CHAPTER 5

RESULTS AND DISCUSSION

5.1.0 INTRODUCTION

Water is an important and essential resource of our earth. The chemical composition of groundwater is related to the soluble products of rock weathering and changes with respect to time and space. The chemistry of groundwater undergoes drastic changes as it comes in contact with aquifer. Water is shaped by unification of two hydrogen atoms with single oxygen atom with an asymmetrical bonding angle of 105º which gives rise to polar characteristic to water molecule. Water is effective in dissolving ions, increases its dielectric constant and its molecules come together with ions to form hydrated ions. When surrounded by water the thermal agitations of ions in minerals are greater to overcome the weaker charge of attraction, thus allow large number of ions to dissociate into aqueous solution. Groundwater is viewed as electrolytic solution due to presence of major and minor dissolved constituents present in ionic form. A charged species in water forces a local rearrangement in structure and those nearby reorient themselves because of charge. Zone of influence immediately adjacent to ion is known as hydration sheath form the bulk solution. Within random region water molecule are less oriented and they are in bulk solution or hydration sheath.

Mass can exist in substances as separate gas or solid phase or liquid phase or mass dissolved in water itself and mass occurring in water as ionic molecule or solid phases.
These phases undergo transport and reaction which distribute mass among various ionic species or between liquid and solid phase. Rate of reaction and mass transport processes vary according to reaction and equilibrium states. Strength of equilibrium is the ability to apply concept of thermodynamics for estimation of equilibrium and other constants as a function of temperature (Nordstorm and Munoz 1979). Considering thermodynamic point of view, equilibrium state is the state of maximum stability towards a close physiochemical system and it may also proceed to an irreversible process (Stumm and Morgan, 1970). Chemistry of most groundwater is powerfully altered by materials through which they pass through. When groundwater moves along flow lines from recharge to discharge, gets affected by variety of geochemical processes. In recharge area soil zone undergoes a net loss of mineral matter to flowing water.

5.2.0 Water Chemistry

5.2.1 pH

The pH of the water is an indicator of its quality and geochemical equilibrium for solubility calculation (Hem 1985). The pH indicates the state of equilibrium reaction in which the water precipitates. The groundwater in Nagapattinam Coastal region is generally alkaline with pH ranging from 6.4 to 9.4 with an average of 8.1. The pH is lower in 2009 PRM but higher in other seasons. It was found to fluctuate in certain locations with few abnormalities.
5.2.2 Electrical Conductivity (EC)

The Electrical Conductivity (EC) of rain water is 0.05 μs/cm (Hem 1991). In this study area, it is ranging from 380 to 6450 μs/cm with an average of 1954 μs/cm. The Highest EC value of groundwater sample was observed during 2009 PRM when compared with other seasons.

5.2.3 Total Dissolved Solids (TDS)

The Total dissolved solids (TDS) ranges from 240 mg/l to 4140 mg/l with an average of 1259 mg/l. TDS was higher in 2009 PRM followed by 2007 POM, 2007 PRM and 2009 POM indicating the dilution of groundwater during monsoonal period.

5.2.4 Anions

The order of dominance of anions in the study area during four different seasons are given in Table: 5.1

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<tr>
<th>Season</th>
<th>Dominant Anions</th>
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<tbody>
<tr>
<td>2007 POM</td>
<td>Cl⁻ &gt;HCO₃⁻ &gt;SO₄²⁻ &gt;NO₃⁻ &gt;F⁻</td>
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<td>2007 PRM</td>
<td>Cl⁻ &gt;HCO₃⁻ &gt;SO₄²⁻ &gt;NO₃⁻ &gt;F⁻</td>
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Table: 5.1 The order of dominance of anions in different seasons
5.2.4 a) Bicarbonate

Bicarbonate represents the major sum of alkalinity. Alkalinity in water is the measure of its capacity of neutralization. It is formed mainly due to the action of atmospheric CO\textsubscript{2} and CO\textsubscript{2} released from organic decomposition. In the study area bicarbonate ranges from 71 mg\textsubscript{l}^{-1} to 897 mg\textsubscript{l}^{-1} with an average of 306.6 mg\textsubscript{l}^{-1}. The concentration of HCO\textsubscript{3} is higher in 2009 POM and lesser in 2007 POM indicating that the contribution from carbonate chemical weathering process and also as from chemical industries (Mondal et al, 2004).

5.2.4.b) Chloride

The dominant anion is chloride followed by bicarbonate in 2009 PRM season and this ion is decreases in other seasons. In the study area Cl\textsuperscript{-} ranges from 31.5 mg\textsubscript{l}^{-1} to 1887.6 mg\textsubscript{l}^{-1} with an average of 465 mg\textsubscript{l}^{-1} indicating the leaching of Cl\textsuperscript{-} from topsoil/weathered zone and Base Exchange reactions (Freeze and Cherry, 1979). Cl\textsuperscript{-} concentration is also higher in most of the places than the permissible limit of 500 mg\textsubscript{l}^{-1} (WHO, 2004), it's also an indicator a longer distance of migration of groundwater along the flow path or anthropogenic impact or greater residence time.

5.2.4.c) Sulphate

Sulphate is commonly found in minor concentration due to lesser break down of organic substances from weathered Soil/Water (Miller 1979; Craig and Anderson 1979; Singh et al, 1994). The highest desirable limit of Sulphate in groundwater is 200 mg\textsubscript{l}^{-1}
and the maximum permissible limit is 400 mg/l (WHO, 2004). The concentration of 
$\text{SO}_4^{2-}$ in the study area ranges from 3 mg/l to 317 mg/l with an average of 60.9 mg/l. 
Sulphate concentration is higher in 2007 POM and lesser in 2007 PRM. The contribution 
of dissolved Sulphate ion varies in mineral like Gypsum, Marcasite (Anandhan, 2005). 
The other sources of this ion may also be due to bacterial fixation, the impact of 
Fertilizers and other anthropogenic sources.

5.2.4.d) Nitrate

The Nitrogen plays a dominant role in life cycle process of plants and animals. 
The Nitrate concentration in groundwater is mainly due to the organic, industrial 
effluents, fertilizer or nitrogen fixing bacteria, leaching of animal dung, sewage and 
septic tanks leakage through soil and water matrix to groundwater (Chidambaram, 2000). 
They get accumulated and decomposed during the monsoon period and also by the 
agricultural activity (Karanth 1991). The concentration of Nitrate in the study area ranges 
from 0.1 mg/l to 147 mg/l. The average Nitrate concentration in groundwater of 
Nagapattinam Coastal Region is within the permissible limit of 14.4 mg/l (WHO, 2004) 
in all the seasons. The higher concentration of nitrate may be due to the septic tank 
leakage into the shallow aquifers or due to the impact of fertilizers.

5.2.4.e) Fluoride

Fluoride concentration of ground water samples in Nagapattinam Coastal Region 
ranging from 0.1 mg/l to 13.43 mg/l with an average of 0.7 mg/l. The $F^-$ was higher in
2009 POM and less in 2009 PRM periods indicating the impact of dilution during the monsoon. The higher concentrations may be due to the industrial impact near the SIPCOT region at karaikal.

5.2.5 Cations

The order of dominance of cations in the study area during four different seasons are given in table 5.2

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Table : 5.2 The order of dominance of cations in different seasons.

5.2.5.a) Sodium

Sodium is the important and most abundant alkali metal which is highly mobile and soluble in groundwater. The concentration of Sodium in ground water sample in the study area varies from 6 mg/l to 1062 mg/l, with an average of 334.2 mg/l. Sodium concentration is higher in 2009 PRM and lesser in 2009 PRM, it’s indicating the contribution from weathering process of Na\(^+\) Plagioclase in gneiss along with the dissolution of Kankar or from the sea water intrusion as the study area is a coastal region with other anthropogenic sources.
5.2.5.b) Calcium

Calcium is an important element in many geochemical processes. Natural source of Calcium may be from minerals like Calcite, Plagioclase and Hornblende are the primary sources for Calcium in groundwater. In study area the Calcium concentration is ranging from 10 mgl\(^{-1}\) to 144 mgl\(^{-1}\) with an average of 40.8 mgl\(^{-1}\). Ca\(^{2+}\) was higher in 2009 PRM and lower during 2007 PRM.

5.2.5.c) Magnesium

Magnesium in groundwater are mainly due to the leaching of Magnesium bearing minerals from Mafic and Ultramafic rocks like Pyroxenite, Peridotite, Dunite, Anorthosite and Gabbro. Mg\(^{2+}\) ranges from 4.90 mgl\(^{-1}\) to 131.22 mgl\(^{-1}\) with an average of 35.6 mgl\(^{-1}\). Magnesium concentration is higher in 2009 PRM.

5.2.5.d) Potassium

Potassium in groundwater is generally lesser due to its lesser mobility (Herman Bouwer, 1978). It may be released due to weathering of Mica and Orthoclase Feldspars. K\(^+\) ions are released during weathering are generally used up in the formation of secondary minerals (Mathews, 1982). K\(^+\) ranges from 0.10 mgl\(^{-1}\) to 176 mgl\(^{-1}\) with an average of 23.2 mgl\(^{-1}\). Higher concentration is noted in 2007 POM and lesser in 2009 PRM. Potassium in most of the samples are well within the prescribed limit with fewer abnormalities irrespective of seasons may be due to urban pollution and fertilizer leaching.
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Table: 5.10 Hydrochemistry of Groundwater POM 2009 (Expressed in mg/l)
The whisker plot shows that the Na\(^+\) and Cl\(^-\) have the higher range of concentrations and lower values in SO\(_4^{2-}\) found in all seasons. The overall trend of cation and anion are remaining same in all seasons irrespective of depth.
5.3.0 SPATIAL DISTRIBUTION

The attribute values of the specific locations were used to create a spatial data, in order to obtain an overall behavior of the electrical conductivity in the study area. The spatial data of electrical conductivity gives a general trend of the characteristics of the anions and cations present in water. This initially provides us first hand information about the geochemically active regimes (Chidambaram, 2000; Srinivasamoorthy, 2004; Anandhan, 2005). Spatial distribution of EC of groundwater samples of Nagapattinam Coastal Region was done for all four different seasons (Fig. 5.2 a,b,c,d).

In PRM 2007, EC ranges from 500 – 4410 µs/cm. Higher EC was observed in center portion of the study area ranges from 2500 – 4400 µs/cm.

In POM 2007, EC ranges from 380– 4480 µs/cm. In 75% of study area EC ranges from 1200 – 3800 µs/cm. Particularly the centre portion of the study area observed higher EC ranges from 1800 to 4000. The SE portion of the study area also observed higher EC.

The study reveals that in PRM 2009, EC ranges from 450-6450 µs/cm. Higher EC ranges from 2000 to 6000 µs/cm was noted in regions covered by the centre portion of the study area.

In POM 2009, EC ranges from 430 – 4090 µs/cm. Higher EC observed in Centre portion of the study area ranges 1700- 3800. In this post monsoon, higher EC was also noted in the NE portion of the study area.
EC for the year 2007

Fig: 5.2a

Fig: 5.2b

EC for the year 2009

Fig: 5.2c

Fig: 5.2d

Fig: 5.2 a,b,c,d Spatial distribution of EC of groundwater samples
5.4.0 WATER CLASSIFICATION

In recent years greater emphasis is given to quality of groundwater due to its increasing usage. To establish quality criteria, a measure of chemical, physical and bacterial constituents has to be compared with recommended limits of water quality, for proper protection and development of groundwater basins.

The voluminous raw hydro geochemical data analyzed is often processed manually for interpretation. To simplify the interpretation of the data, a computer program ‘WATCLAST’ written in C++ (Chidambaram, 2003) was used for calculation and graphical representations. The parameters used are summarized in Table 5.11. The Program requires milligram per liter (mg/l) concentration of Ca$^{2+}$, Mg$^{2+}$, Na$^+$, K$^+$, Cl$^-$, HCO$_3^-$, SO$_4^{2-}$ and other parameters including TDS, EC and pH.

5.4.1 Comparison with Drinking Water Standard

The quality of water is determined by number of factors like geology, soil, weathering, presence of industries, emission of pollutants, sewage disposal and other environmental conditions, with which it alters from the point of its entry to exit. All the above said aspects alter chemical composition of the groundwater, which plays a significant role in determining the water quality for various utility purposes. Criteria used for classification of water for particular purpose is not suitable for other standards. Better results can be obtained by combining chemistry of all the ions than the individual or paired ionic character (Handa, 1964; Hem, 1985).
## Parameters of study

<table>
<thead>
<tr>
<th>Parameters of study</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Percentage of Permissible Error</td>
<td>Freeze and Cherry (1979)</td>
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<td>2. Piper’s Classification</td>
<td>Piper (1944)</td>
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<td>3. Johnson’s Plot</td>
<td>Lawrence and Balasubramanian (1994)</td>
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<td>4. USSL Classification</td>
<td>Wilcox (1955)</td>
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<td>5. Gibbs Plot</td>
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<td>6. Handa Classification</td>
<td>Handa (1964)</td>
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<td>7. Indices Base Exchange and Water Type</td>
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<td>8. Permeability Index and Plot</td>
<td>Doneen (1948)</td>
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<td>9. Residual Sodium Carbonate</td>
<td>Eaton (1950)</td>
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<td>10. Sodium Absorption Ratio</td>
<td>Richards (1954)</td>
</tr>
<tr>
<td>15. Sodium Percentage</td>
<td>Todd (1980)</td>
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**Table 5.11.** The parameters used in preparation of ‘WATCLAST’ Programme
<table>
<thead>
<tr>
<th>Season</th>
<th>pH</th>
<th>Temp°C</th>
<th>EC</th>
<th>TDS</th>
<th>Ca⁺</th>
<th>Mg⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Cl⁻</th>
<th>HCO₃⁻</th>
<th>SO₄⁻</th>
<th>NO₃⁻</th>
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<tr>
<td></td>
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<td>380</td>
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<td>12</td>
<td>6</td>
<td>32</td>
<td>1</td>
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<td>5</td>
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<tr>
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<td>2610</td>
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<td>114</td>
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<tr>
<td></td>
<td>Min</td>
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<td>26.7</td>
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<td>104</td>
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<td>144</td>
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<td>-</td>
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<td>-</td>
<td>-</td>
<td>200</td>
<td>-</td>
<td>200</td>
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<td>50</td>
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<td>ISI 1995</td>
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<td>-</td>
<td>500</td>
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<td>-</td>
<td>200</td>
<td>-</td>
<td>200</td>
<td>-</td>
<td>45</td>
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</table>

**Table: 5.12** Range of ionic concentration including well head parameters
The suitability of water for different purposes like drinking, industrial and irrigation are assessed due to its extensive development. Drinking water standard is based on the presence of objectionable taste, odors or colors along with the presence of substances with adverse physiological effects. The portability of drinking water is mainly based on the permissible limit of certain parameters. When water exceeds the permissible limit, it is unfit for human consumption.

The Table 5.12 exhibits the range of ionic concentration in groundwater of the study area and prescribed specifications of WHO (2004) and ISI (1995). Groundwater is near acidic to alkaline (6.4 to 9.4) and mostly oxidizing. Parameters exceeding permissible limit have been identified in most of the locations indicating higher ionic concentration. EC, TDS, Ca\(^{2+}\), Mg\(^{2+}\), Na\(^{+}\), Cl\(^{-}\), F\(^{-}\), SO\(_4^{2-}\), HCO\(_3^{-}\), and NO\(_3^{-}\) exceed the maximum permissible limit of WHO (2004) in all the seasons. HCO\(_3^{-}\) is also within the permissible limit of ISI (1995) standard for few locations indicating precipitation of CO\(_3^{2-}\) as scales in pipelines (Rangarajan and Balasubramanian, 1990). TDS is higher and exceeding ISI standard (1995) limits for drinking water in all seasons. Most of the samples fall above 500 mg\text{l}^{-1} and there are minor representations of samples in all the season between 200-500 mg\text{l}^{-1} categories. Most of the groundwater samples in the study area are unfit for domestic and drinking purpose.

5.4.2 Irrigation Quality

An assessment of the suitability of groundwater for irrigation is based on an assessment of the content of sodium compared to the total cations in the system. High Sodium waters are not suited for irrigation activities because the sodium ion engages in
cation exchange processes which tend to affect the ability of soils to sustain crop productivity. The Na⁺ ion adsorbs onto cation exchange sites, causing soil aggregates to disperse, thus reducing soil permeability. The work of Wilcox (1955) demonstrated that irrigation waters enriched in Na⁺ results in cation exchange reactions whereby Na⁺ is taken up and Magnesium and Calcium are released into the water. On other hand, the use of Ca-enriched waters for irrigation leads to the release of Na⁺ ion from cation exchange sites, and the preferential adsorption of the Ca²⁺ ions onto the cation exchange sites. In addition, high salinity waters have the tendency to reduce the osmotic potentials of irrigation crops over time. Usually the sodium percent and the EC (which measures the salinity of water) are used collectively to assess the quality of water for irrigation activities. In this study, the Wilcox diagram (Wilcox, 1955) which plots the sodium hazard against the EC was used to assess the quality of the four major groundwater classes in the study area for irrigation activities. Excessive Na⁺ causes soil mineral particles to disperse and water penetration to decrease (Jalali, 2007). High Na⁺ effects become apparent when infiltration rate of a soil is reduced to the extent that the crop is not adequately supplied with water. The problem of high Na⁺ waters is more severe in Clay-rich soils: it is much more severe in Montmorillonitic soils and least in Maolinitic soils (Jalali, 2007).

Hence the suitability of groundwater for irrigation purpose is mainly based on the estimation of the parameters like SAR, Na%, RSC. Total Na concentration and EC are important in classifying the water for irrigation purposes (Wilcox, 1955). Sodium percentage is calculated against major cations and expressed in terms of SAR.
5.4.3 Salinity Hazard

The poor quality waters due to high electrical conductivity will cause Salinization (Ghafoor et al., 1990, 1993). It is imperative to find good quality of irrigation water by increasing the depth or by changing the site of tube well. Excess salt increases the osmotic pressure of the soil solution that can result in a physiological drought condition. Even though the field appears to have plenty of moisture, the plants wilt because insufficient water is absorbed by the roots to replace that lost from transpiration. Based on Electrical Conductivity, waters are classified into four major classes (Richards 1954). The boundary values between the individual classes are 250, 750 and 2250 μscm$^{-1}$. These limit values were determined on the basis of the relationship between the electrical conductivity of waters and the electrical conductivity of saturated soil extracts.

- Low-Salinity Water (EC < 250 μscm$^{-1}$) can be used for irrigation
- Medium-Salinity Water (250 < EC < 750 μscm$^{-1}$) can be used if the soil is washed with a moderate amount of water.
- High-Salinity Water (750 < EC < 2250 μscm$^{-1}$) cannot be used on soils with restricted drainage.
- Very High-Salinity Water (EC > 2250 μscm$^{-1}$) is not suitable for irrigation under ordinary conditions, but it can be used under very special circumstances.
Fig: 5.3 Wilcox classification of ground water for irrigation purpose
The Wilcox classification of ground water for irrigation purpose (Fig.5.3) applied by United State Salinity Laboratory for obtaining the classification of irrigation water. This diagram shows that during the pre and post monsoon the samples fall in C3 and C4 category (High Salinity Hazard).

5.4.4 Sodicity Hazard

Salinity, Sodicity and Toxicity generally need to be considered for evaluation of the suitable quality of groundwater for irrigation (Todd, 1980) and (Shainberg and Oster, 1976). The Sodicity hazard is determined by absolute and relative cation concentrations. If the content of Sodium is high, the Sodicity hazard is high and vice versa. If Calcium and Magnesium are dominant, the hazard is low. The classification of irrigation water with respect to SAR is mainly based on the effect of exchangeable Sodium on the physical condition of the soil.

Low Sodium Water (SAR = 0 to 10)

Medium Sodium Water (SAR = 10 to 18)

High Sodium Water (SAR = 18 to 26)

Very High Sodium Water (SAR > 26)

The Sodium Absorption ratio is calculated by using the epm values in the formula given below;

\[ \text{SAR} = \frac{Na}{\sqrt{\frac{Ca+Mg}{2}}} \]
The values of Sodium adsorption ratio and groundwater Electrical Conductivity are the main criteria that characterize the degree of soil salinization and alkalization hazards in the processes of fluctuation of the shallow mineralized groundwater, or in flow regime processes if such groundwater is used for irrigation. The unfit waters due to high Electrical Conductivity will cause salinization (Ghafoor et al, 1990) and (Goyal and Jain, 1982). The unfit water samples (containing excess of carbonate and bicarbonate) for irrigation will precipitate soil solution Calcium and increase solution Sodium, resulting in soil dispersion (Emerson and Bakker, 1973) as well as impaired nutrient uptake by plants. Most of the samples of Post and Pre Monsoon fall in the low Sodium hazards region are distributed from S1 to S2 category (Low to High). Many samples have good representation in S2 and S3 category on both seasons and few representations in S4 category (Very high Sodium hazards).

In general, the increase of ion concentration results in the unsuitability of water for irrigation purpose. Higher Electrical Conductivity and Sodium hazards are noted during both seasons. Majority of samples during this post monsoon season fall under C2S1, C3S1, C3S2, C4S3 and C4S4 categories. The cluster of Pre monsoon season most of the samples fall in C3S1 and C3S2 category this may be due to dissolution of minerals, dispersivity of ions, agricultural practices etc. In POM season the quality is comparably better to the PRM season with samples representing C3S1 category. In general, the applications of Gypsum in these soil increases soil permeability (Ghafoor, 1993).
5.4.5. Water Infiltration Rate (Doneen)

An infiltration problem related to water quality occurs when the normal infiltration rate for the applied water or rainfall is appreciably reduced and water remains on the soil surface for long duration or infiltrates too slowly to supply the crop with sufficient water to maintain acceptable yields. Although the infiltration rate of water into soil varies widely, it can greatly be influenced by the quality of irrigation water, soil factors; such as structure, degree of compaction, organic matter content and ions, which can also greatly influence the intake rate. The two most common water quality factors which influence the normal infiltration rate are the salinity of water and its Sodium content relative to the Calcium and Magnesium content. High salinity water will increase infiltration. Low salinity water or water with high Sodium to Calcium and Magnesium ratio will decrease infiltration. Both factors may operate at the same time. The infiltration rate generally increases with increasing salinity and decreases with either decreasing salinity or increasing Sodium content relating to Calcium and Magnesium and SAR. Therefore, the two factors, salinity and SAR provide information on its ultimate effect on water infiltration rate. The Permeability Index (PI) of the water was derived by Doneen, (1948) by using major cations and HCO$_3^-$ concentration using the following expression;

$$PI = \left[ \frac{\text{Na}+(\text{HCO}_3^-)}{\sqrt{\text{Ca}+\text{Mg}+\text{Na}}} \right] \times 100$$

Permeability index is an important factor which influences quality of irrigation water, in relation to soil for development in agriculture. Another effect of high Na$^+$ concentrations in irrigation water is related to the bicarbonate ion concentration. Toxicities related to the Bicarbonate ion arise when soils are deficient in Iron and other
micronutrients. The PI of a water sample measures the collective concentrations of Na\(^+\) and HCO\(_3^-\) relative to the total cation content of the water. Permeability indices of the water samples in each of the water classes in the area were calculated as part of the assessment of the irrigation quality of groundwater from the study area. PI was plotted together with the SAR content of the groundwater samples. Three water types are clearly distinguishable similar to Doneen’s chart: Class I waters are the ‘Suitable’ Types for Irrigation and are characterized by Low PIs; Class II waters are generally ‘Acceptable’; Class III waters are ‘Not Suitable’ for irrigation.

Based on permeability index and SAR a new plot has been designed and samples fall in Class I, Class II and Class III to find out suitability of groundwater for irrigation purpose(Fig:5.4 a,b,c,d). All the samples during PRM and POM samples are fall in Class II and Class I. Samples of Class I indicate Good Permeability and can be used for irrigation purpose. The most of the samples of POM and PRM show good representation in the Class I indicating that they can be used for irrigation purpose. It is interesting to note in this diagram that there is a linear relationship of the SAR and PI in Class I and it reduces in Class II and III.
Fig: 5.4.a,b Suitability of groundwater for irrigation purpose
Fig: 5.4.c,d Suitability of groundwater for irrigation purpose
5.4.5.a Crop Salt Tolerance

Crop salt tolerance also needs to be taken into account when assessing the suitability of water and soil for irrigation. The potential impact of irrigation water quality on soil structure can be evaluated using ECi (EC of infiltrating water) and SAR values. The salt content of the soil water in the crop’s root zone referred to as the average root zone salinity (ECse) which is important in assessing the crops that are suitable for growing in particular soil.

The average ECse can be calculated using the measured ECi of the irrigation water. Average root zone leaching fractions for four soil types are listed in (Table 5.13). It requires estimation of the average root zone leaching fraction (LF) of the soil under irrigation, i.e. the proportion of applied water moving below the root zone. This is shown in (Fig 5.5).

<table>
<thead>
<tr>
<th>Soil Type</th>
<th>Average Root Zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>0.6</td>
</tr>
<tr>
<td>Loam</td>
<td>0.33</td>
</tr>
<tr>
<td>Light Clay</td>
<td>0.33</td>
</tr>
<tr>
<td>Heavy Clay</td>
<td>0.2</td>
</tr>
</tbody>
</table>

**Table 5.13** Average root zone leaching Fraction for different soils
5.4.6 Classification for Domestic Purpose

According to Wilcox classification (1955) the water is classified based on the Na% with respect to the other cations present in water. Na% of the samples during PRM 2007 and 2009 for almost 24% of the samples, fall in Permissible category (Table 5.14). Many representations (45%) of samples are noted in Doubtful class and 27% in the Unsuitable category and rest in the good category. In POM 2007 and 2009 Na% for almost 45% of the samples, fall in doubtful category and 20 to 25% samples are unsuitable and 25% of the samples are in Permissible category and rest in good category.

\[
\text{Na\%} = \frac{\text{Na} + \text{K}}{\text{Ca} + \text{Mg} + \text{Na} + \text{K}} \times 100
\]

In Na% Eaton (1950) classification of groundwater for irrigation purposes, 25% of the samples fall in Safe category for irrigation purposes during both seasons. 75% of samples fall in unsafe category during all seasons.

In addition to SAR and Na%, the excess carbonate and bicarbonate in groundwater over the sum of Calcium and Magnesium also influences the Unsuitability of groundwater for irrigation. This is defined as Residual Sodium Carbonate (R.S.C) (Opnanari, 1989). The SAR indicates the relative proportion of Sodium to Calcium + Magnesium whereas; Residual Sodium Carbonate is an index, which indicates the Sodium Hazards (Sodification of soil). The unfit water samples (containing excess of Carbonate and Bicarbonate) for irrigation will precipitate Calcium in soil from solution
and increase of Sodium in solution, resulting in soil dispersion (Emerson and Bakker, 1973) and well as impaired nutrient uptake by plants (Kanwar and Chaudhry, 1968). This is defined as Residual Sodium Carbonate (R.S.C) (Richards, 1954). High concentration of Sodium in irrigation water can result in the degradation of soil structure. This will reduce water infiltration into the soil surface and down the profile, and limit aeration, leading to reduced crop growth.

\[
RSC = (CO_3^{2-} + HCO_3^-) - (Ca+Mg)
\]

During both pre and post monsoons 75% of the samples fall in Good category. (Table 5.14). It is to be noted that 25% of samples of both seasons fall in the medium and bad category.

Hardness refers to the reaction with soap and formation of scale. It increases the boiling point and do not have adverse effect on human health. In the study area 60% of the samples fall in the Moderately Hard category during pre and post monsoons. Few of the remaining samples of both the seasons fall in Very Hard category(20%) (Table 5.14). Few samples also represent Slightly Hard category (20%).

\[
TH = 2.497 \text{Ca} + 4.115 \text{Mg} \quad \text{(Todd, 1980)}.
\]

Chloro-Alkaline indices i.e. 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 matrix when both the indices are positive. All the ionic concentration is expressed in epm. 70 % of the ground water samples of the study area exhibit exchange of (Na\(^+\)K\(^+\)) in the rock to Ca\(^{2+}\), Mg\(^{2+}\) in groundwater by
### Table: 5.14 Watclast Classification for the domestic purpose

<table>
<thead>
<tr>
<th>Na% Wilcox (1955)</th>
<th>USGS Hardness</th>
<th>TDS Classification (USSL,1954)</th>
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<tr>
<td>Excellent</td>
<td>&lt;250</td>
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</tr>
<tr>
<td>Good</td>
<td>250-750</td>
<td>200-500</td>
</tr>
<tr>
<td>Permissible</td>
<td>750-3000</td>
<td>100-3000</td>
</tr>
<tr>
<td>Doubtful</td>
<td>3000-15000</td>
<td>5000-15000</td>
</tr>
<tr>
<td>Unsuitable</td>
<td>&gt;15000</td>
<td>&gt;25000</td>
</tr>
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</table>

| Na% Eaton (1950)  |  |  |
|-------------------|  |  |
| Excellent         | <50            | Na+<0.14                      |
| Good              | 50-150         | 0.14-0.84                     |
| Permissible       | 150-500        | 0.85-2.3                      |
| Doubtful          | 500-1500       | 2.3-10                        |
| Unsuitable        | >1500          | >10                          |

| S.A.R. Richards (1954) |  |  |
|-------------------------|  |  |
| Excellent               | <0.25          | 2                          |
| Good                    | 0.25-1         | 1                          |
| Fair                    | 1-2            | 2                          |
| Poor                    | >2             | 3                          |

| R.S.C. Richards (1954)  |  |  |
|-------------------------|  |  |
| Excellent               | <1             | 1                          |
| Good                    | 1-2            | 2                          |
| Medium                  | 2-5            | 3                          |
| Bad                     | >5             | 4                          |

| EC Wilcox (1955)        |  |  |
|-------------------------|  |  |
| Excellent               | <250           | 200                        |
| Good                    | 250-750        | 500                        |
| Permissible             | 750-2250       | 1500                       |
| Doubtful                | 2250-5000      | 5000                       |
| Unsuitable              | >5000          | >15000                     |

| Table: 5.14 Watclast Classification for the domestic purpose |  |  |
|------------------------------------------------------------|  |  |


Scholler (1965) Index to Base Exchange during all seasons. The rest of the samples (25%) of both seasons (Table 5.14) fall in (Na’K’) groundwater to Ca$^{2+}$, Mg$^{2+}$ rock category. It is calculated by the following expression;

$$\text{CAI 1} = \frac{[\text{Cl}-(\text{Na+K})]}{\text{Cl}}$$

$$\text{CAI 1} = \frac{[\text{Cl}-(\text{Na+K})]}{[\text{SO}_4+\text{HCO}_3+\text{CO}_3+\text{NO}_3]}$$

Scholler classification (1967) for the dominance of anion exhibits that Type I ($r\text{HCO}_3 > r\text{SO}_4$) is predominant in all the samples.

Groundwater extracted from the study area for various purposes is transported by metallic pipes that may or may not be suitable for the transport. This fact is highlighted using Corrosivity Ratio (CR) proposed by Ryzner (1984). The formula for calculating CR is;

$$\text{CR} = \frac{[(\text{Cl}/35.5) + (\text{SO}_4/96)]}{2(\text{HCO}_3)} \times 100$$

It varies with seasons from 70% to 80% fall in unsafe category during PRM2007, POM2007, PRM2009 and POM2009 and rest of the samples fall in safe category irrespective of season.

The Styfzands classification (1989) based on the Chloride concentration in groundwater exhibits that Brackish and Brackish-salt categories. 65%, 70%, 65% and 45% of samples fall in Brackish Category during PRM2007, POM2007, PRM2009 and POM2009 respectively. 20%, 15%, 25% and 30% of samples fall in Fresh Brackish Category during PRM2007, POM2007, PRM2009 and POM2009 respectively (Table 5.14). The rest of samples are representations in Fresh Category. The higher concentration of Chloride in groundwater may be due to sea water intrusion (Senthilkumar et al, 2008).
5.5.0 GEOCHEMISTRY

5.5.1 Mechanism controlling water chemistry

Gibbs, (1970) put forward a Boomerang envelope model to describe the controls of natural water chemistry and classified the controls of surface water chemistry to three types, namely rock control, evaporation/crystallization, and precipitation (Fig.5.6). In general, the rainfall dominated water has Na\(^+\) and Cl\(^-\) as major ions; the weathering dominated water has high Ca\(^{2+}\) and HCO\(_3^-\) concentration, and the evaporation/crystallization dominated water is characterized with high Na\(^+\) and Cl\(^-\) contents (Meybeck, 2003). By plotting total dissolved salt concentrations against relative proportions of the principle anions for many surface waters in the world, he obtained a curve with two arms. Proceeding along the lower arm to the right, waters become lower in salt concentration and achieve a composition resembling rain water (indicated by a high Cl\(^-\) to HCO\(_3^-\) ratio). This arm indicates an increasing dominance of precipitation and thus dilution of dissolved solids. Proceeding to the right along the upper arm, waters with high salt concentrations are encountered, in which Cl\(^-\) (and Na) become dominant, due to the high solubility of NaCl. This arm indicates a dominance of evaporation in determining water chemistry. On the left side (where the arms join) waters can be found in which rock and soil weathering is the dominant process (i.e. without much interference of dilution or evaporation). This simple model has been widely used, but for some cases it is not reproducible. For example, Kilham,(1990) showed that the envelope of data for African waters is shaped like an alchemist’s retort rather than a boomerang. In fact, many
Fig 5.6.a Gibbs plot for the groundwater samples in POM 2007 (after Gibbs, 1970)

Fig 5.6.b Gibbs plot for the groundwater samples in PRM 2007 (after Gibbs, 1970)
Fig 5.6.c Gibbs plot for the groundwater samples in POM 2009 (after Gibbs, 1970)

Fig 5.6.d Gibbs plot for the groundwater samples in PRM 2009 (after Gibbs, 1970)
other factors, such as local variations in hydrologic flow paths and local biogeochemical processes, can easily modify surface water chemistry to exceed the bounds of the original Gibbs envelope. Thus, the controls on water chemistry are different between different regions, and it is necessary to investigate in detail for each individual geological cell.

The samples of the study area during the PRM07 (Fig.5.6.b) in the cation plot fall in the Rock Weathering zone and the anion plot shows both weathering and evaporation dominance. In the PRM09 samples (Fig.5.6.d) fall in weathering zone and evaporation in cation plot. But in the anion plot most of the sample falls in the weathering dominance region. In POM07 (Fig.5.6.a) and POM09 seasons (Fig.5.6.c) the samples in the cation plot are concentrated near the weathering and evaporation boundary. But in anion plots more number of samples falls in evaporation zone than the pre monsoon seasons. The basic concept of the diagram is based on the TDS and few ion ratios but still few samples which fall outside the boomerang plot and those of higher TDS which fall in the evaporation zone may also be due to anthropogenic sources other than the natural sources like rain, weathering and evaporation.

Still the impact of human activities on water chemistry does not have a perfect signature on this method of evaluation or it is considered that original Gibbs envelope implies that the impacts of human activities on water chemistry are relatively weak.
5.5.2 Piper Facies

Hydrogeochemical facies interpretation is a useful tool for determining the flow pattern and origin of groundwater masses. Piper (1944) classified hydrogeochemical facies using trilinear diagram. It consists of two lower triangular fields and a central diamond shaped field. All the three fields have incorporation of major ions only. The Triangular fields are plotted separately with epm values of cations (Ca$^{2+}$, Mg$^{2+}$) alkali earth, (Na$^+$+ K$^+$) alkali, (HCO$_3^-$) weak acid and (SO$_4^{2-}$ and Cl$^-$) strong acid. Water facies can be identified by projection of plots in the central diamond shaped field. This plot has been applied by several authors to understand the hydrogeochemical facies (Karanth, 1991; Chidambaram, 2000; Subramani, et al., 2005; Anandhan, 2005; Jasrotia, 2007; Pandian and Sankar, 2007). The trilinear piper diagram is one way of comparing quality of water.

The published studies variably report groundwater that are fresh to saline, alkaline to acidic, and often have moderate to high chloride concentrations. Examples include America (Foster, 1950; Thorstenson et al., 1979; Chapelle, 1983; Chapelle and Knobel, 1985), Australia (Blake, 1989; Herczeg et al., 1991; Habermehl, 1980, 1983, 1986; Jankowski and McLean, 2001), France (Batard et al., 1982; Blavoux et al., 1982), Germany (Griesshaber et al., 1992), Niger (Andrews et al., 1994), Portugal (Aires-Barros et al., 1995, 1998; Marques et al., 2000, 2001), Siberia (Chudaev et al., 2001; Shandet al., 1995), Spain (Cero´n and Pulido-Bosch, 1999; Cero´n et al., 1998, 2000), Switzerland (Wexsteent al., 1988), and Turkey (Greber, 1994).
Fig: 5.7.a Piper plot exhibiting the chemical facies of groundwater samples for POM
Fig: 5.7.b Piper plot exhibiting the chemical facies of groundwater samples for PRM
The evolution of ground water chemistry represented by the samples falling in Figure 5.7a,b shows that most of the PRM07 samples are NaCl type showing the dominance of sodium and chloride as the study area is located along the coast most of the samples show contamination by Sea water with the dominance of Na\(^+\) and Cl\(^-\) ions. During the PRM09 and POM07 are represented by Na Cl HCO\(_3\) type and followed by Na Cl. The POM09 shows dominance of Na Mg Cl HCO\(_3\) type followed by Na Cl HCO\(_3\) and then by Na Cl. The study area being coastal alluvial terrain during PRM higher concentration of mono valant anions and cations are noted. Later POM results in dissolution of minerals and there by introducing the dissolved carbonates which results in Na Cl HCO\(_3\) type. The evolutionary trend of the geochemical nature of ground water in the study area during different seasons can be represented as follows

\[
Na^+Cl^- \rightarrow Na^+HCO_3^- \rightarrow Na^+HCO_3^- & Na^+Cl^-
\]

This indicates that post monsoon samples are enriched with sodium, bicarbonate and chloride types and, from this it is evident that sea water and tidal channel/canals plays a major role in controlling the groundwater chemical composition in the coastal shallow aquifer, which consists of recent alluvium. Nageswara [26] conducted study on groundwater salinity of the shallow aquifers in the central Kerala and inferred that saltwater encroachment into shallow aquifers can be minimised by construction of tidal barriers. The removal of sodium ions from seawater which has infiltered into fresh water aquifer has been described by a number of workers by the method of ion exchange [28, 31]. Sodium ion present in seawater will exchange to Ca\(^{2+}\) ions. The conversion of
calcium bicarbonate water to sodium bicarbonate water in many aquifers is also undoubtedly due to ion exchange [4, 13]. The freshwater will change into NaHCO₃ type water [3].

Groundwater typing based chemical composition falls in the following subdivision: (1) Na–Cl; (2) Na–Cl–HCO₃; and (3) Na–Mg–Cl; The chemical evolution of the regions groundwaters from fresh to the three evolved end members (Na–HCO₃, Na–Cl, and Na–Mg–Cl). Furthermore, Fig. 5.7 a,b shows that Na–HCO₃-rich groundwater have a ratio of Na/ HCO₃ very close to unity at all salinities. This, when accompanied by the absence of suitably Cl-poor calcium bicarbonate groundwater, shows that these waters do not evolve from Ca–HCO₃ groundwater that undergo normal ion exchange. (Schofield and Jankowski, 2004)

The result of a seawater intrusion into an originally freshwater coastal aquifer with the exchange complex already equilibrated with Ca–HCO₃ freshwaters. On the contrary, an enrichment of Na⁺ together with a depletion of Ca²⁺ plus Mg²⁺ drives the composition along the other trend, thus towards the Na–HCO₃ water type. In this case the trend indicates an ongoing refreshening of an originally saline aquifer already equilibrated with Na-bearing exchange complex.

There are substances which absorb and exchange their cations, with cations present in the groundwater. The exchange process of Na⁺ in water for Ca²⁺ and Mg²⁺ 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 soils are
usually hard when dry (Wilcox, 1955). Variation of anions from recharge to discharge varies from $\text{HCO}_3^- \rightarrow \text{Cl}^-$ type due to the dissolution of ions in the pathway or due to precipitation and removal of $\text{HCO}_3^-$ from the aqueous system (Tirumalesh et al, 2007).

5.5.3 Ion Exchange

The ion exchange pool at any location in a flow path exemplifies water–rock interaction and atmospheric inputs, and ions will exchange at the mineral surfaces that reflect clay mineralogy, water pH, and water chemistry (Bullen and Kendall, 1998). There are various factors influencing the chemical composition of groundwater. According to Magariitz and Luzier, (1985), the variation in the major element chemistry of groundwater is controlled by dissolution precipitation, oxidation-reduction, and the behavior of Calcium and Sodium by ion exchange reactions. Ion exchange has fundamental importance in water-rock interactions (Howard and Lloyd, 1983). Under a given set of conditions various cations are not equally replaceable and do not have the same replacing power. The replacing power of ions generally is in Clay minerals is $\text{Na}^+ < \text{K}^+ < \text{Ca}^{2+} < \text{Mg}^{2+}$. This means that $\text{Ca}^{2+}$ will replace $\text{Na}^+$ more easily than $\text{Na}^+$ will replace $\text{Ca}^{2+}$, but there is no single universal replace ability series. The series also varies depending on the population of exchange sites and the nature of clay minerals (Grim, 1968). Chapelle et al, (1983) and Al-Ruwaih, (1984) point out that cation exchange reactions alter water composition along the flow path in a groundwater flow system. The order in which the dissolved cations $\text{Ca}^{2+} \text{Mg}^{2+}$, $\text{K}^+$ and $\text{Na}^+$ are removed from solution agrees with the relative stability of the cations on the exchange surface. The systematic
changes in cation composition of groundwater have been interpreted as direct evidence of exchange reactions. The chemical composition of groundwater may therefore be used to trace groundwater flow. It was assumed that ion exchange takes place and the concentration of mono- and di-valent cations varies along the flow path. Because ion exchange process and the flow down gradient both proceed directly as a function of time, the process variable tends to increase with distance of flow along hydrological gradients. The flow system can be considered an ion exchange system. The initial groundwater changes composition changes via ion exchange reactions. In the case of mono-valent cations replacing divalent cations, this process can be represented by the equation:

\[ A^{2+}_{\text{aq}} + 2BE_x \leftrightarrow 2B^+_{\text{aq}} + AE_x \]  

Equation (1)

Notations are defined as follows: A\(^{2+}\) is a divalent cation dissolved in (aq) water, B\(^{+}\) is a mono-valent cation dissolved in water; and E\(_x\) is exchanging substrate. In the groundwater the concentration of mono and divalent can be represented by the equation:

\[ A^{2+}_{\text{aq}} \leftrightarrow 2B^{+}_{\text{aq}} \]  

Equation (2)

Equation (2) gives a linear trend between mono and divalent ions. In every ion exchange system the slope is -2 in the plot of A\(^{2+}\) Vs. B\(^{+}\). The distance of the straight line to the axes depends on the initial water quality and characteristic of each ion exchange system. Between selected initial and final points in the system:

\[ \Delta [A^{2+}_{\text{aq}}] = -\frac{1}{2} \Delta [B^{+}_{\text{aq}}] \]  

Equation (3)
where A indicates the differences between the initial and final points. The minus sign denotes the opposite change in the molar concentration of mono and divalent cations. Selection of initial and final points may be arbitrary. Equation (3) is valid along the flow path, towards the direction of groundwater flow.

The ratio of $\text{Mg}^{2+}$/ $\text{Ca}^{2+}$ indicates that the samples range from 0.18 to 2.5 during POM07 (Fig.5.8a) and from 0.18 to 2.65 during POM09 (Fig.5.8c). Clusters of samples fall between 0.26 and 3.55 during PRM07 (Fig.5.8b) and between 0.1 and 2.06 during PRM09 (Fig.5.8d). The samples in general show wide representation below 1 and there are higher values of the ratios noted in the POM07, PRM07 and PRM09 than POM09, though there are higher representation of values in all the seasons. The high $\text{Mg}^{2+}$/ $\text{Ca}^{2+}$ ratio strongly indicates that the sea water intrusion containing high concentrations of $\text{Mg}^{2+}$. In general, freshwater was dominated by calcium and seawater by magnesium. The $\text{Mg}^{2+}$/ $\text{Ca}^{2+}$ ratio provided an indicator for delineating the sea–freshwater interface Mondal et al. (2008)

It is more difficult to model the weathering of Silicate. A general reaction of Sarin et al. (1989) for Silicate weathering is written as follows:

$$(\text{Na, K, Ca}^{2+}, \text{Mg}^{2+}) \text{Silicate} + \text{H}_2\text{CO}_3 = \text{H}_2\text{SiO}_4 + \text{H}_2\text{CO}_3 + \text{Na}^+ + \text{K}^+ + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{Solids}$$
**Fig: 5.8 a** The ratio of $\text{Mg}^{2+} / \text{Ca}^{2+}$ Plot for POM 2007
Fig: 5.8 b The ratio of $\text{Mg}^{2+}$/ $\text{Ca}^{2+}$ Plot for PRM 2007
Fig: 5.8 C The ratio of $\frac{\text{Mg}^{2+}}{\text{Ca}^{2+}}$ Plot for POM 2009
**Fig: 5.8 d** The ratio of $\text{Mg}^{2+}$ / $\text{Ca}^{2+}$ Plot for PRM 2009
It is seen from these weathering reactions that the major ion chemistry of river water alone cannot unambiguously distinguish between the major ion sources. This is because the dissolution of evaporates with complex chemical compositions in the desert areas largely obscures weathering products, giving rise to similar solution composition by different weathering reactions. However, if the above weathering reactions serve as the main source of major ions, stoichiometric analysis would still provide some qualitative information on identification of the weathering sources of these water in the study area.

5.5.3 a Na⁺/Cl⁻ Ratios

Although Na concentrations are somewhat higher than Cl⁻ concentrations, both are present in nearly equivalent amounts (Fig. 5.9). It can be concluded that Cl⁻ and for the most part, Na⁺, are derived from Halite.

\[ \text{Na}^+ \text{Cl}^- \rightarrow \text{Na}^+ + \text{Cl}^- \]

Some of the Na, however, appears to be derived from other processes, as the Na+/Cl- ratio is greater than 1, especially in the more concentrated winter waters. Some may be derived from other Na-bearing silicate minerals such as Albite (Stallard and Edmond, 1983, 1987). Weathering of Albite produces Kaolinite and Na+ ions (Hudson-Edwards et al, 2001). The major ionic ratio Na/Cl ranges from 0.7 to 1.0 in the samples from all Indian saltwater intruded states which is quite comparable to the seawater ionic ratio of 0.85.
Ratio of Na\(^+\)/Cl\(^-\) shows that almost all the samples are less than unity. Cl\(^-\) is greater during all the seasons higher value of Na is noted only in few samples in all the seasons. HCO\(_3\)\(^-\) concentration is higher in the POM09 in most of the samples. Majority of the PRM samples show lesser concentration of HCO\(_3\)\(^-\) then in monsoon and POM samples. This may be due to dissolution of CO\(_3\)\(^-\) salts after PRM. There are three possibilities of addition of Na into the system in the study area viz., weathering of feldspar, ion exchange and saltwater intrusion

\[ 2\text{NaAlSi}_3\text{O}_8 + 2\text{H}^+ + 9\text{H}_2\text{O} \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{Na}^+ + 4\text{H}_4\text{SiO}_4 \]

Albite                                      Kaolinite

The weathering of Plagioclase Feldspar also results in the release of Ca\(^{2+}\) and Na\(^+\) into the groundwater, the congruent dissolution of Plagioclase and K-Feldspar, consistent with the reactions

\[ \text{Na}_{0.62} \text{Ca}_{0.38} \text{Al}_{1.38}\text{Si}_{2.62} \text{O}_8 + 2.76\text{H}^+ + 5.24\text{H}_2\text{O} \leftrightarrow 0.62\text{Na}^+ + 0.38 \text{Ca}^{2+} + 1.38\text{Al} (\text{OH})_2^+ + 2.62 \text{H}_4\text{SiO}_4 \]

\[ \text{K}_{0.95} \text{Na}_{0.05} \text{Al}_{1.00} \text{Si}_{3.00}\text{O}_8 + 6\text{H}_2\text{O} + 2\text{H}^+ \leftrightarrow 0.95\text{K}^+ + 0.05\text{Na}^+ + \text{Al}(\text{OH})_2^+ + 3\text{H}_4\text{SiO}_4 \]

The excess value of Na\(^+\) in groundwater was probably attributed to the direct cation exchange process at the seawater–freshwater interface. Usually, the composition of fresh groundwater in the coastal watershed was often dominated by Ca\(^{2+}\) and HCO\(_3\)\(^-\) ions, which resulted from the carbonate aquifer dissolution. In seawater, the most dominant
ions are Na\(^+\) and Cl\(^-\); and aquifer systems in direct contact with seawater due to seawater intrusion will mostly have Na\(^+\) in the aquifer's matrix. When seawater intrudes into coastal aquifers, an exchange of cations occurs (Appelo and Postma, 2005).

Ca\(^{2+}\)/Na\(^+\) shows that the ratio is less (Fig 5.9) than 1.84 in most of the samples of the POM07 and less than 2.4 during PRM07 and < 4.66 during PRM09. Still lesser ratio is noted in the POM09 sample but they fall well below 0.85. Na\(^+\) is probably not derived solely from silicate weathering. There is a good representation of samples from 0.1 to 0.5 during the all the seasons. Higher value of Ca\(^{2+}\) is noted in three samples may be attributed to the weathering of Plagioclase. The dominance of Cl\(^-\) ion and Ca\(^{2+}\) over Na persist in all the seasons, this is mainly due to sea water intrusion and the ion exchange process. Cl/SO\(_4\) ratio is higher during all the seasons except during POM09.
Fig: 5.9 The relationship of Ca\(^+\)/Na\(^+\) to Cl\(^-\)/SO\(_4\)\(^-\).
5.5.3.b (Ca+ Mg)/HCO$_3$ Ratios

The diagram (Fig 5.10) shows that the relationship of pH to (Mg$^{2+}$ +Ca$^{2+}$)/HCO$_3^-$ ratio. The pH determines the nature of Carbonate present in water as H$_2$CO$_3^-$, HCO$_3^-$ and CO$_3^{2-}$, in acidic to alkaline pH conditions. The pH of study area ranges from acidic to alkaline condition, there is no clear demarcation of pH with regard to season. The pH can be classified into three categories as <7.5, 7.7-8.5 and >8.5. The first category is dominated by samples of the 2007 and most of the samples irrespective of period of sampling are grouped between the second category. Though there are representations of all the samples in the third category but it is dominated by POM09. This process also helps us to evaluate the H$^+$ ions circulation in the groundwater. Higher concentration of H$^+$ ions available during the POM is neutralized by the process of Sea water intrusion, weathering and dissolution. Further during PRM the pH reduces due to the exchange of cations in Clay/Rock matrix with H$^+$ ions in groundwater or due to the availability of neutralizing ions.
Fig: 5.10 The relationship of pH to (Mg$^{2+}$+Ca$^{2+}$)/HCO$_3^-$
The (mCa²⁺ +mMg²⁺-mSO₄²⁻) versus (mNa⁺ +mK⁻ - mCl⁻) relationship provides information on the geological sources of Ca²⁺ and Mg²⁺ in the aquifer. To account for meteoric Ca²⁺ from the dissolution of evaporative gypsum (CaSO₄⁻), an amount of Ca²⁺ equal to the concentration of SO₄²⁻ is subtracted from the sum of Ca²⁺ and Mg²⁺ ions. Calculation of the value of Na⁺ 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 the diagram. It is to be noted that the ‘Y’ axis crosses ‘X’ axis at 1 i.e the line along which (Ca+Mg)*/HCO₃⁻ is equal to unity (Fig 5.11). Field 1 has higher ratio of (Na+K)*/HCO₃⁻ and (Ca+Mg)*/HCO₃⁻, with Na⁺ + K⁺– Ca²⁺ + Mg²⁺ - HCO₃⁻ water type, Field 2 shows the dominance of excess (Ca + Mg)* and higher (Na+K)*. This shows that this field has the dominance of excess (Ca²⁺+Mg²⁺)* and (Na+K)*, with no significant indications of influencing anions, it may be due to contamination. Field 3 has the dominance of excess anion Cl⁻ over Na+K and higher (Ca+Mg)* which may be due ion exchange with Ca-Mg-Cl water type. Field 4 represents Ca-Mg-HCO₃-Cl water type.

Dissolution of carbonate minerals may take place not only to the attack of H₂CO₃ derived from dissolution CO₂⁻ in the water, but also to the attack of H₂SO₄²⁻ produced by input of atmospheric SO₂²⁻ into the waters or by oxidation of sulfides. The reaction as follows describes the dissolution of Carbonate minerals by both of H₂CO₃⁻ and H₂SO₄²⁻:
\[3Ca_{x}Mg_{1-x}CO_{3}^{-} + H_{2}CO_{3}^{-} + H_{2}SO_{4} = 3xCa^{2+} + 3(1-x)Mg^{2+} + 4HCO_{3}^{-} + SO_{4}^{2-}\]

One more possible source of SO\(_{4}^{2-}\) may be from dissolution of sulfate evaporate, but this source for Sulfate ion cannot be simply distinguished on stoichiometry. Several waters from the study area show excess [HCO\(_{3}^{-}\)+SO\(_{4}^{2-}\)] over [Ca\(^{2+}\)+Mg\(^{2+}\)]. This indicates dissolution of Na\(^{+}\) and K\(^{+}\) Silicate minerals is needed to account for this anion excess.

From the stoichiometry of these waters, we show that a considerable amount of [Ca\(^{2+}\)+Mg\(^{2+}\)] is balanced by SO\(_{4}^{2-}\). Assuming that SO\(_{4}^{2-}\) is balanced only by Ca\(^{2+}\) and Mg\(^{2+}\), the balance \([Ca^{2+}+Mg^{2+}]^*\) which is given by subtracting SO\(_{4}^{2-}\) valences from the total [Ca\(^{2+}\)+Mg\(^{2+}\)] equivalences, should be accounted for by weathering of Carbonate and/or Silicate rocks by carbonic acid. Accordingly, ratio of \([Ca^{2+}+Mg^{2+}]^*/[HCO_{3}^-]\) represent the relative amounts of Ca\(^{2+}\) and Mg\(^{2+}\), respectively from Carbonate and Silicate weathering and normally should be less than 1.

Under the same consideration, we assume that the balances of K\(^{+}\) and Na\(^{+}\), \([Na^+ +K^+]^*\), given through subtracting Cl\(^-\) valences from the total Na\(^{+}\)+K\(^{+}\) equivalent values of individual water sample, equalize amounts from Carbonate and/or Silicate weathering. Co-variation of \([Na^+ +K^+]^*/[HCO_{3}^-]\) Vs \([Ca^{2+}+Mg^{2+}]^*/[HCO_{3}^-]\) in these waters, as shown in Fig. 5.11, shows relative contributions of weathering to the chemical constituents of the waters. In Figure 5.11 most of the waters plot close to the point of intersection the two lines, namely of \([Ca^{2+}+Mg^{2+}]^*/[HCO_{3}^-]\) < 1 and \([Na^+ +K^+]^*/[HCO_{3}^-]\) = 0, indicative of dominance of Carbonate dissolution. The groundwater from the study area of all seasons, plots in the (Field-1) First quadrant. On the other hand, the waters of the PRM mostly fall into the (Field 4)
Fig: 5.11 The relationship of \((m\text{Ca}^{2+} + m\text{Mg}^{2+} - m\text{SO}_4^{2-})\) Vs \((m\text{Na}^+ + m\text{K}^+ - m\text{Cl}^-)\)
fourth quadrant, showing excess of both Cl over \([\text{Na}^+ + \text{K}^+]^*\), which may not be ascribed to weathering either of Silicate, or of Carbonate and of evaporate minerals. Probably, sea water intrusion, anthropogenic inputs, like fertilizer, are responsible for the excess of ions in the waters.

Simple cation exchange between \(\text{Ca}^{2+}\) or \(\text{Mg}^{2+}\) and \(\text{Na}^+\) in rocks might also very well explain the excess Na concentration, especially in the monsoon samples (Varsanyi and Kovacs, 1997; Stimson et al., 2001).

5.5.3. c Base Exchange

Most of the samples are clustered around 0.5 and \(\text{Ca}^{2+}/(\text{HCO}_3^- + \text{SO}_4^{2-})\) values around 0.1-0.2 indicating sea water intrusion. The Base Exchange is less prominent in the study area irrespective of the season few samples fall near unity or represent excess of \(\text{Na}^+\) (Fig 5.12). This indicates that the weathering is also one of the important factors during these seasons. Though the ion exchange process is also represented by few samples during this season the weathering is more prominent than other process.
Fig: 5.12 Base exchange plot
5.5.3.d Chadha Plot

The proposed diagram, the difference in milliequivalent percentage between alkaline earths (Calcium plus Magnesium) and alkali metals (Sodium plus Potassium), expressed as percentage reacting values, is plotted on the X axis, and the difference in milliequivalent percentage between weak acidic anions (Carbonate plus Bicarbonate) and strong acidic anions (Chloride plus Sulphate) is plotted on the Y axis. The resulting field of study is a square or rectangle, depending upon the size of the scales chosen for X and Y co-ordinates. The milliequivalent percentage differences between alkaline earths and alkali metals, and between weak acidic anions and strong acidic anions, would plot in one of the four possible sub-fields of the proposed diagram.

The main advantage of the proposed diagram is that it can be made simply on most spreadsheet software packages. The square or rectangular field describes the overall character of the water. The proposed diagram has all the advantages of the diamond-shaped field of the Piper diagram and can be used to study various hydrochemical processes, such as base cation exchange, cement pollution, mixing of natural waters, sulphate reduction, saline water (end-product water), and other related hydrochemical problems. In order to define the primary character of water, the rectangular field is divided into eight sub-fields, each of which represents a water type, as follows:

1. Alkaline Earths Exceed Alkali Metals.

Fig: 5.13 Chadha plot
3. Weak Acidic Anions Exceed Strong Acidic Anions.

4. Strong Acidic Anions Exceed Weak Acidic Anions.

5. Alkaline earths and weak acidic anions exceed both alkali metals and strong acidic anions, respectively. Such water has temporary hardness. The positions of data points in the proposed diagram represent Ca\(^{2+}\)–Mg\(^{2+}\)–HCO\(_3\)\(^-\) type, Ca\(^{2+}\)–Mg\(^{2+}\) dominant HCO\(_3\)\(^-\) type, or HCO\(_3\)\(^-\) dominant Ca\(^{2+}\)–Mg\(^{2+}\) type waters.

6. Alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions. Such water has permanent hardness and does not deposit residual Sodium Carbonate in irrigation use. The positions of data points in the proposed diagram represent Ca\(^{2+}\)–Mg\(^{2+}\)–Cl\(^-\) type, Ca\(^{2+}\)–Mg\(^{2+}\) dominant Cl\(^-\) type, or Cl\(^-\) dominant Ca\(^{2+}\)–Mg\(^{2+}\) type waters.

7. Alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions. Such water generally creates salinity problems both in irrigation and drinking purposes. The positions of data points in the proposed diagram represent Na\(^+\)–Cl\(^-\) type, Na\(_2\)SO\(_4\)\(^{2-}\) type, Na\(^+\) dominant Cl\(^-\) type, or Cl\(^-\) dominant Na\(^+\) type waters.

8. Alkali metals exceed alkaline earths and weak acidic anions exceed strong acidic anions. Such waters deposit residual Sodium Carbonate in irrigation use and cause foaming problems. The positions of data points in the proposed diagram represent Na\(^+\)–HCO\(_3\)\(^-\) type, Na\(^+\) dominant HCO\(_3\)\(^-\) type, or HCO\(_3\)\(^-\) dominant Na\(^+\) type waters.
This is a modified version of the expanded Durov diagram (Burdon and Mazloum, 1958). The same procedure was successfully applied by Vandenbohede et al., (2010) in a coastal aquifer to determine the evolution of two different hydrogeochemical processes within a freshwater lens. The hydro-chemical processes suggested by Chadha., (1999) are indicated in each of the four quadrants of the graph. These are broadly summarized as:

Field- 5. Ca-HCO₃ type Recharging Waters

Field- 6. Ca-Mg-Cl type Reverse Ion-Exchange Waters

Field- 7. Na-Cl type End-Member Waters (Sea water)

Field -8. Na-HCO₃ type Base Ion-Exchange Waters

The resultant diagram is exhibited in (Fig 5.13): Field -5 (Recharging water) when water enters into the ground from the surface it carries dissolved carbonate in the form of HCO₃⁻ and the geo-chemically mobile Ca. Field- 6 (Reverse ion-exchange) waters are less easily defined and less common, but represent groundwater where Ca²⁺ + Mg²⁺ is in excess to Na⁺ + K⁺ either due to the preferential release of Ca²⁺ and Mg from mineral weathering of exposed bedrock or possibly reverse base cation-exchange reactions of Ca²⁺ + Mg²⁺ into solution and subsequent adsorption of Na on mineral surfaces. Field 7 (Na⁺- Cl⁻) waters are typical sea water mixing and are mostly constrained to the coastal areas; Field 8 (Na⁺-HCO₃⁻) waters possibly represent Base Exchange reactions or an
evolutionary path of groundwater from Ca-HCO$_3$ type fresh water to Na - Cl mixed sea water, where Na$^+$ - HCO$_3^-$ is produced by Ion Exchange processes.

The plot show that majority of samples of study area fall in Field -7 (End member waters type) with few representation in Field -6, 8 and 5, indicating reverse ion exchange and base exchange and recharge respectively. Few PRM07 show field 6 indicating the dominance of Reverse ion exchange.

In general, the nature of the sample scatter in the plot shows that Na$^+$ K$^+$ is predominant in cations. In anions most of the samples shows dominance of Cl$^-$, SO$_4^{2-}$. Field-7 shows good representation of all the samples irrespective of season indicating the impact of sea water intrusion, followed by Reverse Ion Exchange and Base Ion Exchange processes and Recharge nature is also noted in very few samples.

5.5.4 Spatial Distribution of Ca$^{2+}$/ Na$^+$ ratio

The spatial distribution of the Ca$^{2+}$/ Na$^+$ ratio for different seasons (Fig 5.14 a,b,c and d) shows that the lowest value during PRM 2007(Fig:5.14b) occurs in the maximum of the study area in all directions. During POM 2007 (Fig.5.14a) only NE and middle of the study area have the lowest value. The POM 2009 (Fig.5.14c) shows maximum area in lower concentrations and NW, SE shows slightly higher concentration. During the PRM 2009 (Fig.5.14d) lower concentrations are noted in the maximum area and higher concentration found in NW. and slightly higher values in SE of the study area.
Fig: 5.14 a,b Spatial distribution of the Ca$^{2+}$/Na$^+$ ratio for the year 2007
**Fig: 5.14 c,d** Spatial distribution of the Ca$^{2+}$/Na$^+$ ratio for the year 2009
The distribution of this ratio is higher and lower in almost all formations in various seasons. It shows that lithology is not the major factor. The higher values indicate the dominance of the Calcium ion over the Sodium ion. The Calcium might be obtained from the minerals like Hornblende, Biotite, Anorthosite or the Calcic Plagioclase. It is also chiefly derived from the raw materials used for tanning process like lime. Since Sodium is the dominant ion in all the seasons major portion of the study area has a ratio lesser than 1. The Na might have derived from the process of natural weathering of minerals or from the usage of raw materials for tanneries like Sodium Chloride, Sodium Carbonate, Sodium Bi-Carbonate and Sodium Sulfate.

5.5.5 IONIC STRENGTH

Ionic strength (IS) 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, 1990).

\[ I = 0.5 \sum m z^2 \]

Where \( m \) is the concentration of a given ion in moles per liter and \( z \) is the charge on that ion. The terms in the summation include one for each ionic species present. A monograph, which simplifies calculation of ionic strength from analytical data in milligrams per liter, has been published by Hem (1961). The approximate value of Ionic Strength can also be computed from the specific conductance of the solution if this has been measured (Lind, 1970). However, calculation should not be made unless one should
have some knowledge of what the principal dissolved species present in the solution. If the composition is unknown for water with a specific conductance of 1,000 μ mhos, calculated value of IS could range from 0.0085 to 0.027.

The ionic strength ranges from 0.005 to 0.055. The distribution of the ionic strength in the samples varies from lower to higher ranges. There is no significant demarcation of the IS with season (Fig 5.19). The higher ionic strength indicates longer residence time or greater interaction with the host rock (Chidambaram et al, 2007) or dissolution of more components in the groundwater system, during the monsoon season. Since, there was no clear demarcation between the ionic strength of the samples for different seasons. A frequency histogram and the frequency curve were drawn (Fig. 5.20) to find out the distribution of samples in different frequency intervals. During PRM07 and PRM07 the distribution is bi-modal ranges. Distribution of samples at lower (0.013 - 0.025) and higher (0.035-0.040) values were noted during PRM07. Similarly the lower values (0.015-0.020) and another higher value (0.038) was noted at PRM09. The POM07 samples show higher distribution around (0.013 and 0.020) and that of POM09 show high distribution around (0.0075-0.0175) though higher values of ionic strength are noted in POM07 and PRM07 the frequency distribution shows that more samples are concentrated at the low ionic strength regions. It is evident that lesser ionic strength is noted in the post monsoon season samples and both higher and lower ionic strength grouping is more common in PRM. The process of dilution during the monsoon reduces the ionic strength of the samples during POM.
Fig: 5.15 Log pCO₂ Vs Ionic Strength
5.5.6 PARTIAL PRESSURE OF CARBON DIOXIDE (pCO₂)

In hydro-geological studies, the equilibrium of Calcium Carbonate in contact with natural water, either surface or groundwater is one of the most important geochemical reactions. Neutral water exposed to CO₂ in the atmosphere will dissolve CO₂ equal to the partial pressure. The CO₂ will react with H₂O to form H₂CO₃, a weak acid, and resulting solution will have a pH of about 5.7. Soil CO₂ from organic decomposition is another more important study in groundwater. As Calcite and Dolomite are soluble in acid solution, even rainwater will dissolve Carbonate rocks. Likewise, a change in pH can result in precipitation of CaCO₃ from a solution that was at equilibrium prior to the pH shift. The equilibrium constants for the various reactions in Carbonate equilibrium are as follows:-

Carbonate equilibrium constants at 25º C;

1. \[ \text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} \]
   \[ K_{\text{CaCO}_3} = \frac{\dot{a}\text{Ca}^{2+} \dot{a}\text{CO}_3^{2-}}{\dot{a}\text{CaCO}_3} = 10^{-8.35} \]

2. \[ \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \]
   \[ K_{\text{H}_2\text{CO}_3} = \frac{\dot{a}\text{H}^+ \dot{a}\text{HCO}_3^-}{\dot{a}\text{H}_2\text{CO}_3} = 10^{-6.4} \]
Fig: 5.16 Histogram representing the frequency distribution of the ionic strength
3. \[ \text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \]

\[ K_{\text{H}_2\text{CO}_3} = \text{H}^+ \text{HCO}_3^- = 10^{-10.3} \]

\[ \text{pH}_2\text{CO}_3 \]

4. \[ \text{H}_2\text{O} + \text{CO}_2 \leftrightarrow \text{H}_2\text{CO}_3 \]

\[ K_{\text{CO}_2} = \text{H}_2\text{CO}_3 = 10^{-1.5} \]

\[ \text{pCO}_2 \]

Partial pressure of CO\(_2\) (pCO\(_2\)) in rivers are commonly out of equilibrium with atmosphere. Two possible explanations for this apparent paradox are: (1) River waters (particularly perennial rivers) contain a significant fraction of high CO\(_2\) groundwater and (2) the rate of re-equilibrium with the atmosphere (by releasing the excess CO\(_2\)) is relatively slow (Stumm and Morgan, 1996; Holland, 1978). The Log P\(_{\text{CO}_2}\) (Raymahashay, 1986) for each samples are determined to study its relation to recharge (Prasanna et al., 2009, Chidambaram et al., 2009). Log P\(_{\text{CO}_2}\) value, during POM09 ranges from -1.43 to -4.2 (Fig 5.22). Lower values were observed in the samples of POM, indicating recharge. The ionic strength does not show any linearity with log P\(_{\text{CO}_2}\) values except for few samples in PRM. This may be due to higher pH or lesser neutralizing ions like Ca\(^{2+}\) (Raymahashay, 1986).
Fig: 5.17 Log pCO$_2$ Vs pH
An increase in the Carbon dioxide partial pressure during water-rock interaction influences the process of mineral dissolution. Carbon dioxide may be generated by several processes. In the absence of Calcite in mineral assemblage, saturation in Calcite and high pH may be easily reached during dissolution of Plagioclase in water with dissolved CO$_2$ coming from atmosphere and soil, and under such condition, for instance of Kaolinite saturation (Venturelli et al, 2003). The most of the Pre-Monsoon samples exhibit higher pCO$_2$ values > -2.5. The log pCO$_2$ values linearly decreases with pH. Higher pH shows lesser Log pCO$_2$ which is more significant during Monsoon season, which also indirectly indicates that, the fresh water recharge or atmosphere interaction with system. The higher values of log pCO$_2$ coincide with lesser values of pH indicating rock water interaction which is more prominent during both seasons.

It is also interesting to note that pH decreases from 8 to 6.5 with increase in log pCO$_2$. This systematic decrease of the log pCO$_2$ with season shows there is less interaction of the groundwater system with the atmosphere during the non-monsoon seasons the process of ion exchange or sea water intrusion may be prominent during the Non Monsoon season.

5.5.7 Chloride Vs Bicarbonate

Chloride ion usually plays a minor role in groundwater, but it is a dominant ion in seawater. In contrast, HCO$_{-1}^{3}$ is usually the most abundant negative ion in groundwater. There is such a large difference between the proportions of Cl$^{-}$ and HCO$_{-1}^{3}$ in groundwater and in seawater, that the ratio between these two ions (i.e. the ratio:
Cl−/HCO−1 3) is a useful index of the presence of seawater in groundwater. Hence, an increase of chloride content in groundwater is the most reliable indicator of the first stage of salt-water intrusion in groundwater. Goswani (1969) presented field studies at Digha (India) and, making use of Cl−1 content of water samples, he delineated the groundwater body on isochlor of 500 ppm and Cl−/HCO−1 3 ratio of 0.66. The boundary zone of the 300–500 isochlors demarcates the diffusion zone of seawater (Freeze and Cherry, 1997). The ionic ratio Cl/CO3 + HCO3 with a value of 2.91 to 3.5 clearly indicates the marine incursion as a value more than 2.8 is considered to be an indices of the serious contamination. The average seawater has a ratio of about 2.3 (Goldberg, 1963).

The Electrical conductivity of the groundwater when compared with the Cl/HCO3− ratio indicates that there exists a liner relationship between these parameters. There is an increase of this ratio with conductivity and 30% of the sample irrespective of season fall above 2250μs/cm. almost 40% of the samples during PRM have Cl/HCO3− ratio >2 indicating the dominance of sea water intrusion, though there are representations of samples of POM they are comparatively lesser than PRM. It is also evident from the figure the linearity of increase varies according to the season where good positive relation exists during PRM than POM. The relation between Ionic strength of the sample to that of Cl/HCO3 ratio also behave in the similarly to that of EC; but at lower log pCO2 (<-2.75) shows higher Cl/HCO3 values (>2) during POM and during PRM the higher ratios are noted above higher log pCO2 values.
Fig: 5.18 Log pCO₂ Vs Cl⁻/HCO₃⁻
5.6.0 REMOTE SENSING

5.6.1 Traditional classification systems

The traditional classification systems deals with land cover and/or land-use (Danserau, 1961; Fosberg, 1961; Trochain, 1961; Eiten, 1968; UNESCO, 1973; Mueller-Dombois and Ellenberg, 1974; Anderson et al., 1976; Kuechler and Zonneveld, 1988; ECE-UN,1989; UNEP/FAO, 1994; CEC, 1995; Duhamel, 1995; Thompson, 1996) are limited in their capacity of storage of classes and often do not contain the whole variety of occurring land covers or land-uses. Some describe (semi) natural vegetation in great detail while accommodating cultivated areas in a single class or vice versa. More important, they are based upon the approach of class names and class descriptions that do not consistently use a set of criteria to make class distinctions (Jansen and Di Gregorio, 1998a). Furthermore, the criteria used are often not inherent characteristics but describe the environmental setting of the land cover and land-use, respectively. The distinction between land cover and land-use is not always appreciated or adhered to in the above mentioned classifications (Louisa Jansen, and Antonio Di Gregorio, 2002). In the present classification the land use was classified into Settlements, Crop, Forest land, Water body, Mud, Rivers and others.
Fig: 5.19 IRS-1D LISS III Satellite Image of 2000
Fig: 5.20 IRS-P6 LISS III Satellite Image of 2009
5.6.2 Visual Image Interpretation

The products, obtained from the landuse and land cover mapping by visual interpretation of satellite imageries are give in Fig: 5.19 and 5.20 corresponding to 2000 and 2009 respectively. By careful examination of these images six different units are discernible. They include: 1. Built-up land, 2. Agriculture land containing presently fallow and fallow lands, 3. Forest, 4. waste lands containing water logged land, machy land, land without shrub, sandy area and barren rocky area, 5. Water bodies containing lakes, tanks and creeks and others which contain salt pans and other features.

5.6.3 Digital image processing

The digital image processing has been acting as an indispensable tool in the extraction of information from the remotely sensed digital data. This tool has also been utilized to deal with recording of reflectance characteristics of several objects. Typical spectral reflectance characteristics for healthy green vegetation and dead or senescent vegetation generally reflect 40 – 50% of the incident Near Infra Red (NIR) energy (0.7 to 1.1 Micrometers) with the chlorophyll in the plants absorbing approximately 80 to 90% of the incident energy in the visible region of (0.4 to 0.7 micrometer) part of the spectrum (Jensen, 1986). Dead or senescent vegetation reflects a greater amount of energy than the healthy vegetation throughout the visible spectrum. Conversely it reflects less than green vegetation in the reflective infra red region.
It is often useful to display, in image form, the difference in the amount of electromagnetic radiation received by a sensor in different wave bands that are recorded at the same time or to display the same wave bands that are recorded at different times (Curran, 1988). Such an image is achieved by ratioing or subtracting the DN (Digital Number) of pixels in one image with the corresponding pixels in another image and then the result is contrast stretched. This ratio or Difference – Image will suppress details, common to the two images and will enhance the details that are different in the two images (Sabins, 1978; Condit & Chavez, 1979; Townshend, 1981 and Jensen, 1986).

The present study involves three main steps. In the first step, the spatial distribution based on the groundwater level, Electrical conductivity and rainfall data were plotted. Second step involves the classification of satellite data for 2000 and 2009 using land use types. Analysis of satellite data includes registration, classification to identify the land use /land cover using supervised classification comparison (Fig: 5.21 & 5.22). Finally the land use types were correlated with the spatial plots of EC, WL and rainfall.

The spatial distribution of the Electrical conductivity of groundwater during 2000 shows that the EC value ranges from <260 to >2870 micro mho/cm. and the highest value is occupied in the central part of the study area, which is indicated by the deeper water table. The electrical conductivity of the 2009 ground water ranges from greater than 360 to less than 3660 micro mhos/cm. The spatial pattern of EC during 2009 is similar to that of the 2000 but the area occupied by the higher EC has increased in the central part of the region and it is also to be noted that the average Conductivity of the groundwater in the
region has also increased. The delivery of sediments eroded from agricultural areas is also responsible for the supply of nutrients, pesticides, and heavy metal contaminants to river channels (e.g. Boers, 1996; De Wit and Behrendt, 1999; Verstraeten and Poesen, 2002), which can have an impact on the water quality of rivers and coastal areas. Sediment delivery also impacts on channel and floodplain morphology (e.g. Asselman and Middelkoop, 1995; De Moor et al., 2008), the ecological functioning of floodplains (Richards et al., 2002), and sediment deposition rates in reservoirs and ponds (Verstraeten and Poesen, 1999). Comparison of this landuse with the decadal change in the groundwater conditions helps to identify the threat and its region of salinity impact (Nobi, et al 2009).

The Modern scientific technologies of remote sensing and digital image processing are extremely useful in periodic assessment of the coastal landuse and land cover changes and analyze them to formulate better management(Klemas, 1986; Specter and Gaylee, 1990). Land cover mapping serves as a basic inventory of land resources for all levels of government, environmental agencies and private industry throughout the world (Vijith and Satheesh, 2007). The classification was done under the following heads (Table: 5.15) as crop, forest, saltpan, mud, settlements, water bodies (dry & wet) and others (Fig: 5.21 & 5.22). The plain terrain (others) is converted into crop land and Built-up area (settlement) is increase compared with year 2000 to 2009.

The study area has an Agricultural land (crop) of 747.8 (25.10%) sq.kms during 2000 and 919.57 (30.87%) sq.kms during 2009. Settlement covers 64.23 sq.kms (2.16%)
<table>
<thead>
<tr>
<th>Land use</th>
<th>AREA IN SQ.KMS</th>
<th>AREA IN %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CROP</td>
<td>747.8</td>
<td>+ 919.57</td>
</tr>
<tr>
<td>OTHERS</td>
<td>1712.81</td>
<td>- 1544.16</td>
</tr>
<tr>
<td>SETTLEMENT</td>
<td>64.23</td>
<td>+ 92.86</td>
</tr>
<tr>
<td>FOREST</td>
<td>18.55</td>
<td>- 18.52</td>
</tr>
<tr>
<td>WATERBODY</td>
<td>9.42</td>
<td>- 5.62</td>
</tr>
<tr>
<td>RIVER DRY</td>
<td>28.83</td>
<td>+31.21</td>
</tr>
<tr>
<td>RIVER WET</td>
<td>117.15</td>
<td>-98.64</td>
</tr>
<tr>
<td>SALT</td>
<td>24.27</td>
<td>+ 28.8</td>
</tr>
<tr>
<td>MUD</td>
<td>255.64</td>
<td>-239.32</td>
</tr>
</tbody>
</table>

Table: 5.15 Land use/Land cover classification.
during the year 2009 and 92.86 (3.12%) Sq.Km during 2000. Water body covers an area of about 9.42 Sq.Km (0.32%) in year 2000 and 5.62 (0.19%) Sq.Km during 2009 because the area is dry condition. Mud area and others have decreased.

There is an increase of cropland during August 2009, from 747 sq.km to 919 sq.km. This is because the imagery of 2000 was a scene captured during May 2000 (i.e. summer) and the imagery captured for 2009 was during August (i.e.) after the onset of the SW monsoon, when the agricultural activities get initiated. Others include the grass lands and dry lands they show higher area occupied during May 2000 and becomes lesser during August 2009 this is mainly due to the increase of agricultural activities along the river channels after the onset of monsoon. It is observed that when the surrounding landscape patterns change, the environmental conditions (e.g. microclimate) produced along these edges (the boundaries between surrounding forests and the cool temperate forest) may be modified and it influences the interior regions (Murcia, 1995; Bannerman, 1998).

In Settlement there is a drastic increase in population in a decade and hence it is reflected in the settlement area from 2000 to 2009. There is just 1% increase in the area occupied by the settlements. There is no much variation in the area covered by mud, salt pan, Forest and water body. Forest cover change detection has been done, through visual interpretation of satellite data by Roy and Joshi (2002), Rogan et al. (2002), Le Hegarat-Mascle et al. (2006), Reis and Yomralioglu (2006) and Panigrahy et al. (2010).
Fig: 5.21 Land Use Land Cover of the study area of 2000
Fig: 5.22 Land Use Land Cover of the study area of 2009
The river wet region shows a significant decrease during 2009 as it may be due to the increase in the agricultural land. It is also noted that the both the monsoon were prevalent dominantly during 2000 and only NE monsoon was more prominent during 2009. A slight decrease in mud may be due to the increase in the salt marsh regions in the southern part of the study area at the swampy mangroves. This may be due to siltation’s along the in the swampy mangroves. Swamp forest is a particular type of wetland, classified by the Ramsar Convention as “freshwater, tree-dominated wetlands” in category (Xf) (Ramsar Convention Secretariat, 2006). These ecosystems maintain a rich diversity of species and also contribute to regulate river flows, thus helping to slow erosion processes and control floods (Hauenstein, González, Peña-Cortés, & Muñoz-Pedreros, 2002, 2005; Richardson, 1994). Wetland areas have been recognised internationally for their high biological and environmental value, and as providers of ecosystem services. Swamp forests have often been threatened by the destruction of their habitat by clearing for agricultural land, grazing and firewood extraction. These, leave remnant patches following human land conversion activities due to the fact that swamp forests occupy land of lower agricultural value (Ramírez et al., 1983, 1996; San Martín et al., 1988; Squeo, Arancio, & Cavieres, 2001). It must be considered that wetlands are sensitive to interventions in their river basins and surrounding landscape, so that any alteration in the territory may affect both physical-biological interactions with the wetland and the quality and flow of water (Furukawa, Inubushi, Ali, Itang, & Tsuruta, 2005; Osumba, Okeyo-Owuor, & Raburu, 2010; Yule, 2010).
Fig: 5.23 Change detection of Land use pattern
The decrease in wetlands with shrubs/grass is due to rapid urbanization and industrialization along the coastline. These anthropogenic activities had limited the entry of high tides and backwaters onto the main land, which are main sources of wetlands along Vedaranyam coast. Similarly, decrease in woody vegetation (Mangroves and Coconut trees) is also due to the above anthropogenic activities. Fallow lands have been increased because most of the wetlands have been converted to fallow lands due to non availability of tidal water/backwater and moisture, (Prabaharan,2010).

The comparison of the land use changes during the study period (Fig:5.23) and the electrical conductivity of groundwater show that the conductivity has increased during the recent years and the crops land in this region have reduced due to the saline nature of the ground water and the settlement has increased in this regions. The major variation on the land use pattern is noted along the central part of the study area where the groundwater conductivity has increased. Hence it is clear that the groundwater quality plays a major role in the land use pattern change in the study area. Detection and characterization of change in key resource attributes allows resource managers to monitor landscape dynamics over large areas, including those areas where access is difficult or hazardous, and facilitates extrapolation of expensive ground measurements or strategic deployment of more expensive resources for monitoring or management (Li et al., 2003; Schuck et al., 2003).
The present study shows that satellite remote sensing based land cover mapping is very effective for coastal land use/land cover changes. The study has been conducted with the high resolution satellite data IRS P6 LISS III data the study area falling in the coastal region of the Tamilnadu shows minor changes in the land use pattern for the periods from 2000 to 2009.

There is an increase in the settlement and swampy region and there is a decrease in the others. The major variation on the land use pattern is noted along the central part of the study area where the groundwater conductivity has increased. Hence it’s clear that the groundwater quality plays a major role in the land use pattern change in the study area. Hence, this is an essential tool for future planning and management of coastal regions by the virtue of their fragile ecosystem it has been observed that important coastal land use types like Agricultural (crop), settlement increased.

5.6.4 Normalised Differential Vegetation Index

The Normalised Vegetation Index map is also prepared by using the Remote Sensing data with NDVI Ratio. It assess the target being observed contains live green vegetation or not. NDVI is used to simply and quickly identify vegetated areas and their condition and it remains the most well known and used index to detect live green plant canopies in multispectral remote sensing data.

\[
\text{NDVI} = \frac{\text{NIR}-\text{RED}}{\text{NIR}+\text{RED}}
\]
Fig: 5.24 Normalized Vegetation Index map of year 2000
Fig: 5.25 Normalized Vegetation Index map of 2009
RED and NIR stand for the spectral reflectance measurements acquired in the red and near IR regions respectively. NDVI ratio varies between -1.0 and +1.0. The NDVI of an area containing dense vegetation (green) represents positive values (0.1 to 0.3). The very low positive and negative values indicate Rivers, Water bodies. High values of range from 0.3 to 0.5 represent forests.

5.7.0 STATISICAL ANALYSIS

Multivariate analyses, such as cluster, factor and discriminate analysis, aim to interpret the governing processes through data reduction and classification. They are widely applied mainly to spatial data in geochemistry (Papatheodorou et al, 1999; Papatheodorou et al, 2002a), hydrochemistry (Voudouris et al, 1997; Lambrakis et al, 2004), mineralogy (Seymour et al, 2004) and even in marine geophysics (Papatheodorou et al, 2002b). The use of these methods to water quality monitoring and assessment has increased in the last decade, mainly due to the need to obtain appreciable data reduction for analysis and decision (Vega et al, 1998; Helena et al, 2000; Lambrakis et al, 2004). Multivariate treatment of environmental data is widely used to characterize and evaluate groundwater quality (Vengosh and Keren, 1996; Suk and Lee, 1999; Helena et al, 2000; Lambrakis et al, 2004; Panagopoulos et al, 2004) and it is useful for evidencing temporal and spatial variations caused by natural and human factors linked to seasonality. Data reduction was carried out for four different seasons by using statistical applications like Correlation, Factor Analysis and Cluster Analysis.
5.8.0 Correlation

Pearson’s correlation coefficient is also known as Karl Pearson’s correlation coefficient. Pearson’s correlation coefficient is the method of measuring the correlation. This method was developed by Karl Pearson and is therefore named Pearson’s correlation coefficient. Pearson’s correlation coefficient is known as the best method of measuring the correlation, because it is based on the method of covariance. Pearson’s correlation coefficient gives in aquifer about the degree of correlation as well as the direction of the correlation.

Assumptions in calculating the Pearson’s correlation coefficient

a. **Independent of case:** In Pearson’s correlation of coefficient, cases should be independent to each other.

b. **Distribution:** In Pearson’s correlation coefficient, variables of the correlation should be normally distributed.

c. **Cause and effect relationship:** In Pearson’s correlation coefficient, there should be a cause and effect relationship between the correlation variables.

d. **Linear relationship:** In Pearson’s correlation coefficient, two variables should be linearly related to each other, or if we plot the value of variables on a scatter diagram, it should yield a straight line.
Properties in Pearson’s correlation coefficient

The following are the properties of Pearson’s correlation coefficient:

a. **Limit of the Pearson correlation coefficient:** Karl Pearson’s correlation coefficient value lies between +1 to -1.

b. **Pure number:** Pearson’s correlation coefficient is a pure number and it is independent of the unit of measurement. For example, if one variable’s unit of measurement is in inches and the second variable is in quintals, even then, Pearson’s correlation coefficient value does not change.

c. **Symmetric:** Pearson’s correlation of the coefficient between two variables is symmetric. This means that if we calculate the Pearson’s correlation coefficient between X and Y or Y and X, the value of Pearson’s correlation coefficient will remain the same.

Probable error and Karl Pearson’s correlation coefficient

Probable error is used to determine the reliability of Pearson’s correlation coefficient. The following formula is used to determine the value of probable error:

\[
P.E. = 0.6745 \frac{1 - r^2}{\sqrt{N}}
\]
Where:

\[ P.E = \text{Probable error} \]

\[ r = \text{Pearson’s correlation coefficient} \]

\[ N = \text{Number of observations} \]

If the absolute value of Pearson’s correlation coefficient is greater than 6 times probable error, then the Pearson’s correlation coefficient is taken to be significant. If the absolute value of Pearson’s correlation coefficient is less than 6 times probable error, then the correlation coefficient will be insignificant.

**Degree of correlation**

a. **Perfect correlation:** If Pearson’s correlation coefficient value is near \( \pm 1 \), then it said to be a perfect correlation.

b. **High degree of correlation:** If Pearson’s correlation coefficient value lies between \( \pm 0.75 \) and \( \pm 1 \), then it is said to be a high degree of correlation.

c. **Moderate degree of correlation:** If Pearson’s correlation coefficient value lies between \( \pm 0.25 \) and \( \pm 0.75 \), then it is said to be moderate degree of correlation.

d. **Low degree of correlation:** When Pearson’s correlation coefficient value lies between 0 and \( \pm 0.25 \), then it is said to be a low degree of correlation.
e. **No correlation**: When Pearson’s correlation coefficient value lies around zero, then there is no correlation. The formula for Pearson’s correlation takes on many forms. A commonly used formula is exhibit below.

\[ r = \frac{\sum x y - \frac{\sum x \sum y}{N}}{\sqrt{\left( \sum x^2 - \frac{\sum x^2}{N} \right) \left( \sum y^2 - \frac{\sum y^2}{N} \right)}} \]

A simpler looking formula can be used if the numbers are converted into z scores:

\[ r = \frac{\sum z_x z_y}{N} \]

where \( z_x \) is the variable X converted into z scores and \( z_y \) is the variable Y converted into z scores.

Correlation analysis carried out by using bi variate correlation using Pearson’s method. This was carried out for different dataset and it indicates hydro geochemical complexity in the region with less positive and less negative correlation. During the PRM2007 good correlation is exhibited between, Ca\(^{2+}\) with SO\(_4^{2-}\), Na\(^+\) with Cl\(^-\) and HCO\(_3^-\) and NO\(_3^-\) with K\(^+\). The PRM09 shows correlation of Cl\(^-\) with HCO\(_3^-\), Na\(^+\), SO\(_4^{2-}\) and Mg\(^{2+}\); Na\(^+\) with Cl, HCO\(_3^-\) and SO\(_4^{2-}\); Mg has good correlation with Cl and SO\(_4^{2-}\) and Ca with SO\(_4^{2-}\). POM07 good correlation is exhibited between, Ca\(^{2+}\) with SO\(_4^{2-}\), Na\(^+\) with Cl and HCO\(_3^-\) and NO\(_3^-\) with K\(^+\). The POM09 season shows good correlation of Ca-SO4; Mg-SO4; Na-Cl-SO4-HCO3; K-NO3 and Cl with Na and Mg. The major ion exhibiting correlation with other ions in almost all seasons is Cl\(^-\), Na\(^+\) and HCO\(_3^-\).
This is mainly possible due to the impact of sea water intrusion and leaching of the secondary salts precipitated along the pores of the formations (Chidambaram et al, 2009). Temperature also plays a significant role in PRM and POM indicating the thermodynamic control over the groundwater chemistry.

5.9.0 FACTOR ANALYSIS

Factor analysis, which includes principal component analysis (PCA), is a very powerful technique applied to reduce the dimensionality of a data set consisting of a large number of inter-related variables, while remaining as much as possible the variability present in data set. This reduction is achieved by transforming the data set into a new set of variables, the principal components (PCs), which are orthogonal (non-correlated) and
are arranged in decreasing order of importance. Mathematically, the PCs are computed from covariance or other cross-product matrix, which describes the dispersion of the multiple measured parameters to obtain eigen values and eigenvectors. Principal components are the linear combinations of the original variables and the eigenvectors (Wunderlin et al, 2001). Varifactors (VFs), a new group of variables are obtained by rotating the axis defined by PCA. Varimax rotation distributes the PC loadings such that their dispersion is maximized by minimizing the number of large and small coefficients (Richman, 1986). Besides considerable data reduction, entire data set variability is described through few VFs/PCs without losing much information. Further, grouping of the studied variables according to their common features by VFs helps in data interpretation (Vega et al, 1998; Morales et al, 1999; Helena et al, 2000; Simeonov et al, 2003; Singh et al, 2004).

Principal Component Analysis (PCA) is a multivariate statistical technique used for data reduction and for deciphering patterns within large sets of data (Wold et al, 1987; Farnham et al, 2003). Principal components are nothing more than the eigenvectors of a variance covariance or a correlation matrix of the original data matrix. By themselves they may provide significant insight into the structure of the matrix not available at first glance. PCA results vary considerately depending on whether the covariance or correlation matrix is used when large differences exist in the standard deviation of the variables (Davis, 1986). When the correlation matrix is used, each variable is normalized to unit variance and therefore contributes equally. The concentrations of elements studied
in the groundwater samples of the research area vary differently and the PCA is therefore applied to the correlation matrix for the present study. Thus the raw data matrix was first centered about zero by subtracting the means from each column and then dividing each of the values within each column by the column standard deviation. The eigenvectors of the correlation matrix are principal components and each original observation is converted to what is called principal component score by projecting it onto the principal axes. The elements of the eigenvectors that are used to compute the scores of the observations are called principal component loadings. Because the correlation matrix is symmetrical, the eigenvectors are mutually orthogonal. Typically, the raw data matrix can be reduced to two or three principal component loadings that account for the majority of the variance. The first principal component loading explains the most variance and each subsequent component explains progressively less. As a result, a small number of factors usually account for approximately the same amount of information as the much larger set of the original observations do. The PC loadings can be examined to provide further insight into the processes that are responsible for the similarities in the trace element concentrations in the groundwater samples. PC scores of each groundwater sample can be plotted together to investigate similarities between them.

5.9.1 PRM 2007

The results of FA extracted for four different factors during PRM2007 (Table:5.16 a and b) representing 82% of the total data variability.
<table>
<thead>
<tr>
<th>Factor</th>
<th>Loadings</th>
<th>TDV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor I</td>
<td>Na, Cl, HCO₃</td>
<td>26.7</td>
</tr>
<tr>
<td>Factor II</td>
<td>Ca, Mg, SO₄</td>
<td>24.6</td>
</tr>
<tr>
<td>Factor III</td>
<td>K, NO₃</td>
<td>19.4</td>
</tr>
<tr>
<td>Factor IV</td>
<td>F</td>
<td>11.9</td>
</tr>
</tbody>
</table>

**Table 5.16a** Factor analysis of the PRM2007 samples (Varimax rotated)

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<tbody>
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<td>Ca²⁺</td>
<td>0.3</td>
<td>0.84</td>
<td>0.38</td>
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<tr>
<td>Mg²⁺</td>
<td>0.12</td>
<td>0.82</td>
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<tr>
<td>Na⁺</td>
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</tr>
<tr>
<td>K⁺</td>
<td>0.0</td>
<td>0.04</td>
<td>0.88</td>
<td>-0.01</td>
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<tr>
<td>Cl⁻</td>
<td>0.80</td>
<td>0.39</td>
<td>0.06</td>
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<tr>
<td>HCO₃⁻</td>
<td>0.87</td>
<td>0.81</td>
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<tr>
<td>SO₄²⁻</td>
<td>0.29</td>
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<tr>
<td>NO₃⁻</td>
<td>0.03</td>
<td>0.01</td>
<td>-0.05</td>
<td>0.97</td>
</tr>
<tr>
<td>F⁻</td>
<td>0.01</td>
<td>0.09</td>
<td>0.87</td>
<td>-0.04</td>
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</tbody>
</table>

**Table 5.16b** Factor Representations and total data variability
The association of the ion in Factor I indicates a predominant seawater source for these ions (Table: 5.16a). Water in pans near to the coast often has a composition similar to seawater from wet and dry deposition of cyclic salts that originate as sea-spray or vapour, or from dissolution of salt formed by evaporation of a remnant of seawater isolated following a marine regression (Herczeg and Lyons, 1991). Dissolution of relict marine salt deposits occurs at coastal but not inland pans in the study area. Rainfall adjacent to the coast will have a chemical signature similar to seawater (Soderberg, 2003) and is consistent with the global average coastal rainfall signature (Faure, 1992). The theory of cyclic wetting and drying may explain the similarity to seawater of ion ratios in water entering the inland pans (Drever and Smith, 1978). In semi-arid to arid climates, rain is likely to evaporate from the soil before it has a chance to infiltrate, resulting in a build up of salts in or on the soil. Capillary evaporation of shallow groundwater will also concentrate salts near the surface during the dry summer months. A period of heavy rain can infiltrate and dissolve salts accumulated in the soil, leading to recharge by a relatively saline solution, with the signature of coastal rainfall (Drever and Smith, 1978).

The factor II shows that cyclic wetting and drying results in the most conservative and soluble solutes maintaining a seawater signature from the catchment into the pans, but less soluble solutes may be affected by processes in the catchment. The SO$_4^{2-}$, Ca$^{2+}$, Mg$^{2+}$, deviate from seawater. Isotope studies in Namibia (Eckardt and Spiro, 1999) and Australia (Chivas et al., 1991) have shown that oxidation of organic dimethyl sulphide gas (DMS) released from productive upwelling coastal waters is an important source of SO4 inland. The enrichment in SO4 compared to Cl in the pan waters may reflect similar
input of DMS from the adjacent Cape Columbine coastal upwelling cells. Dissolution of
dust results in relatively higher concentrations of Ca and alkalinity in rainwater than in
seawater (Faure, 1992), but these elements are also affected by water-rock interactions
occurring in the pan catchment, such as mineral weathering and ion sorption (Herczeg
and Lyons, 1991). The distribution of dolomite in pan sediments may reflect the slow
kinetics of dolomite formation at low temperatures (Warren, 1999; Parkhurst and
Plummer, 1993), which may partially be overcome by removal of SO4 from solution
through SO4-reducing microbial processes (Vasconcelos et al., 1995; Baker and Kastner,
1981). A byproduct of SO4 reduction is HCO3, formed through oxidation of organic
matter (Last, 1990; Compton, 1988; Lyons et al., 1984).

Factor III shows the association of K and NO\textsubscript{3} indicating impact of fertilisers and
factor IV is indicated by Fluoride, fluoride in all inflow waters and most brackish-saline
pan waters is enriched in salt pans (Smith and Compton, 2004) compared to seawater,
whereas F is depleted relative to seawater in brine pan waters, displaying a trend similar
to alkalinity.

5.9.2 PRM 2009

Onset of monsoon in the study area has a significant impact on the groundwater
chemistry. Four different factors (Table: 5.17 a and b) were extracted representing
83.12\% of the TDV. The representation of the factors are almost similar to the factors
represented in the PRM 2007 except for the increased impact of fertilizers represented as
factor II than that of the Salt pan influence other than the other two factors I and IV
remains the same.
Table 5.17 a Factor analysis of the PRM 2009 samples (Varimax rotated)

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<tr>
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</thead>
<tbody>
<tr>
<td>Ca&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.10</td>
<td>0.44</td>
<td>0.80</td>
<td>0.12</td>
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<tr>
<td>Mg&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>0.19</td>
<td>-0.02</td>
<td>0.91</td>
<td>-0.11</td>
</tr>
<tr>
<td>Na&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.95</td>
<td>-0.01</td>
<td>0.08</td>
<td>0.12</td>
</tr>
<tr>
<td>K&lt;sup&gt;+&lt;/sup&gt;</td>
<td>0.05</td>
<td>0.91</td>
<td>0.10</td>
<td>0.01</td>
</tr>
<tr>
<td>Cl&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.74</td>
<td>0.34</td>
<td>0.24</td>
<td>0.27</td>
</tr>
<tr>
<td>HCO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.76</td>
<td>0.06</td>
<td>0.50</td>
<td>0.20</td>
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<tr>
<td>SO&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;2-&lt;/sup&gt;</td>
<td>0.67</td>
<td>-0.08</td>
<td>0.03</td>
<td>-0.36</td>
</tr>
<tr>
<td>NO&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.02</td>
<td>0.00</td>
<td>0.00</td>
<td>0.93</td>
</tr>
<tr>
<td>F&lt;sup&gt;-&lt;/sup&gt;</td>
<td>0.07</td>
<td>0.92</td>
<td>0.11</td>
<td>0.00</td>
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</table>

Table 5.17 b Factor Representations and total data variability

<table>
<thead>
<tr>
<th>Factor</th>
<th>Loadings</th>
<th>TDV (%)</th>
</tr>
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<tbody>
<tr>
<td>Factor I</td>
<td>Na,Cl, SO4, HCO3</td>
<td>28.09</td>
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<tr>
<td>Factor II</td>
<td>K, NO3</td>
<td>22.14</td>
</tr>
<tr>
<td>Factor III</td>
<td>Ca, Mg, SO4</td>
<td>20.15</td>
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<tr>
<td>Factor IV</td>
<td>F</td>
<td>12.74</td>
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Table 5.18 a Factor analysis of the POM2009 samples (Varimax rotated)

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<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>0.01</td>
<td>0.8</td>
<td>0.3</td>
<td>0.0</td>
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<tr>
<td>Mg$^{2+}$</td>
<td>0.02</td>
<td>0.9</td>
<td>-0.1</td>
<td>-0.1</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.09</td>
<td>0.2</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.0</td>
<td>0.2</td>
<td>0.9</td>
<td>0.0</td>
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<tr>
<td>Cl$^-$</td>
<td>0.8</td>
<td>0.5</td>
<td>0.1</td>
<td>0.1</td>
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<tr>
<td>HCO$_3^-$</td>
<td>0.9</td>
<td>0.8</td>
<td>0.0</td>
<td>0.1</td>
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<tr>
<td>SO$_4^{2-}$</td>
<td>0.4</td>
<td>0.1</td>
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<td>-0.2</td>
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<tr>
<td>NO$_3^-$</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.9</td>
</tr>
<tr>
<td>F$^-$</td>
<td>0.0</td>
<td>-0.1</td>
<td>0.9</td>
<td>0.0</td>
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</table>

Table 5.18 b Factor Representations and total data variability

<table>
<thead>
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<th>Factor</th>
<th>Loadings</th>
<th>TDV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Factor I</td>
<td>Na$^+$, Cl$^-$ and HCO$_3^-$</td>
<td>26.67</td>
</tr>
<tr>
<td>Factor II</td>
<td>Ca$^{2+}$, Mg$^{2+}$, Cl$^-$, SO$_4^{2-}$</td>
<td>26.33</td>
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<tr>
<td>Factor III</td>
<td>K, NO$_3^-$</td>
<td>19.73</td>
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<td>Factor IV</td>
<td>F$^-$</td>
<td>11.54</td>
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<tr>
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</tr>
<tr>
<td>Ca^{2+}</td>
<td>0.02</td>
<td>0.1</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>0.44</td>
<td>0.46</td>
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<tr>
<td>Na^+</td>
<td>0.96</td>
<td>0.04</td>
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<td>K^+</td>
<td>0.14</td>
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<td>Cl^-</td>
<td>0.88</td>
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<tr>
<td>HCO_3^-</td>
<td>0.88</td>
<td>0.06</td>
</tr>
<tr>
<td>SO_4^{2-}</td>
<td>0.32</td>
<td>0.23</td>
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<tr>
<td>NO_3^-</td>
<td>0.09</td>
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<tr>
<td>F^-</td>
<td>0.31</td>
<td>-0.46</td>
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**Table 5.19 a** Factor analysis of the POM 2007 samples (Varimax rotated)

<table>
<thead>
<tr>
<th>Factor</th>
<th>Loadings</th>
<th>TDV (%)</th>
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<tbody>
<tr>
<td>Factor I</td>
<td>Na^+, Cl^- and HCO_3^-</td>
<td>32.25</td>
</tr>
<tr>
<td>Factor II</td>
<td>K, NO_3^-</td>
<td>21.99</td>
</tr>
<tr>
<td>Factor III</td>
<td>Ca^{2+}, SO_4^{2-}</td>
<td>18.40</td>
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**Table 5.19 b** Factor Representations and total data variability
The POM 2009 season shows four significant factors (Table: 5.18 a and b) representing about 84.26% of TDV. The representation of the factor loadings shows that all the four factors represented in the PRM07. In this season also it behaves in a similar manner. $K^+$ is also a common constituent of soluble fertilizers or could come from livestock excrement (Conrad et al, 1999). Whitehead (1979) has suggested that surface waters draining industrialized and urban areas contain considerably more iodine than those draining rural areas.

5.9.4 POM 2007

In POM season is represented by three factors (Table: 5.19 a and b) with TDV of 75% the Factors representations are as follows. The representation of these factors are similar to that of the PRM09, but still small variations in the ion representation is noted in factor III where Mg is not represented in this season, this may be due to the dilution effect in the ground waters after the monsoon.

5.10.0 Factor Score

The representation of the factors spatially was carried out by plotting the contours for the scores of different samples to the factors. The chief factor or the first factor generally provides an overall idea about the variations in water chemistry in the study area. In general it is understood that there are three basic parameters which determine the groundwater chemistry of this region irrespective of season, they are; 1. Sea water intrusion, 2. Salt pans and 3. Application of fertilisers. Hence to determine the samples representing the key factor i.e. the saltwater intrusion is plotted for different periods.
Fig: 5.26 a  

Fig: 5.26 b  

Fig: 5.26 Factor Score Contour of Post Monsoon
Fig: 5.27 Factor Score Contour of Pre Monsoon
PRM07 (Fig: 5.27a), POM07 (Fig:5.26 a), PRM09 (Fig:5.27b) and POM09 (Fig:5.26 b).

It is interesting to note that during all the periods the factor 1 is represented in the central part of the study area showing the positive values and the area of representation increased with time, moreover it is interesting to note that the area occupied by sea water intrusion is lesser during POM and higher in PRM.

5.11.0 CLUSTER ANALYSIS

The attention of Q-mode factor analysis is devoted to interpret the inter-object relationships in a data set rather than the inter variable relationships explored by the principal component analysis. A similarity matrix that consists of coefficients of proportional similarity between samples is first established in Q-mode analysis. The most widely used similarity measure in Q-mode factor analysis is the cosine q coefficient of proportional similarity (Davis, 1986),

\[
\text{cosine } \theta_y = \frac{\sum_{k=1}^{m} X_{ik} X_{jk}}{\sqrt{\sum_{k=1}^{m} X_{ik}^2 \sum_{k=1}^{m} X_{jk}^2}}
\]

This expresses the similarity between object i and object j by regarding each as a vector defined in m-dimensional space. The value of cosine q ranges from 1 for two collinear vectors to 0 for two orthogonal vectors. Since cosine q measures only the angular similarity, it is sensitive only to the relative proportions of the variables and not to their absolute magnitudes.
This means that a concentrated sample exhibits the same similarity matrix to one that is more dilute if the relative proportions of the elements are the same. Therefore in Q-mode factor analysis, the Q-mode factor loadings rather than the scores are plotted if the relationships between samples are to be known.

5.11.1 Hierarchical Cluster Analysis

Cluster analysis comprises a series of multivariate methods which are used to find true groups of data. In clustering, the objects are grouped such that similar objects fall into the same class (Danielsson et al, 1999). Hierarchical cluster analysis is the most widely applied techniques in the earth sciences and is used in this study. Hierarchical clustering joins the most similar observations, and then successively the next most similar observations. The levels of similarity at which observations are merged are used to construct a dendrogram. Some measure of similarity must be computed between every pair of objects. In this study, a standardized m-space Euclidian distance (Davis, 1986,) \( d_{ij} \) is used

\[
d_{ij} = \sqrt{\sum_{k=1}^{m} (X_{ik} - X_{jk})^2}
\]

where \( X_{ik} \) denotes the kth variable measured on object i and \( X_{jk} \) is the kth variable measured on object j. A low distance shows the two objects are similar or ‘close together’, whereas a large distance indicates dissimilarity.
5.11.1a Q Mode

The hierarchical cluster was carried out by Wards methods and using Squared Euclidian distance method for all the four seasons (Fig 5.22 a, b,c and d). All the seasons show three major clusters.
Dendrogram using Average Linkage (Between Groups) POMO7

Rescaled Distance Cluster Combine

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Fig:5.28 a
Dendrogram using Average Linkage (Between Groups) for POME

Rescaled Distance Cluster Combine

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Fig: 5.28 b

180
Dendrogram using Average Linkage (Between Groups) PRM 07

Rescaled Distance Cluster Combine

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Fig: 5.28 c
Dendrogram using Average Linkage (Between Groups) PRM09

Rescaled Distance Cluster Combine

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Fig: 5.28 d
The cluster 1 samples are few in number and they fall along the coastal region south of Karaikkal and along the northern part of the Nagpattinam region. Cluster 2 falls along the mentioned two regions in the study area near the salt pan regions close to Vedaranyam and few patches north of Karaikkal. This is more prominent around the tributaries of the major rivers present in the study area.

5.12.0 Comparision of Groundwater Samples

The comparison is calculated by the similarity coefficient between the samples (including pre and post Monsoon) with the sea water of the study area. This is done by means of a linear regression logarithm. Similar samples that have correlation coefficients close to the correlation coefficient table ratios were taken into account rather than the absolute values. Therefore, samples being diluted by precipitation may still have a correlation coefficient with respect to its original composition even though the quality of dissolved minerals is very different. The difference in absolute concentration is expressed by the Euclidean distance.

$$D_{ij} = \sqrt{\sum_{k=1}^{n} \left( \frac{X_{ik} - X_{jk}}{n} \right)^2}$$

where $X_{ik}$ denotes the $K^{th}$ variable measured on samples $i$ and $X_{jk}$ is the $K^{th}$ variable measured on sample $j$, in all ‘$n$’ variables are measured on each sample and $D_{ij}$ is the distance between sample $i$ and sample $j$.

This is obtained by comparison of seven parameters, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Na}^{+}$, $\text{K}^{+}$, $\text{Cl}^{-}$, $\text{HCO}_3^{-}$ and $\text{SO}_4^{2-}$ where samples with correlation coefficient values greater the 0.95 are displayed in Table 5.20. The comparison is done with all the samples, first with that of seawater.
Higher correlation was found in the samples of POM09-14, PRM09-14, POM09-19, POM09-03 and POM07-14. It is to be noted that in all the seasons sample 14 (Karuvi) shows good correlation with the sea water, as it is located along the river bank. The pre monsoon season shows precipitation of salts along the pore spaces and during the post monsoon the salts precipitated in these spaces are leached to the ground water. This results in more correlation of this sample during post monsoon to sea water. Thus, it is evident that the mechanism that has altered the groundwater is not the direct infiltration but due to precipitation and dissolution of the salts entrapped from sea water (Chidambaram et al 2010).
Parameters Used: Ca²⁺, Mg²⁺, Na⁺, K⁺, Cl⁻, HCO₃⁻ and SO₄²⁻.

<table>
<thead>
<tr>
<th>Main Sample Index</th>
<th>Sample</th>
<th>Correlation Coefficient</th>
<th>Euclidean distance</th>
<th>Used correlation Points</th>
</tr>
</thead>
<tbody>
<tr>
<td>684</td>
<td>POM09-14</td>
<td>0.991</td>
<td>3992.322</td>
<td>7</td>
</tr>
<tr>
<td>721</td>
<td>PRM09-14</td>
<td>0.987</td>
<td>3993.688</td>
<td>7</td>
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<tr>
<td>689</td>
<td>POM09-19</td>
<td>0.986</td>
<td>3994.561</td>
<td>7</td>
</tr>
<tr>
<td>673</td>
<td>POM09-03</td>
<td>0.981</td>
<td>4161.592</td>
<td>7</td>
</tr>
<tr>
<td>647</td>
<td>PRM07-14</td>
<td>0.978</td>
<td>3994.455</td>
<td>7</td>
</tr>
<tr>
<td>620</td>
<td>POM07-24</td>
<td>0.977</td>
<td>4315.483</td>
<td>7</td>
</tr>
<tr>
<td>628</td>
<td>POM07-32</td>
<td>0.977</td>
<td>4315.483</td>
<td>7</td>
</tr>
<tr>
<td>671</td>
<td>POM09-01</td>
<td>0.975</td>
<td>4137.114</td>
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<td>602</td>
<td>POM07-06</td>
<td>0.975</td>
<td>3766.286</td>
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</tr>
<tr>
<td>710</td>
<td>PRM09-03</td>
<td>0.973</td>
<td>4184.196</td>
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<tr>
<td>634</td>
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<td>0.972</td>
<td>4294.151</td>
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<td>PRM09-28</td>
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<td>3639.966</td>
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<tr>
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<td>PRM07-06</td>
<td>0.966</td>
<td>4071.305</td>
<td>7</td>
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<td>708</td>
<td>PRM09-01</td>
<td>0.962</td>
<td>4214.597</td>
<td>7</td>
</tr>
<tr>
<td>743</td>
<td>PRM09-36</td>
<td>0.962</td>
<td>4200.379</td>
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<tr>
<td>669</td>
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<td>0.962</td>
<td>4181.555</td>
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<tr>
<td>706</td>
<td>POM09-36</td>
<td>0.961</td>
<td>4219.575</td>
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<tr>
<td>632</td>
<td>POM07-36</td>
<td>0.96</td>
<td>4143.963</td>
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<tr>
<td>636</td>
<td>PRM07-03</td>
<td>0.96</td>
<td>4206.785</td>
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<tr>
<td>598</td>
<td>POM07-02</td>
<td>0.959</td>
<td>4325.542</td>
<td>7</td>
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<tr>
<td>656</td>
<td>PRM07-23</td>
<td>0.957</td>
<td>4067.093</td>
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<td>618</td>
<td>POM07-22</td>
<td>0.953</td>
<td>4305.19</td>
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<td>638</td>
<td>PRM07-05</td>
<td>0.952</td>
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<td>601</td>
<td>POM07-05</td>
<td>0.946</td>
<td>4091.868</td>
<td>7</td>
</tr>
</tbody>
</table>

**Table: 5.20** Comparision of groundwater samples
5.13.0 Percent of mixing

The chemical compositions of different samples of the study area for different seasons are compared with the chemical composition of the sea water in the study area (Xue et al. 2000). The same samples of different seasons were selected to identify the mixing proportion. This was done by using the following formula:

\[ \text{PRM07-14 + Sea Water composition (\% in question)} \rightarrow \text{POM09-14} \]

The sample PRM09-14 was attempted to mix with the sea water composition of the Palayar (Chidambaram et al 2010) to obtain the composition of POM09-14, as POM09-14 has very good correlation to sea water than PRM09-14. It was optimized to obtain the composition and it was found that only 0.008\% mixture of sea water with the PRM09-14 (Table: 5.22) resulted in the composition.

Another trial was also attempted to mix the least correlated composition in the table POM07-05 (Table: 5.21) with the sea water composition to obtain the POM09-14 composition. It was evident that only 0.06\% of sea water with the POM07-05 would result in a composition similar to POM09-14. Hence it is understood that the region is dominantly of saline water and only a very minor variation in composition exist.
<table>
<thead>
<tr>
<th>Solution 1</th>
<th>POM07-05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution 2</td>
<td>sea water</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Percentage of solution 1 in target solution 90%-99%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution 1</td>
</tr>
<tr>
<td>Solution 2</td>
</tr>
</tbody>
</table>

| Na+ | 464 | 994.1 | 941.09 | 888.08 | 835.07 | 782.06 | 729.05 | 676.04 | 623.031 | 570.021 | 517.01 | 5765 |
| K+ | 10 | 28.1 | 26.29 | 24.48 | 22.67 | 20.86 | 19.05 | 17.24 | 15.43 | 13.62 | 11.81 | 191 |
| Ca2+ | 53 | 150.5 | 140.75 | 131 | 121.25 | 111.5 | 101.75 | 92 | 82.25 | 72.5 | 62.75 | 1028 |
| Mg2+ | 68 | 76.32 | 75.488 | 74.656 | 73.824 | 72.992 | 72.16 | 71.328 | 70.496 | 69.664 | 68.832 | 151.2 |
| Cl- | 868.78 | 1804.902 | 1711.29 | 1617.68 | 1524.07 | 1430.45 | 1336.84 | 1243.2 | 1149.62 | 1056.01 | 962.39 | 10230 |
| HCO3- | 350 | 419.3 | 412.37 | 405.44 | 398.51 | 391.58 | 384.65 | 377.72 | 370.79 | 363.86 | 356.93 | 1043 |
| SO42- | 139 | 140.1 | 139.99 | 139.88 | 139.77 | 139.66 | 139.55 | 139.44 | 139.33 | 139.22 | 139.11 | 150 |

Table: 5.21 Percentage of mixing sample: POM 2007-05
<table>
<thead>
<tr>
<th>Solution1</th>
<th>PRM09-14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution2</td>
<td>Seawater</td>
</tr>
</tbody>
</table>

Percentage of solution 1 in target solution 0.9991 to 0.999

<table>
<thead>
<tr>
<th>Solution1</th>
<th>1</th>
<th>0.9991</th>
<th>0.9992</th>
<th>0.9993</th>
<th>0.9994</th>
<th>0.9995</th>
<th>0.9996</th>
<th>0.9997</th>
<th>0.9998</th>
<th>0.9999</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solution2</td>
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<td>0.0009</td>
<td>0.0008</td>
<td>0.0007</td>
<td>0.0006</td>
<td>0.0005</td>
<td>0.0004</td>
<td>0.0003</td>
<td>0.0002</td>
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<table>
<thead>
<tr>
<th>Na+</th>
<th>706</th>
<th>710.553</th>
<th>710.103</th>
<th>709.654</th>
<th>709.204</th>
<th>708.755</th>
<th>708.305</th>
<th>707.86</th>
<th>707.406</th>
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<tbody>
<tr>
<td>Ca2+</td>
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<td>60.871</td>
<td>60.785</td>
<td>60.699</td>
<td>60.613</td>
<td>60.527</td>
<td>60.441</td>
<td>60.355</td>
<td>60.269</td>
<td>60.183</td>
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<tr>
<td>Mg2+</td>
<td>42</td>
<td>42.098</td>
<td>42.089</td>
<td>42.079</td>
<td>42.069</td>
<td>42.059</td>
<td>42.05</td>
<td>42.04</td>
<td>42.03</td>
<td>42.021</td>
<td>151.2</td>
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<td>Cl-</td>
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<td>1050.47</td>
<td>1049.66</td>
<td>1048.84</td>
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<td>1047.21</td>
<td>1046.4</td>
<td>1045.57</td>
<td>1044.76</td>
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<td>236</td>
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<td>236.439</td>
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<td>7.4</td>
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Table: 5.22 Percentage of Mixing sample: PRM 2009-14