater samples fall in Class I and Class II categories, indicates water is good for irrigation purpose (Fig. 11).

Percent Sodium (Na%)

Na^+ is an important cation which in excess deteriorates the soil structure and reduces crop yield (Srinivasamoorthy, 2004). When the concentration of Na^+ is high in irrigation water, Na^+ tends to be absorbed by clay particles, displacing Mg^{2+} and Ca^{2+} ions. This exchange process of Na^+ in water for Ca^{2+} and Mg^{2+} in soil reduces the permeability and eventually results in soil with poor internal drainage. Hence, air and water circulation is restricted during wet conditions and such soil are usually hard when dry (Collins and Jenkins 1996; Satesh et al. 1999). The Na% is calculated using the formula given below:

$$Na\% = \frac{\text{Na}^+ + \text{K}^+}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+} * 100$$

Where the concentrations are reported in meq/L.

According to Wilcox classification (1955), the water is classified based on the Na% with respect to the other cations present in water. Na% for groundwater falls in permissible to doubtful category and surface water falls in good to permissible category (Table 3). In Na% Eaton (1950) classification of groundwater for irrigation purposes (Table 3), majority of surface and groundwater samples fall in safe category.

Residual Sodium Carbonate (RSC)

In addition to the SAR and Na%, the excess sum of carbonate and bicarbonate in groundwater over the sum of calcium and magnesium also influences the unsuitability of groundwater for irrigation. This is designed as Residual Sodium Carbonate (R.S.C) (Richards 1954). The RSC is calculated by using the formula given below:

$$RSC=(HCO_3^-+CO_3^{2-})-(Ca^{2+}+Mg^{2+})$$

Where the concentrations are reported in meq/L.

In surface and groundwater, most of the samples fall in good category indicating water is fit for irrigation purpose (Table 3). According to chloride classification by Stuyfzand (1989), majority of samples in both surface and groundwater (Table 3), fall in fresh category indicating water is fit for agriculture purpose.

Hardness of the water

Hardness of the water refers to the soap neutralizing power of water. Hardness refers to the reaction with soap and scale formation. It increases the boiling point and do not have adverse effect on health of human. According to USGS hardness, most of the surface water samples fall in slightly hard category and majority of groundwater samples fall in moderately hard category (Table 3). In Handa (1964) classification, Permanent hardness (Non Carbonate hardness, NCH) is higher in both surface and groundwater samples, when compared to the temporary hardness (Carbonate hardness CH), indicates such hardness cannot be removed easily from the water (Table 3).

Conclusion

A detailed hydrochemical analysis of the Perumal Lake revealed the following:

1. The overall evaluation during the study period showed that the surface and groundwater in the area is alkaline in nature.
2. The abundance of the cations and anions are $Na^+ > Ca^{2+} > K^+ > Mg^{2+}$ and $Cl^- > HCO_3^- > SO_4^{2-}$ in groundwater; $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ and $HCO_3^- > Cl^- > SO_4^{2-}$ in surface water.
3. Higher EC concentration in surface water was observed in the southern part of the Lake. The river water enters the lake along this region, which increases the ionic concentrations.
4. In Piper plot majority of surface water showed mixed CaMgCl facies and in groundwater changes from mixed CaMgCl to NaCl facies indicates the longer residence time of groundwater in the shallow aquifers.
5. Study of $\delta^{18}O$ and δD signatures in groundwater samples belongs to Alluvium formation recharged from meteoric water. Few water-rock interactions in groundwater samples are noted in Tertiary formation.

6. From the Gibb's diagram, chemical weathering has been identified as the dominant factor in controlling the groundwater hydrogeochemistry.

7. The chemical concentration of ions in surface water is within the permissible limit for drinking purpose. Groundwater in one third of the study area exceeds the permissible limit of Cl^- , Na^+ , K^+ and Ca^{2+} concentrations.

8. Based on the USSL diagram, most of the groundwater samples fall under high salinity and low sodium hazard, which need adequate drainage to overcome salinity problems for irrigational purposes. Surface water samples are good for irrigation in almost all types of soil with little danger of exchangeable sodium. However, PI values indicate that surface and groundwater samples are suitable for irrigation.

9. The values of SAR, NA% and RSC for surface and groundwater are within permissible limit.

The conclusions derived indicate that the water is relatively free from pollution and anthropogenic influences except in few locations for salt water intrusion and the geochemical process dominantly controls the groundwater chemistry of the region.

Acknowledgement

The authors wish to express thanks to Centre for water resource, development and management (CWRDM), Kozhikode, India for helping in the stable isotope analysis of the water samples. The authors are grateful Mr.M.Vasanthavigar for the preparation of maps. They are also thankful to the Department of Earth Sciences, Annamalai University, India for their cooperation.

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Table 1. Geological Succession of the study area

Era	Age	Formation	Lithology
Quaternary	Recent to Sub- Recent	Alluvium & Laterite	Soils, alluvium and coastal sand, clays, kankar and Laterite
-----UNCONFORMITY-----			
Tertiary	Mio-Pliocene	Cuddalore sandstones	Sandstone- Argillaceous and pebble bearing grits, clays (Variegated) with lignite Seams and pebble beds.
-----UNCONFORMITY-----			
Cenozoic	Lower Eocene to Palacocene	Gopurapuram, formations	black clays or shales, grey colored sandstone, calcareous sandstone, shales and siliceous Limestone with fossils
-----UNCONFORMITY-----			

Table 2. Chemical Concentrations of surface and groundwater samples collected in the study area. (All values in mg/L except EC in $\mu\text{s}/\text{cm}$ and pH)

S.NO	Type	pH	EC	Ca	Mg	Na	K	Cl	HCO ₃	SO ₄	PO ₄	H ₄ SiO ₄	TDS
G1	Groundwater	7.54	3640.00	140.00	45.60	275.86	34.70	460.85	219.60	248.33	5.01	14.14	2380.00
G2		7.11	2220.00	52.00	14.40	269.30	21.10	354.50	183.00	67.24	5.13	109.70	1271.00
G3		7.16	3020.00	108.00	21.60	222.99	92.00	265.87	329.40	216.14	3.11	120.86	1960.00
G4		8.46	4490.00	52.00	33.60	505.75	50.50	478.58	549.00	192.12	1.85	95.21	2790.00
G5		7.17	2937.00	128.00	40.80	206.90	8.20	389.95	292.80	72.05	4.46	198.07	1660.00
G6		6.13	409.00	20.00	7.20	41.00	7.20	88.62	36.60	14.39	4.26	73.88	303.00
G7		6.31	488.00	24.00	12.00	36.70	6.30	106.35	36.60	13.24	4.95	59.10	286.00
G8		7.12	870.00	40.00	14.40	72.30	5.80	141.80	158.60	7.76	4.93	51.06	609.00
G9		7.07	791.00	36.00	4.80	68.97	12.30	106.35	158.60	5.91	5.09	72.01	497.00
G10		7.30	1040.00	40.00	16.80	76.90	8.20	124.10	195.20	0.68	5.13	53.55	627.00
G11		8.33	1130.00	64.00	*BDL	68.97	11.60	124.10	158.60	3.69	0.14	47.37	679.00
G12		6.98	1510.00	60.00	7.20	68.97	23.90	124.10	85.40	96.06	0.17	61.53	912.00
S1	Surface water	6.95	594.00	28.00	9.60	50.57	7.10	70.90	85.40	48.03	0.04	42.33	357.00
S2		7.01	594.00	40.00	0.00	80.46	8.30	70.90	170.80	45.27	4.60	47.49	416.00
S3		7.74	736.00	44.00	12.00	43.90	7.50	70.90	85.40	73.60	4.82	46.62	433.00
S4		7.29	644.00	20.00	*BDL	91.95	6.10	88.63	85.40	48.03	0.36	41.61	390.00
S5		7.37	682.00	28.00	14.40	57.47	7.50	88.63	73.20	89.61	0.33	50.91	423.00
S6		6.98	706.00	22.00	7.20	57.47	7.10	88.63	85.40	23.42	0.50	49.50	416.00
S7		7.40	711.00	32.00	7.20	57.47	7.00	88.63	85.40	35.01	0.10	39.18	370.00
S8		7.43	615.00	32.00	2.40	57.47	7.40	70.90	109.80	9.61	4.84	37.66	431.00
S9		8.09	405.00	28.00	9.60	22.99	8.00	70.90	97.60	3.56	0.35	17.02	240.00
S10		7.29	426.00	28.00	4.80	34.48	6.70	70.90	97.60	3.83	0.75	25.34	257.00
S11		6.81	268.00	20.00	9.60	22.99	6.40	53.18	85.40	4.48	0.33	51.50	160.00
S12		6.96	282.00	30.00	2.40	18.39	16.30	53.18	85.40	4.26	3.12	46.38	172.00
S13	6.81	268.00	20.00	16.80	16.09	6.80	70.90	85.40	4.62	0.53	14.14	161.00	
S14	6.95	274.00	16.00	26.40	13.20	7.50	53.18	85.40	19.21	6.04	109.69	192.00	
S15	7.14	722.00	36.00	2.40	68.97	11.00	124.10	85.40	4.10	3.82	51.98	505.00	
S16	7.91	859.00	40.00	7.20	45.50	7.10	88.63	85.40	19.21	0.20	35.81	527.00	

*BDL=below detectable limit

Table 3. Result of WATCLAST program

Category	Grade	GW		Category	Grade	GW		Category	GW	
		n=12	n=16			n=12	n=16		n=12	n=16
Na% Wilcox (1955)										
Excellent	0-20	0	0	Soft	<75	0	1	<200	0	4
Good	20-40	0	5	Slightly Hard	75-150	3	14	200-500	3	10
Permissible	40-60	8	7	Moderately Hard	150-300	6	1	500-1500	5	2
Doubtful	60-80	3	3	VeryHard	>300	3	0	1500-3000	4	0
Unsuitable	>80	1	1	IBE Schoeller (1965)						
Na% Eaton (1950)										
Safe	<60	8	12	(Na+k)rock->Ca/Mg g.w.		6	8	Ca-Mg Facies	0	0
Unsafe	>60	4	4	(Na+k)g.w.->Ca/Mg rock		6	8	Ca-Na Facies	12	16
S.A.R. Richards (1954)										
Excellent	0-10	11	16	Type I		10	14	Na Facies	0	0
Good	10-18	1	0	Type II		0	0	Anion facies		
Fair	18-26	0	0	Type III		2	2	HCO ₃ Facies	0	0
Poor	>26	0	0	Type IV		0	0	HCO ₃ -Cl-SO ₄ Facies	0	0
R.S.C. Richards(1954)										
Good	<1.25	11	16	Safe		<1	10	Cl- Facies	5	0
Medium	1.25-2.5	0	0	Unsafe		>1	2	Hardness Classification (Handa, 1964)		
Bad	>2.5	1	0	Chloride Classification (Stuyfzand, 1989)						
Excellent	<250	0	0	Extremely fresh		<0.14	0	A1	0	0
Good	250-750	2	15	Very fresh		0.14-0.84	0	A2	2	8
Permissible	750-2250	6	1	Fresh		0.84-4.23	7	A3	8	5
Doubtful	2250-5000	4	0	Fresh/Brackish		4.23-8.46	1	Temporary Hardness (CH)		
Unsuitable	>5000	0	0	Brackish		8.46-28.21	4	B1	0	0
				Brackish-salt		28.21-282.1	0	B2	0	0
				Salt		282.1-564.1	0	B3	2	3
				Hyperhaline		>564.3	0			

GW=groundwater; SW=surface water, n=number of samples

Table 4. Comparison of chemical compositions with WHO standard

Parameter	WHO Standards 2004	Surface water		
		Range		Polluted samples (S.No.)
		Min	Max	
pH	6.5 – 8.5	6.81	8.09	-
TDS (mg/L)	500-1000	160.00	527.00	-
Calcium (mg/L)	100	16.00	44.00	-
Magnesium (mg/L)	50	2.40	26.40	-
Chloride (mg/L)	250	53.18	124.10	-
Sulphate (mg/L)	250	3.56	89.61	-
Sodium (mg/L)	200	13.20	91.95	-
Potassium (mg/L)	20	6.10	16.30	-
Bicarbonate (mg/L)	125-350	73.20	170.80	-

Parameters	WHO Standards 2004	Groundwater		
		Range		Polluted samples (S.No.)
		Min	Max	
pH	6.5 –8.5	6.13	8.46	-
TDS (mg/L)	500-1000	286.00	2790.00	G1 - G5
Calcium (mg/L)	100	20.00	140.00	G1,G3,G5
Magnesium (mg/L)	50	4.80	45.60	-
Chloride (mg/L)	250	88.62	478.58	G1 - G5
Sulphate (mg/L)	250	0.68	248.33	-
Sodium (mg/L)	200	36.70	505.75	G1 - G5
Potassium (mg/L)	20	5.80	92.00	G1-G4, G12
Bicarbonate (mg/L)	125-350	36.60	549.00	G4

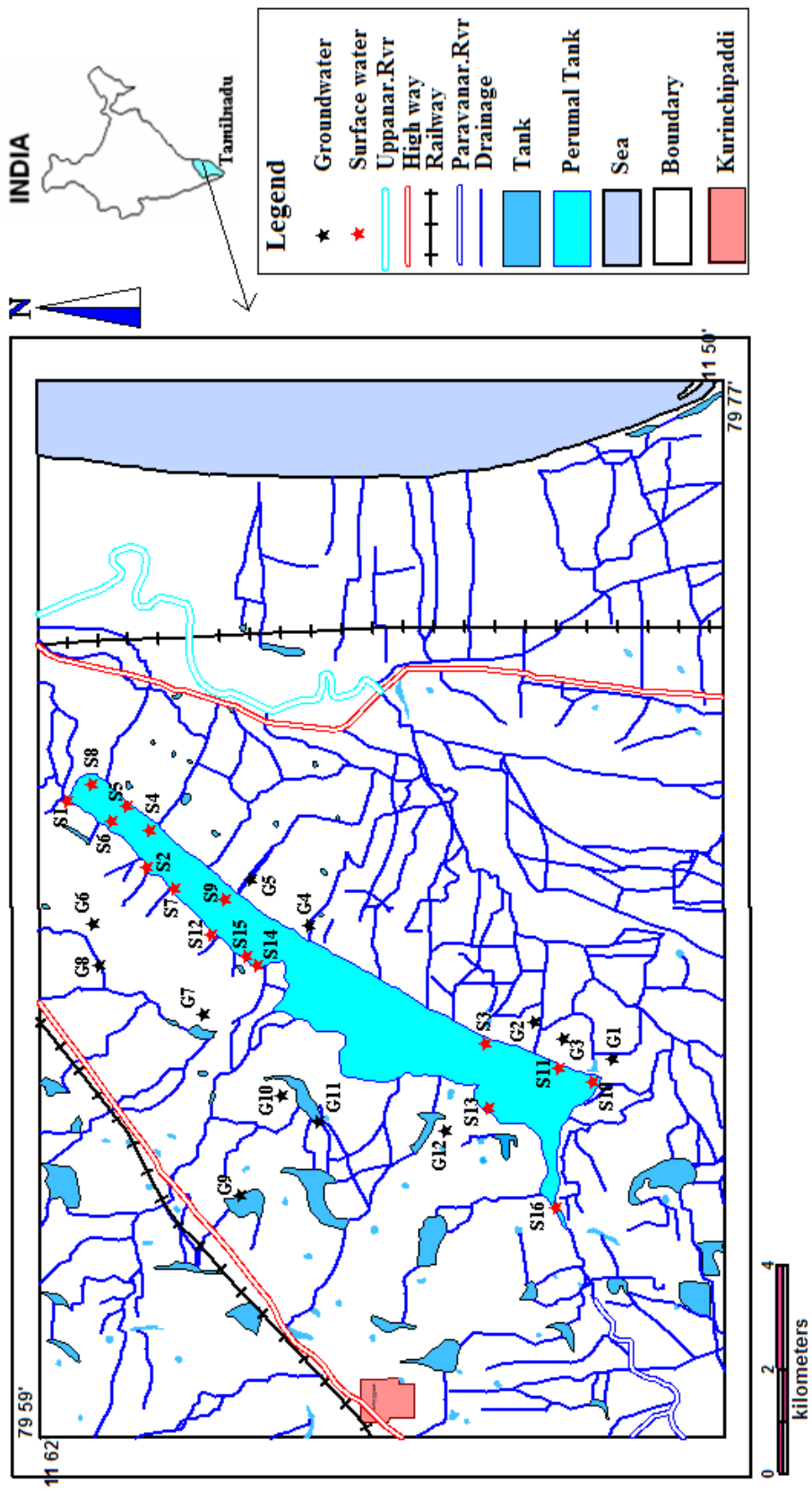


Fig. 1 Map showing the location of the study and samples locations

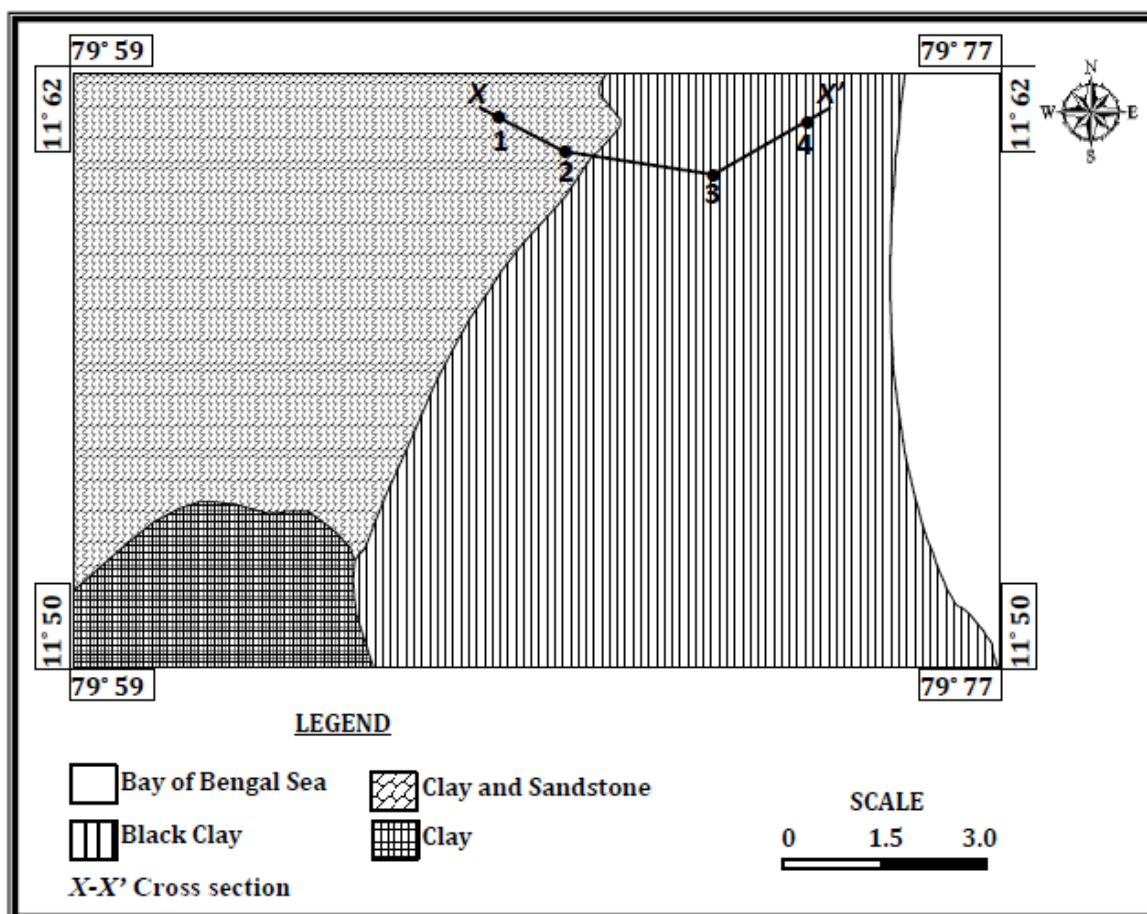


Fig. 2 Geology map of the study area

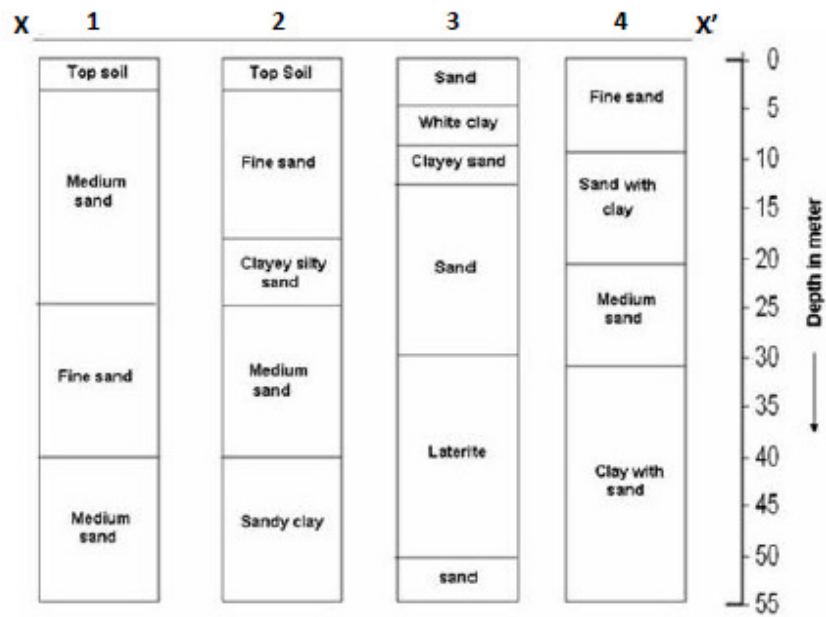


Fig. 3 Lithological cross section along X-X' in Figure 1 (after Prasanna et al. 2008)

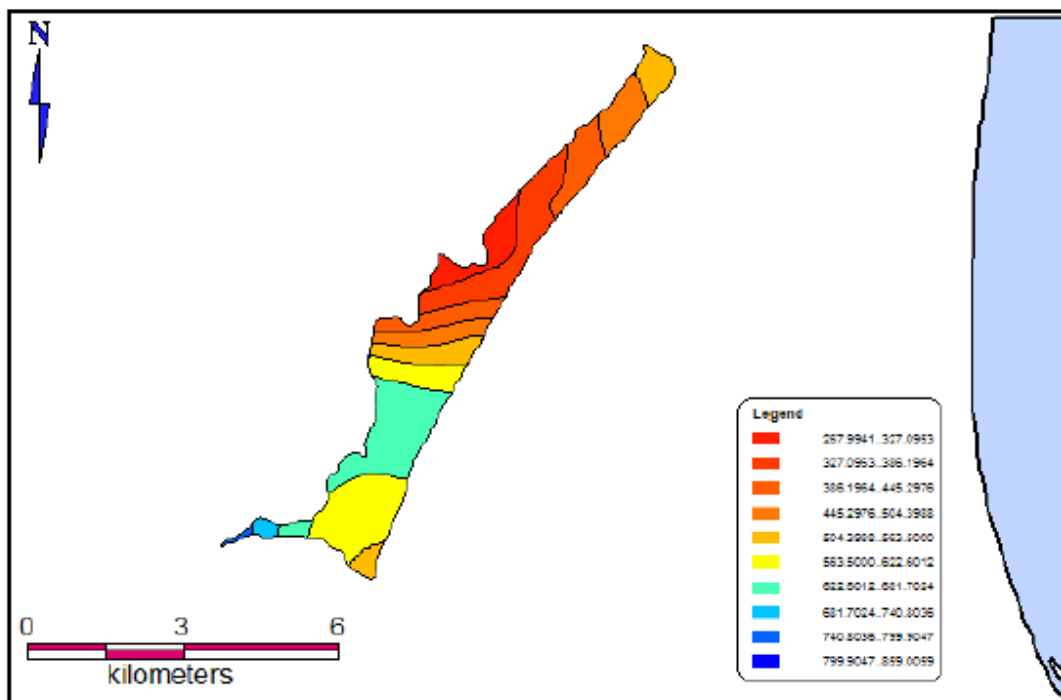


Fig. 4 Spatial distribution of EC ($\mu\text{s}/\text{cm}$) in surface water

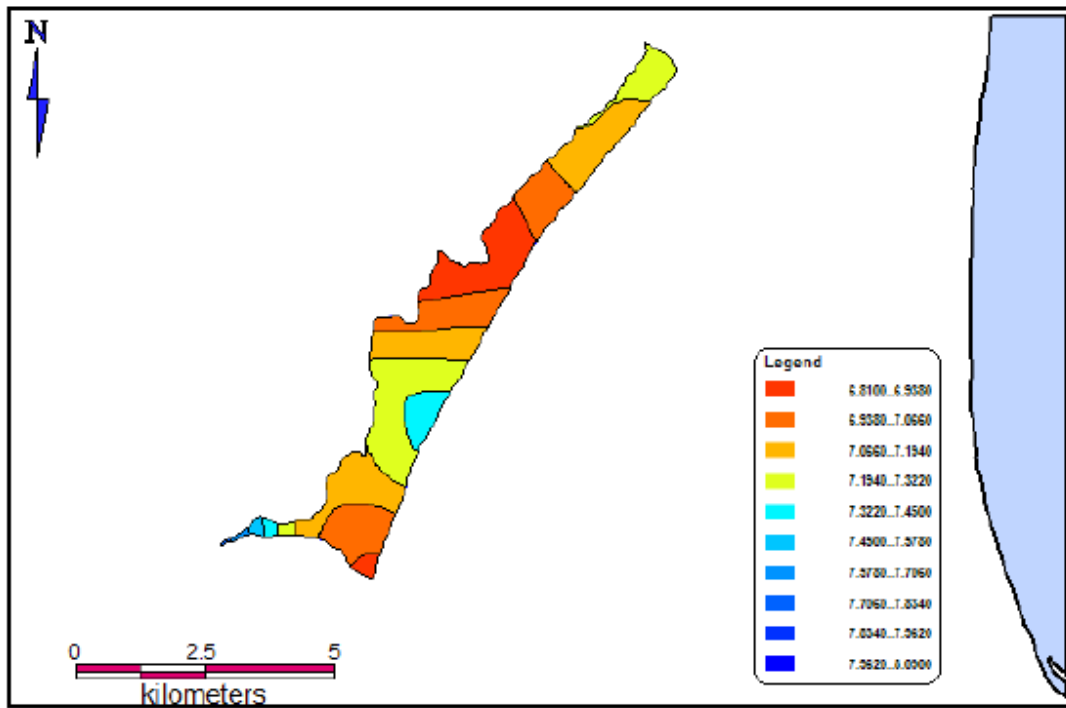


Fig. 5 Spatial distribution of pH in surface water

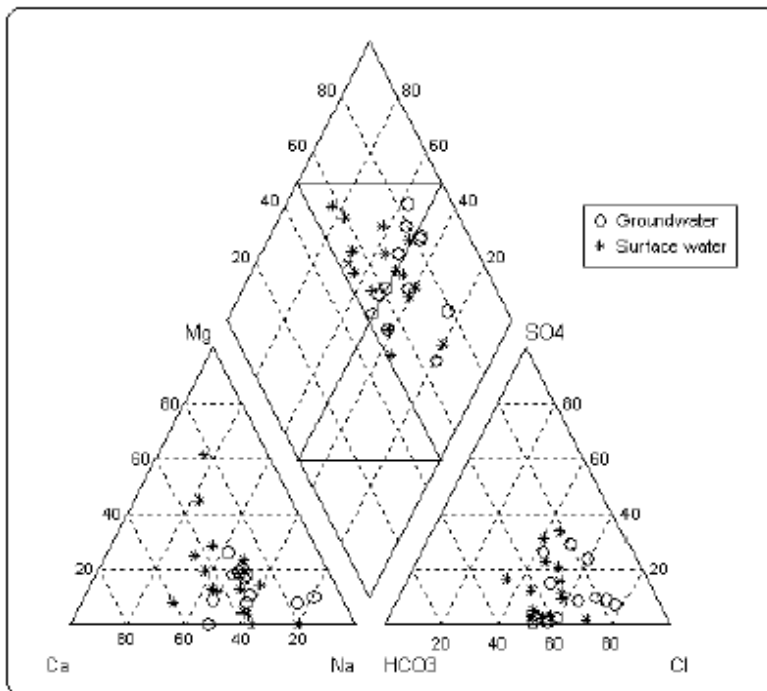


Fig. 6 Piper Plot

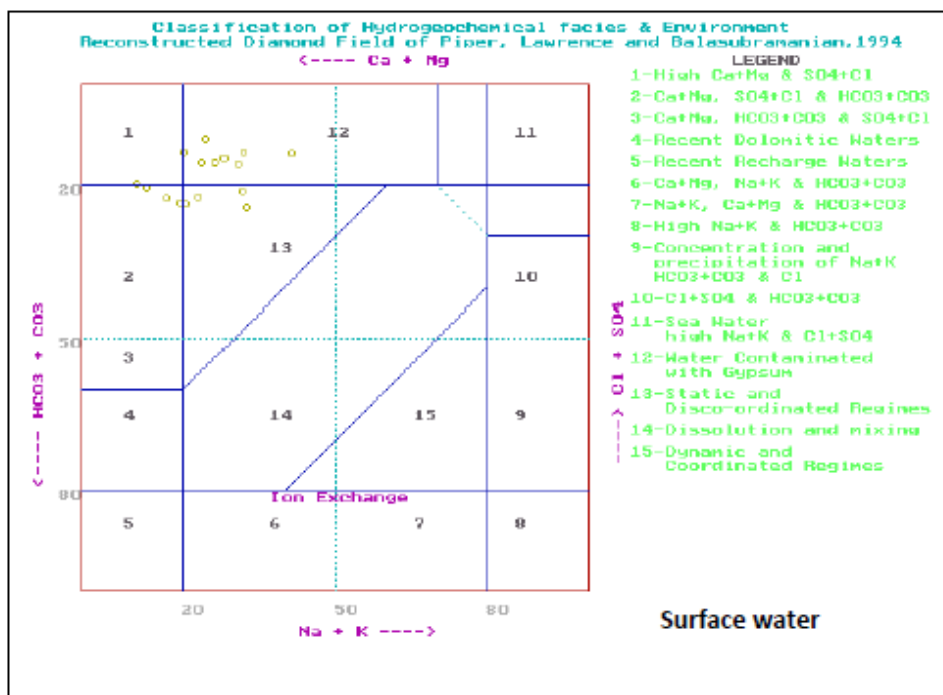
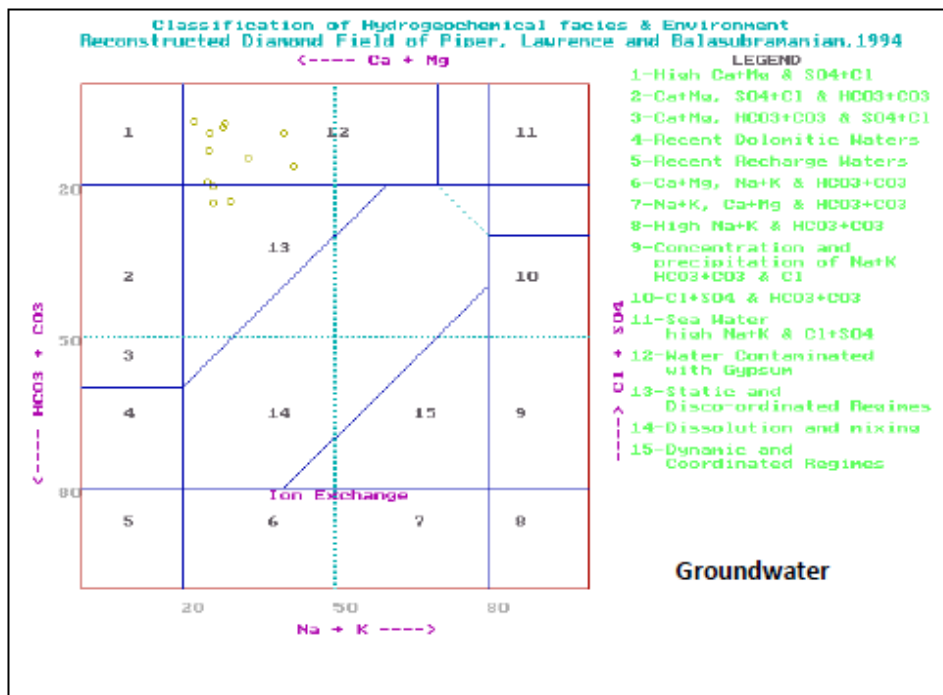


Fig. 7 Johnson's plot

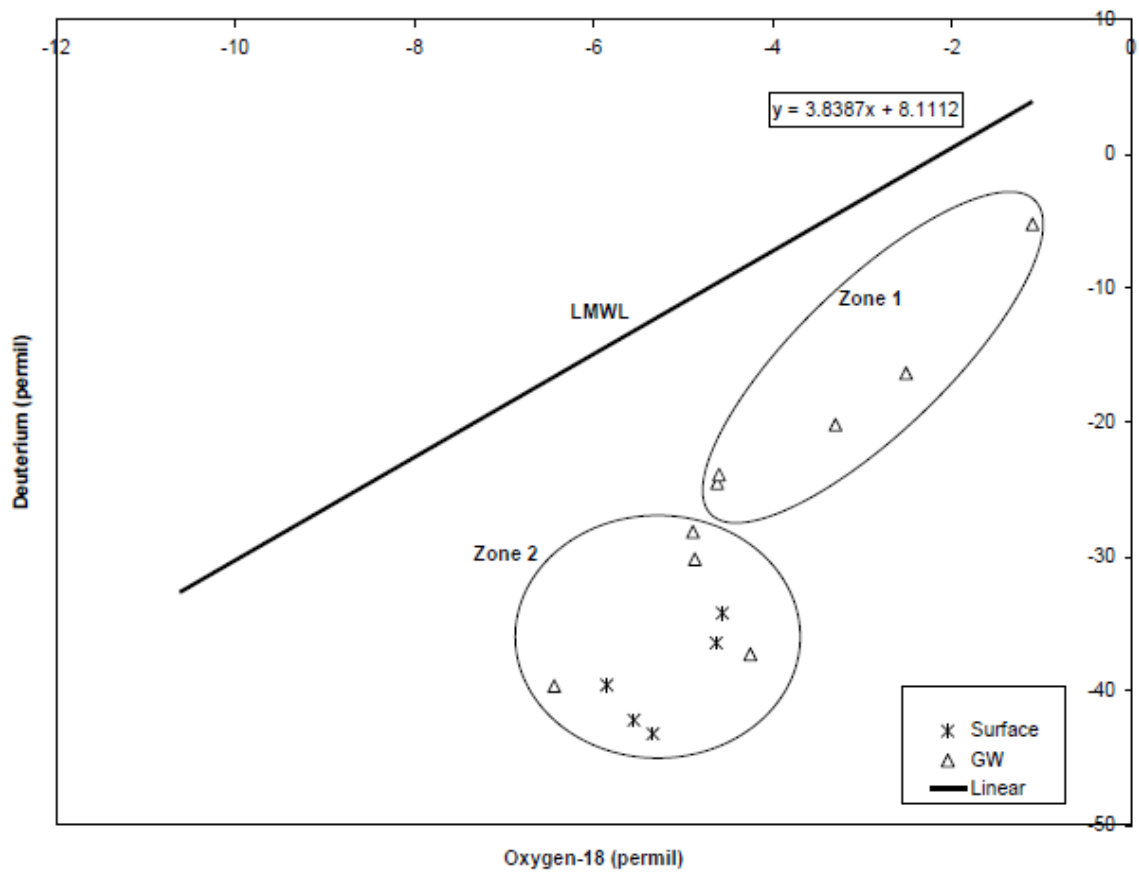


Fig. 8 Relation between Oxygen 18 and Deuterium

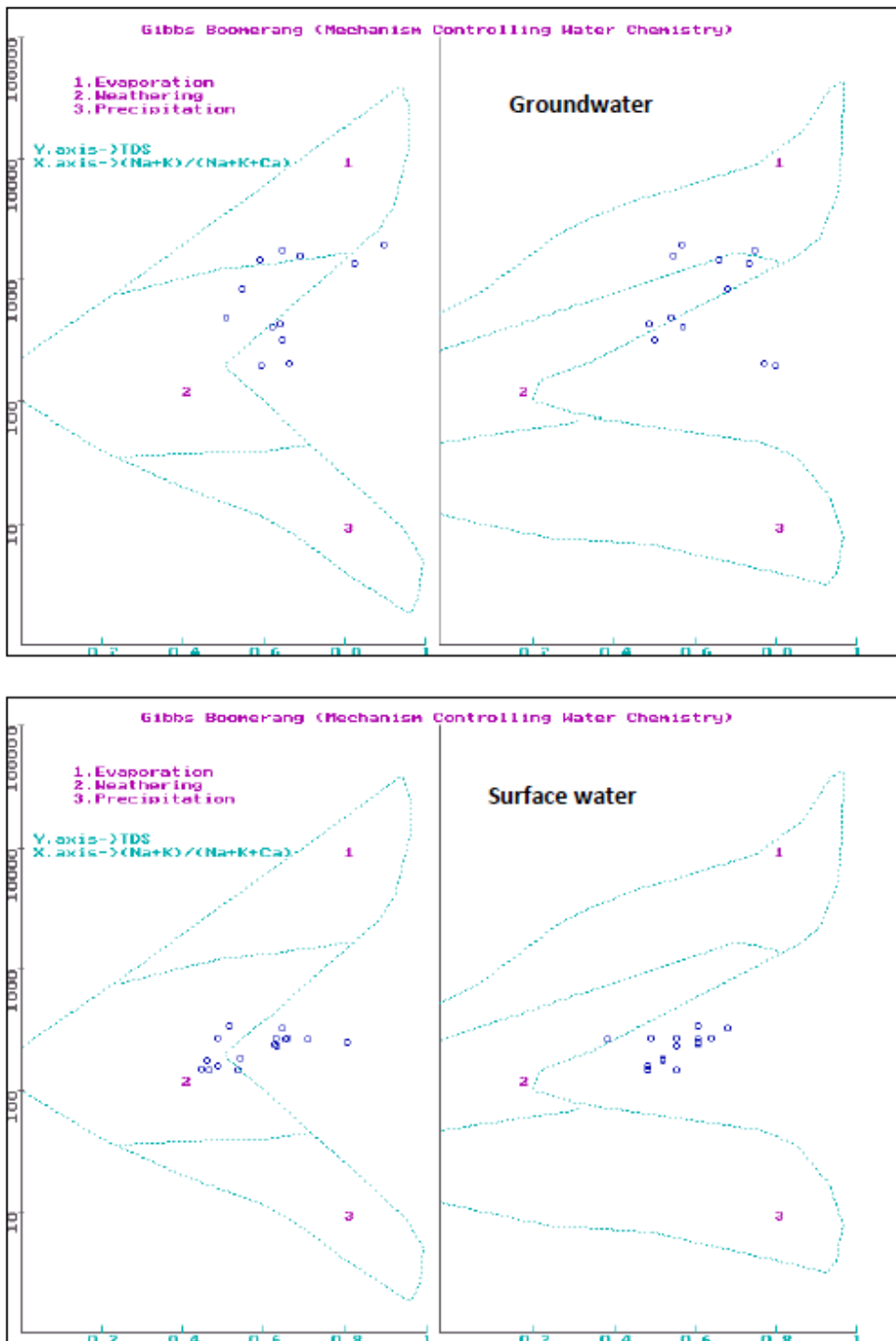


Fig. 9 Gibbs plot

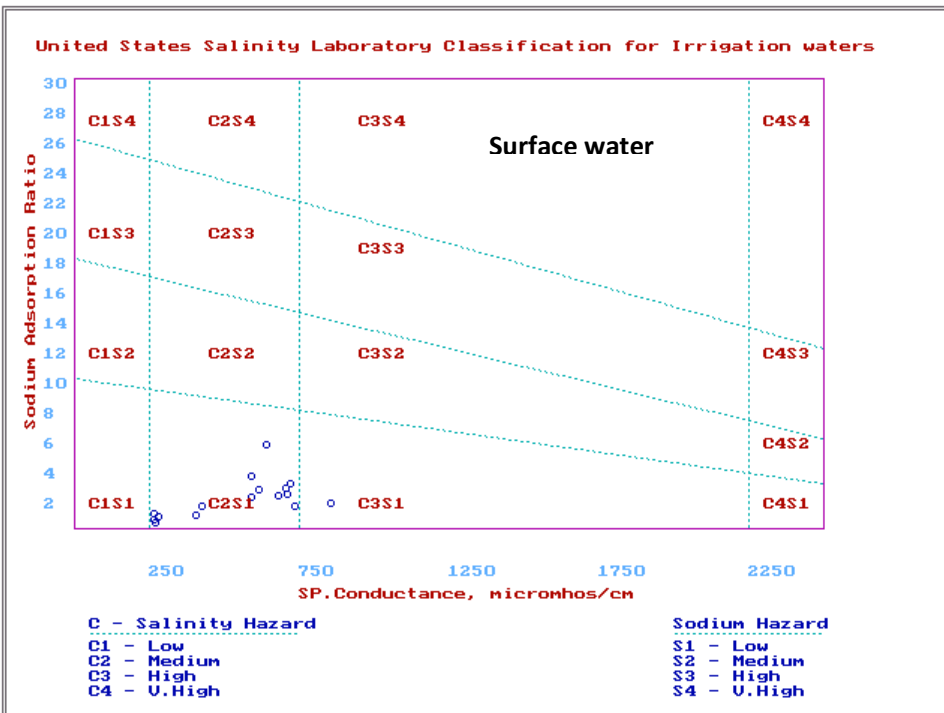
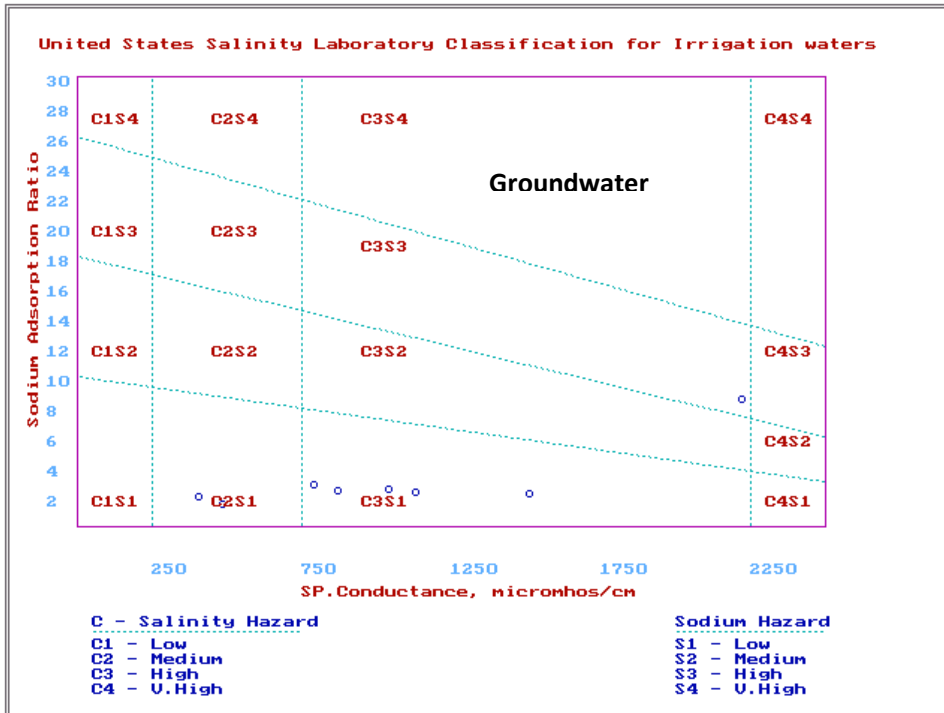


Fig. 10 USSL diagram

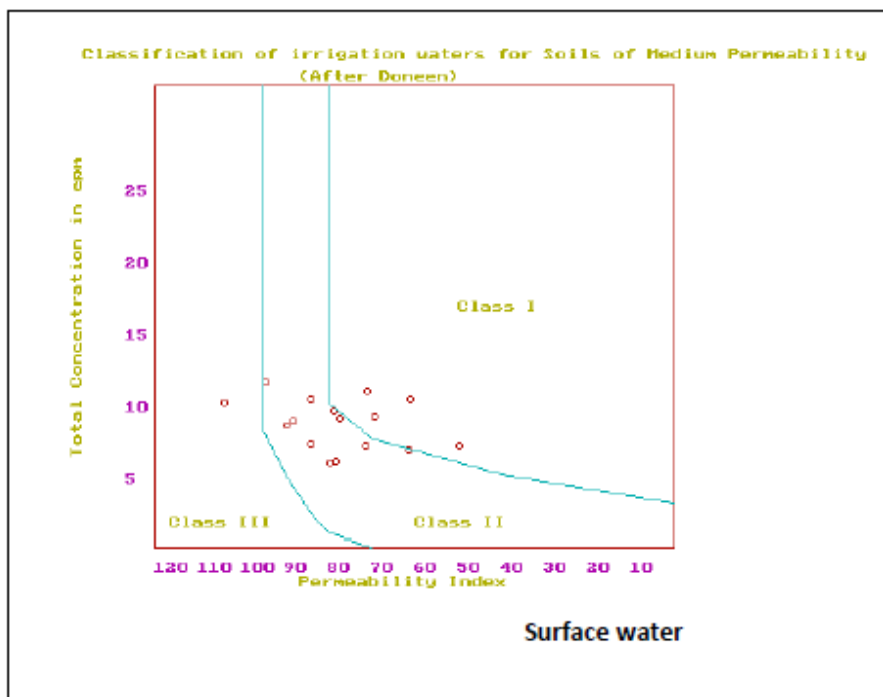
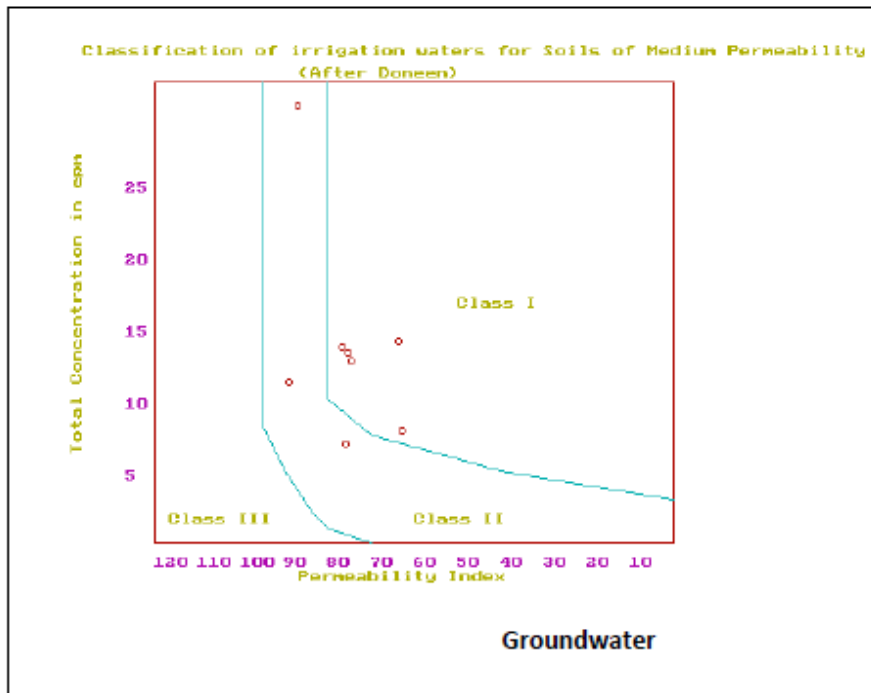


Fig. 11 Doneen plot