CHAPTER - V
GEOCHEMICAL STUDY

5.1. Introduction:

The utilization of groundwater has been increased at an alarming rate worldwide in the recent decades. In large parts of the India, the exploitation of groundwater has increased to the highest degree, particularly for irrigation, industrial and drinking purposes due to frequent failures of monsoon. The groundwater demand is terrifically increased due to the rapid urbanization and industrialization. Now-a-days, it is accepted that the quality of the groundwater is equally important as its quantity. Both the quantity and quality of the groundwater is affected by over exploitation. So the withdrawal of groundwater must be regulated to avoid the sea water incursion, by that we can maintain the quantity and quality of the groundwater for current and future needs. The natural and anthropogenic effects including local climate, geology and agricultural practices also have an influence on water quality.

The evaluation and classification of the groundwater based on its quality can be done by examining its chemical characteristics. The deviations in the ion chemistry of the groundwater can be used to categorize the geochemical processes controlling the groundwater quality. The ion exchange reaction is the process of replacement of ions in the solution by ions absorbed from the neighboring aquifers; this strategy can also be studied using the geochemical analysis of the groundwater. When the atmospheric gases like carbon dioxide (CO$_2$) mixes with the water in the precipitation form, it reacts with the minerals on the earth surface. This process is called weathering. Major inorganic constituents in the water originate from weathering. The solid phase formed because of weathering is soils and the liquid phase is leachate, which runs off as surface water and/or infiltrates and becomes a part of the groundwater (Hounslow, 1995).
The nature of the rock formations, atmospheric precipitation, topography, soils, quality of the recharged water and subsurface geochemical processes create a notable alteration in groundwater quality. The compositions of the rock minerals have a great role in deciding the concentration of inorganic ions in the groundwater. The rising of groundwater levels along with an increasing trend of salinity may be generally because of the dissolution of rocks or mineral salts (Ballukraya and Ravi 1995; SubbaRao 2008; Latha and Rao 2012).

The materials dissolve in water in many ways. One of them is just the material get dissolved in water without any change in the material ie, solute in the water. This process depends on the temperature and pressure in the groundwater environment. In this case, the material is seen as a complete molecule in the water. For example when sugar dissolves in water it exists as individual sugar molecules with minimum to maximum concentration. But in other hand, when an ionic solid dissolves in water it break down into individual ions. which is known as dissociation. The common salt, sodium chloride (NaCl) when dissolves with water it is divided in to sodium (Na\(^+\)) ions and chloride (Cl\(^-\)) ions. The existence of the charged ions in groundwater is because of dissociation. The silicon is commonly considered to exist as uncharged SiO\(_2\) molecules. The major ions existing in a typical groundwater are Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^-\), SO\(_4\)\(^{2-}\), HCO\(_3\)\(^-\) and CO\(_3\)\(^{2-}\) (Hounslow, 1995). As the CO\(_3\)\(^{2-}\) ion is absent in the groundwater samples collected from the study area, the chemical analysis for all other major ions were carried out in this study.
Figure 5.1 Location map showing water sampling stations
5.2. Methodology

A total of 69 groundwater samples were collected from dug wells and tube wells during the months January and June of 2012 representing both the post monsoon and pre monsoon seasons respectively (Fig. 5.1). After 10 minutes of pumping, the groundwater samples were collected and stored in one liter HDPE bottles, which are pre-cleaned (acid-washed) and thoroughly rinsed with distilled water. The groundwater samples were analyzed for the physico-chemical parameters like pH, electrical conductivity, sodium, potassium, calcium, magnesium, bi-carbonate, chloride, and sulphate by following the standard procedures of APHA (1989).

The pH (hydrogen ion concentration) and electrical conductivity (EC) were measured using Eutech digital portable meters at the field itself. The instruments used for finding the pH and EC were calibrated as per the guidelines given by the manufacturer. The standard buffer solutions of pH 4.01, 7 and 10.01 were used to calibrate the pH meter. The EC meter was calibrated using the buffer solutions having conductivity 84µS/cm and 1408 µS/cm. The concentrations of Calcium (Ca\(^{2+}\)) and magnesium (Mg\(^{2+}\)) ions in the groundwater were estimated by ethylene diamine tetra acetic acid (EDTA) titration. Flame photometer was employed to estimate the concentrations of sodium (Na\(^{+}\)) and potassium (K\(^{+}\)) ions.

The bicarbonate (HCO\(_3\)) ions in the groundwater samples were determined by using acid titrimetric method, in which the sulphuric acid with 0.01N (Normality) is used. Chloride (Cl\(^{-}\)) ion concentration is calculated using argentometric (AgNO\(_3\)) titration. Spectrophotometer is employed to find out the sulphate (SO\(_4^{2-}\)) concentration. The total hardness (TH) is calculated from the amount of calcium and magnesium ions by the following equation (Todd 1980).

\[
TH=2.497Ca^{2+} + 4.115Mg^{2+}\text{ mg/l}
\]  

(1)
The accuracy of the results obtained is confirmed by calculating the ion-balance error (Mandel and Shiftan 1981) which was found to be around 10%.

5.3. Water quality:

The quality of the groundwater can be categorized for its suitability for different purposes depending upon some specific standards. In this study, the drinking water quality standards are obtained from World Health Organization (WHO 1997) and Bureau of Indian Standards (BIS 1991) guidelines. The quality of groundwater in the study area is compared with these standards to find its fitness for drinking. The ranges of chemical parameters in the groundwater and their comparison with the WHO standards and Indian standards for both the post monsoon and pre monsoon seasons are given separately (Table 5.1 & Table 5.2).

5.3.1. pH:

pH is the measure of hydrogen ion concentration in a solution. It is an important factor which maintains the carbonate and bicarbonate levels in groundwater (Jameel and Hussain, 2011). Hydrolysis, dissociation and oxidation processes are the three major sources of hydrogen ions in natural waters (Hounslow, 1995). The pH in the collected groundwater samples ranges from 6.35 to 8.74 with an average of 7.87 in the post monsoon, which shows majority of the groundwater samples are somewhat alkaline in nature. The slight alkalinity shows the occurrence of weak basic salts in the soil (Jameel, 2002). The pH values may be increased by removing CO$_2$ from a solution or by adding a base to that solution (Hounslow, 1995). But the pH values of the groundwater in the pre monsoon season vary from 5.63 to 7.9 with an average of 6.9, shows the groundwater is slightly acidic during pre monsoon. The low pH tends to favor the dissolution of carbonates and hydroxides. The acidity found in groundwater may be due to the acid mine
### Table 5.1 Ranges of chemical parameters and their comparison with the WHO and the Indian standards for drinking water (Post-monsoon)

<table>
<thead>
<tr>
<th>Chemical Parameter</th>
<th>Concentration of ions</th>
<th>Range of standards (Desirable to Permissible)</th>
<th>Sample well numbers exceeding Permissible limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.35-8.74</td>
<td>7.87</td>
<td>7.0 -9.2</td>
</tr>
<tr>
<td>TDS (mg/l)</td>
<td>48 - 17024</td>
<td>1243</td>
<td>500-1500</td>
</tr>
<tr>
<td>Ca$^{2+}$ (mg/l)</td>
<td>2 - 2290</td>
<td>124</td>
<td>75-200</td>
</tr>
<tr>
<td>Mg$^{2+}$ (mg/l)</td>
<td>0.6 – 1067</td>
<td>73</td>
<td>30 - 150</td>
</tr>
<tr>
<td>Na$^+$ (mg/l)</td>
<td>16 – 795</td>
<td>138</td>
<td>50 - 200</td>
</tr>
<tr>
<td>K$^+$ (mg/l)</td>
<td>1.3 – 225</td>
<td>22</td>
<td>10 - 12</td>
</tr>
<tr>
<td>HCO$_3^-$ (mg/l)</td>
<td>24 – 716</td>
<td>267</td>
<td>300 - 600</td>
</tr>
<tr>
<td>SO$_4$$^{2-}$ (mg/l)</td>
<td>1.5 – 115</td>
<td>36</td>
<td>200 - 600</td>
</tr>
<tr>
<td>Cl$^-$ (mg/l)</td>
<td>18 – 3624</td>
<td>363</td>
<td>250 - 600</td>
</tr>
<tr>
<td>TH (mg/l)</td>
<td>60 – 5992</td>
<td>609</td>
<td>100 - 500</td>
</tr>
</tbody>
</table>
Table 5.2 Ranges of chemical parameters and their comparison with the WHO and the Indian standards for drinking water

(Pre-monsoon)

<table>
<thead>
<tr>
<th>Chemical Parameter</th>
<th>Concentration of ions</th>
<th>Range of standards (Desirable to Permissible)</th>
<th>Sample well numbers exceeding Permissible limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.63 - 7.91</td>
<td>6.9</td>
<td>7.0 - 9.2</td>
</tr>
<tr>
<td>TDS (mg/l)</td>
<td>75 - 6406</td>
<td>767</td>
<td>500 - 1500</td>
</tr>
<tr>
<td>Ca²⁺ (mg/l)</td>
<td>20 - 196</td>
<td>86</td>
<td>75 - 200</td>
</tr>
<tr>
<td>Mg²⁺ (mg/l)</td>
<td>1.26 - 220</td>
<td>41</td>
<td>30 - 150</td>
</tr>
<tr>
<td>Na⁺ (mg/l)</td>
<td>8 - 338</td>
<td>121</td>
<td>50 - 200</td>
</tr>
<tr>
<td>K⁺ (mg/l)</td>
<td>2 - 151</td>
<td>29</td>
<td>10 - 12</td>
</tr>
<tr>
<td>HCO₃⁻ (mg/l)</td>
<td>12 - 622</td>
<td>178</td>
<td>300 - 600</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/l)</td>
<td>0.45 - 155</td>
<td>42</td>
<td>200 - 600</td>
</tr>
<tr>
<td>Cl⁻ (mg/l)</td>
<td>16 - 1526</td>
<td>123</td>
<td>250 - 600</td>
</tr>
<tr>
<td>TH (mg/l)</td>
<td>75 - 1157</td>
<td>382</td>
<td>100 - 500</td>
</tr>
</tbody>
</table>
drainage, acid precipitation and the surface introduction of acids to a dumping site (Hounslow, 1995). The low pH in groundwater does not cause any notable harmful effect (Jameel and Hussain, 2011).

5.3.2. Total Dissolved Solids (TDS):

TDS is the measurement of the large amount of inorganic salts and minor amount of organic materials dissolved in water. TDS reflects the quantity of minerals dissolved in water (Adhikary et al., 2012). Owing to differences in solubility of minerals, the TDS varies in diverse geological regions (WHO 2004). Generally the quantity of total dissolved solids (TDS) rises with the residence time of groundwater (Zaporozec, 2004). The total dissolved solids (TDS) in the groundwater differs from 48 to 17024 mg/l with an average value of 1243 mg/l in the post monsoon period and the variation in pre monsoon period was between 73 and 6406 mg/l with a mean of 767 mg/l. For both the seasons, 46% of the samples surpass the desirable limit (500 mg/l) of both the WHO and BIS standards. Raise of TDS in the study area may be because of the saline water infiltration from nearby sea, estuaries and salt pans and seepage of waste water from the surrounding agricultural lands. The domestic sewage along with channel water may percolate into the groundwater, which may lead to increase in TDS values (Ward 1994). The groundwater classification based on TDS corresponding to salinity is given in the Table 5.3.

<table>
<thead>
<tr>
<th>TDS (mg/l)</th>
<th>Water Class</th>
<th>Number of samples</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Post monsoon</td>
<td>Pre monsoon</td>
</tr>
<tr>
<td>1000 - 3000</td>
<td>Saline</td>
<td>9</td>
<td>14</td>
</tr>
<tr>
<td>3000 - 10000</td>
<td>Moderately saline</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>&gt; 10000</td>
<td>Highly Saline</td>
<td>2</td>
<td>_</td>
</tr>
</tbody>
</table>

Table 5.3 Classification of groundwater on the basis of TDS (USGS, 2000)
5.3.3 Total Hardness (TH):

The hardness of the groundwater is possibly because of the leaching of calcium and magnesium ions into groundwater (Srinivasamoorthy et al. 2011c). Carbonate, bicarbonate, sulfate, chloride and nitrate are some of the anions responsible for hardness in groundwater (Jameel and Hussain, 2011). The hardness of the water boosts its boiling point and it has no significant effects on human beings. The hardness of the groundwater samples varies from 60 to 5992 mg/l with an average value of 609 mg/l in post monsoon season, which indicates that the groundwater is normally hard in the post monsoon season. 20% of the samples has the hardness well above the maximum permissible limit of WHO (500mg/l).

The amplification of hardness is due to the increase of calcium and magnesium ions in the groundwater, this may be due to the leaching effect of precipitation and other geochemical processes. In the pre monsoon season, the value of hardness is between 75 and 1157 mg/l having an average value of 382 mg/l. During the pre monsoon season, 25% of samples in the study area contain hardness above the permissible limit of WHO (500 mg/l). The hardness of groundwater can affect both industrial and domestic uses when the water is heated; in that instance it becomes a water quality issue (Hiscock, 2005). The classification of the groundwater based on hardness is given in the Table 5.4.

<table>
<thead>
<tr>
<th>Total Hardness (mg/l)</th>
<th>Water Class</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Post monsoon</td>
</tr>
<tr>
<td>75 - 150</td>
<td>Moderately hard</td>
<td>2</td>
</tr>
<tr>
<td>150 - 300</td>
<td>Hard</td>
<td>23</td>
</tr>
<tr>
<td>&gt; 300</td>
<td>Very Hard</td>
<td>41</td>
</tr>
</tbody>
</table>

Table 5.4 Classification of groundwater on the basis of Total Hardness (TH)
5.3.4. Major Cations:

The major cations present in the groundwater are calcium (Ca\(^{2+}\)), magnesium (Mg\(^{2+}\)), sodium (Na\(^+\)) and potassium (K\(^+\)). The concentration of these constituents mostly depends on the type of geological formations in contact with the groundwater during its flow (Zaporozec, 2004). The order of abundance of cations is generally in the order Na\(^+\) > Ca\(^{2+}\) > Mg\(^{2+}\) > K\(^+\) for both the seasons. Even the concentrations of the ions change, in general, there is no notable change in the order of abundance in both the seasons.

5.3.4.1. Sodium:

The sodium ion in the groundwater may be from halite dissolution and from silicate weathering reaction (Meyback, 1987). Feldspars, clay minerals, evaporites and industrial wastes are also some of the major sources of sodium (Todd 1980). Sodium may also get into the groundwater due to irrigation return flow and anthropogenic activities (Jeevanandam et al, 2007). Higher concentration of sodium in the groundwater may be due to cation exchange reaction (Ramkumar et al. 2012). The sodium concentration in groundwater is also enhanced by intrusion of domestic sewage and percolation of channel water having high ionisable salts (Jameel and Hussain, 2011).

The Na\(^+\) ion concentration in the study area ranges from 16 to 795 mg/l with a mean value 138 mg/l and 8 to 338 mg/l with an average of 121 mg/l for post monsoon and pre monsoon respectively. During the post monsoon season, 13% of samples cross the permissible limit (200 mg/l) of WHO. But in the pre monsoon period only 11.5% of total samples are found to have more Na\(^+\) ions than the permissible limit of WHO (200 mg/l). In the coastal areas salinization results due to the mixing of sea water with groundwater also increases the sodium
ion count in the groundwater (Jeevanandam et al, 2007). The salt pans seen in the study area are also responsible for the elevated sodium ion concentration. The continuous ingestion of groundwater with elevated sodium content may cause hypertension, congenial heart disease and kidney problems (Raju et al 2011).

5.3.4.2. Potassium:

The major sources of potassium (K$^+$) are potash feldspar (KAlSi$_3$O$_8$), mica (KAl$_2$(AlSi$_3$)O$_{10}$(OH)$_2$) and less commonly, leucite (KAlSi$_2$O$_6$) and sylvite (KCl) (Hounslow, 1995). The high concentration of potassium in the groundwater may be due to the weathering of silicate minerals from igneous and metamorphic rocks (Karanth 1987). So the presence of silicate minerals from igneous and metamorphic rocks also increases the concentration of potassium in groundwater. Feldspars, Micas and clay minerals are also some of the sources of potassium (Todd 1980). The concentration of potassium in the post monsoon season is between the minimum value 1.3 mg/l to a maximum value of 225 mg/l. The variation of potassium concentration in the pre monsoon period is 2 to 152 mg/l.

The mean value of K$^+$ concentration in the groundwater is 22 and 29 for post and pre monsoon respectively. 26% of samples in the post monsoon and 48% of samples in pre monsoon season exceed the permissible limit (12 mg/l) of WHO. The percolation of excessive potassium fertilizers and manures into the groundwater used in the surrounding agricultural fields in the study area is also a reason for the increase of potassium values. The K$^+$ ions are derived from ion exchange reactions also. The usual sinks of the potassium are plants and clays.

\[
\text{Clays + K}^+ \rightarrow \text{illite}
\]
Above reaction is one of the common clay reactions, which reduces the potassium ion concentration in the groundwater (Hounslow, 1995). The more concentration of sodium and potassium in the presence of suspended matter can crosses foaming which accelerates scale formation and results in corrosion in boilers (Todd 1980).

5.3.4.3. Calcium:

The sources of calcium are calcite, aragonite, dolomite, gypsum, feldspars and clay minerals (Hounslow, 1995; Todd 1980). The higher concentration of calcium and magnesium may be due to the excessive use of fertilizers, manures in the agricultural fields for higher production. Elevated calcium concentration may be due to the ion exchange reaction and the low values may be due to reverse cationic exchange reaction (Jacob et al. 1999). The Ca$^{2+}$ ionic concentration for the post monsoon varies from 2 to 2291 mg/l with an average of 124 mg/l where as for the pre monsoon, the concentration of Ca$^{2+}$ is in the range of 22 to 196 mg/l with a mean value of 86 mg/l. 7% of samples in the post monsoon season exceeds the permissible limit of both WHO and BIS (200 mg/l). In the pre monsoon season, all samples are within the permissible limit of both WHO and BIS. If the calcium and magnesium in groundwater is beyond the permissible limits they produce encrustation in water supply and have an adverse effect on domestic use (Raju et al 2011).

5.3.4.4. Magnesium:

The most common source of large quantities of magnesium in natural waters is dolomite (Hounslow, 1995). The other reason for higher Ca$^{2+}$ and Mg$^{2+}$ concentration is the cationic exchange of Ca$^{2+}$ and Mg$^{2+}$ with Na$^{+}$, i.e., the Na$^{+}$ ions are replaced with the Ca$^{2+}$ and Mg$^{2+}$. The lower values are because of the reverse cationic exchange reaction in which the Na$^{+}$ ion replaces
the Ca$^{2+}$ and Mg$^{2+}$ ions and reduces their concentrations (Jacob et al. 1999). In the post monsoon, the magnesium concentration varies from 0.6 to 1067 mg/l with an average of 73 mg/l. For the pre monsoon Mg$^{2+}$ concentration ranges from 1.26 to 220 mg/l with an average of 41 mg/l.

During the post monsoon period, 7.2% and 14.5% of the samples exceeds the permissible limits of WHO (150 mg/l) and BIS (100 mg/l) respectively. During the pre monsoon season, only one sample found to have excess magnesium content crossing the permissible limit of the WHO. But 7.2 % of the samples have crossed the permissible limit of BIS. The excess of Mg$^{2+}$ along with high sulphate content may have a laxative effect and also causes corrosion in the water distribution system, notably in waters having low alkalinity. The increased concentration of magnesium in groundwater would adversely affect the soil quality by changing it alkaline when used for irrigation purposes, which results in poor crop yields (Ramkumar et al. 2012).

5.3.5. Major anions:

The major anions present in the groundwater are chloride (Cl$^-$), sulphate (SO$_4^{2-}$), bicarbonate (HCO$_3^-$), and carbonate (CO$_3^-$) (Hounslow, 1995). The carbonate is not detectable in the groundwater samples from the study area. The major anion abundance for the post monsoon was in the order Cl$^-$ > HCO$_3^-$ > SO$_4^{2-}$. During pre monsoon, the order of anion abundance changes as HCO$_3^-$ > Cl$^-$ > SO$_4^{2-}$.

5.3.5.1. Bi-Carbonate:

The major source of bicarbonate (HCO$_3^-$) in the groundwater is the atmosphere (CO$_2$) ie., CO$_2$ reacts with soil and releases HCO$_3^-$ into the groundwater (Tyagi et al. 2009; Vasanthavigar et al. 2010). The bicarbonate ion in the groundwater also arises due to the sulphate reduction reactions (Hounslow, 1995). The bicarbonates in groundwater may be also due to the oxidation
and decomposition of organic pollutants (Sadhana 1994). The HCO$_3^-$ ion concentration varies
from 24 to 716 mg/l with an average value of 267 mg/l for the post monsoon and 12 to 622 mg/l
with a mean value 178 mg/l during the pre monsoon. Only 5.8% of the groundwater samples in
the study area had exceeds the permissible limit of 600 mg/l, suggested by both WHO and BIS
during post monsoon season. In the premonsoon season, only one of the total samples (W43)
contains bicarbonate content more than the permissible limit of both WHO and BIS. If the
bicarbonate ions in groundwater exceed the permissible limits, it indicates that CO$_3$ may
precipitate as scales in pipelines and in turn affects the pumping systems (Rengarajan and
Balasubramanian, 1990).

5.3.5.2. Chloride:

Generally chloride is the major anion present in the natural waters. The chlorine in the
groundwater originates from both the natural sources like chloride rich rocks and anthropogenic
sources like runoff containing inorganic fertilizers, animal feeds, irrigation drainage and
seawater intrusion in coastal area (O’Brien and Majewski 2002; Aghazadeh et al. 2011). The
high concentration of chloride indicates the pollution by industries and by organic wastes of
animals (Jameel and Hussain, 2011). The high chloride values in groundwater are also because
of high soil porosity and permeability (Jain et al. 2003).

The amount of chloride ion in the groundwater varies from 18 – 3624 mg/l in post monsoon and
from 19 – 1526 mg/l in pre monsoon. The chloride concentration in the groundwater has mean
value of 363 and 123 mg/l for the post monsoon and pre monsoon season respectively. During
the post monsoon season, 15.9% of groundwater samples have higher concentratrion of chloride
ion exceeding the permissible limit 600 mg/l suggested by WHO. But only 7.2 % of samples
exceed the permissible limit of 1000 mg/l as per BIS guidelines. During the pre monsoon season only two of the groundwater samples (W51, W52) exceed the permissible limit of WHO. But only one of the sample has the chloride concentration exceeding the permissible limit of BIS (W52). Chloride along with higher concentration of sodium increases the salinity in groundwater. Groundwater with more concentration of chloride is less preferable in food processing industries, textile processing industries, paper manufacturing and synthetic rubber manufacturing industries (Todd 1980).

5.3.5.3. Sulphate:

The major sources of sulphate are the minerals of pyrite, gypsum and anhydrite. Under certain conditions the sulphates may be derived from organic sulphur compounds also (Hounslow, 1995). The accumulation of soluble salt in the soil, usage of excess sulphate fertilizers and other anthropogenic activities also increases the concentrations of sulphate (Jameel and Hussain, 2011). The sulphate concentration in the groundwater in the post monsoon varies from 1.5 to 115 mg/l with an average of 36 mg/l and in pre monsoon it varies from 0.45 to 155 mg/l with an average of 42 mg/l. During both the pre monsoon and post monsoon season, the groundwater samples from the study area has the sulphate ions within the permissible limits of WHO (600 mg/l) and BIS (400 mg/l). Minimum concentration of sulphate is found in the study area due to its lesser breaking down of organic substances from weathered soils/water (Miller 1979). Combination of sulphate with calcium forms an adherent heat - retarding scale (Todd 1980). Undesirable effects like gastro - intestinal irritation and some respiratory problems in human beings are associated with intake of groundwater with higher concentration of sulphate (Maiti 1982; Subramani et al, 2005).
5.4. Spatial Variations:

Geographic Information System (GIS) has emerged as a powerful tool for generating the spatial distribution maps. GIS can be used for analyzing, storing, and displaying spatial data. Several geological areas including environmental and engineering studies uses the spatial data obtained from GIS analysis to make better decisions (Stafford 1991; Goodchild 1993; Burrough and McDonnell 1998; Lo and Yeung 2003).

The spatial distribution maps were prepared to illustrate the seasonal variation in concentrations of several chemical parameters using Inverse Distance Weighted (IDW) raster interpolation technique of the spatial analyst module in ARCGIS. The common formula used in the IDW interpolation method was,

$$
\hat{Z}(s_0) = \sum_{i=1}^{N} \lambda_i Z(s_i)
$$

Where, \( \hat{Z}(s_0) \) is the value we are trying to predict for \( s_0 \), \( N \) is the number of measured sample points surrounding the prediction location that will be used in the prediction, \( \lambda_i \) is the weights assigned to each measured point that we are used here. These weights will decrease with distance; \( Z(s_i) \) is the observed value at the location \( s_i \). Comparing several interpolation techniques, IDW with a squared distance expression gives the more reliable results (Burrough and McDonnel, 1998, Mathes and Rasmussen, 2006).

The seasonal variation of major chemical parameters (TDS, TH, Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^-\), SO\(_4\)\(^{2-}\) and HCO\(_3\)\(^-\)) in the groundwater samples from Agastheeswaram taluk of Kanniyakumari district is spatially depicted in the figures prepared using the ArcGIS 9.2 software. These diagrams show the spatial variation of the different chemical parameters over the entire study area.
area. The total ionic budget is found to be more in the post monsoon season comparing the pre monsoon season.

The total dissolved solids spatial maps for both seasons (Fig.5.2) shows that there is no major change in the overall distribution of the TDS. But comparing to the post monsoon season, the TDS is considerably less the post monsoon season. In the case of hardness (Fig.5.3), during both the seasons majority of the samples are within the permissible limit of both WHO and BIS. The sodium distribution maps (Fig.5.4) are also similar in both the seasons. Comparing both the seasons, the sodium concentration is low in the pre-monsoon season. In the case of K spatial maps (Fig.5.5), the overall distribution illustrates, the distribution of potassium is more in the pre-monsoon season. In majority of Wells the potassium is found to be more than the permissible limits.

The spatial distribution maps of calcium (Fig. 5.6) depicts that the calcium in the groundwater of the study area is generally within the permissible limits, the case of both the seasons. In the post monsoon season, fewer wells in the southern side of the study area shows very high concentration of calcium. Mg distribution maps (Fig.5.7) also depicts that majority of the samples in the study area where having a permissible amount of magnesium except two or three samples. In the case of anions, the chloride distribution maps (Fig.5.8) shows that the concentration is more in the post monsoon season. The southern side regions near Manakudy and the upper Central region around the Nallur are showing more concentration of chloride crossing the permissible limits. But in pre-monsoon season, majority of the samples are within the desirable limit of WHO (2004). Only a smaller area near to Manakudy has higher concentration of chloride.
In the spatial maps of sulphate distribution (Fig.5.9), there are no notable changes in the concentration of sulphate during both the seasons. In both the seasons, the groundwater from the south and central parts are found to have more sulphate ions. The bicarbonate ion distribution maps (Fig.5.10) shows that majority of the samples from the study area are having a desirable amount of bicarbonate in the groundwater. But in the post monsoon season the $\text{HCO}_3^-$ ion is the dominant anion, which is found to be more in the Central, East and southern parts of the study area.

From the overall spatial analysis, the regions around Manakudy and Nallur in the southern side and upper central region of the study area seemed to be highly contaminated in both the seasons. The saline intrusion around Manakudy and the runoff of excess fertilizers from the surrounding agricultural lands and percolation of domestic sewage in Nallur may be the reason for the contamination of groundwater in these areas. The bicarbonate concentration is more in the central and northwestern side of the study area may be because of rock water interaction.
Figure 5.2 Spatial distribution of total dissolved solids (TDS) during (a) post monsoon (b) pre monsoon
Figure 5.3 Spatial distribution of total hardness (TH) during (a) post monsoon (b) pre monsoon
Figure 5.4 Spatial distribution of sodium (Na\(^+\)) during (a) post monsoon (b) pre monsoon
Figure 5.5 Spatial distribution of potassium (K⁺) during (a) post monsoon (b) pre monsoon
Figure 5.6 Spatial distribution of calcium ($\text{Ca}^{2+}$) during (a) post monsoon (b) pre monsoon
Figure 5.7 Spatial distribution of magnesium (Mg$^{2+}$) during (a) post monsoon (b) pre monsoon
Figure 5.8 Spatial distribution of chloride (Cl\textsuperscript{−}) during (a) post monsoon (b) pre monsoon
Figure 5.9 Spatial distribution of sulphate ($\text{SO}_4^{2-}$) during (a) post monsoon (b) pre monsoon.
Figure 5.10 Spatial distribution of bicarbonate (HCO$_3^-$) during (a) post monsoon (b) pre monsoon
5.5. Hydrogeochemical processes:

5.5.1. Piper Diagram:

Piper diagram was used to find the origin of groundwater. The water type and some other geochemical processes like precipitation, mixing and ion-exchange in the study area can be analysed using the Piper diagrams. Characterization of the geochemical nature of the groundwater in the study area is done by depicting the ionic concentrations in the piper diagram (Piper 1944). The Piper diagrams (Fig. 5.11) predicts the hydrochemical processes happening in the study area.

During both the seasons the alkaline earth elements (Ca\(^{2+}\) + Mg\(^{2+}\)) exceed the alkali elements (Na\(^{+}\) + K\(^{+}\)). In the post monsoon the strong acids (SO\(_4\)\(^{2-}\) + Cl\(^{-}\)) exceed the weak acids (CO\(_3\)\(^{-}\) + HCO\(_3\)\(^{-}\)) and both the acids had balanced levels in the pre monsoon period. The anion triangle shows the Cl\(^{-}\)dominating next with HCO\(_3\)\(^{-}\) in the case of post monsoon and HCO\(_3\)\(^{-}\) dominates in pre monsoon season. The sulphate ion is completely non dominant in both seasons. Cation triangle shows that majority of samples falls in no dominant region for both season but comparing all other cations, Ca\(^{2+}\) is found to be the major cation.

Few samples falls on the right corner in the diamond region of Piper diagram suggests those stations are in a saline region. A small number of samples falling on the left corner of the Piper diagram indicates that groundwater from those stations are affected by temporary hardness. Comparing to the post monsoon season, the alkali metals content, i.e. Na\(^{+}\) + K\(^{+}\) is dominating in the pre-monsoon season.
Figure 5.11 Piper diagrams illustrating the chemical composition of groundwater.

a. Post monsoon
b. Pre monsoon
In both the seasons, majority of the samples have mixed Ca-Na-HCO$_3$ and mixed Ca-Mg-Cl as the dominating hydrochemical facies. According to the water type classification by Piper, the major water types are Ca- Mg- Cl- SO$_4$ and Ca- Mg- HCO$_3$. Majority of the samples falling in the centre of the cation triangle shows that the ion exchange is the dominant process the study area (Hounslow, 1995).

5.6. Mechanism of rock water interaction:

5.6.1. Gibbs Plots:

Gibbs (1970) established in the mechanism which controls the chemical composition of water and provides the close relationship existing between chemical composition of groundwater and aquifer lithology. Gibbs plots are based on the three significant natural mechanisms viz. atmospheric precipitation, rock weathering and evaporation controlling the major ion chemistry of the groundwater. Two plots proposed by Gibbs are

i) TDS versus Cl$^-$/( Cl$^-$+ HCO$_3^-$)

ii) TDS versus (Na$^+$+ K$^+$)/( Na$^+$+ K$^+$+ Ca$^{2+}$)

Both the plots are drawn for both the post monsoon and pre-monsoon seasons (Fig. 5.12 & Fig. 5.13). The Gibbs plots clearly shows majority of the samples fall on the rock dominant region, which shows the rock weathering was the most important chemical process in the study area. So the aquifer environment determines the ion combination in the groundwater. Different combination of cations and anions in the groundwater can get by weathering of different sources of rocks (Garrels and Mackenzie 1967). Next to rock weathering, majority of samples falls on the evaporation dominant area. This show the anthropogenic activities also play a key role in the chemical composition of the groundwater from the study area.
Figure 5.12 Gibbs diagrams showing the mechanisms controlling the chemistry of groundwater.

- a. Major cations vs TDS for post monsoon
- b. Major cations vs TDS for pre monsoon
Figure 5.13 Gibbs diagrams showing the mechanisms controlling the chemistry of groundwater.

a. Major anions vs TDS for post monsoon
b. Major anions vs TDS for pre monsoon
5.6.2. Ions Scatter diagrams:

Factors that increase the ionic ratios in the groundwater were discussed. Categorization of ionic ratios of potential source is also essential to identify them. Plotting Na\(^+\) - Cl\(^-\) scatter plot (Sami 1992) indicates the salinity and the mechanism of acquiring salinity. The sodium chloride ions obtained from halite dissolution or indirectly from ocean and from salt water intrusion, which became the primary source of sodium and chloride content in the groundwater. If the chloride ion concentration is more than the sodium ion concentration then the water may be derived from brines, where the reverse ion exchange has occurred. In the diagrams (Fig. 5.14(a), Fig. 5.14(b)) we can notice the correlation of sodium and chloride for both the post monsoon and pre-monsoon season. In both the figures, we can find most of the samples below the equiline, which shows the additional chloride may be from other geochemical processes like rock water interactions (Prasanna et al 2011).

In the figures (Fig. 5.14(c) and Fig. 5.14(d)), it seems that most of the points or falling along and above the 1:1 trend line shows high Ca\(^{2+}\) and Mg\(^{2+}\) content when compared to HCO\(_3^-\) in the study area. This suggests the ions have resulted from weathering of sulphate and carbonate minerals (Datta and Tyagi 1996). The plot of (Ca\(^{2+}\) + Mg\(^{2+}\)) versus HCO\(_3^-\) marks the carbonate weathering is dominant in few stations during the post-monsoon season. The placement of more sample points along (Ca\(^{2+}\) + Mg\(^{2+}\)) side in some stations shows the reverse ion exchange processes is the source of calcium and magnesium ions in the groundwater in that stations (Prasanna et al 2011).

The (Na\(^+\) + K\(^+\)) was plotted against Cl\(^-\) (Fig. 5.15(a), Fig. 5.15(b)) shows the silicate weathering is dominant in several stations during the pre monsoon season. The Na\(^+\) + K\(^+\) versus
Cl⁻ plots also shows the alkali metals when compared to chloride were less dominant in the post monsoon season and more dominant in the pre-monsoon season. Because silicate weathering corresponds to the excess of (Na⁺ + K⁺) by Cl⁻ values (Stallard and Edmond, 1983). The relationship between EC and (Na⁺ / Cl⁻) in the groundwater was plotted and it furnish the evidence of evaporation (Jankowski and Acworth, 1997). The scatter diagram of EC versus Na⁺/Cl⁻ (Fig. 5.15(c), Fig. 5.15(d)) shows the trend line was inclined having a small negative slope with the increasing of EC, which shows the evaporation is not the dominant process. But the same result was given by Gibbs diagrams as rock water interaction is the dominant process in the study area, which justifies this result.

From the combined study of the ions scatter diagrams, these diagrams show the groundwater was controlled by rock water interface which likely be from calcium and magnesium silicate weathering and from carbonate weathering. The Gibbs plots also depicts that the rock water interaction is the dominant hydrochemical process in the study area, which confirm this process.
Figure 5.14 Ion scatter diagrams of the groundwater in the study area.

a. Na$^+$ versus Cl$^-$ scatter plot for post monsoon
b. Na$^+$ versus Cl$^-$ scatter plot pre monsoon
c. HCO$_3^-$ versus (Ca$^{2+}$ + Mg$^{2+}$) plot for post monsoon
d. HCO$_3^-$ versus (Ca$^{2+}$ + Mg$^{2+}$) plot for pre monsoon
Figure 5.15 Ion scatter diagrams of the groundwater in the study area.

a. Cl$^-$ versus (Na$^+$+K$^+$) plot for post monsoon
b. Cl$^-$ versus (Na$^+$+K$^+$) plot for pre monsoon
c. EC versus Na$^+$/Cl$^-$ plot for post monsoon
d. EC versus Na$^+$/Cl$^-$ plot for pre monsoon
5.7. Irrigation water Quality:

In addition to the chemical characteristics of the groundwater, the irrigation also depends on factors like soil texture and composition, crops grown and irrigation practices in that area (Srinivasamoorty et al. 2011a). Percent sodium (Na%), sodium absorption ratio (SAR) and residual sodium carbonate (RSC) are some of the parameters used to determine the water quality for irrigation in a region.

5.7.1. Sodium percent:

Classifying the groundwater for irrigation based on its sodium content is important. Since the sodium in water reacts with the soils and reduces its permeability which affects the plant growth (Srinivasamoorthy et al. 2013). The sodium content in groundwater can be expressed in the term percent sodium (Na%). The sodium percentage or percent sodium can be calculated using the formula,

\[
Na\% = \frac{(Na^++K^+) \times 100}{(Ca^{2+}+Mg^{2+}+K^++Na^+)}
\]

where all the concentrations are reported in meq/l.

The classification of groundwater based on Na% put forward by Wilcox (1955) is given in the Table 5.5. The Wilcox diagram (Wilcox 1955) was drawn between electrical conductivity (EC) and percent sodium (Na%) to classify the groundwater based on its suitability for irrigation (Fig. 5.16).

Irrespective of the seasons majority of the samples fall in the excellent to good and good to permissible regions. Less than 10 percentages of samples fall in the doubtful to unsuitable and unsuitable regions. In these regions the soils have high EC and the Ca\(^{2+}\) and Mg\(^{2+}\) ions replaces
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Range</th>
<th>Water Class</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>POM</td>
</tr>
<tr>
<td>Na% (Wilcox, 1955)</td>
<td>&lt; 20</td>
<td>Excellent</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>20 - 40</td>
<td>Good</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>40 - 60</td>
<td>Permissible</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>60 - 80</td>
<td>Doubtful</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>&gt; 80</td>
<td>Unsuitable</td>
<td>_</td>
</tr>
<tr>
<td>SAR (Richard, 1954)</td>
<td>&lt; 10</td>
<td>Excellent</td>
<td>68</td>
</tr>
<tr>
<td></td>
<td>10.0 - 18</td>
<td>Good</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>18 - 26</td>
<td>Doubtful</td>
<td>_</td>
</tr>
<tr>
<td></td>
<td>&gt; 26</td>
<td>Unsuitable</td>
<td>_</td>
</tr>
<tr>
<td>RSC (Richard, 1954)</td>
<td>&lt; 1.25</td>
<td>Good</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>1.25 - 2.50</td>
<td>Doubtful</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>&gt; 2.50</td>
<td>Unsuitable</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 5.5 Classification of groundwater on the basis of Na%, SAR and RSC for irrigation
Figure 5.16 Rating of groundwater samples by Wilcox diagram on the basis of EC and %Na.

a. Post monsoon
b. Pre monsoon
the Na$^+$ ion when absorbed by the clay particles, which reduces the permeability and internal drainage and makes the soil hard and unfit for irrigation (Gaofeng et al. 2010).

**5.7.2. Alkalinity Hazard:**

The alkalinity hazard in the groundwater can be found by calculating the sodium adsorption ratio (SAR). The SAR is determined using the following formula (Karanth 1987):

$$\text{SAR} = \frac{Na^+}{\sqrt{Ca^{2+} + Mg^{2+}/2}}$$  \hspace{1cm} (3)

where all concentrations are expressed in meq/l.

The classification of groundwater based on the SAR values is shown in the Table 5.5. The salinity hazard of the groundwater is measured from its electrical conductivity (EC) values. The salinity in the groundwater mainly originates from weathering of the rocks, leaching from the topsoil and some anthropogenic activities. Along with these processes climate also had a minor influence. The classification of groundwater for irrigation purposes based on EC and SAR values can be studied by sketching the United States salinity diagram (USSL 1954). The USSL diagrams for both the post monsoon and pre-monsoon seasons (Fig. 5.17) are plotted by taking salinity hazard (EC) and alkalinity hazard (SAR) in X and Y axes respectively.

The USSL diagrams shows 85% of samples for both the post and pre monsoons falls in the C2S1 and C3S1 region, which shows a medium to high salinity in the groundwater of the study area. Other areas are affected by very high salinity. Some special type of irrigation like salt tolerance cropping can be done in those areas which are affected by high salinity.
Figure 5.17 Salinity and alkalinity hazard of groundwater samples depicted in USSL Diagrams
   a. Post monsoon
   b. Pre monsoon
5.7.3. Residual Sodium Carbonate (RSC):

Residual sodium carbonate is another parameter used to check the fitness of groundwater for irrigation purposes. The RSC in groundwater is mainly due to the water having higher concentration of bicarbonate ions, which precipitates the Ca$^{2+}$ and Mg$^{2+}$ ions as their carbonates and increases the Na$^{+}$ ions which increases the sodium carbonate in the groundwater (Srinivasamoorthy et al. 2013). The RSC is calculated by the following equation (Eaton 1950),

$$\text{RSC} = (\text{HCO}_3^- + \text{CO}_3^{2-}) - (\text{Ca}^{2+} + \text{Mg}^{2+})$$

(4)

all the concentrations are expressed in meq/l.

The classification of groundwater for irrigation based on the RSC values is presented in Table 5.5. According to this classification 71% of samples are within doubtful limit with RSC<2.5 for Post monsoon and 91% of samples are within the doubtful limit for the pre monsoon season which shows the residual sodium carbonate decreases in the pre monsoon period. Polluted agricultural returns and localized pollution are also some of the reasons for high residual sodium carbonate content (RSC). Prolonged usage of groundwater with high RSC will affect the crop yields space (Srinivasamoorthy et al 2011a).

5.8. Ion exchange:

The concentration of ions in groundwater varies when there is an exchange with the ions of its aquifer environment during the periods of movement and residence (Latha and Rao 2012). Chloroalkaline Indices 1 and 2 are calculated for the groundwater samples in the study area suggest the ion exchange taking place in the groundwater (Prasanna et al. 2011). They are calculated using the following formulas:
CAI 1 = \[\text{Cl}^- - (\text{Na}^+ + \text{K}^+)\] / \text{Cl}^- \quad (5)

CAI 2 = \[\text{Cl}^- - (\text{Na}^+ + \text{K}^+)\] / \((\text{SO}_4^{2-} + \text{HCO}_3^- + \text{CO}_3^{2-} + \text{NO}_3^-)\) \quad (6)

where the concentration of ions is in meq/l.

Both the indices, CAI 1 and CAI 2 are negative if there is an exchange between alkaline Earth metal ions (calcium or magnesium) in the groundwater with alkali metal ions (sodium and potassium) in the aquifer material, and if reverse ion exchange takes place both these indices will be positive (Schoeller 1965). The obtained results show that 58% of samples show positive for both the indices during the post monsoon period and only 7% of samples show positive in the pre monsoon period. These Chloroalkaline indices calculated for the collected samples shows the reverse cationic exchange is the leading process in the post monsoon and normal ion exchange is the leading process in the pre monsoon season.

5.9. Statistical Approach:

The statistical analysis of the geochemical parameters can be done by applying several methods. Here the correlation analysis is applied to study the statistical and scientific correlation between various chemical parameters. Electrical conductivity (EC), calcium (Ca^{2+}), magnesium (Mg^{2+}), Sodium (Na^{+}), potassium (K^{+}), bicarbonate (HCO_3^-), chloride (Cl^-) and sulphate (SO_4^{2-}) are the chemical components used for forming the correlation coefficient matrix. The correlation coefficient values which reveal the correlation between the parameters are always between -1 to +1. Generally the geochemical parameters exhibiting correlation coefficient > 0.7, are considered to have strong correlation. If the correlation coefficient values are between 0.5 and 0.7, a moderate correlation was seen (Giridharan et al, 2008). The tables (Table 5.6 & Table 5.7) shows
the correlation coefficient matrix of various elements in the Agastheswaram taluk of Kanniyakumari district for both post and pre monsoon seasons.

The correlation matrices show high values and low values of positive correlation among the chemical constituents. In the groundwater of the study area, generally the chemical budget of ions depends on several factors such as rock-water interactions, anthropogenic activities, river water seepage and saline water intrusions. During post monsoon season a good correlation is obtained between EC and all other parameters, which shows that the electrical conductivity is influenced by all chemical parameters. Observing the table, a very high correlation (0.97, 0.83) is obtained between Na$^+$ and EC, in both the seasons. This is an important result which shows, the concentration of Na$^+$ can be affected by ionic exchange reactions between groundwater and clay minerals, which shows the sodium concentration is locally increased in relation to the clay interbeddings in the subsurface layers (Cimino et al. 2008).

Potassium (K$^+$), magnesium (Mg$^{2+}$) and calcium (Ca$^{2+}$) also shows good to moderate correlation with EC for both the seasons. In the case of anions, Cl$^-$ and SO$_4^{2-}$ show better correlation with EC during both the seasons. The sodium and chloride shows a good correlation during both the seasons shows the presence of salinity in the groundwater. The positive correlation between Na$^+$ and Cl$^-$ (0.73, 0.72) indicates both the elements may be derived from saline water intrusion (Srinivasamoorthy et al, 2011c).
### Correlation coefficient – post monsoon – season-1

<table>
<thead>
<tr>
<th></th>
<th>EC</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>HCO₃⁻</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
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<td>EC</td>
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<td>0.583</td>
<td>0.887</td>
<td>0.965</td>
<td>0.597</td>
<td>0.71</td>
<td>0.664</td>
<td>0.71</td>
</tr>
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<td>Ca²⁺</td>
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<td>0.221</td>
<td>0.58</td>
<td>0.263</td>
<td>0.509</td>
<td>0.327</td>
<td>0.509</td>
<td></td>
</tr>
<tr>
<td>Mg²⁺</td>
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<td>0.481</td>
<td>0.516</td>
<td>0.495</td>
<td>0.516</td>
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<td></td>
</tr>
<tr>
<td>Na⁺</td>
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<td>0.621</td>
<td>0.828</td>
<td>0.73</td>
<td>0.828</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K⁺</td>
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<td>0.552</td>
<td>0.515</td>
<td>0.552</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>HCO₃⁻</td>
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<td>1</td>
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<td></td>
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</tr>
<tr>
<td>Cl⁻</td>
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<td></td>
</tr>
<tr>
<td>SO₄²⁻</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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</table>

Table 5.6 Correlation matrix for the water samples during post monsoon

### Correlation coefficient – pre monsoon – season-2

<table>
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<tr>
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<th>EC</th>
<th>Ca²⁺</th>
<th>Mg²⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>HCO₃⁻</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
</tr>
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<td>0.829</td>
<td>0.639</td>
<td>0.181</td>
<td>0.969</td>
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<td>Ca²⁺</td>
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<td>0.496</td>
<td>0.42</td>
<td>0.252</td>
<td>0.475</td>
<td>0.596</td>
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</tr>
<tr>
<td>Mg²⁺</td>
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<td>0.662</td>
<td>0.303</td>
<td>0.252</td>
<td>0.607</td>
<td>0.689</td>
<td></td>
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</tr>
<tr>
<td>Na⁺</td>
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<td>0.62</td>
<td>0.378</td>
<td>0.719</td>
<td>0.888</td>
<td></td>
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</tr>
<tr>
<td>K⁺</td>
<td>1</td>
<td>0.294</td>
<td>0.55</td>
<td>0.687</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCO₃⁻</td>
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<td>0.006</td>
<td>0.294</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Cl⁻</td>
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<td></td>
<td></td>
<td></td>
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</table>

Table 5.7 Correlation matrix for the water samples during pre monsoon
The sodium ion is also having a good correlation with sulphate ion during both the seasons. The moderate correlation was obtained between calcium and sodium indicates the influence of cation exchange reactions (Kim et al, 2004). Generally, the correlation coefficient values of HCO$_3^-$ with other parameters are good to moderate (> 0.5) during post monsoon season. It has low values of correlation coefficient during pre monsoon season, which shows the carbonate weathering was more during post monsoon.

According to Douglas and Leo (1977), Giridharan et al (2008) three different sets of strong relationship can exist between major cations and anions.

1. A highly competitive relation can be obtained between ions having different valence number but same charge. Eg. Ca$^{2+}$ and Na$^+$. 
2. An affinity ion relationship was seen between ions processing same valence but different charges. Eg. Na$^+$ and Cl$^-$. 
3. A non-competitive relationship exists between ions having same valence and same charge. Eg. Na$^+$ and K$^+$. 

According to the above classifications, the results from the correlations coefficient matrices (Table 5.7 & Table 5.8) show a highly competitive relationship exists between Na$^+$ and other bivalent ions Ca$^{2+}$, Mg$^{2+}$ during both the seasons. In the case of affinity ion relationship, a good correlation was obtained between the single valence oppositely charged ions Na$^+$, K$^+$ and HCO$_3^-$, Cl$^-$ during the post monsoon season. But the affinity ion relationship was less for bicarbonate ion with other single valence positive ions during pre monsoon season. A significant competitive ion relationship exists between Na$^+$ and K$^+$, the single valence positive ions during both the seasons. In the case of anions the single valence negatively charged HCO$_3^-$ and Cl$^-$ ions registers a good
correlation during post monsoon season and very low positive correlation during pre monsoon season.

5.10. Summary of geochemical analysis:

The geochemical quality assessment of groundwater in Agastheeswaram taluk shows the groundwater is slightly alkaline during the post monsoon and it turns as slightly acidic in the pre monsoon season. The order of cationic abundance is $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+} > \text{K}^+$ and most of the samples where $\text{Ca}^{2+}$ replaces $\text{Na}^+$ in the post monsoon season by cationic exchange reactions. The hydrogeochemistry also reveals the order of anionic supremacy is $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$ in the post monsoon and the major anion trend changes as $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ in the pre monsoon which is due to the carbonate weathering in the pre monsoon season.

The groundwater usage for drinking purposes is restricted in the wells 40, 41, 51, 52, 54, 61, 68 and 69 representing the areas Nallur, Koilvila, Manakudy, Puthalam, Rajakkamangalam, Pallam and Thengamputhoor respectively of Agastheeswaram taluk because of high content of TDS, $\text{Na}^+$, $\text{Cl}^-$ and hardness. High salinity with medium sodium hazard at some locations shows the groundwater is not suitable for regular agricultural activities. The observed chemical variations in both seasons may be because of rock-water interactions, ion-exchange reactions and percolation of agricultural waste water from the surrounding agricultural fields. From the geochemical analysis, generally the groundwater from majority of the stations in the study area is suitable for domestic and irrigation usage and some needs remedial measures.