CHAPTER-I

INTRODUCTION

1.1 GENERAL INTRODUCTION

Scientists and environmentalists now appear to be strongly committed to collaborate in finding long-term solutions to the vexing environmental problems. In order to achieve substantial development, environmental protection shall constitute an integral part of the development process and cannot be considered in isolation from it. Developed countries have long identified major environmental hazards and have successfully implemented monitoring and remedial programmes to minimize the risk involved. On the other hand, developing countries lack such measures or they are lagging far behind and however try to they follow them.

The chemistry of groundwater is mainly controlled by the geochemical reactions along the direction of flow. It is necessary to identify these geochemical reactions\(^1\) in the aquifer in order to assess the distribution of major ion chemistry of the region. Safe drinking water is necessary for the survival and the demand for safe drinking water\(^2\) has been increased, even though one billion people are still in lack of safe water. The usage of groundwater increased in many cities in India, including Chennai city due to the increase in population and industrial sectors which lower the groundwater level. As a consequence of population explosion, urbanization, industrialization and modern agricultural techniques, the massive waste disposals to
the environment have paved a new system of water borne sewage and sludge, and it has been proved to be pollution potential and threat to the environmental purity.

1.1 ENVIRONMENTAL POLLUTION

Environmental pollution is the biggest menace to the human race on this planet today. It means adding impurity to environment. The growths of cities, industrialization, urban waste and pollution are an important part of history. From the rise of the first urban settlements until the emergence of mega cities in the 20th century, the scale and intensity of pollution has increased. The root cause for environmental degradation is mainly human activities with nature under the false ego that human is the master of nature. Environmental stress limits may vary from country to country depending upon the development stages. India, occupies 7th place among the industrially developing countries of the world and 2nd place among the world population. Because of population explosion and rapid industrialization, the massive industrial effluents and city sewage emissions into the environment daily, has crossed the critical limits and become harmful to all organisms, including human. Even though, industrialization is the key factor for the economic development of a nation, each industry is associated with the emission of dangerous or potentially hazardous pollutants directly or indirectly to the environment, which leads mainly to water, air and soil pollution. There are two types of sources for pollution. One is point source which is due to the domestic waste and industrial wastes and another one is non point source which is due to surface runoff and atmospheric deposition.

The environment consists of earth, water, air, plants and animals. If we pollute them, then the existence of man and nature will be hampered. It is true that trees are
being cut down rapidly. Our earth is becoming warmer. If pollution continues, the day
is not far when our earth will be a boiling pan and become a desert. Otherwise it will
be covered with sea water causing destruction of mankind. Pure air is always needed
for inhaling. If we take pure air, our health improves. On the other hand impure air
causes diseases and impairs our health and causes the death. Smoke pollutes the air. It
is the root of air pollution. The smoke which is discharged from industries and
automobiles are the mixture of carbon monoxide, carbon dioxide and methane etc.
These are all poisonous gases. These causes lung-cancer, tuberculosis etc. which take
a heavy toll of life.

The water of rivers and seas is being constantly polluted all over the world by
various dangerous chemical and biological wastes. Mills and factories discharge very
harmful waste waters into many rivers and sea. The water of the Ganges flowing by
the side of both Varanasi and Calcutta is extremely polluted and contains all sorts of
dangerous bacteria. It is really very strange and laughable that large number of the
Indians regard this water as holy. They even drink this water for salvation. There is no
doubt that the fish that grow in such waters are poisonous too. Reckless application of
chemical fertilizers, insecticides and pesticides pollutes the soil. Vegetables and fruits
are quite injurious today, because they contain the poison of insecticides and
pesticides. If the air we breathe, the water we drink and the soil which produces our
crops, vegetables and fruits, all become more and more impure, then our chances of
good health and longevity will be very less and less. Environment pollution is a
serious menace to our existence. Realising the danger, we must plant trees in large
number to absorb impure air. Impure water from industries can be sent back for
purification and then it can be used for irrigation purpose.
1.2.1 **Sewage Pollution**

Due to increase in population, it is difficult to manage the amount of sewage produced during the flood or the failures of treatment plant and sometimes the untreated sewage water entered into river and coastal water.

1.2.2 **Petroleum Pollution**

Leakage of petroleum products such as oil and gasoline, enters the water through the ships and marine terminals and this also happens due to offshore oil rigs, runoff from parking lots, factories etc. It happens mainly due to the accidents such as oil rigs, pipelines or oil tankers.

1.3 **WATER**

Each water molecule consists of two hydrogen atom and an oxygen atom. Each hydrogen atom is united to oxygen atom by sharing a pair of electrons. As the oxygen atom has eight electrons, and hydrogen atom has one electron, in a water molecule, three nuclei are surrounded by ten electrons. The bond thus developed by the attractions between positively changed hydrogen atoms of one water molecule and negatively charges oxygen atom of another water molecule is termed as hydrogen bond. This hydrogen bond is responsible for the joining several water molecules together and forming a three-dimensional structure (Fig-1.1) Most of the anomalous properties of water can be explained on the basis of the presence of hydrogen bonds. These properties (Table-1.1) include high specific heat capacity, heat of vaporization, unique density behavior, polarity, dielectric constant low viscosity and high surface tension, etc., that make it fit for its special role in living system and use in industrial and urban development’s.
Figure-1.1 Structure of water molecule

Table-1.1 Physical Properties\(^5\) of water

<table>
<thead>
<tr>
<th>S.No</th>
<th>Property</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Heat of Formation (at 25°C)</td>
<td>285.89</td>
<td>kJ/mole</td>
</tr>
<tr>
<td>2</td>
<td>Ionic Dissociation Constant(at 25°C)</td>
<td>(10^{14})</td>
<td>M(^1)</td>
</tr>
<tr>
<td>3</td>
<td>Heat of Ionization (at 25°C)</td>
<td>55.71</td>
<td>kJ/mole</td>
</tr>
<tr>
<td>4</td>
<td>Apparent Dipole Moment</td>
<td>6.24(10^{-30})</td>
<td>C.m(^e)</td>
</tr>
<tr>
<td>5</td>
<td>Viscosity (at 25°C)</td>
<td>0.895</td>
<td>m.Pa.S (=cP)</td>
</tr>
<tr>
<td>6</td>
<td>Density (at 25°C)</td>
<td>0.998</td>
<td>g/cm(^3)</td>
</tr>
<tr>
<td>7</td>
<td>Freezing Point</td>
<td>0.0</td>
<td>°C</td>
</tr>
<tr>
<td>8</td>
<td>Boiling Point</td>
<td>100.0</td>
<td>°C</td>
</tr>
<tr>
<td>9</td>
<td>Dielectric Constant (at 17°C)</td>
<td>81.0</td>
<td>MHz</td>
</tr>
<tr>
<td>10</td>
<td>Electrical Conductivity (at 25°C)</td>
<td>&lt;10(^{-8})</td>
<td>S/cm</td>
</tr>
<tr>
<td>11</td>
<td>Velocity (at 25°C)</td>
<td>1496.3</td>
<td>m/s(^{-1})</td>
</tr>
</tbody>
</table>

The natural water is a mixture of H\(_2\)O molecules (with possible nine combinations) because of the fact that both hydrogen and oxygen have isotopes \(^1\)H, \(^2\)H (D), \(^3\)H (T), \(^{16}\)O, \(^{17}\)O and \(^{18}\)O. According to chemistry, it can be classified into three categories \textit{viz.}, simple, H\(_2\)O; heavy, D\(_2\)O and super heavy, T\(_2\)O waters. The physical, chemical and biological composition of water is influenced to a greater extent by different factors, including regional climates and geomorphology, physical variables (temperature, turbidity, pressure), chemical variables (pH, TDS, EC, DO, individual anions, cations, nutrients and toxic variables (biocides and trace metals).
1.4 WATER POLLUTION

The history of water pollution goes with the history of man itself when he first arrived at this planet. All activities of early man like clearing of trees, burning, cultivation and piling of midden influenced the bodies of water. The cutting of forest results in an increased runoff altering the river biology. Agriculture caused an increased erosion of soil causing treated silting and increase of salts in streams. Natural source of pollution like leaf-fall in the forested areas increased the organic matter and water bodies to affect fish. Such conditions might be prevailing, beyond doubt, throughout the history since the invasion of plants on the earth crust, even much before the arrival of man. However, the most serious problems of water pollution resulted by human activities. The reference of white colour and small red threads in the foul mud in the writings of Aristotle indicates that the effects of sewage were known to the ancient people. As there was no treatment facility of these wastes at that time, it is quite certain that these wastes might have brought quite severe problems of river and groundwater pollution. The waste water disposal on land became a common practice almost throughout the world. In recent years, water pollution occurs when the discharging of untreated sewage into the water bodies as a result which alter the physical, chemical and biological properties and make it unfit for drinking and domestic applications. Pollutants are directly or indirectly discharged into water bodies without adequate treatments. Fresh and clean water is the basic need of human requirements; yet it has been observed that millions of people worldwide are deprived of this. Unsanitary conditions coupled with the lack of potable or drinking water has often been cited as the factors responsible for the ill health of rural population. About 3 million people get affected every year by water borne diseases.
1.5 GROUNDWATER POLLUTION

The volume of groundwater is much greater than that of all freshwater lakes and streams. Underground water plays an important role in the overall water balance of the environment. Groundwater is a primary source of freshwater in several towns and rural areas. The existing utilization of groundwater in India is currently estimated to be 45000 million m$^3$. It is widely used as a source of water for irrigation, industrial and household applications. The contribution of groundwater to total irrigation is about 40% in India. However, 98 % of the fresh water available to human beings and stored in aquifers, mainly in the weathered and fractured zones. Groundwater can remain in the subsurface from days to millennia depending on the length of the flow path, influenced significantly by long term changes in climate, unlike many surface waters; groundwater that makes it valuable as a resource is its physical and chemical quality, i.e., minimal concentrations of dissolved mineral salts, suspended solids, bacteria and viruses. Over the last two decades, issues of groundwater pollution have become aware of the health threat posed by contamination through urban development without adequate attention to sewage and wastes disposal and rapid industrialization. Groundwater pollution has originated from disposal on land water bodies, leaching of heavy metal ions from mineral rocks to a shallow sandy aquifer, which affect groundwater hydrology and cause damage to soil, plants and animals, including human beings. The major causes are spread of epidemics, chronic diseases, skin and stomach diseases and soil fertility. Besides hygiene diseases like trachoma, scabies, leprosy are also caused due to contaminated water.
1.6 WATER QUALITY STANDARDS

Water quality standard is a major tool for the quality appraisal of water sources\(^6\) \textit{i.e.}, whether it is suitable\(^7\) for drinking, domestic, irrigation and industrial purposes or not? World Health Organization (WHO), American Public Health Association (APHA), Environmental Protection Agency (EPA), American Water Works Association (AWWA), American Standard for Testing Materials (ASTM), Bureau of Indian standards (BIS), Indian Council of Medicinal Research (ICMR), US Public Health Association (USPHA) and European Economic Community (EEC) have amended the specific recommended standard limits (Table-1.2) for various WQPs.

\begin{table}[h]
\centering
\begin{tabular}{lcccc}
\hline
WQPs & USPH & WHO & EPA & ICMR & BIS \\
\hline
pH & - & 7.0-8.5 & - & 6.0-9.2 & 6.5-8.5 \\
TDS & 500 & 500 & - & 500 & 500 \\
TH & 600 & 300 & - & 300 & 300 \\
Cl\(^-\) & 250 & 200 & 350 & 250 & 250 \\
SO\(_4^{2-}\) & 230 & 200 & 250 & 200 & 200 \\
Ca\(^{2+}\) & - & 75 & - & 75 & 75 \\
Mg\(^{2+}\) & - & 50 & - & 50 & 30 \\
TA & - & - & - & 200 & 200 \\
EC & - & - & - & - & 750-2250 \\
Na\(^+\) & - & - & 20 & - & - \\
K\(^+\) & - & - & - & - & 12 \\
COD & - & - & - & - & 10 \\
BOD & - & - & - & - & 5.0 \\
\hline
\end{tabular}
\caption{Drinking water standards\(^7\)\(^-\)\(^9\) *}
\end{table}

*\textbf{Units}: All the parameters are given in ppm, excluding EC-\textmu mhos/cm, pH

Water quality parameters (WQPs) are also widely used to construct\(^8\), planning of specific water and waste water treatment system for chemists, engineers, scientists and technologists. The presence of heavy metals in water system constitutes to be one of the most pervasive environmental issues of recent time. Although, control
technologies have been applied to many industrial and municipal sources, the total quantity of these substances released to the environment remains staggering. The standard limits for heavy metals in drinking water are given in Table-1.3. The chemistry and toxicity of a few heavy metals are described below:

**Table-1.3 Drinking water standards for heavy metals**

<table>
<thead>
<tr>
<th>Trace Elements</th>
<th>USPH</th>
<th>WHO</th>
<th>EPA</th>
<th>ICMR</th>
<th>BIS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>0.01</td>
<td>0.01</td>
<td>0.05</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Lead</td>
<td>0.05</td>
<td>0.05</td>
<td>0.1</td>
<td>0.01</td>
<td>0.1</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.05</td>
<td>0.05</td>
<td>0.02</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Copper</td>
<td>1.0</td>
<td>1.5</td>
<td>3.0</td>
<td>3.0</td>
<td>0.5</td>
</tr>
<tr>
<td>Zinc</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Mercury</td>
<td>-</td>
<td>0.001</td>
<td>0.001</td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

*Units: All the parameters are given in ppm, excluding EC-μ.mhos/cm,pH

1.6.1 CADMIUM

It is a highly toxic heavy metal commonly present with the ores of zinc, rock phosphate and in coal. Fishes and other aquatic life show high tendency of its bi-accumulative nature. Hence which is classified as a soft acid, preferentially competing with sulfides and it mostly occurs as a divalent ion; chemically it closely resembles zinc and occurs as an iso-morphous replacement in zinc ores. It is estimated that about 25,000 to 30,000 tons of cadmium are released into the environment every year, about half the quantity is released from the weathering of rocks, into river water and then to the oceans. Release of cadmium from human activities is estimated to be 4,000 to 13,000 tons per year, with the major contributions from mining activities, and burning of fossil fuels. Cadmium can enter into atmosphere due to the burning of fossil fuels (e.g., coal fired electrical plants) and from the burning of household wastes.
Cadmium in trace amounts is industrially important act as a toxicant and it is biologically non-essential. Primarily the cadmium is used in electroplating, low melting point alloys, solders, battery, polyvinyl chloride and pigments. A maximum acceptable concentration of 0.005 mg L$^{-1}$ for cadmium in drinking water has been established on the basis of health considerations. The acute oral lethal dose of cadmium for man has not been well established; however several hundred milligrams are found to be lethal consumption of water containing 13 to 15 mg L$^{-1}$ of cadmium has caused vomiting and gastrointestinal cramps. In living organisms, especially human beings, acute cadmium poisoning occurred due to the exposure to fumes during the melting or pouring of cadmium metals.

1.6.2 ARSENIC

Arsenic is considered to be a semimetal, as it does not possess all the properties of true metals. It is widely distributed in the earth crust and in biosphere. The arsenic pollution may arise by use of herbicides, fungicides, insecticides, electronics and catalysts and from industries along with burning of fossil fuels. Arsenic also shows the tendency of bioaccumulation in the body tissues which represent the sources of arsenic in natural waters.

The major arsenic compounds are Arsenite (As$^{3+}$), arsenate (As$^{5+}$), Arsenious acids (H$_3$AsO$_3$, H$_2$AsO$_3^-$, HAsO$_3^{2-}$), arsenic acids (H$_3$AsO$_4$, H$_2$AsO$_4^-$, HAsO$_4^{2-}$), Dimethylarsenate (DMA), Monomethylarsenate (MMA), Arsenobetaine (AB) and Arsenocholine (AC). In aerobic waters, arsenic acid predominates only at extremely low pH. As (III) halogenides are more toxic than other inorganic arsenic compounds. Toxicity of trivalent arsenic to human beings is caused by its binding to Thiol anions.
and SH groups of enzymes which inhibit some enzymatic activities. Inhalation or exposure to arsenic trioxide causes irritation of nasal mucosa with perforation of the nasal septum, dermatitis and conjunctivitis. Arsenicals may also act as skin conduct allergens\textsuperscript{18-20}. Arsine and arsenates are most toxic of all the arsenicals, and have been found to be highly toxic to many species in aquatic environment.

\section*{1.7.3 \textsc{Lead}}

Lead enters the environment through auto exhaust and industrial sources. It is present in the form of impurities in inorganic fertilizer. The primary form of lead in nature is galena (PbS), a relatively insoluble ore. Lead is also occurs as Plattnerine (PbO\textsubscript{2}), Cerussite (PbO\textsubscript{3}) and Anglesite (PbSO\textsubscript{4})\textsuperscript{21}. The different oxidation states like 0, +2 and +4 are possible for lead. However, lead is complexed by both inorganic and organic ligands present in aquatic system. In systems with very high Cl\textsuperscript{-} concentrations, such as estuaries and sea water, PbCl\textsuperscript{+} is the dominant species. The other significant species are PbHCO\textsubscript{3}\textsuperscript{+}, PbCO\textsubscript{3}\textsuperscript{0} and PbOH\textsuperscript{+}.

The concentration of lead in groundwater can be varied significantly, depending on the corrosivity of the water. While corrosivity varies greatly with water quality, but hard water is generally less corrosive than soft water. Nevertheless, hard water alone does not always guarantee that there will be no elevated lead levels. Excessive concentration lead causes structural alterations in chromosomes and binds strongly to mitochondrial membranes\textsuperscript{22}. The maximum acceptable lead concentration for chronic exposure in soft water has been found to be 4 to 8 \(\mu\text{g} \text{L}^{-1}\). Acute toxicity is caused by 1.0 to 1.5 mg L\textsuperscript{-1} of dissolved lead. Ionic lead is an active form of the element.
1.6.4 MERCURY

Mercury is a shiny silver white metal found in small amounts in the earth crust. It combines with other elements to form inorganic and organic compounds. Mercury is used for a wide variety of industrial and domestic applications. The burning of fossil fuels, the smelting of Sulphide ores, cement manufacture and heating of other materials containing mercury, release about $10^4$ tons of mercury into the global atmosphere per year\(^{23}\). Mercury carried by wind and rain, is found throughout the environment mostly due to release of naturally occurring mercury from rock and soil. Burning of coal, oil and incineration of materials that contain mercury, like batteries. Many other industrial operations added a huge amount of Hg to the oceans and other natural waters\(^{24}\). The speciation of mercury in the environment is complex, not only because of its various oxidation states (0, +1 and +2) but also because of biotic and abiotic methylation and the volatility of several forms of Hg.

Dissolved inorganic species are probably HgCl\(_4^{2-}\) in sea water and Hg(OH)\(_2\) and Hg(OH)Cl in fresh water under aerobic conditions\(^{25}\). World attention was focused on the toxicity of mercury in 1950s when many fatalities occurred among people living near Minamata bay (Japan), as a result of eating fish and shellfish from the bay\(^{24}\). The poisoning was eventually traced to methyl mercuric chloride, which had been discharged into the bay from a vinyl chloride plant and had been accumulated by the marine aquatic life\(^{24}\).

The methylated forms of mercury are much more toxic than inorganic forms and can be transported from water through the food chain by virtue of their much higher solubility in lipids than in water. These organic forms of mercury are better
able to pass through the food chain barrier and through the human placenta\textsuperscript{26}. The mercury in its organic form has concentrated in the food chains with high concentration in fish and shellfish, which concentration 3000-10000 times over the ambient concentration. Methyl mercury is much more toxic to humans than the other forms as it can be absorbed almost entirely by the intestine.

### 1.6.5 ZINC

Zinc is an essential and beneficial element in body growth. Concentration above 5mg/l may cause a bitter astringent taste and opalescence in alkaline water. Zinc most commonly enters the domestic water supply from deterioration of galvanized iron and dezincification of brass. Zinc in water may also come from industrial water pollution. The most important uses of this metal and its alloys are in manufacture of brass, cosmetics, battery, paints and agricultural applications\textsuperscript{27}.

Zinc hydrolysis is negligible below pH 6. At pH 4 – 7, predominant species of zinc are Zn\textsuperscript{2+} in fresh waters; Zn\textsuperscript{2+} and ZnCl\textsuperscript{+} in seawater. At pH > 7.5, Zn(OH)\textsubscript{2} is the major species in both the environments. The bioavailability of zinc critically depends on its chemical form. Zinc is a component of many enzymes and it is involved in the synthesis of RNA and DNA. It diminishes the toxicity of cadmium and copper. The epidermis contains a high proportion of the total amount of zinc in the body and a zinc deficiency can result in skin diseases\textsuperscript{28}. Zinc has relatively low toxicity towards aquatic organisms\textsuperscript{29} and its toxicity diminishes with increasing hardness and increasing pH of the water.
1.6.6 COPPER

Copper is a widely distributed metal in nature and it is extensively used by human beings. It is an essential metal required by almost all living organisms in some of their enzyme systems. Deficiency of copper may lead to certain physiological disorders in both plants and animals, but at higher concentration it works essentially as a pollutant. In nature copper is found in a variety of minerals, important of which include copper pyrites (CuFeS$_2$), Charcocite (Cu$_2$S), Indigo copper (CuS) and bornite (Cu$_5$FeS$_4$). Anthropogenic origin of copper is mainly form mining activities, use of copper fungicides, industrial applications such as metallurgical units and alloys manufactures, copper electroplating and chemical industries.

Mining effluents and industrial wastes sometimes they create serious river pollution problems. Cu$^{2+}$ is dominant species and their complexes with OH$^-$ and CO$_3^{2-}$ are strong, but those with Cl$^-$ and SO$_4^{2-}$ are relatively weak in acidic environments (pH < 7). In pH 6-8, the predominant species are Cu$^{2+}$, as Cu(OH)$_2$, CuHCO$_3^+$, CuCO$_3$ and CuOH$^+$. The toxicity of copper to the aquatic biota has been well established$^{30}$. The carbonatocopper complexes are found to be nontoxic, anionic hydroxycopper complexes contribute 15 to 18 % to the observed toxicity, while free copper plus neutral and cationic hydroxycomplexes are responsible for 60 to 70 % of the toxicity observed$^{31}$. The organic chelator has the ability to detoxify ionic copper species$^{32,33}$.

Humic acid, glutamic acid and EDTA, ligands significantly reduce the toxicity of copper to marine bacteria. Copper can be solubilized by using certain microorganisms and copper is toxic to most aquatic life. Algae are very sensitive to
copper and can be killed at concentrations as low as 0.5 mg/L. Copper has also shown varying toxicities towards different species of fish. In higher organisms, copper interfere with –SH groups of certain enzymes and can result in rain damage.

1.8 SOFTWARE APPLICATIONS ON WATER QUALITY PARAMETERS

Software applications like Aquachem, GIS, SPSS, XLSTAT and the brief description of these software tools used have been described below. These techniques are used to explain the influence of various ions in groundwater might be a better understood.

1.7.1 AquaChem

Aqueous geochemical data analysis was well defined by using aquachem\textsuperscript{34}. It provides the numerical analysis of geochemical data sets and plots the graph for the modelling the water quality. This analysis tool covers a wide range of unit conversions, charge balances, sample comparison, statistical analysis, trend analysis and much more. It has a standard database for the water quality standards for each parameter if any samples exceeds the allowable limit then it appears with specific color to identify the problems. The aqua chem graphical plotting techniques include Piper, Stiff, Durov, Schoeller, Ternary diagrams, radial plots, scatter graphs etc. We used the Piper Diagram to characterise the quality of water and to analyse whether anion and cation is dominating and responsible for the quality of the water. These plots provide unique interpretation of the samples between the groundwater and aquifier materials.
1.7.2 Geographic Information System

A geography information system is a computer system designed to capture, store, manipulate, analyze, manage, and present all types of spatial or geographical data. The first known use of the term geographic information system was by Roger Tomlinson in the year 1968. Spatial variation is very important in day to day life, so they developed a tool called geographic information system (GIS) which helps us to know our geographic knowledge. Location in the earth space-time may be recorded as date/time of occurrence and x, y and z coordinates representing longitude, latitude, and elevation respectively. All earth based spatial-temporal location and extent references should ideally be related to one another and ultimately to a real physical location or extent.

1.7.3 Statistical Study

Statistical package for the social sciences (SPSS) is used to analyze highly complex data and manipulation to create tables and graphs using simple instruction. It has the capability of handling large amounts of data and can perform all the possible analysis. SPSS is used commonly in health researchers, education researchers, data miners and water analysis. Principle component analysis and factor analysis can be perfectly monitored by SPSS.

1.7.4 Control Methods of Water Pollution

The presence of different pollutants in the waste waters makes it almost impossible to treat all the wastes in the same manner. The wastes originating from
various sources can be broadly divided into two categories, that is biological wastes and non-biological wastes. The biological waste include those whose origins are primarily from living or previously living sources like sewage, and discharges of effluents from tanneries, paper and pulp mills, food manufacturing plants etc., such wastes have a predominance of degradable organic matter and are generally treated quite differently from non-biological wastes. The non-biological wastes are rich in nondegradable matter consisting of solids and liquids in suspended or dissolved form including various inorganics and organics, many of which may be highly toxic to biological life.

Most of the chemicals released in effluents are generally soluble in water. They form aqueous solutions and therefore cannot be separated by ordinary physical processes like screening, settling and filtration. The removal of dissolved solids and liquids from wastes following methods can be employed that is neutralization, oxidation, reduction, reverseosmosis, ionexchange and carbon adsorption. The carbon adsorption method is chiefly employed than other methods. Which is used to remove dissolved organics such as saturated oil, alkanes, chlorinated hydrocarbon, dyes, benzene and many other high molecular weight compounds.

Adsorption as a water treatment process has aroused considerable interest during recent years. Activated carbon with surface area of 110.35 – 146.06 \( \text{m}^2 \text{g}^{-1} \) from sunflower seed were applied to removal of acid blue\(^{38}\). AC produced from jack fruit peel, (carbonized by chemical method) to treat and remove malachite green from wastewater obtained from a dye industry\(^{39}\). Adsorption of methylene blue on Malaysia bamboo based activated carbon\(^{40}\). Low cost and non-conventional
adsorbents like activated carbon, Lignite, Fly ash, Neem tree leaves are used as adsorbents for removing COD of Industrial waste water.

Activated carbon is a commonly used adsorbent in sugar refining, chemical and pharmaceutical industries, and water and wastewater treatment, barring the development of new technologies, industrial need for activated carbon will only increase in future. Though its capacity is lower than that of commercial grade activated carbon, the low material cost makes it an attractive option for the treatment of industrial waste water containing organic pollution. Lecus aspera commonly known as ‘Thumbai’ is distributed throughout India from the Himalayas down to Ceylon.

The leaves of the Lecus aspera can be obtuse, linear; they can reach up to lengths of 8.0 cm, and be 1.25 cm broad. The epidermis of the stem is covered in a thick waxy cuticle and contains few traversed stomata. The roots of the Lecus aspera contain epidermal cells which are very narrow and closely packed together. This research examines the adsorption and treatment of dissolved organic pollutants in groundwater from a nearby industrial site in Chennai city using granular activated carbon produced from stems, roots and leaves of Lecus Aspera.

1.8 METAL SPECIATION

Speciation studies of metals may be defined as the process of identifying and quantifying the different and definite metal ion species present in analytical samples.
Total metal concentrations, both in environment and bio-samples are increasingly demanded by the society, due to their toxicity and normally quantified by Atomic Absorption Spectroscopy (AAS) techniques. However, chemists have recognized toxic trace metals present in true samples (sediments, urine, serum etc.,) in a most varied physico-geochemical forms and concluded that metals bio-geochemical distribution and their toxicity will be dictated by the specific species, accordingly with oxidation states and the ability to react with the bio systems\(^{43}\).

For example, Cr (III) is essential and nontoxic element however, Cr (VI) is highly toxic. Similarly, As (III) is much more toxic\(^{44}\) than As (V). Total metal determination by AAS a technique as mentioned before is insufficient to-day and sometimes misleading for assessment of metal toxicity in food or sediment samples. Hence, additional “speciation” information are being increasingly needed both in environmental and biological issues. Heavy metal speciation was first introduced (Goldberg) in 1954 for better understanding of biogeochemical cycling of trace metals in seawater. Measurement techniques are used to measure the concentration of one or more forms of the elements of choice, have no useful inherent ability to respond only to particular forms. For convenience this may be described as total techniques for speciation. They are Atomic Absorption Spectroscopy (AAS)\(^{45}\), Atomic Emission Spectroscopy (AES)\(^{46}\), Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)\(^{47}\), Atomic Fluorescence Spectroscopy (AFS)\(^{48}\), X-Ray Fluorescence Spectroscopy (XFS)\(^{49}\), Neutron Activation Analysis (NAS)\(^{50}\), Electronic Spectroscopy\(^{51}\) and Magnetic Resonance Spectroscopy\(^{52}\). In recent years, the development of new concepts for metal speciation measurement to water, air and soil, reliable \textit{in-situ} measurements, focused on voltammetric measurements and
biogeochemical process, new bioanalytical sensors, modern micro-total-analytical systems and rugged submersible probes based on specifically designed mechanics, electronics and software.

1.9 REVIEW OF LITERATURE

Groundwater is a major source of water supply and food production on irrigated agricultures worldwide. It also plays an important role in sustaining rivers, lakes and wetlands during dry periods and it is essential for many ecosystems. The degradation of groundwater quality is a major and severe problem that lies in all over the world. Especially in south India, the capital of Tamilnadu (Chennai) has experienced an impressive growth in population and industry. The environmental consequences of this are causing concern about the impacts of pollution. Water pollution is one of the most serious environmental problems in Chennai; waste water discharges emit various kinds of pollutants.

These substances include household chemicals, such as oil waste, agricultural chemicals, industrial chemicals, inorganic and heavy metals. Due to the environmental persistence, these pollutants can cause contamination of surface water and groundwater which are the main water resources for drinking water production in Chennai city. In addition inadequate wastewater treatment facilities can fail to remove pollutants and therefore their levels can be considerably high in receiving water. The removal of these pollutants, even present at low concentrations, is an established challenge in the production of tap water and drinking water from surface water and groundwater. If most of the fertilizer industry, polymer industry, and oil refinery industry were located in and around this area, they produce nitrate, sulphate, chloride,
and metals contaminated product, which either directly are indirectly enter into the ground water medium.

Some of the wells around these areas are closed due to these reasons. In order to Investigate their impact of industrial pollution on groundwater of these areas, the brief study on water quality (Major ion chemistry of environmental samples around sub-urban of Chennai city) have been carried out by Kumaresan et al., 53. These studies revealed discharge of huge quantities of solid and liquid wastes, which are dumped into their premises or let out in the adjoining low-lying areas, resulting in brackishness of groundwater and most of the major ions are anthropogenic in origin. Further research has also been carried out by the Mohamed Sheriff et al., 54.

Now a day’s domestic wastage have been dumped in the Coovum river, which affects the quality of groundwater and it had been studied and concluded that all the physico-chemical parameters were having higher concentration55. Elango et al.,56 have investigated the hydrochemical qualities of ground water in Chengalpet region, South India to find out the ground water suitability for domestic and irrigation purposes using Gibbs, Piper and Durov diagrams. A measure of pollution load in lake water, on the basis of water quality index (WQI) and National Sanitation Foundation (NSF) was conducted57 in Trichy, south India. From the results, all sampling sites were found to have enormous amount of pathogenic bacteria and high BOD values Loganathan et al.,58 have evaluated status of groundwater at Chennai city to find out the present investigations made on the groundwater of north and south Chennai revealed that the water quality was within the ISI standard except the few parameters this may due to the intrusion of sea water, industrial effluents intrusion into the
groundwater and improper maintenance of the sewage system during the period of 2006 to 2007. Raman.N have reported most of the parameters of water are not in the acceptable limit accordance with the IS 10500 drinking water quality standards in pallavaram solid waste landfill site in Chennai\textsuperscript{59}. Appasamy and Lindquist\textsuperscript{60} have reported the presence of high concentration of ammonia, phosphate, feacal coliform bacteria and organic matter in the water ways on Adayar and Cooum rivers of Chennai city.

Various studies on the impact of domestic waste and city sewage\textsuperscript{61-67}, municipal solid waste landfills\textsuperscript{63}, urban aquifer\textsuperscript{61}, coastal sea water intrusion\textsuperscript{61, 68}, tannery effluents\textsuperscript{64} on groundwater quality in Tamil Nadu, India have been reported and concluded that the water quality degradation has been increased with increase of population growth, urbanization and industrialization. Sathyakumary \textit{et al.}\textsuperscript{69} have reported the groundwater quality of coastal Kanyakumari district, south India that the quality of groundwater in many of the sampling stations, showed (physico-chemically) safe nature for drinking purposes.

Nalawade \textit{et al.}\textsuperscript{70} have reported the Heavy metal pollution index is useful tool in evaluating overall pollution of groundwater and surface water pollution. Assessment of major river water qualities in India, river Godavari\textsuperscript{71}, Ganga river\textsuperscript{72} at haridwar, Yamuna river\textsuperscript{73} at Madura, Athrabanki river\textsuperscript{74} near Paradip (A.P), Ram Ganga river\textsuperscript{75} at Moradabad have been carried out and reported that contaminations occurred through mixing of the untreated industrial, domestic sewage in to river systems. On the global level Labu river water systems (Malaysia)\textsuperscript{76}, river Pinios (Thessalia-Greece)\textsuperscript{77}, Calabar river (Nigeria)\textsuperscript{78}, Manuherikia river (Newzeeland)\textsuperscript{79},
Odra river basin\textsuperscript{80}, have also been analyzed. The results showed that the river waters are badly polluted with industrial trace metal pollutants such as, Cd, Cu, Pb, Cr, As, Hg, Mn, and Zn. Saffran, K have reported The water quality index\textsuperscript{81} produces a number between 0 for worst water quality and 100 for best water quality. The water pollution pattern, sources and classification of pollution load index based on WQI are examined in water and sediment sample analysis\textsuperscript{82}. The method of principal component is a special case of the more general method of factor analysis in water treatment have reported by P.K Mohapatra \textit{et al.},\textsuperscript{83} and Nimal kumar \textit{et al.},\textsuperscript{84} Principle component analysis was used to help distinguish between different geochemical states and to identify trends in the changing groundwater chemistry as the site was undergoing in situ bioremediation\textsuperscript{85}.

Removal of color, COD and lignin of pulp and paper wastewater by using wood ash had reported by Netnapid Tantemsapya \textit{et al.},\textsuperscript{86} Removal of Erichrome Black T by using mosambi peel activated carbon as an adsorbent has been carried out U.V. Ladhe, \textit{et al.},\textsuperscript{87} The adsorption and treatment of organic contaminants using activated carbon from waste Nigerian bamboo was investigated\textsuperscript{88}. To compare the adsorption efficiency of activated carbon prepared from animal horns (AHC), which is both a waste and a pollutant and a commercial activated carbon (CAC) with respect to uptake of the organic components responsible for the chemical oxygen demand (COD) of industrial wastewater have reported by Emmanuel O. \textit{et al.},\textsuperscript{89} S. J. Allen. \textit{et al.},\textsuperscript{90} have reported decolourisation of wastewater using eco-friendly adsorption. The adsorption of dissolved organic matter (DOM) on granular-activated carbon (GAC) as a pretreatment to reverse osmosis (RO) desalination of membrane bioreactor (MBR) effluents was studied by Shirra Gur-Reznik \textit{et al.},\textsuperscript{91}. Another study was to investigate
the suitability of using activated carbon (AC), limestone (LS) and mixture of both (LS:AC) as low cost media for the post-treatment of treated effluent to remove COD and Colour\textsuperscript{92}. Adsorptive apple pomace and wheat straw\textsuperscript{93} and the value of adsorption intensity $1/n < 1$ shows a normal adsorption. While $1/n > 1$ is indicate of cooperative adsorption have reported by atkins\textsuperscript{94}.

1.10 DESCRIPTION OF STUDY AREA

Chennai is a fourth largest metropolitan city in India and also is a capital of the state of Tamil Nadu and lies between lat. $12^\circ57'30"$–$13^\circ8'50"$N and long. $80^\circ12'10"$–$80^\circ18'20"$E and forms part of the survey of India. Chennai had four major parts that are north, west, south and central Chennai. It is located at an altitude of 8 meters approximately from the mean sea level. This area spread towards the northeast of Tamil Nadu and occupies a total area of 174 square kilometers. The average annual rainfall is about 1300 mm (51 inches). The city is splashed by Cooum river and Adyar river which flow through the centre of the city. Both the rivers are linked with each other through Buckingham canal. According from (2011 census) 4.68 million residents and so many industries located in and around this area.

The area of north Chennai stands as thriving trade and commerce center in the city. The northern regions spread out as a continuous land strip lying adjacent to the sea that is Bay of Bengal. The presence of the second major port here makes it an important trade centre. The northern localities house some of the reputed manufacturing companies of India. The automobile industries located here are attractions in themselves. Tandaiyarpet in north Chennai is located the fishing
The harbour makes up a popular attraction in the north. The region is inhabited by a local population, most of which are employed in the popular industries located here. The eastern boundary of the northern localities is limited by the famous Buckingham canal.

The area of west, south and central Chennai lies in between 13.08329°N latitude and 80.27000°E longitude and 12 km away from the north Chennai. Some of the localities that fall in Chennai south include K.K.Nagar, Nungampakkam, Mylapore, Saidapet, Adayar and Velachery. Some important tourist attractions located in the southern suburbs are Elliot's beach, Guindy park, Periyar Science and Technology Centre, Kapaleeswarar Temple, Karaneeswarar Temple, Santhome etc.,

In Chennai three types of soils are found. These are the sandy soil, clay soil, hard rock. Sandy soil is generally found in the places located by the river banks and coastal areas. In clay-soil is found at Tandaiyarpet, Aynavaram, Kilpauk, Anna Nagar, Villivakkam, Koyamedu, Vadapalani, K.K.Nagar, Nungamakkam, Royapettah and George Town. In hard rock are found, near Adayar, Taramani, Velachery, St.thomas Mount, Adambakkam and Guindy. Most of the cities around Chennai contain clay soil. Freshwater reservoirs, lakes namely Poondi, Sholavaram, Redhills, Veeranam to cater the daily needs of water for Chennai area.

1.10.1 SAMPLING STATIONS

Groundwater samples have been collected from residential areas situated near by industrial site of Chennai city during the period April 2011 – 2013. Sub-urban stations have been selected for investigation on the basis of geographical locations
and population density as well as industrial site, where greater pollution impacts expected to groundwater quality. Chennai has more than 1400 factories. Most of these factories are situated in the northern part, particularly Manali, Ennore, Ambattur and Thiruvottriyur.

The major groups of industries are those that generate electricity (35%), manufacture rubber, plastics, purify petroleum and coal products (9.5%), transport of equipment (9.5%), machinery and machine tools (9.3%), paper and paper products (5.5%), metal products (5%) and others (27%). The sampling area like Madavaram (N₁-N₆), Manali (N₇-N₁₂), Tandaiarpettai (N₁₃-N₁₈), Tiruvottiyur (N₁₉-N₂₄), Ernavur (N₂₅-N₃₀), Ennore (N₃₁-N₃₆) are highly populated and unhygienic, associated with open drains for sewage and effluents from industries, which enters into nearby residential sites. The sampling site of west Chennai include Vadapalani (W₁-W₃), Kilpauk (W₄-W₆), Annanagar (W₇-W₉), Ambattur (W₁₀-W₁₄), Ayanavaram (W₁₅-W₁₆), which is also a thickly populated with small scale industries.

The sampling site for Chennai south includes Adayar (S₁-S₄), Nungampakam (S₅-S₆), K.K.Nagar (S₆-S₇), Mylapore (S₈-S₁₀), Saidapet (S₁₁-S₁₃), Velachery (S₁₄-S₁₆) which is also a thickly populated and the river water along with domestic sewage may percolate into the groundwater.

The sampling site for Chennai central, Egmore (C₁-C₃), Virukampakkam (C₄-C₇), Triplicane(C₈-C₁₀), Rayapettai(C₁₁-C₁₃), Georgetown (C₁₄-C₁₆), which is splashed by Cooum river and Adyar river which flow through the centre of the city. South part of Chennai city was hard rock formations with overburden soils. Details of sampling stations and respective sites and location of bore wells are given in (table-1.5 and fig.1.2).
Figure 1.2 Study Area Map of Chennai City, Tamil Nadu, India
<table>
<thead>
<tr>
<th>Sl.No</th>
<th>Sample Code</th>
<th>Location of Borewells in North Chennai(N)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>Madavaram</td>
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<tr>
<td>I</td>
<td>N_1</td>
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<td></td>
<td></td>
<td>Tandaiyar pettai</td>
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<tr>
<td>III</td>
<td>N_13</td>
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<td></td>
<td></td>
<td>Ernavur</td>
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<td></td>
<td>N_2</td>
<td>Rajaji nagar</td>
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<td></td>
<td>N_3</td>
<td>Avvair street</td>
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<tr>
<td></td>
<td>N_4</td>
<td>Periyar street</td>
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<tr>
<td></td>
<td>N_5</td>
<td>Thirumurugan nagar</td>
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<tr>
<td></td>
<td>N_6</td>
<td>Pandiyan street</td>
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<td></td>
<td></td>
<td>Manali</td>
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<td></td>
<td></td>
<td>Thiruvalluar street</td>
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<tr>
<td>II</td>
<td>N_7</td>
<td>Thiruvalluar street</td>
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<td></td>
<td></td>
<td>Tiruvottiyur</td>
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<tr>
<td></td>
<td>N_8</td>
<td>Bharathiyar street</td>
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<td></td>
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<td>Balaraman street</td>
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<td></td>
<td>N_10</td>
<td>SP koil street</td>
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<tr>
<td></td>
<td>N_11</td>
<td>M.G.R.Nagar</td>
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<td></td>
<td>N_12</td>
<td>Tamarai kulum 2^n d st.</td>
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<td></td>
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<td>3^rd cross street</td>
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<td>Nehru nagar street</td>
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<td>Indira street</td>
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<td>Anna kalani street</td>
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<td></td>
<td></td>
<td>Annamalai street</td>
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<tr>
<td>VI</td>
<td>N_19</td>
<td>3^rd cross street</td>
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<td></td>
<td>N_20</td>
<td>Mada vidi street</td>
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<td>N_24</td>
<td>Anna kalani street</td>
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<td>N_25</td>
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<td></td>
<td>N_27</td>
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<td>N_28</td>
<td>Indiragandhi kuppam</td>
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<tr>
<td></td>
<td>N_30</td>
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<td></td>
<td>N_31</td>
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<td></td>
<td>N_32</td>
<td>Svm nagar</td>
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<td>N_33</td>
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<td>N_34</td>
<td>Kamaraj nagar</td>
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<td></td>
<td>N_35</td>
<td>Christ nagar</td>
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<td></td>
<td>N_36</td>
<td>Gandhi nagar</td>
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<td>Location of bore wells in West Chennai (W)</td>
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<tr>
<td>VII</td>
<td>W₁</td>
<td>Valliyammai Street</td>
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<td>W₂</td>
<td>Eswar Nagar</td>
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<td></td>
<td>W₃</td>
<td>Vinayager Street</td>
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<td></td>
<td>W₄</td>
<td>Vasu Street</td>
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<td>W₅</td>
<td>Sivsankar Street</td>
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<td></td>
<td>W₆</td>
<td>Kumaran Nagar</td>
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<td></td>
<td>W₇</td>
<td>Bharathi Colony</td>
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<td></td>
<td>W₈</td>
<td>MGR Nagar</td>
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<td></td>
<td>W₉</td>
<td>7&lt;sup&gt;th&lt;/sup&gt; cross street</td>
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<td>W₁₀</td>
<td>Padmavathi Nagar</td>
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<td>W₁₁</td>
<td>Sathyapuram</td>
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<td>W₁₂</td>
<td>ThiruvangadamNagar</td>
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<td></td>
<td>W₁₃</td>
<td>Kalidasan Street</td>
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<td>Kamaraj Street</td>
</tr>
<tr>
<td></td>
<td>W₁₅</td>
<td>A.K.Swami Nagar</td>
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<tr>
<td></td>
<td>W₁₆</td>
<td>Mettu Street</td>
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</tbody>
</table>

Table-1.4 Continuation...
Figure-1.3 (a) Background of Chennai city, south India
Additive industry in (Central Chennai)

Paper industrial effluent (Thandaiyarpettai)

Polymer industry in (Thiruvottiyur)

Discharged effluent (Ambattur)

Figure-1.3.(b) Background of Chennai city, south India
1.11 NEED FOR THE STUDY

Groundwater quality is controlled by many factors such as rainfall, hydrologic fluctuation and climate. Groundwater is an important natural source of water supply all over the world. Rapid urbanization and increased industrial activities has resulted in the degradation of water quality. There are several states in India where more than 90% populations are dependent on groundwater for drinking and other purpose. The quality of water may depend on geology of particular area and also vary with depth of water table and seasonal changes and composition of dissolved salts depending upon source of the salt and soil, subsurface environment. The main objective of the study is to evaluate the effect of industrial pollution into the groundwater and problems associated with water quality in and around Chennai city, south India. In recent years, Chennai city has experienced an impressive growth in population, industry, the environmental consequences of this are causing concern about the impacts of pollution. Water pollution is one of the most serious environmental problems in Chennai city. Hence, the author has chosen this title of the study with the following aims and objectives.

- To assess the groundwater quality in and around Chennai city.
- To assess the groundwater quality trends in and around Chennai city.
- To assess the trace metals in groundwater in and around Chennai city.
- To statistically analyze the data, using Water Quality Index (WQI), Heavy Metal Pollution Index (HPI), Principle Component Analysis (PCA), Factor Analysis (FA) and Correlation Studies.
➢ To remove the organic pollutants from groundwater using the adsorbent like activated carbon of Lecus Aspera.

➢ To assess the groundwater suitability for potable purposes in Chennai city, south India.
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