CHAPTER-7

MAJOR ION HYDROCHEMISTRY
A wide range of chemical substances is soluble in water. These substances dissociate into negative and positive charged ions and having concentration more than 1 ppm in water are termed as major ions (Davis and Dewiest, 1966). It normally makes up more than 96% of the dissolved minerals in groundwater. Major ions are, for the most part conservative and having long residence time.

Major ion concentration plays a vital role in determining the chemical composition of water. These are the most important chemical parameters that ascertain the water quality and its usefulness for drinking, irrigation and industrial purposes. Major ion concentration may help to differentiate between contaminated and non-contaminated zone in groundwater as well as sources of pollution. Certain major ions in groundwater like chlorides (Cl\(^-\)) act as important tracer to determine the direction of groundwater movement, area of recharge and discharge, relative age of groundwater movement of pollutants, sea water intrusion, groundwater modeling, etc.

Major ions like Ca\(^{+2}\), Mg\(^{+2}\), Na\(^+\), K\(^+\), Cl\(^-\), SO\(_4\)\(^{-2}\), HCO\(_3\)\(^-\) and CO\(_3\)\(^{-2}\) in groundwater are highly variable depend on natural and anthropogenic factors. The natural variability of major ions in groundwater largely depends on local geological, climatic and geographical condition of the area. Whereas anthropogenic factors i.e. mining, industrialization, urbanization, etc. may also control variation in major ions concentrations in groundwater depends on the extent of human activities in the concerned area. The details
DISTRIBUTION OF MAJOR IONS

CHLORIDE (Cl⁻)

Chloride ion is one of the most important sources of salinity in water. Higher salinity in water is responsible for higher concentration of chloride ions. Thereby, elevated concentration of chloride ions makes water unpalatable and therefore unfit for drinking and livestock watering (Champman, 1992).

Chloride salts being highly soluble and free from chemical reactions with aquifer material and remains stable once they inter in solution. Chloride content in water may exceed the Sodium due to Base Exchange reaction.

The highest desirable and maximum permissible levels of Chloride in drinking water are 200mg/l and 600mg/l respectively (WHO, 1984). The Indian Council of Medical Research (ICMR, 1975) recommended desirable and maximum permissible limits of Chloride as 200 and 1000mg/l respectively.

Chloride concentration in the study area ranges from 574.11 to 17.36mg/l and 637 to 16.61mg/l in deep aquifer during pre-monsoon and post-monsoon periods (2002-2003) respectively. On the other hand in shallow aquifers, it ranges from 1165.66 to 30.48mg/l and 1092.80 to 22.15mg/l during pre-monsoon and post-monsoon periods (2002-2003) respectively. The highest Chloride concentration occurs at Pinnalur (637.14mg/l) and lowest at Mudanai (16.61mg/l) in deep aquifer, whereas in
shallow aquifers the highest values are observed at Cuddalore (11653.66mg/l) and lowest at Kuzhakollai (22.15mg/l).

The chloride distribution map of deep (Fig.26) and shallow aquifer (Fig.27) show, the chloride concentration is lower (<50.00mg/l) in recharge area whereas in mining, Thermal Power Plants and south and south east of lignite mining area observed between 100 to 893.23mg/l of chloride. The abnormally high concentration of chloride in south and south-east of Lignite mines are due to excessive depressurization of upper confined aquifer and infiltration of mines water, industrial effluents and agricultural returned flow. The second most important belt showing the abnormally high concentration of chloride is reported along the Cuddalore coastal belt. Wherein, high rate of urbanization and industrialization results excessive withdrawal of groundwater and invite seawater intrusion landward.

In general, chloride concentration in the study area increases gradually from recharge to discharge areas. The chloride contours are almost parallel in the north east and bend towards south, which inferred groundwater flow towards south east. The chloride concentration in shallow aquifer is more than that of deep aquifers. Shallow aquifers are more vulnerable to contamination due to dissolution, seepage of mines water and industrial effluent that let out into agricultural fields, ponds, drains, etc. wherein, parting clay lies at the bottom of upper confined aquifers (deep aquifers) which may prevent downward movement of pollutants; hence it prevents contamination of lower confined aquifers. High concentration of chloride gives salty taste and corrosive effects on metals as well harm the plant growth.
Fig. 26: Chloride distribution map (deep aquifer)
Fig. 27: Chloride distribution map (shallow aquifer)
In the study area, chloride concentration is well within the permissible limits except at few places. Hence, the groundwater is suitable for drinking and irrigation purpose in the investigated area.

**CALCIUM (Ca\(^{+2}\))**

Calcium (Ca\(^{+2}\)) is one of the important cation present in these waters. It is quickly dissolved from calcium enriched rocks especially carbonate and sulphates. The solubility of calcium carbonate depends upon the dissolved CO\(_3\). The hardness of water is mainly controlled by salt of calcium and magnesium. Calcium in water is mainly derived from dissolution of calcium from calcium enriched rocks, leaching from soils and application of fertilizers in agricultural fields, returned flow of irrigation water, and infiltration of mines water and industrial effluents, dissolution of soil and other anthropogenic impacts.

The highest desirable and maximum permissible limits of calcium in drinking water recommended by Indian Standard Institute (ISI, 1983) and World Health Organization (WHO, 1984) is 75 and 200mg/l respectively. Calcium is essential for the growth of human body, which require 0.70 to 2.00gm/day. In case of pregnant and lactating women and growing children however, require high doses of calcium. However, high concentration of calcium may also adversely affect the human health such as formation of gallbladder and kidney stone and urinary disorders.

Calcium concentration in the study area range from 178.90 to 10.41mg/l and 135.37 to 10.93mg/l in deep aquifer during pre and post-monsoon periods (2002-2003) respectively. In shallow aquifer, calcium content ranges from 525.05 to 8.02 and 404.40 to 8.00mgl during pre and post-monsoon respectively. Wherein, maximum value observed at
Cuddalore (404.40mg/l) and lowest at Keezhakollai (8.00mg/l). The highest value of calcium at Cuddalore is due to impact of seawater in this region. Calcium concentration in and around mining area is generally higher as compared to area outside the mining zone. In majority of deep tubewells, Calcium concentrations are lower than the shallow aquifer. In general, calcium concentration in the study area falls within the prescribed limit as given for drinking water by WHO (1984) and ISI (1985) except at few places.

MAGNESIUM (Mg^{++})

Magnesium is one of the common elements present in natural water and main contributor of hardness in water along with calcium. In general, magnesium concentration is very less compared to calcium in most natural groundwater. It may be due to relatively less abundance of magnesium rich minerals in rocks (Hem, 1970). The principal sources of magnesium in water are weathering of Ferro-magnesium rich rocks and magnesium rich carbonate rocks.

Magnesium is one of the most important nutrients for the growth of human organism. Magnesium deficiency results structural dis-functioning and severe diarrhea, chronic renal failure and protein caloric malnutrition (WHO, 1973). Whereas, higher concentrations of magnesium may causes cathartic and diuretic (Lehr et. al., 1980).

The maximum permissible and highest desirable limit of Magnesium for drinking water is 100mg/l and 30mg/l respectively (ISI, 1983, WHO, 1984). Whereas, Indian Council of Medical Research (ICMR, 1975) has recommended 50mg/l and 100mg/l, the maximum desirable limit and maximum permissible limit respectively.
In the study area, magnesium concentration ranges from 72.74 to 1.20mg/l and 59.98 to 1.26mg/l in deep aquifer during pre and post-monsoon periods respectively. The highest value was recorded at Cuddalore town (Pachchayamkuppam) 72.74mg/l. The abnormally high value of magnesium indicates presence of Ca-Mg rich evaporates and clays such as montmorillonite rich in magnesium (Bovwer, 1978). The lowest value of magnesium observed at Umangalam (1.20mg/l). About 64.00% and 81.00% of deep-water samples fall within the maximum permeable limit suggested by ISI (1983) and WHO (1984) during pre and post-monsoon period respectively. Whereas, according to Indian Council of Medical Research (ICMR, 1975), 89% and 94% of deep tubewells samples fall within the maximum permissible limit during pre and post-monsoon period respectively. Magnesium concentration at Nadiyapattu and Andikuppam were found below the detection limits. No sample in the study area found above the highest desirable limit.

In shallow water samples, calcium concentration range from 805 to 4.36mg/l and 726.68 to 2.46mg/l during pre and post-monsoon periods respectively. Maximum value of magnesium was recorded at Cuddalore (805.0mg/l), it may be due to salt water intrusion in the coastal belt. About 64% and 68% of water samples fall within the maximum permissible limits as suggested by ISI (1983) and WHO (1984) during pre and post-monsoon periods respectively. Whereas, during pre and post-monsoon periods 74 and 86% of water samples lies within the maximum permissible limit as per ICMR (1974), respectively. Magnesium concentration along the Cuddalore coastal belt (at Cuddalore, Alapakkam, Selambemangalam, etc.) was
observed to be above the maximum permissible limits, which may be due to seawater intrusion.

The spatial distribution of magnesium concentration in shallow aquifers was more than the deep aquifers. In pre-monsoon period, magnesium concentration showed higher values in both deep and shallow aquifers as compared to post-monsoon period. It is due to infiltration of rain water along with leached ions will dilute shallow aquifers first and might have taken a large time to reach the deep confined aquifers. Thus, the lower confined aquifers are better in quality than the upper confined aquifers in the study area.

In general, magnesium concentrations in the study area fall within the permissible limit except in the mining area and the south and southeast region. It may be due to the seepage of pumped out mines water and industrial effluent into agricultural fields, down stream drainage, ponds, etc. in the south and south east of the mine area.

**SODIUM (Na⁺)**

Sodium is one of the most abundant constituents of the earth crust and is present in natural water since its salts are highly soluble in water. The concentration of sodium in groundwater depends on local geological, hydrogeological and climatic conditions and anthropogenic activities such as mining, urbanization, industrialization, etc.

Sodium concentration is the most important parameter to determine the suitability of surface and groundwater for various purposes (i.e. drinking, industrial and irrigation) especially irrigation. Higher concentration of sodium in water results is reduction of soil permeability, soil aerations and
circulations of water, thereby affecting plants growth and enhances the soil salinity.

Sodium is an essential element for the growth of human body. However, higher concentration of sodium also adversely affects the person's suffering from cardiac diseases, renal diseases pertaining to circulatory system and high blood pressure. The guideline limit of Sodium in drinking water is 200mg/l (WHO, 1984).

Sodium concentration in the study area range from 563.10 to 20.22 mg/l in deep aquifer during pre-and post-monsoon periods (2002-2003) respectively. Maximum concentration of the sodium was observed at Erumbur (563.10mg/l) and lowest at Nadiyapattu (20.22 mg/l). The higher value of sodium concentration observed in the south east and south of lignite mines, it may be due to infiltration of mines water and industrial effluents. Sodium concentrations in Cuddalore aquifers were low as compared to alluvial aquifers. About 77% and 79% of water samples fall within the maximum permissible limit during pre-monsoon and post-monsoon respectively.

In shallow aquifers, sodium concentration ranges from 6422.75 to 8.97mg/l and 6193.56 to 18.98mg/l during pre- and post-monsoon periods (2002-2003) respectively. Whereas, highest value observed at Cuddalore (6422.76mg/l), which could be were mainly due to seawater intrusion. While abnormally high concentration of sodium in the south and south east of lignite mines, may be due to infiltration of mines water and industrial effluents. However, low concentration of sodium in west and north west of lignite mines observed in some parts of Cuddalore Formation and area unaffected by lignite mining and associated industrial activities. About 39%
and 38% of water samples having sodium concentration above the recommended limit in pre-monsoon period (2002).

Sodium is the most dominant cation that occurs in the study area. In general, sodium concentration in deep aquifers fall within recommended limits for drinking water except at few places. Whereas, sodium concentration in shallow aquifers is abnormally higher i.e. about 40% of the samples have above the recommended limits. Hence, shallow aquifers are least suitable for drinking and irrigation purposes in the study area.

**POTASSIUM (K⁺)**

Potassium concentrations in natural waters are normally found lower then those of sodium. It may be due to relative resistance of potassium-enriched rocks to weathering (Goldetech, 1938) and also due to reaction with the clay minerals. The chief sources of potassium in groundwater are weathering of potassium silicate rocks, rainwater and application of K-fertilizers. Concentration of potassium in soil may also increase due to application of high doses of potassium rich fertilizers, which may disturb the existing equilibrium conditions between various stages of water circulation and the medium. In addition to the other factors such as nature of clays, pH, organic matter, moisture content in the soil may also control the potassium concentration in the soil.

In the study area, potassium is the least abundance among cations. Its concentration varies from 169.30 to 1.17mg/l and 146.48 to 1.10mg/l in deep aquifers during pre- and post-monsoon periods respectively. Maximum concentration of potassium was observed at Pachchayamkappam (146.48mg/l), which may be due to the effect of seawater intrusion in these areas.
In shallow aquifer, potassium concentration ranges from 489.88 to 0.39mg/l and 468.70 to 0.56mg/l during pre- and post-monsoon periods respectively. Maximum concentration of potassium was observed at Pinnalur (468.70 mg/l), which may be due to excessive application of potassium fertilizers. Abnormally high concentrations of potassium were observed along the Cuddalore coastal belt.

In general potassium concentration were found high in shallow aquifers than in deep aquifers in major part of the study area. It is mainly due to application of K-fertilizers, whereas abnormally high concentrations of potassium in coastal track were may be due to seawater intrusion.

In general, potassium concentrations in groundwater were low in comparison to other cations except at few places in the study area, where excessive application of K-fertilizers to enhance the crop production and impact of seawater in coastal belt. However, potassium is more toxic to fish and shell than calcium, magnesium and sodium (Brown et al., 1970).

**BICARBONATE (HCO₃⁻)**

Bicarbonate is one of the common anion present in natural waters. Alkalinity and hardness in water are largely controlled by the presence of dissolved carbon dioxide in water. Sources of bicarbonate in groundwater are dissolution of carbonate rocks, released carbon dioxide by decaying of organic matter and also presence of carbon dioxide in soil and atmosphere.

The carbon dioxide present in atmosphere has react with water to form weak acid termed as carbonic acid which dissolved the calcium carbonate present in soils and rocks enrich with calcareous matter.
\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & = \text{H}^+ + \text{HCO}_3^- \\
\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} & = \text{Ca}^{++} + 2\text{H}_2\text{CO}_3^-
\end{align*}
\]

Carbonate concentration in water having 600mg/l is considered safe and good for drinking and irrigation purpose (WHO, 1984).

In deep water aquifers, bicarbonate concentration ranges from 411.80 to 26.40mg/l and 384.64 to 27.86mg/l during pre- and post-monsoon periods (2002-2003) respectively. The highest value is recorded at Visur (411.80mg/l), which may be due to proximity to Cretaceous limestones. Bicarbonate concentration in the south and south east of lignite mines were also relatively high because of impact of mines water and industrial effluents draining in these areas.

In shallow water aquifers, bicarbonate concentration ranges from 680 to 24.41mg/l and from 500.60 to 20.33mg/l during pre- and post-monsoon periods respectively. Where highest concentration observed at Pinnalur (i.e. 680.18mg/l). In phreatic aquifer, bicarbonate concentration is more than in the deep aquifer. The higher concentration of bicarbonate observed in south and south cast of the lignite mines, which may be due to infiltration of mines water.

**SULPHATE (SO\text{4}^-)\)**

Sulphate is one of the most abundant anion in natural water. The principal sources of sulphate in groundwater are the results oxidation of sulphide mineral present in lignite, Sedimentary and Igneous rocks and volcanic emanations. Furthermore, the application of soil amendments (i.e. gypsum, pyrite, etc.), industrial discharge and atmospheric precipitation may also add significant amount of sulphate to groundwater (Chapman, 1992).
Concentrations of sulphate in groundwater were largely controlled by oxidation, reduction, precipitation and solution processes.

The highest desirable and maximum permissible limits of sulphate in drinking water are 200mg/l and 400mg/l (ICMR, 1975, WHO, 1984) respectively. Whereas, Indian Standarded Institute (ISI, 1984) as suggested highest desirable and maximum permissible limits of sulphate are 150mg/l and 400mg/l respectively. Sulphate concentration more than 250mg/l may cause gastrointestinal irritation. Elevated sulphate concentration may have laxative effects (WHO, 1984). Whereas, sulphate concentration exceed 500mg/l may impart better taste.

In deep water aquifers, sulphate concentration ranges from 561.95 to 5.93mg/l and 464.93 to 3.06mg/l during pre- and post-monsoon periods respectively. Whereas, abnormally highest concentrations were observed at Erambur (561.95mg/l), Pinnalur, Valayamadevi, the area nearer to mines water which discharge their effluents in the south and south east of lignite mines. Abnormally high concentration has also been noticed along the coastal belts especially at Cuddalore, which may be probably due to the saltwater intrusion. About 25.50% of the samples in the pre-monsoon season having sulphate concentration more than the highest desirable limit. They were mainly confined to lignite mining and associated industrial regions and south and south-east of it which may be due to seepage of mines water let out from lignite pits into down gradient drains, ponds, nallas, etc. In general, sulphate concentration is higher in pre-monsoon period than those of post monsoon period.

Sulphate concentration in shallow aquifer ranges from 1921.22 to 13.45mg/l and 1610.44 to 12.86mg/l during pre- and post-monsoon periods
respectively. Abnormally high concentration were found south and south east of lignite mines and around mining area as a result of oxidation of marcasite (FeS$_2$), which occurs sporadically in lignite deposits, Cuddalore sandstones and aquifer Sands in different forms. About 42.10% and 23.68% of water samples having sulphate concentration more than highest desirable limit during pre-monsoon and post-monsoon period respectively. Whereas, 18.42% and 13.45% samples have sulphate concentration more than maximum permissible limit during pre- and post-monsoon periods respectively.

In general, sulphate concentration in groundwater was more in phreatic aquifer than in deep aquifer and also more in pre-monsoon period than in post-monsoon period.

Sulphate is the most dominant anion present in the study area. Higher concentration of sulphate in the upper confined aquifer (deep aquifer) during pre-monsoon is the results of oxidation of H$_2$S enriched mines water pumped out from aquifer gets seeped into the groundwater and also by the oxidation of lignite beds (Karanth, 1987).

**CARBONATE (CO$_3$$^-$)**

Carbonate concentration in the major part of the study area are very low, and large number of samples having concentration below detection level. The low concentrations of carbonates are due to the absence of carbonate rocks in the area. The higher concentration found in the mines and south and south east of mines are due to leaching of mines water and industrial effluents. Whereas, high concentration in the central part of the Mine-II, are due to the presence of highly mineralized zone in deeper
aquifers. High concentrations of carbonate in coastal track may be due to effect of seawater.

**TOTAL DISSOLVED SOLID (TDS)**

Total dissolved solids (TDS) represent the total concentration of anions and cations in water and it gave an idea about the general quality of water. High concentration of TDS corresponds to higher concentration of major cations and anions in water.

Total Dissolved Solid (TDS) concentration, more than 2000-3000mg/l is considered to be too salty to drink ñ (Allan, et. al., 1979). The palatability of water depends upon the concentration of TDS in water. If TDS level less is than 600mg/l is considered to be good whereas more than 1200mg/l in drinking water is non-palatable (WHO, 1984). The permissible limit of TDS in drinking water lies in between 500 to 1500mg/l (ICMR, 1975).

In the study area, TDS ranges from 2043.80 to 110.33mg/l and 1743.80 to 104.89mg/l in deep aquifers during pre- and post-monsoon periods respectively. The highest concentration has been observed in the south and south east of the lignite mines, where untreated mines water and industrial effluents draining into agricultural fields and down streams drainages, ponds, lakes, etc. and peculate downward and ultimately enhance the TDS concentration in groundwater. Majority of deep wells are good in quality except few pockets lies central part of the Mine-II, along Gadilam river flow zone, south and south-east of mines and Coastal track in the study area. The TDS concentration in deep aquifer is high during pre-monsoon and lower in post-monsoon season. About 74.46%and 80.83% water samples fall within the safe limit for drinking and domestic purposes during pre- and post-monsoon periods respectively.
In shallow water zone, TDS concentration range from 21930.71 to 64.93mg/l and 20181.70 to 84.45mg/l during pre-and post-monsoon period respectively. The distributions of TDS in shallow aquifers are similar to that of deep aquifers. In shallow aquifers, in general the TDS concentration is more than the deep aquifer. About 50.00% and 76.94% of the water samples fall within the fresh water range during pre-and post-monsoon periods.

**TOTAL HARDNESS (TH)**

Total hardness in water is mainly due to the presence of Ca$^{++}$ and Mg$^{++}$ and significant amount of iron and manganese if present are also included. Sum of the calcium and magnesium hardness is termed as general hardness. Hardness in water is divided into carbonate and non-carbonate hardness. Where carbonate hardness referred as temporary hardness and hardness remained in the water after boiling is called permanent hardness (Chapman, 1992). Public acceptability of hardness vary from community to community depending upon local factors.

The maximum permissible limit and highest desirable limits of hardness is 600mg/l and 300mg/l respectively (ISI, 1983). Whereas, maximum permissible limit recommended by WHO (1984), for drinking water is 500mg/l. In general hard water does not have adverse effect on human being. It is generally reported that the cardiovascular diseases are confined in the areas having soft water (Crawford, 1972).

In the study area, total hardness range from 706.37 to 24.05mg/l and 539.86 to 33.14mg/l in deep aquifer during pre- and post-monsoon period respectively. Higher hardness was observed along the coastal zone, south and south east of lignite mines, mining-cum-industrial complex and along the Gadilam river flow zone. Higher hardness in the mining area, south,
southeast of mines may be due to leaching of mine spoils, infiltration of mines water and industrial effluents discharged in down stream. While in the Coastal belt and Zone of Gadilam River flow it may be the results of dissolution of anhydrate, gypsum and calcareous sandstones. About 8.51% of water samples in the study area are soft in pre- and post-monsoon periods.

In shallow aquifers, total hardness ranges from 4627.13 to 29.70 mg/l and 4063.43 to 26.82 mg/l during pre- and post-monsoon periods respectively. Highest hardness values were noticed at Cuddalore, which may be due to effect of seawater intrusion. In Phreatic aquifers, only 5.26% of water samples fall under the soft water categories while 25.53%, 10.65 and 55.31% lies under moderately hard, hard and very hard water categories during pre-monsoon period.

In deep tube-wells groundwater is less hard in comparison to shallow aquifers and also hardness increases in pre-monsoon period. In general, major part of the study area, groundwater is generally hard and very hard and is within the permissible limits except at a few places.

**HYDROGEN ION CONCENTRATION (pH)**

Hydrogen ion (pH) concentration is an important variable in water quantity assessment and soil fertility as it influences growth of plants and soil organisms and it affects the sensibility of water for drinking, industrial and irrigation purposes.

The pH is a measure of the acidity and alkalinity of water and is very important character of water quality evaluation. Hydrogen ion (pH) concentration is defined as the negative of the logarithm to the base 10 of the hydrogen ion concentration (i.e. \[
\text{pH} = \log_{10}([H^+])
\]). The pH ranges from 0 to
14 where less than 7 indicates an acidic solution and more than seven indicates an alkaline while 7 indicates neutral solution.

Temperature plays very important role in determining the pH at which neutrality occurs (Freeze and Chery, 1979). The pH in groundwater principally controlled by the balance of dissolved carbon dioxide, carbonates and bicarbonates ions (Fletcher 1987).

The highest desirable limit of pH for public water supply ranges in between 7 and 8.5, while the maximum permissible limit varies form 6.5 to 9.2 (WHO, 1984).

In the study area, pH value varies from 5.90 to 9.20 in the deep aquifers and 4.20 to 9.80 in the shallow aquifers during pre and post monsoon periods, highest value is recorded at village Pachchayankuppam (pH = 9.20) and lowest at village Nanakuppam (pH = 5.90). In case of shallow aquifers highest values are also recorded at Pachchayankuppam (pH=9.80) and lowest value at Vadakvellur (pH = 4.20).

In general, the groundwater in the area is alkaline in nature. However, acidic water was noticed only in few wells at lignite yard, southern part of the Mine-II, U Mangalam, Edakuppam, etc. The values of the pH on the whole are within the permissible limits except at few places in and around the mining and thermal power plants areas.

**ELECTRICAL CONDUCTIVITY (EC)**

Electrical conductivity is a measured of the ability of an aqueous solution to conduct electrical currents and it depends on the concentration of ionized substances present in water. In other words, the electrical conductivity is defined as reciprocal of the electrical resistance of one cubic
centimeter material at 25°C (Cutcheon et. al. 1993). It gives an idea about extent of mineralization and magnitudes of salinity in water. The electrical conductivity of 400 μmhos/cm at 25°C is considered suitable for human consumption (WHO, 1984).

The electrical conductivity values in the study area ranges from 3386 to 206 μmhos/cm and 36718 to 120 μmhos/cm in deep and shallow aquifers during pre and post monsoon periods (2002-2003) respectively. In post-monsoon period, electrical conductivity ranges from 3096 to 146μmhos/cm and 31993 to 131μmhos/cm in deep and shallow aquifers respectively. The highest EC value was noticed at Erambur (3386 μmhos/cm) in deep aquifers due to infiltration of mine water and industrial effluents, and Base exchange reaction occurring in the sediments rich in sands, silts and calcareous sandstones.

The high value of EC found in a wells south east of lignite and lowest north west of mines. The higher value of EC in the south east of mines may be due to seepage of mines water discharge into natural and man made drains flowing down gradient of the area (i.e. south east). The high value of EC was also observed along the Cuddalore coastal belt, which may be due to the seawater intrusion.

In shallow aquifers highest EC value were observed at Cuddalore (i.e. 36718 μmhos/cm) it may be due to salt-water intrusion because of rapid industrialization and vibration along the Cuddalore coastal belt especially around the Cuddalore and Porto Nova towns.

In general, EC value increase from north west to south east direction following the general hydraulic gradient. In Tertiary Cuddalore Formation,
the EC values are generally low in comparison to Recent alluvium formation in the north and southeast.

A perusal of iso-conductivity map of deep (Fig.28) and shallow aquifers (Fig.29) shows north and north western part of the area falls in the ranges of 250 to 750 μmhos/cm whereas in north east and eastern part fall in the range more than 1500 μmhos/cm.

High degree of mineralization and salinization occurs in the proximity of thermal power plant and lignite mining areas and east and south of lignite mines as well as Cuddalore coastal belt. In shallow aquifers, EC value is comparatively more than deep aquifer. In general, the groundwater is fit for drinking and irrigation purposes in the study area except in the Neyveli lignite and Industrial complex area and south east of lignite mines as well as Cuddalore belt, where groundwater quality is very poor.
Fig. 28: Iso-conductivity map (deep aquifer)
Fig. 29: Iso-conductivity map (shallow aquifer)
2. GRAPHIC REPRESENTATION OF HYDRO-CHEMICAL DATA

The most important task in the groundwater study is compilation and presentation of hydrochemical data in a convenient way for visual explanation and interpretation of water quality. For which, graphic methods are used to display, comparing similarity and dissimilarity in cations and anions in a deep and shallow aquifers and also for pre-and post-monsoon data. A large number of graphic methods have been developed for representing large number of hydrochemical data viz. bar graph, vector diagram, pattern diagram, stiff, tri-linear diagram, etc. In the present study, tri linear diagram have been used for the presentation of chemical data because all other diagram provide quick visual comparison of individual chemical data but not suitable to display large number of chemical data, for which Tri-linear diagram is most suited.

2.1 TRI-LINEAR DIAGRAM

There are various methods of Tri-linear Plotting (Palmar, 1911, Hill, 1940, Piper, 1944). Of which, Piper’s Diagram has been used in the present study. The greatest application of Tri-linear diagram is to represent large number of hydro-chemical data for critical study of groundwater quality. Piper’s Diagram consists of three distinct fields of which two triangular fields and one diamond shaped field. In the right and left triangular fields, major anions (Cl\(^-\), SO\(_4\)\(^-\), HCO\(_3\), CO\(_3\)\(^-\)) and cations (Mg\(^{++}\), Na\(^+\), K\(^+\), Ca\(^{++}\)) are plotted in percentage respectively. While overall characteristic of water is represented in the diamond shape field by single point plotting which is intersection point, projected from the right and left triangle in the diamond field.
2.2 HYDROCHEMICAL FACIES

The concept of hydrochemical facies was developed by Back (1961, 1966), Margan & Winner (1962) and Seaber (1962), to represent chemical composition of water in a convenient way by identifiable groups. Ophari and Toth (1989) had defined hydrochemical facies as distinct zones, having cations and anion concentrations described within defined compositional categories. According to Back (1966) hydrochemical facies is a function of lithology, solution kinetics and flow patterns of the aquifer. Hydrochemical facies have been identified on the basis of relative dominance of major cations and anions. For considering domination, 50% of the reacting value (out of total cations and total anions separately) has been considered as threshold value. In case of no clear dominance, relative abundances of individual parameters have been considered. Major cations and anions percentage value are plotted on Piper’s Diagram to infer the hydrochemical facies in the study area. The plot of the hydrochemical data in Piper’s diagram of deep and shallow water aquifers is shown in Fig 30 & 31. It is inferred from the Tri-linear diagram, 53.19% and 61.70% of water samples fall in Na + K- type facies, 4.25% and 2.12% Mg-type facies. 2.12% Ca-type and 40.44% and 34.66% belong to no dominant type in deep aquifers during pre- and post-monsoon period respectively. While in anion categories, 55.33% and 51.04% no dominant- type, 25.53% and 27.65% HCO₃ +CO₃ -type, 17.20% and 21.77 Cl -type and 2.12% SO₄ -type during pre- and post-monsoon periods respectively.

In shallow aquifers, 76.31% and 86.82% of water sample belong to Na + K type, 21.06 and 10.55% no dominant type and 2.63% Ca-type of water observed during pre and post monsoon period respectively. In case of
Cations Facies

A. Magnesium (Mg) Type
B. Calcium (Ca) Type
C. Sodium (Na) Type
D. No Dominant Type

Anions Facies

E. Sulphate (SO₄) Type
F. Bicarbonate (HCO₃) Type
G. Chloride (Cl) Type
H. No Dominant Type

Fig. 30: Tri linear diagram (Shallow aquifer)
Cations Facies
A. Magnesium (Mg) Type
B. Calcium (Ca) Type
C. Sodium (Na) Type
D. No Dominant Type

Anions Facies
E. Sulphate (SO$_4$) Type
F. Bicarbonate (HCO$_3$) Type
G. Chloride (Cl) Type
H. No Dominant Type

Fig. 31: Tri linear diagram (deep aquifer)
anion category, and 39.47% Cl-type, 7.89% and 5.24% SO₄- type, 18.42% and 21.05% HCO₃ + CO₃ type and 34.22% no dominant type during pre- and post monsoon periods (2002-03) respectively.

Interpretation of hydro-chemical facies of groundwater from Piper’s diamond field for pre and post-monsoon of deep and shallow aquifers shows continuous mixing between Cl and HCO₃ with few representations of SO₄. The trend of Na and Ca-type facies in deep and shallow aquifers are similar while varies with seasons. HCO₃ + Cl-type and SO₄ + Cl-type dominate the anions during post and pre-monsoon periods (2002-03) respectively. Na + K and SO₄ + Cl-type dominate the diamond field in the pre- monsoon period. On the other hand, mixed trends are observed in major cations and SO₄ + Cl + HCO₃-type in the post-monsoon period, which may be due to leaching from the mines waste, surface soil, retuned flow of mines and Industrial effluents. Pipers diagram show that the groundwater are contaminated due to weathering process, leaching and dissolution of surface soil, mixing, seepage of mines and Industrial waste water and by secondary precipitation. The Pipers diagram also reveals the fact that deep and shallow aquifers affected by the salinity problems except north and north-west of lignite mines. Hence, groundwater chemistry of deep and shallow aquifers is dominated by chemical weathering processes and impact of lignite mining followed by evaporation, infiltration and leaching of soils, mines water and industrial effluents. In general, Tri-lineat Diagram shows that groundwater in the study area belong to Na + K, SO₄ + Cl and SO₄ + Cl + HCO₃-types.
3. SOURCES, CAUSES, IMPACT AND REMEDIES OF MAJOR IONS ON GROUNDWATER

The abnormally high concentrations of major ions in mining area and, south and south east of mines are mainly due to large-scale exploitation of lignite, over exploitation of aquifer and associated industrial activities (i.e. two pit head giant thermal power plants, fertilizer plant, briquetting and carbonization plant, etc). However, in the coastal belt, abnormality in major ions concentration may be the result of seawater intrusion.

The lignite mining and associated industries producing huge quantity of liquid and solid mines wastes, in addition to huge quantity of flyash produced by thermal power plants. The mine wastes and flyash contains large number of soluble salts. When came in contact with aqueous environment cause dissolution and release of large number of inorganic salts into solution. It enhances the major ion concentration in surface water they ultimately leach to groundwater as well. The seepage of mines water, flyash ponds water and uses of this water for irrigation in down stream villages resulted high concentration of major ions in deep and shallow aquifers. While high concentration of major ions in upper confined aquifers (deep aquifers) may be due to excessive depressurization of this aquifer for mine safety.

The rapid industrialization and urbanization in the Cuddalore costal belt has resulted sharp decline of water level, which in turn invite seawater ingress landward and causing abnormally high concentration of major ions in coastal aquifers.

In the west and north west (i.e. higher hydraulic gradient) of lignite mines have major ions concentration well within the permissible limit. In the
lignite mining and associated industrial areas and south and south east of mines have major ions concentration above the permissible limits.

The high concentration of major ions in groundwater and surface water has adversely affected the water quality for drinking, irrigation and industrial purposes in the study area.

In general, control of groundwater pollutions is more difficult than prevention since groundwater pollution is an irreversible process. Remedial measures to reduce the groundwater and surface water contaminations should first be applied near source of pollution from where it inter into hydrological system. The following remedial measures should be adopt to minimize the water pollution in the study area:

- Covering of mine wastes and dry flyash ponds with lime or limestone, afforestation of spoil dumps, etc.
- To reduce the area of groundwater pumping by constructing close space discharge wells and restricting to lignite bench.
- Treatment of mines and flyash ponds water before discharging into agricultural field drains, ponds, etc.