CHAPTER 4

METHODOLOGY

4.1.0 INTRODUCTION

Hydrogeochemical research requires proper site selection for collection of water samples and appropriate method of analysis. Sampling sites were located taking several factors into considerations like lithology, structure, geomorphology, and river influence, mining, urban, agricultural and availability of wells. Sampling of groundwater has been carried out in and around Nagapattinam Coastal region between 2007 and 2009. A synoptic view of the methodology adopted is noted in the Flow chart (Fig 4.2)

4.2.0 FIELD METHODS

The groundwater samples were collected during January 2007, July 2007, January 2009 and July 2009 to broadly cover seasonal variations of POM (post monsoon) and PRM (pre monsoon) seasons. A total of 148 samples were collected at the rate of 37 samples per season. The sampling locations are plotted and taking into consideration of their uniformity in their aerial disposition. The samples are restricted in the southern part of the study area due to the presence of Vedaranyam Swamp, number of agricultural fields, number of distributary channels and non availability of bore wells. The irrigation is mainly met from tanks and surface waters flows in this part of the study area.
Fig: 4.1 Sample Location map of the study area
<table>
<thead>
<tr>
<th>S.No</th>
<th>Location Name</th>
<th>S.No</th>
<th>Location Name</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>Nallur</td>
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<td>2</td>
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<td>Thiruvilaiyattam</td>
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<td>Mangainallur</td>
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<td>Thirumarugal</td>
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<td>Tiruvengadu</td>
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<td>Nagapattinam</td>
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<td>Thevur</td>
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<td>Tiruppundi</td>
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<td>13</td>
<td>Keelaiyur</td>
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</tr>
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<td>Karuvi</td>
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<td>Voimeedu</td>
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<td>Sembanar koil</td>
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<td>Thopputhurai</td>
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<td>18</td>
<td>Vaitheeshwaran Koil</td>
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<td>Vedaranyam</td>
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<td>19</td>
<td>Mayiladuthurai</td>
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</table>

Table: 4.1 Name of the Sample Locations
Methodology

Groundwater sampling (PRM1, PRM2, POM1, POM2)

pH and EC (in field)

Filtered (0.45μm)

pH, EC, F, Cl, HCO₃, Ca²⁺, Mg²⁺, SO₄²⁻, Na⁺, K⁺, NO₃⁻

- Ion Electrode
- Titration
- UV Spectrophotometer
- Flame Photometer
- Ion chromatography

Modeling (WATQ4F)

Hydrogeochemistry

Classification
Geochemistry
Thermodynamics
Statistics

Saturation Index & Correlation

Result and Discussion

Conclusion

Fig: 4.2 Methodology
4.2.1 Water samples

Ground water sampling locations are shown in figure 4.1. The locations selected for groundwater sampling is given in the table 4.1. One litre of water samples were collected in polyethylene bottle. As a precautionary measure, they were rinsed with 1:1 HNO₃ to wipe out the slightest impurity followed by final washing with distilled water. As the chemical changes are quite apparent in water samples during transit and storage, certain parameters such as Electrical conductivity (EC), pH and Temperature were measured immediately after the sample collection. And then it was sealed and brought to laboratory for analysis and stored properly (4ºC) before analysis. Half the quantity of the collected sample was filtered and acitified for cation analysis while the other half of the each sample preserved for anion determination.

4.2.2 Filtration of Samples

Before estimation of dissolved metals the samples were filtered through 0.45 µm membrane filter paper using vacuum pumps.

4.3.0 LABORATORY METHODS

4.3.1 Water Analysis

Water samples were analysed for major, minor and trace ion concentration by using standard procedures (APHA 1998; Ramanathan 1992; Ramesh and Anbu, 1996).
a) pH and Electrical conductivity

pH and EC of water samples where measured by pH-Conductivity meter model CONSORT C425. The pH electrode is active and stable only after wetting. For this purpose, it was immersed for at least ten hours in 0.1 M HCl or in a buffer of pH 4 to 7. Before using, the reference part of the electrode is topped with 3.5 M KCl solution. After rinsing the electrode with distilled water, it was immersed in a buffer solution of pH 6.87 (25ºC), the CAL knob was adjusted, then the SLOPE knob was adjusted after the immersing the electrode in a buffers solution of pH 4.01 (25ºC). After the instrument is calibrated, pH of each water sample was determined. Three readings of each sample were recorded to get accurate result. The samples were stirred during measurement to promote homogeneity.

As the ions occur in a dissociated form in water medium so they move under the influence of an electrical potential. Therefore by imparting an electrical current to a solution, the conductance of the solution can be determined. The ability of the solution to conduct the current is a function of the concentration and change of the ions which in turn is dependent on the dissolved solids in the water medium. So a rapid determination of TDS can be made by measuring the electrical conductance of a ground water sample (Todd, 1980). Conductance is preferred to its reciprocal i.e., resistance, because it increases with salt content. Specific electrical conductance is defined as conductance of a cubic centimeter of water at a standard temperature of 25º C; a rise of 1º C increases the conductance by about 2% (Todd, 1980).
EC was measured in microsimens per centimetre (µs/cm.). Because natural water contains a variety of ionic and undissociated substances, conductance cannot be simply related to TDS. However, since conductance can easily be measured, the results serve as dependable indicators of dissolved solids. An approximate relation for most natural waters in the range of 100 µs/cm to 5000 µs/cm leads to the following equivalencies (Logan 1961 and Richards 1954).

\[ 1 \text{ meq of cations} = 100 \mu \text{s/cm} \]

\[ 1 \text{mg/l} = 1.56 \mu \text{s/cm} \]

The instrument was first calibrated and set for 0.01M KCl standard (1287 µs/cm. at 25º C). Three readings of each sample were taken and the average was considered. This instrument also has a selection mode for measuring TDS.

b) Temperature

Temperature of the water samples were measured by a standard mercury thermometer of +0.1º C.

c) Bicarbonate

Bicarbonate was determined by following potentiometric titration method. Standards of bicarbonates (ranging from 5 mg/l to 300 mg/l) were prepared. 25 ml of each samples were titrated against 0.006N HCl. End point of the reaction is attained when the solution comes to pH of 4.5. A graph was plotted for standard concentration against volume consumed. Then the concentration of the samples was determined from the graph plotted.
d) Chloride

Chloride, in the form of chloride ion (Cl\(^-\)) is one of the major inorganic anion in water. It was estimated by Mohr’s titration method. Standard solutions of chloride of various concentrations were prepared. 25 ml. of each water and standard solutions were titrated against 0.06N silver Nitrate solution. Potassium chromate was used as an indicator. The colour change is from yellow to pink was taken as end point. Knowing the value of silver nitrate consumed by each sample, the concentration of chloride in each sample was ascertained from graph of standard solution of chloride against volume of silver nitrate consumed.

e) Sulphate

Sulphate was determined by turbidity method. Sulphate standards of concentration ranging from 1 ppm to 100 ppm were prepared from Sodium sulphate in distilled water. 10ml of each standard solution and sample was taken, and diluted to 100 ml with distilled water. 20 ml of sample was taken and 5 ml of conditioning regent (mix 50 ml glycerol with solution containing 30 ml of con. HCl+300 ml of distilled water+100ml of 95% ethyl alcohol+75gm of NaCl) was added and mixed well. The flask is constantly stirred with stirrer. Barium chloride is added while stirring and the turbidity developed was measured on spectrophotometer at 420 nm, after stirring for 5 min in both standards and sample. Note the absorbance value for calculation. The standard curve is attained by plotting absorbance values of standard sulphate solution
was plotted in the graph for the specified ranges. Amount of sulphate present in sample is read from calibration graph.

\[
\text{SO}_4^- \text{ mg} \times 1000
\]

\[
\text{SO}_4^- (\text{mg l}^{-1}) = \frac{\text{X}}{\text{Dilution factor}} \times \frac{\text{Vol. of sample}}{}
\]

f) Fluoride

Fluoride concentration was determined by using Orion fluoride ion electrode mode (94-09, 96-09). The instrument was checked for slope by TISABIII (concentrate with CDTA) by using the meter with mill volt read only mode. Measurements were made with 5 ml of TISAB III for 50 ml of sample. The electrode was rinsed with distilled water, blot-dry and placed into beaker. When stable reading is displayed, mv values for corresponding standard concentration (0.05 mg l\(^{-1}\), 1 mg l\(^{-1}\), 1.5 mg l\(^{-1}\), 2.5 mg l\(^{-1}\), 5 mg l\(^{-1}\), 10 mg l\(^{-1}\), and 100 mg l\(^{-1}\)) were noted. The readings with increasing concentration of standards were repeated after rinsing the electrode with deionized water blot dried and placed into second beaker and reading is displayed. Record the mv value and corresponding standard concentration by using semilogarithmic graph paper. Prepare a calibration curve by plotting mv values on the linear axis, and the standard concentration values on the logarithmic axis. Similar steps are followed for the samples to attain the readings. Using calibration curve prepared the unknown concentration is determined using Orion fluoride ion electrode.
g) Calcium and Magnesium

Calcium and Magnesium was analysed by titrimetry. 20ml of sample was titrated against 0.02N EDTA, after adding ammonium chloride-ammonia buffer and 30-40 mg of Erichrome black-T as indicator. The endpoint was indicated by appearance of steel blue colour. The amount of EDTA consumed for determining total calcium magnesium is noted (B).

The amount of calcium is obtained by titrating 20 ml of sample after adding 2ml of 1N sodium hydroxide, and 30-40mg of Murexide indicator against 0.02m EDTA solution. The end point is denoted by the appearance of blue-violet colour. The amount of EDTA consumed is (A)

\[
0.0004 \times A \text{ ml} \\
Ca^{2+} (\text{mg l}^{-1}) = \frac{-}{\text{Vol. of sample}} \times 10^6
\]

\[
0.00024 \times (B-A) \text{ ml} \\
Mg^{2+} (\text{mg l}^{-1}) = \frac{-}{\text{Vol. of sample}} \times 10^6
\]

h) Sodium and Potassium

Sodium and Potassium was analysed by flame photometer method (ELICO CL 378). The stock solutions for sodium and potassium were prepared, the air valve was opened and the air pressure is adjusted to 10 lbs.sq in the gas valve were opened and the burner is ignited. The gas supply is adjusted to get blue green and stable cones. Place the capillary in distilled water
and set the galvanometer on ‘zero’ with zero knob. Dip the capillary into the standard solution and set the digital reading at 100 by means of sensitivity knob. Feed the capillary with samples to be analysed after analyzing the standard solution and record the readings displayed in the instrument. Prepare the calibration curve with sodium and potassium standards. The concentrations of sodium and potassium in the sample are read from the calibration curves.

i) Nitrate

The Nitrate was analyzed by Consort ion meter C933 using ion selective electrode (31505-003B). By serial dilution of the 0.1M or 1000 ppm Nitrate standard; prepare two Nitrate standards whose concentration is near the expected sample concentration. Measure out 100ml of each standard into individual 150 ml beakers and add 2 ml of ISA to each.

Place the more dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode. Lower the electrode tip into the solution. Adjust the meter to the concentration of the Nitrate standard and fix the value in the memory according to the meter manufacture’s instructions after stabilization of the reading. Rinse the electrode with distilled water and blot dry. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution. Adjust the meter to the concentration of the Nitrate standard and fix the value in the memory according to the meter manufacturer’s instructions after stabilization of the reading. For low level measurements, place the rinsed, dried electrode into a solution containing 100 ml of distilled
water and 2 ml of ISA. After stabilization, fix the blank value in the meter according to the meter manufacturer’s instructions. Place 100 ml of the sample and 2 ml of ISA in a 150 ml beaker. Place the beaker on the magnetic stirrer and begin stirring. Immerse the electrode tip into the solution and wait for the reading to stabilize. Read the concentration directly from the meter display. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tip in the first Nitrate standard.

4.4.0 Remote Sensing Methodology

4.4.1 Data acquisition

The basic or primary data of the present study include the IRS Resourcesat-1 LISS III data obtained from National Remote Sensing Centre (NRSC) Hyderabad. This data relates to the combination of three spectral bands i.e., 2, 3 and 4. These band combinations have been proved very suitable for the identification of vegetation, water, soil/rock and their associations. Secondary or ground truth data constitutes an important data base in remote sensing because they increase the interpretation accuracy and reliability of remotely sensed satellite data by enabling verification of the interpreted details by supplementing it with the information which can not be obtained directly on satellite imagery.

Ground truth data recorded in the field is attributed as collection, verification and measurement of the information about different surface features on the earth which is responsible for the occurrence of specific spectral reflectance behavioral pattern. To ensure better interpretation and more correct
calibration of remote sensing information, limited field checks were conducted. As the terrain is accessible to the remotest corner, field verifications remained very successful.

4.4.2 Visual Interpretation Method

a. Selection of data: In addition to the standard FCC in 1:250,000 scale, Survey of India topo sheets, district statistical reports and other reports relevant to the theme of the present study have been taken into consideration for visual interpretation. The procedures adopted for the visual interpretation of satellite imageries strictly adhered to the norms published by NRSA (1989) and they are described below.

b. Preliminary visual interpretation: The methodology is based on monoscopic visual interpretation of IRS LISS III FCC generated data on 1:250,000 scale for the identification of different land use and land cover classes based on certain interpretation keys and image characteristics like tone, texture, shape, size, pattern, location, association etc. Before going for the interpretation an overall idea about the land use pattern of the study area was carried out by observing the survey of India topo sheet. Some basic land use classes such as forest, marches, human settlements etc., were identified based on the top sheet retrieved information as well as data depicted in other reports.

c. Ground Truth Data Collection and Verification: The ground truth operation was carried out in the month of January. As mentioned earlier the survey program of ground truth data collection was planned in such a way that at least 10% of the area under study was covered. Areas of doubtful
preliminary interpretation were verified by selective field checks and simultaneously information regarding geology, geomorphology and hydrological causes of the phenomena were collected. Final interpretation and modification: Based on ground truth data modifications were effected and land use classes and their boundaries were redefined.

d. Final Cartographic Map preparation and Reproduction: After necessary corrections, the theme details are transferred to base map. Fair drawing of the originals is made as per predesigned specifications and Cartographic symbols.

4.4.3. Digital Image Interpretation Method

Digital data received from the satellites contain some distortions due to various reasons like rotation of earth, variations in satellite position with time and atmospheric interference. They are commonly known as radiometric and geometric errors. Radiometric and geometric corrections were made to eradicate such distortions. The digital image processing exercise comprised the following three successive steps.

1. Image Restoration
2. Image Enhancement
3. Information Extraction

Geometric corrections are usually made to depict the features on the surface of earth in their original state while radiometric corrections are made to cut off the radiation contribution made by the atmosphere so that the true signature of the objects can be represented.
Image enhancement is carried out in order to get the image in a better contrast which helps for the identification of different features. This includes linear contrast enhancement, Hue saturation intensity transformations (HIS), density slicing, edge enhancement etc.,

Information extraction deals with the extraction of maximum information from a digital image by such processes as band ratioing, filtering, principal component analysis etc.,

Since the landaus /land cover classification of Nagapattinam coast by monoscopic visual interpretation of the imagery in 1:250,000 scale, showed notable changes in land use. So digital image processing was felt necessary to get detailed textural information of the area. As the DN values and their distribution controls the texture of the image, so detailed information of the area can be availed out of it. Land use/ Land cover and its change over the years are such information which can be deciphered from the texture of the image. For that purpose multi-temporal data of 2000 and 2009 data was acquired to compare its result which has been obtained by mapping the same themes by means of visual interpretation of hard copy imageries. Land use classification was carried out on both the raw images.

During the present study, the digital image processing was carried out using ERDAS 9.3. Image processing operations, such as rectification & registration and classification are carried out with the following data.


The vectorization of the both imageries was done by using Arcview 3.1. Various supervised classification methods are used to assign an unknown pixel to any one of a number of classes. Generally three algorithms are used for supervised classification.

They are

1. Minimum distance to mean classifier
2. Parallelpiped classifier
3. Maximum likelihood classifier (ML Classifier)

The Gaussian ML classifier quantitatively evaluates both the variance and covariance of training classes. Of the three classifiers, the ML classifier has been most widely used. In the present study the same classification method is adopted.

The choice of the number of training sets was not arbitrary but was according to the histogram which was multimodal and the number of land use classes was almost equal to the number of modes. Before starting the processing work, an FCC was created by taking data on three bands Green, Red and Infrared and they were projected onto the three image plains 1,2 5 of the monitor. More than one site was taken as test set to bring homogeneity and to avoid declassification. DN values nearing a particular class were categorized as the nearest class. After the choice of the test sets, different colors are assigned to these classes. The number of class and their assigned colors are kept similar on both imageries, so that comparative study has been obtained.
4.4.4. Estimation of Normalized Differential Vegetation Index (NDVI)

Band ratioing is one of the best available methods in digital image processing for the extraction of meaningful information using remotely sensed data. Various indices such as Vegetation Index (VI), Normalized Differential Vegetation Index (NDVI) etc., are estimated by the above methods. Of the various indices, NDVI is the most important one as it provides a lot of information about the status of the vegetation of a particular area. NDVI is given by a formula \( \frac{Br-Bg}{Br+Bg} \) where \( Br \) and \( Bg \) are the pixel values in the red and green band respectively.

In the present study IRS LISS III digital data were used in which \( Br \) and \( Bg \) are represented by B4 (Band 4) and B3 (Band 3) respectively. The process of estimating the NDVI values for the vegetation was carried out in ERDAS 9.3. The system provides for the direct estimation of NDVI through a menu option. The NDVI values at different points of the vegetation were recorded by taking the cursor to the concerned position.