METHODOLOGY

3.1 Introduction

The rapid increase in population and economic development has led to severe environmental degradation that undermines the environmental resource base upon which sustainable development depends. The economics of environmental pollution, depletion and degradation of resources has in fact been neglected as compared to the issues of growth and expansion. India has been no exceptions to this worldwide phenomenon, rather the trends of environmental deterioration in India, because of the substantial increase in its population, have been far more prominent as compared to other developing economies, ineffective treatment of domestic wastewater, discharge of highly complex wastes from industries and the polluted runoff from agricultural fields, have resulted in considerable degradation in the quality of water sources.

The fast growing urban areas are responsible for deterioration of the natural resources. It is now very difficult to get clean potable water in such cities. On one hand the development of urban areas is also essential but on the other hand the quality of the environment has to be maintained for survival of the life.

In the present study the overall structure of the study area is taken into consideration while selecting the sampling sites.

3.2 Methods of collection of Groundwater samples

Samples of groundwater were collected and stored in polythene bottles prior to collection of samples, the polythene bottles were thoroughly cleaned and rinsed with distilled water. The collected samples were labeled properly. The number of samples to be collected was decided considering the objective of the study and the fact that while studying mixed industrial and domestic regime water studies it is more reliable to collect many samples from close localities than taking infrequent samples from a large number of distant sampling stations. Since the industrial processes are considerably varied and usually unpredictable, higher number of sample stations from a smaller area are required to be studied to evaluate truly the effect of industrial waste upon the groundwater. Taking in view this aspect in all 45 sample stations was selected. These include 32 dug wells and

13 bore wells spread over an area of approximately 30 sq. km. Sample frequency was greater in the close vicinity of industries to find out the content and impart of industrial effluents on variation in the values of different parameters. The sampling and fieldwork was continued during pre-monsoon and post-monsoon seasons for two consecutive years from 2008 to 2009. Pre-monsoon samples were collected in the month of May and post-monsoon samples were collected in the month of December every year.

3.3 Groundwater Quality Determination

The determination of physicochemical parameters of groundwater samples was carried out by adopting standard method given by APHA (1995) and Trivedi and Goel (1984). The temperature was measured by using thermometer in the field. The pH was measured by using pH meter (Elico Cat No CL54 model) and the conductivity was measured by using Digital Conductivity meter (Elico CM 180 model). TDS was calculated by using the formula $0.64 \times EC$. The chemical parameters like Total hardness (TH), Calcium (Ca), Chlorides (Cl), alkalinity was determined titrimetrically. Magnesium (Mg) was calculated by taking the differential value between TH and Ca concentrations. Sodium (Na) and Potassium (K) was measured by using Elico Flame Photometer (Modal CL 22 D). Sulphate (SO_4) and Phosphate (PO_4) was determined by using Visible Spectrophotometer (SL 171 model, Mini Spec). Eight trace elements namely Lead (Pb), Zinc (Zn), Iron (Fe), Copper (Cu), Chromium (Cr), Manganese (Mn), Cadmium (Cd), Nickel (Ni) were determined by using Atomic Absorption Spectrophotometer (Model, Chemito AA 201).

3.5.1 Physicochemical parameters

Hydrogen Ion Concentration (pH)

The pH of the water, which is a measure of effective hydrogen ion activity, pH value is defined as a negative logarithm of hydrogen ion concentration, more precisely of hydrogen ion activity in moles per liter. It is a quantitative expression for acidity or alkalinity of water. The pH scale extends from 0 to 14 with the value of 7 corresponding to exact neutrality at 25°C. Thus the pH value of absolute pure water is 7. If the pH value is less than 7, the water is said to be acidic in nature and if it is more than 7 the water is

called as alkaline. Normally the pH value of groundwater ranges from 5 to 8. Water with pH between 7 and 8 is ideal and suitable for most of purposes. As per the Indian Standard Institution (1983), the pH values for drinking water should be in between 6.5 to 8.5. The pH was measured by using pH meter (Elico Cat No CL54 model). The pH meter was calibrated for 4.0 and 9.2 buffer solution. All standard precautions necessary for reliable pH determination were observed.

Conductivity

Conductivity is the measure of capacity of a substance to conduct electric current. Conductivity is reciprocal of the resistance. As most of the salts in the natural water are present in the ionic forms, capable of conducting current. Electrical current is the ability of an object to conduct electric current. It depends upon the presence of various ionic species in the water. Specific electrical conductance of water is defined as the conductance of a cubic centimeter of water at standard temperature of 25°C and is measured in micromhos per centimeter or microseimens per centimeter.

The conductivity is measured by using Digital Conductivity meter (Elico CM 180 model). The conductivity meter was calibrated by using 0.1 N KCL solutions and meter was adjusted to 1413 micro mhos/cm

Total Dissolved Solids

Total dissolved solids of groundwater include all solids in solution, whether ionized or not and do not include suspended matter. In natural water dissolved solids are composed of carbonates, bicarbonates, chlorides, sulphate and phosphate. Concentrations of dissolved solids are important parameter in drinking water. Total dissolved solids were calculated by using following formula given by APHA (1995).

TDS = EC X 0.65

Total Hardness

Hardness results from the presence of divalent metallic cations, of which calcium and magnesium are the most abundant in groundwater. Hardness is an important criterion for determining the usability of water for domestic, drinking and many industrial

supplies. Water hardness is the measure of the capacity of the water to react with soap. Hardness of water is not a specific constituent, but variable and complex mixture of anions and cations. Dissolved solvents and polyvalent metallic ions cover it. In fresh water, the principal hardness causing ions are Ca^{++} and Mg^{++} where in the hardness caused by Mg^{++} is permanent in nature.

50 ml groundwater sample was taken and 1ml of buffer solution was added then pinch of Erio-chrome Black-T indicator was added. Contents of the flask were titrated against 0.01N Ethynele Diamine Tetra Actic Acid (EDTA) solution at the end of titration wine red colour changes to blue. The total hardness was estimated by using following formula:

Total hardness in mg/l as $CaCO_3$ = $\underline{ml\ EDTA\ used\ X\ 1000}$

ml of Sample.

Calcium

Calcium is the major constituent of most igneous rock, metamorphic and sedimentary rocks. The principal sources of calcium in groundwater are some member of the silicate mineral group like plagioclase, pyroxene and amphibole among igneous and metamorphic rocks, and limestone, dolomite and gypsum among sedimentary rocks. Silicates mineral are not soluble in water, but weathering breaks them down into soluble calcium products and clay minerals. The carbonates and sulphates of calcium, however, are soluble in most natural waters. Because of its abundance in most rock types and its solubility, calcium is present almost everywhere in groundwater. Calcium is one of the most abundant substances of the natural water. The quantities in natural waters generally vary from 10 to 100 mg/l depending upon the types of rocks. Disposal of sewage and industrial wastes are important sources of calcium.

In 50 ml groundwater sample was taken and 2 ml of 1N sodium hydroxide (NaOH) solution was added. Then approximately 100 to 200 mg of murexide indicator was added. Contents of the flask were titrated against 0.01N Ethynele Diamine Tetra acetic acid (EDTA) solution resulting pink colour changes to purple which indicates the end point of titration. The calcium was determined by using the following formula:

Total Calcium in mg/l　　　=　　　$\dfrac{\text{ml EDTA used x 400.8}}{\text{ml of sample}}$

Magnesium

Magnesium is an important component of basic igneous rocks such as dunites, pyroxenites and amphibolites; volcanic rocks such as basalts, metamorphic rocks such as talc and tremolite-schists; and sedimentary rocks such as dolomite. Most limestones also contain some magnesium carbonate. Olivine, augite, biotite, hornblende, serpentine and talc are some major magnesium bearing minerals. Although in igneous and metamorphic rocks magnesium occurs in the form of insoluble silicates, weathering breaks them down into more soluble carbonates, clay minerals and silica.

In natural water magnesium occurs with calcium, but it concentration generally lower than the calcium. The principal sources in the natural waters are various kinds of rocks, sewages and industrial wastes.

The magnesium was determined by using the following formula:

Mg^{++} mg/l = Total Hardness (as mg/ l $CaCO_3$) – Calcium hardness (as mg/$CaCO_3$) x

　　　　0.244

 Where,

Calcium hardness (as mg/l $CaCO_3$) = Ca, mg/l x 2.497

Sodium

Sodium bearing mineral like albite and other members of plagioclase feldspars, nepheline, sodalite, glaucophane, aegerine etc. are not as widespread or abundant as the calcium and magnesium bearing minerals. Weathering of these minerals releases primary soluble sodium products. However, by far the most significant and important source of sodium in groundwater, with concentration of over 50 ppm of sodium, are the precipitates of sodium salts impregnating the soil in shallow water tracts, particularly in arid and semi-arid regions, sea water influx in coastal areas and connate water. Certain clay minerals and zeolites can increases the sodium content in groundwater by base Exchange reactions. An increase in sodium with concomitant reduction of calcium and magnesium, preponderance of sodium over chloride ions or alteration of calcium bicarbonate to sodium bicarbonate, may be indicative of base exchange enrichment of sodium, if such

changes are not accompanied by an increase in the total mineralization of the groundwater. Most sodium salts are readily soluble in water, but take no active part in chemical reactions as do the salts of alkaline earths. The increasing pollution of groundwater has resulted in a substantial increase in the sodium content of drinking water.

The content of sodium in groundwater was estimated flame photometrically, employing Elico Flame Photometer (Modal CL 22 D). The instrument was operated as per the instructions of the manufacturer. The instrument was calibrated by using sodium chloride (NaCl). The 10, 20, 50, 60 and 100 ppm standard solutions were prepared for sodium.

Potassium

The common source of potassium are the silicate minerals orthoclase, microcline, nepheline, leucite and biotite, in igneous and metamorphic rocks, and evaporates containing highly soluble and in some sedimentary rocks. Although potassium is nearly as abundant as sodium in igneous rocks and metamorphic rocks, its concentrations in groundwater is one-tenth or even one-hundredth that of sodium. Two factors are responsible for the scarcity of potassium in groundwater, one being the resistance of potassium minerals to decompositions by weathering (Goldtich, 1938) and the other the fixation of potassium in clay minerals formed due to weathering. The concentration of potassium (K) in waters varies from area to area.

The content of potassium in groundwater was estimated flame photometrically, employing Elico Flame Photometer (Modal CL 22 D). The instrument was operated as per the instructions of the manufacturer. The instrument was calibrated by potassium chloride (KCl). The 10, 20, 50, 60 and 100 ppm standard solutions were prepared for potassium.

Chloride

Chloride bearing rock minerals such as sodalite and chlorapatite, which are very minor constituents of igneous and metamorphic rocks, and liquid inclusions which comprise very insignificant fraction of the rock volume, are minor sources of chloride in

groundwater. It is presumable that the bulk of the chloride in groundwater is either from atmospheric sources or sea water contaminations. Sea water may also get trapped as connate water during the deposition of sediments. Desiccation of inland basins with initial fresh waters may give rise to highly saline waters. Solutions of halite and other evaporite deposits in sedimentary rocks also give rise to high chloride contents in groundwater. Chlorides may get into water from several sources including rock containing chlorides, agricultural runoff, wastewater from industries, effluent wastewater from wastewater treatment plants and road salting.

Chloride ions are generally present in natural waters and its presence can be attributed to dissolution of salts. 50 ml groundwater sample was taken and 2 ml potassium chromate (K_2CrO_4) solution was added. Contents of the flask were titrated against 0.02 N silver nitrate solution at the end of the titration yellow colour change to red colour. The chloride was determined by using the following formula:

$$Cl \text{ in mg/ } l = \frac{\text{ml of AgNO}_3 \text{ used x Normality of AgNO}_3 \text{x } 35.5 \text{ x } 1000}{\text{ml of sample}}$$

Alkalinity

The primary source of carbonate and bicarbonate ions in groundwater is the dissolves carbon dioxide in rain and snow which, as it enters the soil, dissolves more carbon dioxide. An increase in temperature or decrease in pressure causes reduction in the solubility of carbon dioxide in water. Decay of organic matter may also release carbon dioxide for dissolution. Water charged with carbon dioxide dissolves carbonate minerals, as it passes through soil and rocks, to give bicarbonates. Carbonates dissolution from rocks and precipitation from water is a two way process dependant on the partial pressure of carbon dioxide. The alkalinity of natural waters is due to salts of carbonate, bicarbonates, borates, silicates and phosphates along with hydroxyl ions in free State.

100 ml groundwater sample was taken and add 2-3 drops of phenolphthalein indicator was added, if the colour changes to pink then contents of the flask were titrated against 0.1N hydrochloric acid (HCL) at end of titration pink colour changes to colour less or disappears. It is the phenolphthalein alkalinity (PA). Then 2 to 3 drops of methyl

orange indicator was added to the same contents of the flask and titrated against 0.01N hydrochloric acid (HCL) at the end of titration yellow colour changes to pink gives total alkalinity (TA) of the samples.

Alkalinity was calculated as follows:

Phenolphthalein Alkalinity (PA) as $CaCO_3$ mg/ l =

$$\frac{(\text{ml of HCL used x Normality of HCL}) \times 1000 \times 50}{\text{ml of sample}}$$

Total Alkalinity in mg/l = $\frac{(\text{ml of total HCL used x Normality of HCL}) \times 1000 \times 50}{\text{ml of sample}}$

Sulphate

Sulphate (SO_4) content in groundwater is made possible through oxidation, precipitation, solution and concentration, as the water traverses through rocks. The sources of sulphate in rocks are sulphur minerals, sulphides of heavy metals which are of common occurrence in the igneous and metamorphic rocks. Apart from these natural sources, sulphates can be introduced through the application of sulphatic soil conditioners. Sulphides minerals when oxidized, give rise to soluble sulphates. In view of stability of the dissociated sulphate ion in most environments where it occurs and also of the high solubility of the sulphates of the common cations calcium, magnesium and sodium, sulphate can be present in high concentration in groundwater. Sulphate ions usually occur in natural waters and generally are readily soluble in water. The sulphate was determined by the turbidetric method. For the determining the sulphate 50 ml groundwater sample was taken and 2.5 ml conditioning reagents was added then spoonful of Barium chloride was added to the contents of test tube. The absorption spectra of this precipitated suspension are measured at 420 nm by using Elico Visible Spectrophotometer SL 171 model (Mini Spec).

Initially the optical density was measured for 5, 10, 15, 20, 25, 30, 35 and 40 ppm standard solution. Then the concentration v/s absorbance standard graph was prepared,

then the measured absorbance of groundwater samples of the study area was plotted on the standard graph and the concentration was found out.

Phosphate

Phosphorous is an essential plant nutrient and is extensively used as fertilizers. Phosphate gets adsorbed or fixed as aluminum or iron phosphate in acidic soils or as calcium phosphate in alkaline or neutral soils; as a result, the concentration of phosphate in ground water is usually low, but various chemical processes in soil strata may induce the mobility of phosphate in sub-soil and ground water.

For the determining the phosphate 50 ml groundwater sample was taken and 2 ml ammonium molybdate was added then 5 drops of stannous chloride solution ($Sncl_2$) was added to the contents of test tube. The absorption spectra of this precipitated suspension are measured at 690 nm by using Elico Visible Spectrophotometer SL 171 model (Mini Spec).

Initially the optical density was measured for 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 ml of standard solution. Then the concentration v/s absorbance standard graph was prepared, then the measured absorbance of groundwater samples of the study area was plotted on the standard graph and the concentration was found out.

3.5.2 Trace Elements

The trace constituents are distributed in a variety of rock types. A trace element study of groundwater is important for a variety of reasons such as their significance related to public health problems and their need in relation with plant growth (Gibbs, 1977). Trace elements dissolved in groundwater are defined as chemical elements dissolved in water in minute quantities, always or almost always, in concentrations less than one milligram of trace element in one litre of water (USGS.1993).

Two possible sources of trace elements are trace elements derived from weathering of rocks and trace elements introduced into the water by human activity (Drever, 1982).

1. Weathering of rocks as a source of trace elements in groundwater:

As far as rock source is concerned trace elements can be released into waters as result of

    a. Sulphide- oxidation reactions and

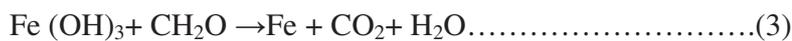b. Reductive dissolution of metal hydroxides (Robertson and Blows. 1995)

It is possible that oxidation of ferrous sulphides occurring as accessory minerals (opaque) in basaltic rocks have been responsible for releasing the metals into the aquifers. The general reactions of this kind are given by Lin-Hua and Atkinsons (1985) as follows:

$$FeS_2 \text{ (solid)} + 8H_2O \rightarrow 2SO_4 + Fe + 16h + 4e \text{ ………………..} (1)$$

Furthermore, hydrous manganese and iron oxides occur as coatings around silicates grains and are ubiquitous in soils and alluvial sediments in the area. The hydrous iron oxides are often amorphous, whereas Mn generally occurs as poorly crystallized birnesite or todorokite (Drever, 1982). Since these hydrous Fe-Mn oxides have extremely high absorption capacity and affinity for heavy metals, many metals like Copper (Cu), Lead (Pb) and Zinc (Zn) etc. are largely present in their oxide phases. The reductive dissolution of these metal oxides or hydroxides release many metals in the waters as follows:

$$MnO_2 \text{ (Birnesite)} + CH_2O \rightarrow Mn + CO_2 + H_2O \text{ ………….. } (2)$$

And

$$Fe(OH)_3 + CH_2O \rightarrow Fe + CO_2 + H_2O \text{ ……………………….} (3)$$

Thus ferric iron hydroxide and manganese oxide reduction not only release Iron (Fe) and Manganese (Mn) to the groundwater, but also metals co-precipitated or adsorbed onto these metal oxides. This could be the reason for the remaining metals to depict similar temporal trends in their concentration.

2. Human activity as a source of trace elements in groundwater:

In order to find out human activities as an additional source of trace elements in groundwater. Naturally occurring contaminants are present in the rocks and sediments. As groundwater flows through sediments, metals such as iron and manganese are dissolved and may later be found in high concentration in the water. Industrial discharges, urban activities, agricultural runoff, groundwater pumpage, and disposal of waste all can affect groundwater quality. Contaminants from leaking fuel tanks or fuel or toxic chemical spills may enter the groundwater and contaminate the aquifer. Pesticides and fertilizers applied to lawns and crops can accumulate and migrate to the water table. The physical properties of an aquifer, such as thickness, rock or sediment type, and location, play a large part in determining weather contaminants from the land surface will reach the groundwater. The risk of contamination is greater for unconfined (water table)

aquifers than for confined aquifers because they usually are nearest to land surface and lack an overlying confining layer to impede the movement of contaminants. Because groundwater moves slowly in the subsurface and many contaminants absorb to the sediments, restoration of a contaminated aquifer is difficult and may require years, decades, centuries, or even millennia (Waller, 1982).

Significance of trace elements in groundwater

In basic rocks, several trace elements can be accommodated in the crystal structure of different minerals. Iron (Fe), Lead (Pb), Zinc (Zn), Copper (Cu), Chromium (Cr), Manganese (Mn), Cadmium (Cd), Nickel (Ni) etc. are the important major and trace elements which occur in these rocks. However, in the groundwater all of them occur as trace elements. Their distribution and occurrence in the ground water depends upon degree of weathering and mobility of these elements during weathering (Handa, 1986). The contamination of ground water by trace element has received great significance during recent years due to their toxicity and accumulative behavior. These elements, contrary to most pollutants, are not biodegradable and undergo a global eco-biological cycle in which natural waters are the main pathways. The major sources of trace element in ground water include weathering of rock minerals, discharge of sewage and other waste effluents on land and runoff water (Table 3.1). The water used for drinking purpose should be free from any toxic elements, living, and nonliving organisms and excessive amount of minerals that may be hazardous to health. Some of the heavy metals are extremely essential to humans, for example, cobalt, copper, etc., but large quantities of them may cause physiological disorders. Cadmium, chromium, and lead are highly toxic to humans even in low concentrations (Jain et al 2009). Trace elements are a major source of pollution in natural waters due to industrial waste disposal and considered highly toxic to aquatic organisms. The compounds of these elements are nonbiodegradable and hence remains suspended or partially dissolved in water columns and get accumulated in many aquatic organisms. The heavy metals in the aquatic environment or in the food web affect aquatic life in various ways. The kidney and liver are reportedly damaged, leading to general body weakness, poor appetite affecting reproductive processes, and changes in physiological activities (Luoma and Carter 1991).

Pollution of groundwater is an impairment of water quality by chemicals, heat or bacteria to a degree, that does not necessarily create and actual public heath hazards, but does adversely affect such water for domestic, farm, municipal or industrial use.

Table 3.1 Trace elements and their sources.

Trace Elements	Source to groundwater
Iron (Fe)	Occurs naturally as mineral from sediment and rock or from mining, industrial waste and corroding metal.
Lead (Pb)	Enters environment from industry, mining, pluming, gasoline, coal, and as a water additive.
Zinc (Zn)	Found naturally in water, most frequently in areas where it is mined. Enters environment from industrial waste, metal plating, and plumbing, and is a major component of sludge.
Copper (Cu)	Enters environment from metal plating, industrial and domestic waste, mining, and mineral leaching.
Chromium (Cr)	Enters environment from old mining operations runoff and leaching into groundwater, fossil-fuel combustion, and cement plant emissions, mineral leaching, and waste incineration. Used in metal plating and as a cooling-tower additive.
Manganese (Mn)	Occurs naturally as a mineral from sediment and rock or from mining and industrial waste.
Cadmium (Cd)	Found in low concentration in rocks, coal and petroleum and enters the ground and surface water when dissolved by acidic waters. May enter the environment from industrial discharge, miming waste, metal plating, water pipes, batteries, paints and pigments, plastic stabilizers, and landfill leachate.
Níkel (Ni)	Occurs naturally in soil, groundwater, and surface water. Often used in electroplating, stainless steel and alloy products, mining, and refining.

(Reference: U.S.Geological survey, 1982)

Many trace elements are essential nutrients however certain trace elements such as As, Cd, and Hg are known to be persistent environment contamination and toxic to

most form of life. Trace elements are generally present in small concentration in natural water system. Their occurrence in groundwater and surface water can be due to natural sources such as dissolution of naturally occurring minerals containing trace elements in the soil zone or the aquifer material or to human activities such as mining, fuels, smelting of ores and improper disposal of industrial wastes.

Trace element analysis

Trace elements namely Iron (Fe), Copper (Cu), Zinc (Zn),Chromium (Cr), Nickel (Ni),Manganese (Mn), Cadmium (Cd), Lead (Pb) were determined by using Atomic Absorption Spectrophotometer (Model Chemito AA 201) as per the standard methods for examination of water and wastewater (APHA, 1995). Hollow cathode lamps of respective metals were used and the instruments was optimize for maximum response. Air and Acetylene were used as oxidant and fuel respectively. The instrument was standardized for the individual elements. Calibration curve was obtained for every metal ion using standard solution. Standard solutions were prepared from 1,000 mg/l stock solution of different metals of interest.