CHAPTER 2
THE STUDY AREA AND METHODOLOGY

Rapid growth of population has multiplied human needs several fold resulting in a fast pace of industrialization and urbanization. To fulfill human requirements, new technologies have been evolved to increase production. In the process of human civilization, the use of cloth itself was a definite stage. With the passage of time cloth became a basic need. In ancient times, this need was fulfilled by cottage industry but with the growth of population and advancement in technology, hand woven cloth gave way to the machine-made cloth in the large number of textile mills. Consumer demand for textile products is ever increasing in domestic as well as in international market resulting in setting up of more and more textile processing industries. Not going far back in the history of textile industry in India, the East India Company started its business by cotton industry (Hussain et al., 2004). Textile industry is one of the largest and oldest organized sectors in India and is also at the same time extremely complex (Dutta, 1994). Usually, 6-7 liters of water are used for producing one meter of cloth (ISI, 1980) and consequently, a very large volume of effluent consisting of a large amount of dyes, pigments and other chemicals is discharged to the environment.

The present work was aimed at evaluating the impact of a textile mill at Rangia (District Kamrup, Assam) on quality of soil and water in the surrounding areas. The textile unit is operating for the last eighteen years. However, no study has been reported on the impact of the continuous operation of the mill on the quality of soil and water of the area.

2.1 Rangia town: Important features

Rangia town (26^0 28′ 11″N, $91^0$37′ 47″E) is the nerve center of the Rangia Civil Sub-Division, the only Sub-Division in the Kamrup (rural) district, situated at a distance of about 60 km from Guwahati ($26^0$11′ N, $91^0$47′ E). The river Borolia flows through the town. The geographical location of Rangia is shown in Figs. 2.1 and 2.2.

The total population of the town is 26,674 (as of March, 2007; Source-Rangia Municipal Board) distributed in ten municipal wards. The demographic profile of the

town reflects a mixed pattern of population, including Hindus and Muslims in almost equal percentage, together with a sizeable Bodo population.

The National Highway No. 31 runs through the town and Rangia is an important Railway junction of the N. F. Railway. These have contributed in a big way towards the overall development of the township in general and communication network in particular. The International Route to Bhutan runs through the town, which is better known as the Rangia-Darranga Road.

In the academic scenario, there are five colleges, three Higher Secondary schools, ten High Schools and nine Lower Primary Schools operating within the town towards fulfilling the academic needs of the student community.

The industrial activity within the town is not very noticeable. There are nine SSI units within the town, which manufacture steel trunks and 'kerahi'. Three stone crusher units are also operating at the outskirts of the township. Two big rice mills are there. In both sides of the Rangia-Darranga road, adjacent to the town, seven brick industries produce large quantities of bricks. Just on the side of the Rangia-Darranga Road, is situated the APOL Mill at a distance of 8 km from Rangia town. In recent times, one industrial park has been established by the state government at a distance of about 6 km from the town on Rangia-Guwahati road (NH 31) and it is expected that this will help in expansion of industrial activities in Rangia. Another contributing factor in this direction is the 'Gram Swaraj Parishad, Rangia'. In close cooperation with Khadi and Village Industries Department, Government of India, this institution has contributed a lot towards generation of employment and motivation for self-employment amongst the enterprising new generation in and around Rangia.

In Rangia town, Government water supply scheme is yet to build up (either by Municipal Board or the State Public Health Engineering department). But in some of the surrounding villages, Public Health Engineering department has installed water supply scheme through deep tube wells but the covering area is very small. The most common source of drinking water for the residents in and around Rangia town is tube-well water. In some public institutions like temples, deep dug-well is also seen as source of drinking water. People find it easier to collect water from such a dug well as only a bucket and a 50-60 feet rope are required and usually no maintenance is called for.

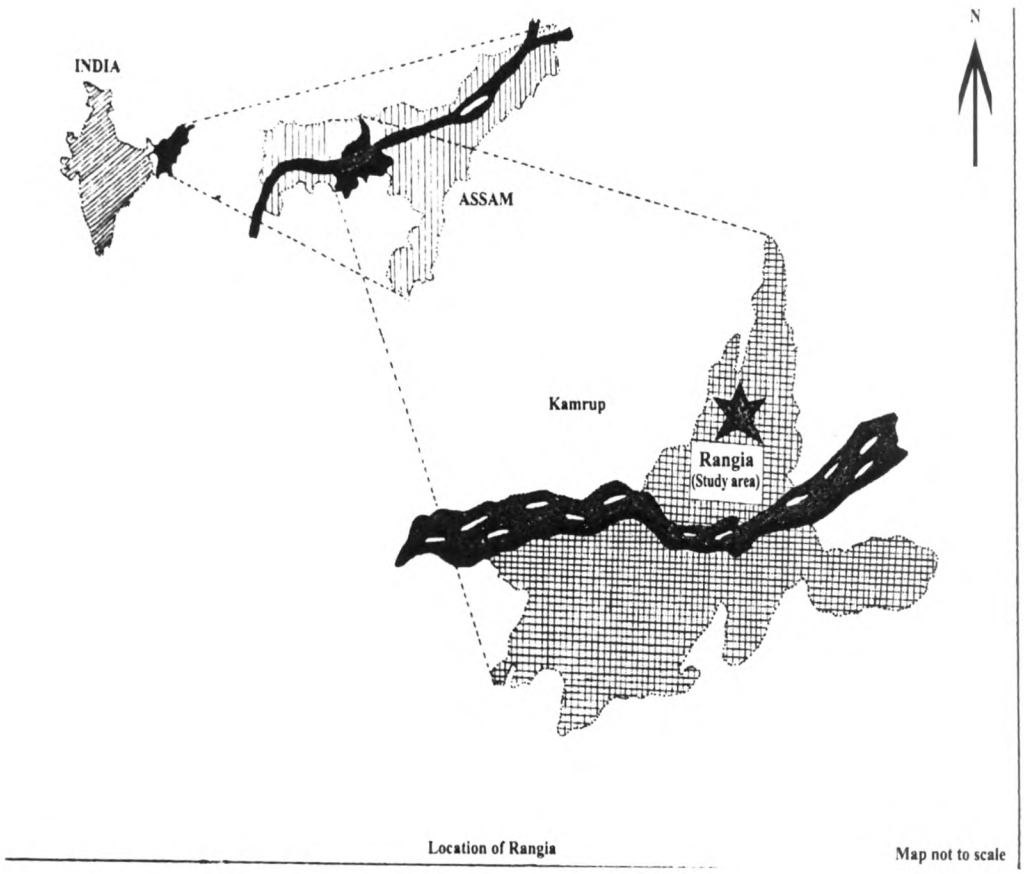


Fig. 2.1. Geographical location of Rangia vis-à-vis its position in the map of India

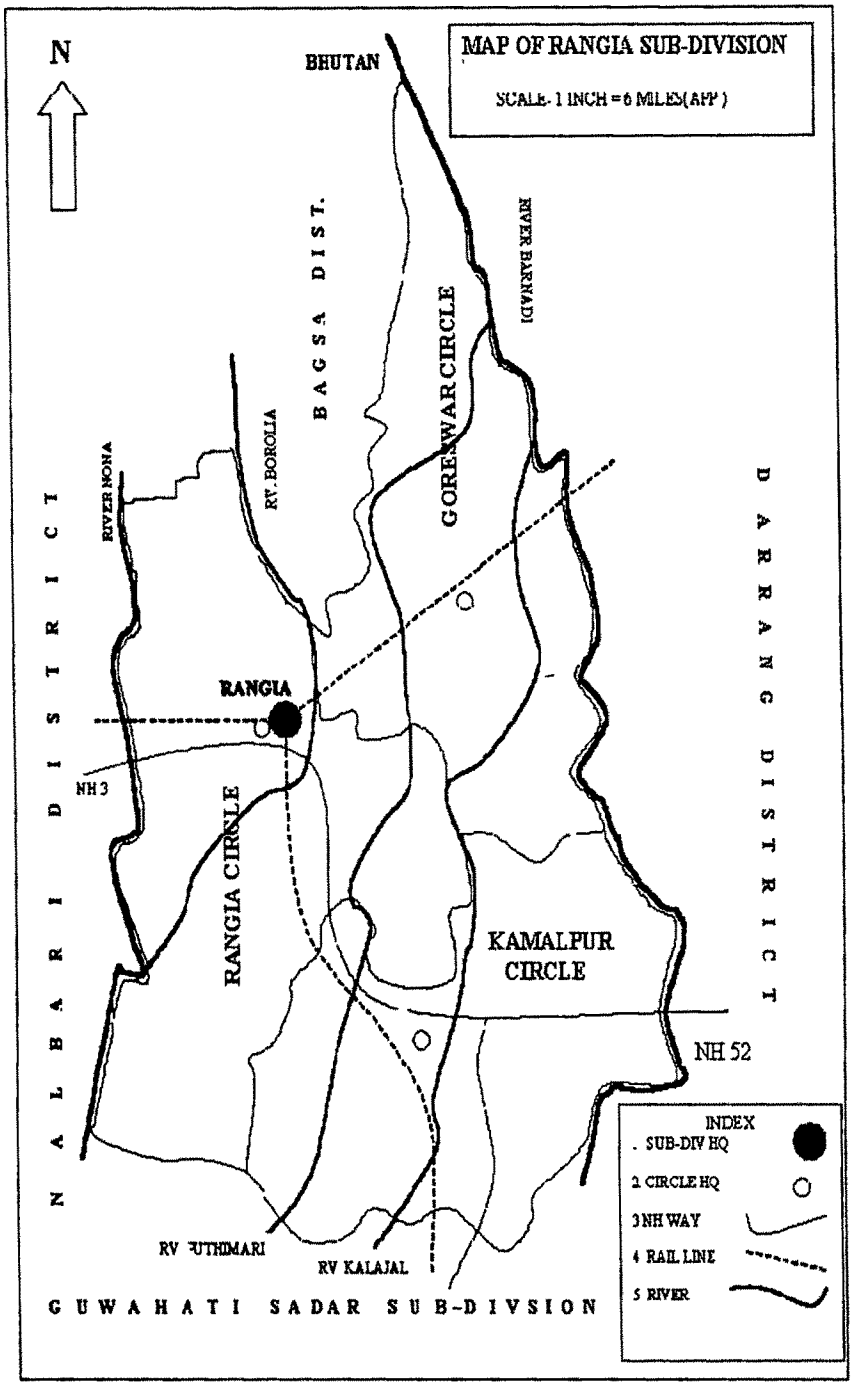


Fig. 2.2. Location of the study area (Rangia) along with the physical features.

Normally the ground water level for domestic tube wells is found at a depth of 20 to 30 m. Irrespective of the sources, the quality of water for the purpose of ordinary domestic use is not good. On storing for an hour or so, the water gets reddish because of the presence of high iron content which is considered by the people as the main problem. Moreover, the high iron content gives a bad taste. The people use water filters made of sand-stone-charcoal to get rid of excessive iron. High iron content gives a visible tinge to water of open tanks.

As far as water-borne diseases are concerned, according to Sub-Divisional Medical and Health office, Rangia, no specific outbreaks have been recorded as yet. But common health problems that occur due to use of unsafe water are quite prevalent like any other place of the state. Such problems are more numerous during the summer season as people require more water intake during these days.

2.2 The Textile Mill

APOL (Assam Polyester Co-operative Society Limited) is Assam's only textile mill near Rangia town in the district of Kamrup, Assam, just 50 kilometers north of Guwahati (26.11W, 91.47E). This unit was officially opened in June 1988 and started commercial production of spinning yarn of 5000 kg/day from November 1988 and weaving and processing from November 1991. The installed capacity of weaving unit was 8000 m/day and that of the processing unit was 20,000 m/day. The mill is producing yarn and cloths, especially viscose, polyester and acrylic fibre. In addition to this, to meet the growing demand of the local weavers, it has started manufacturing polyester mixed cotton yarn of variety of shades, blended with 'Eri' and 'Muga' yarn. The mill has its own dyeing unit with a capacity of 1500-2000 kg/day.

The raw materials required for the mill are bought from different parts of the country. The mill is using three types of fibers for spinning and weaving purpose. These are polyester, viscose and acrylic. Depending upon the types of fabric, the fibers are mixed in different proportions. The Bongaigaon Refinery and Petrochemical Limited (BRPL) supplies polyester whereas the other fibers- viscose and acrylic are taken from Nagda of Madhya Pradesh and Kolkata respectively.

The entire unit is covering an area 38.02 acres (125 bigha) of agricultural land. The Rangia-Bhutan road just passes through the eastern side of the mill. The northern and southern boundaries are covered by scattered residential accommodation while the vast western side is open agricultural land. The effluent of the mill is released through this agricultural land. There is a historical earthen dam at a distance of about 125 meters from the boundary wall of the mill along the western direction. The King Baidyadev built it during the period of 1138-1145 and the dam is about 6.4 km long and 6-8 meter wide. This dam divides that area into two sides (A and B), the side A is between the Mill and the dam, and the side B from the dam and beyond. The side A experiences more effluent load in comparison to side B. Again from the boundary wall of the mill the whole area is sloping downwards towards the western side and a drain across the dam is connecting the vast area (B) to area (A). In the last few years, as reported by the local people, this vast area has gradually lost productivity for all types of crops. The people in the area complain of pigmented water entering their agricultural land. The grazing cattle also refuse to drink this water.

The Mill and its suburbs are shown in Plate 2.1.

2.3 Collection of samples

2.3.1 Sampling frequency

The soil and water samples were collected twice a year in the months of (i) April (pre-monsoon period, before the onset of the monsoon) and (ii) November (post-monsoon period, after all rains stop) for a three-year period.

2.3.2 Soil samples

The locations of the soil sampling sites are shown in Fig. 2.3. During the three-year period, 175 samples of soil were collected from the study area for analysis. The frequency of collection is shown in details in Table 2.1 (a and b).

During the post-monsoon season, soil samples could not be collected from the area between the mill and the earthen dam as the area was occupied by the brick kiln industry. 'Control' soil samples were collected from a place where the effluent from the mill is not likely to have any influence.

Plate 2.1. The Textile Mill and its surroundings – (i) the Mill from its rear (top), (ii) the earthen dam with the side A in front (middle), (iii) Brick manufacturing behind the Mill along with accumulated surface water (bottom, left and right).

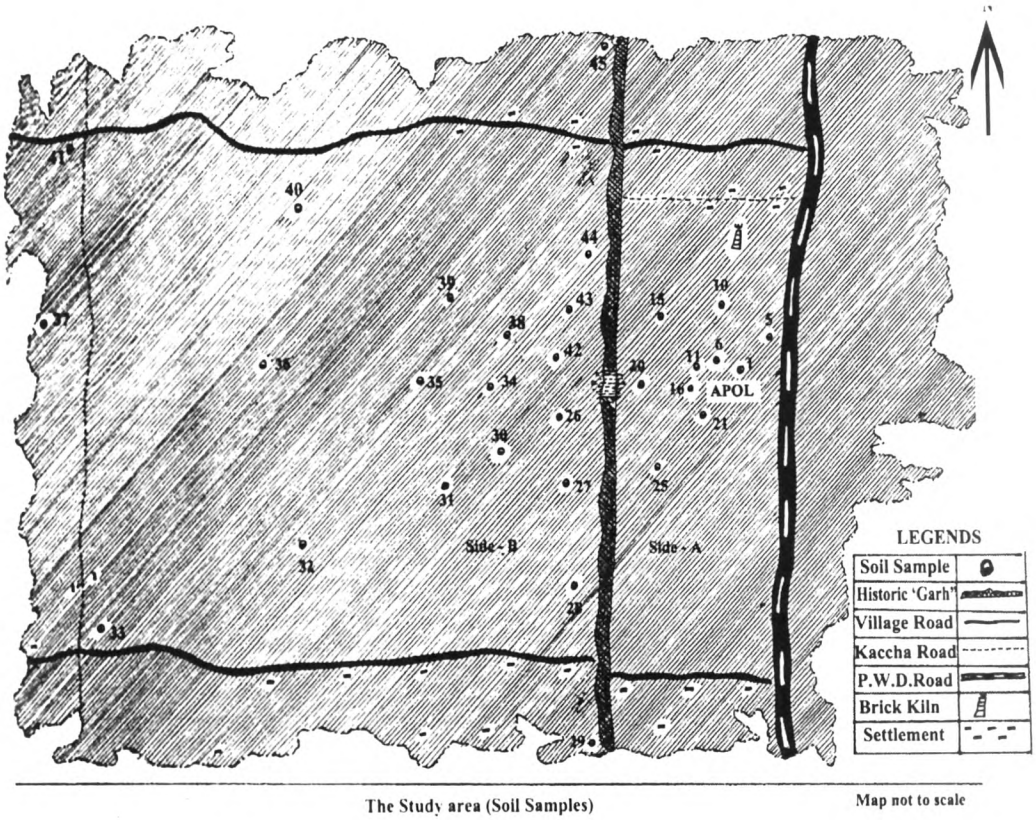


Fig. 2.3. Approximate locations of the soil sampling sites in the study area

Table 2.1a: Frequency of collection of soil samples (side A)

Direction	Distance from the Mill (m)														
	20	40	60	80	100	20	40	60	80	100	20	40	60	80	100
	First Pre-Monsoon					Second Pre-Monsoon					Third Pre-Monsoon				
NE	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√
N	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√
NW	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√
W	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√
SW	√	√	√	√	√	√	√	√	√	√	√	√	√	√	√

Table 2.1b: Frequency of collection of soil samples (side B)

Direction	Distance from the Mill (m)											
	150	200	500	1000	150	200	500	1000	150	200	500	1000
	First Pre-Monsoon				Second Pre-Monsoon				Third Pre-Monsoon			
S					√	√	√	√	√	√	√	√
N					√	√	√	√	√	√	√	√
NW					√	√	√	√	√	√	√	√
W					√	√	√	√	√	√	√	√
SW					√	√	√	√	√	√	√	√

Direction	Distance from the Mill (m)											
	150	200	500	1000	150	200	500	1000	150	200	500	1000
	First Post-Monsoon				Second Post-Monsoon				Third Post-Monsoon			
S	√	√	√	√	√	√	√	√	√	√	√	√
N	√	√	√	√	√	√	√	√	√	√	√	√
NW	√	√	√	√	√	√	√	√	√	√	√	√
W	√	√	√	√	√	√	√	√	√	√	√	√
SW	√	√	√	√	√	√	√	√	√	√	√	√

2.3.3 Water samples

Drinking water samples were collected from 7 sites (one tube well and 6 dug wells, Fig. 2.4) scattered round the mill in five seasons (starting from the post-monsoon season of the first year to the post-monsoon season of the third year) as shown below:

S/N	Source	Distance from the mill
1	Dug well	About 1 km south
2	Tube well	About 1 km south west
3	Dug well	About 1 km south west
4	Dug well	About 1 km north west
5	Dug well	About 1 km north west
6	Dug well	About 1 km north
7	Dug well	About 500 m north

Like soil samples, 'Control" drinking water sample (tube well) was also collected from a far-off area where the effluent from the Mill was not likely to have any effect.

Surface water sample collection was done from 8 sites (4 from side A and 4 from side B) starting from the post-monsoon season of the first year to the pre-monsoon season of the third year. Altogether four sets of surface water samples (2 pre-monsoon, 2 post-monsoon) were collected as shown below:

S/N	Location
1	Surface water accumulation towards the north western boundary of the mill in Side A
2	Surface water accumulation towards the west of the Mill where the effluent is released in Side A
3	Water accumulated at the earthen dam crossing (about 120 m from the boundary wall of the Mill) in Side A
4	Artificial pond filled with effluent water located at the western corner of the boundary in Side A
5	Accumulated water at about 500 m away from the mill (along the earthen dam) in Side B in the northern direction
6	Accumulated water at about 500 m away from the mill (along the earthen dam) in Side B in the southern direction
7	Accumulated water at about 300 m away from the mill in the western direction in Side B
8	Accumulated water at about 800 m away from the mill in the western direction in Side B

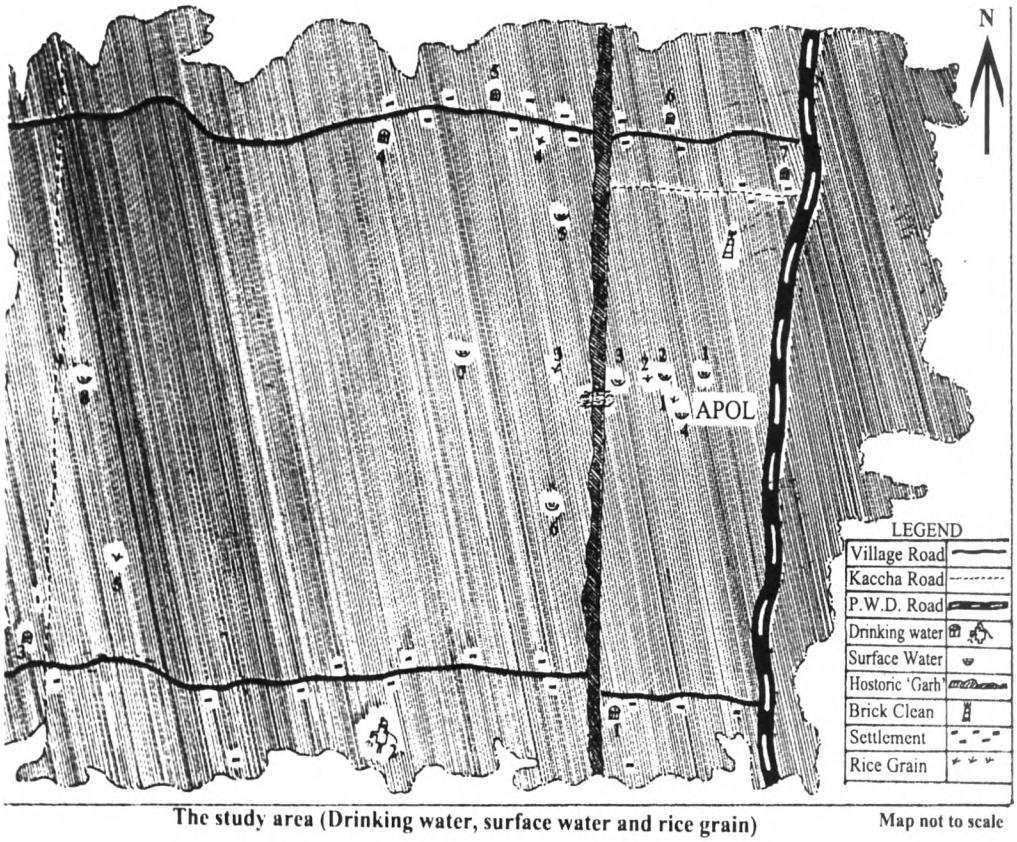


Fig. 2.4. Approximate locations of the sampling sites for drinking water, surface water and rice paddy grains.

2.3.4 Rice grain samples

Rice seeds from 5 sites of the agricultural field in both side A and side B were collected only once during the post-monsoon, harvesting season in the third year along with a 'Control' sample from a field far away from the mill. One of the rice grain (R) samples was taken from close vicinity of the mill (R1) and the other four from distances of about 50 m (R2), 200 m (R3), 500 m (R4) and 1 km (R5) from the mill.

2.4 Selection of parameters for soil analysis and methodology for determination

The parameters selected for analysis along with the method of estimation followed in this work are described below:

2.4.1 pH

The acid-base characteristics of the soil samples can be ascertained from the soil pH. Solubility of various substances present in soil and the potency of toxicity of those substances can be known from its pH. The pH is a very important property of soil as it determines the availability of nutrients, microbial activity and physical condition of the soil. Acidity and alkalinity reflect both H^+ and OH^- ion concentration in soil.

The soil pH was determined by using digital pH-meter (Elico LI 120) in 1:5 soil/water suspension-using buffers for calibration.

2.4.2 Electrical Conductance

Cations and anions present in soil impart electrical conductivity when the soil is made into a suspension in water. Higher the concentration of ions in solution more is its electrical conductance.

Soil conductivity was determined by using a conductivity bridge (Elico CM 180) by using a conductivity cell of cell constant 1.0 in 1:5 soil/water suspensions.

2.4.3 Bulk Density

The soil bulk volume comprises of the soil solids and the pore spaces. The bulk density of soil is calculated for the dry soil and it is assumed that after drying, the soil volume does not change and the pore spaces remain intact.

The bulk density was determined in the laboratory in repacked cubes as per the procedure of Chopra and Konwar (1986) using the following formula for computation:

$$\text{Bulk Density, g/cm}^3 = (W2 - W1) / V \quad (1)$$

where

W1 = Weight of the empty bottle

W2 = Weight of bottle packed with oven dry soil

V = Volume of the bottle, obtained by measuring the volume of water required to fill it completely

2.4.4 Water holding capacity

Water enters an agricultural or horticultural system as either precipitation from rain, hail, snow or dew or irrigation. Water is absorbed by the soil up to point when all the pores of the soil are full. At this point it has reached its storage capacity. Water, which is absorbed by soil because of its polar character, has not left the soil system through drainage or run-off and it is lost through a combination of evaporation from surface stored water and the soil surface and transpiration (evaporation of water from plant leaves). Together these processes are known as evapotranspiration.

Water holding capacity of the soil samples was determined by using circular stainless steel box of known weight (a). The perforated bottom plate of the box was supported on a Whatmann No.1 filter paper and approximately 10 g of the soil was added to the box and weighed (b). The box with the soil was kept dipped overnight with about one fourth of it under water in a Petri dish. After about 16 h, the box was removed from water and allowed to drain off the excess water. When no more water fell from the bottom of the box, it was weighed again (c). The weight of the moist filter paper supported in the box was also measured (m). The water holding capacity was calculated from the following expression :

$$\text{Water holding capacity, \%} = [c - (b + m) \times 100] / (b - a) \quad (2)$$

2.4.5 Hydraulic Conductivity

Hydraulic conductivity is one of the hydraulic properties of the soil as well as soil's fluid retention characteristics. These properties determine the behavior of the soil fluid within the soil system under specified conditions. More specifically, the hydraulic conductivity determines the ability of the soil fluid to flow through the soil matrix system under a specified hydraulic gradient; the soil fluid retention characteristics determine the ability of the soil system to retain the soil fluid under a specified pressure condition. . The saturated hydraulic conductivity is an essential parameter in the analysis and modeling of water flow and chemical transport in the soil (Iversen et. al. 2001).

The mathematical expression for the vertical water flow through soil is called Darcey's law. Darcey stated that the rate of flow increased with an increased depth of water above the soil through which it flowed. The flow decreased with an increased depth of soil. Each soil has different combination of pore sizes and the number of pores and each soil has a different flow rate constant, which is called hydraulic conductivity.

For hydraulic conductivity determination of soil sample, a soil core of 15.5 cm height was made inside an aluminium ring and the core was supported on a filter paper placed on a perforated aluminium plate. This arrangement was placed below a funnel clamped to a rack. Water was delivered to the soil core with an aspirator bottle maintaining a constant head of 2.5 cm above the core and water flowing down the core was collected in a beaker in intervals of 30 minutes. The hydraulic conductivity was calculated from the formula

$$\text{Hydraulic Conductivity (K) cm/min} = QL / HAT \qquad (3)$$

where

Q = Quantity of water collected in cm3

A = Cross sectional area of the inside of the ring in cm2

L = length of the soil core in cm.

H = Total height of water column (core height + water head) in cm

T = Time of flow in minutes

2.4.6 Organic Matter (OM)

Soil organic matter greatly affects the biology of the soil because it provides the main food source for the community of heterotrophic soil organisms. The soil microbial biomass is a labile pool organic matter and comprises 1%–3% of total soil organic matter (Jenkinson and Ladd, 1981). Soil OM is the sum of different pools of soil OM, i.e., active and passive fractions. The active fractions include living biomass, some detritus, and non-humic matter; it comprises about 10-20 % of the total soil OM. Passive fractions include most of the humus physically protected in clay-humus complexes, most of the humin, and much of the humic acids; the passive fraction accounts for 60-90 % of the OM in most soils. The susceptibility of the active fraction to rapid changes explains why even relatively small changes in total soil OM can produce dramatic changes in important soil properties, such as aggregate stability and nitrogen mineralization, which are associated with this OM fraction. The role of OM in soil in relation to soil fertility and physical conditions is widely recognized (Stevenson, 1986; Johnson, 1986)

Walkey and Black method was used to determine the organic matter content in soil. 5 g of the air-dried soil sample was mixed with 10 ml of 1N $K_2Cr_2O_7$ solution and 20 ml of concentrated H_2SO_4 acid in a 500 ml conical flask. Solid Ag_2SO_4 was added to it by gentle stirring so that silver sulphate goes into solution completely. The contents were diluted to 200 ml by adding distilled water. The colour of the solution turned bluish purple on addition of 1 ml of phosphoric acid and 1 ml of diphenylamine indicator. The solution was titrated with ferrous ammonium sulphate till colour changes to brilliant green. The amount of organic carbon was calculated from the formula:

$$\text{Organic Carbon, \%} = [(x - y) / w] \times 0.003 \times 100 \qquad (4)$$

where

x = volume of $K_2Cr_2O_7$ solution

y = volume of ferrous ammonium sulphate required for titration

w = weight of soil sample

The total organic matter of the soil sample was then calculated from the values of organic carbon, obtained as above, using the formula:

$$\text{Organic matter \%} = \text{Organic Carbon \%} \times 1.724 \quad (5)$$

2.4.7 Total Nitrogen

Of the total amount of nitrogen present in soil nearly 95-99 % is in the organic form and 1-5 % in the inorganic form as NH_4^+ and nitrate (NO_3^-) (Troch and Thompson 1993). Normally a plant contains N in the range of 0.2 – 4 % of dried plant tissue. Determination of total nitrogen in soil does not indicate how much amount of it present in soil available for plant intake. During growth and development, an average of only 0.5 – 2.5 % and sometimes rarely 5 %, of the total nitrogen is converted into forms accessible to the plant (Rao et al., 1997).

To determine nitrogen in soil, micro-Kjeldahl method (Jackson, 1967) was adopted. 10 g of soil sample in a 500 ml Kjeldahl flask was mixed with 25 ml of distilled water to make a suspension. The digestion catalyst mixture was prepared by mixing together 20 g $CuSO_4$, 3 g HgO, and 1 g selenium powder. 1 g of this mixture was mixed with 20 g sodium sulphate and was added to the suspension along with 35 ml of concentrated H_2SO_4 with gentle swirling motion. The content was heated at low heat for about 10-30 minutes until the frothing stops. The temperature was then raised rotating the flask after every few minutes interval for about two hours. The digested component was then cooled and the supernatant liquid was transferred to a 100 ml volumetric flask. The residue was washed several times with distilled water and after each washing, the supernatant liquid was transferred to the flask

25 ml of that solution was taken in a micro-Kjeldahl flask and 25 ml of 40 % NaOH was added, and then the mixture was distilled by heating. The distillate was collected in a 250 ml of conical flask containing 25 ml of 4 % boric acid and 5 ml of mixed indicator (the mixed indicator consisted of an alcoholic solution of 0.5 % bromocresol and 0.1 % methyl red in 2:1 ratio). About 100 ml of distillate was taken for titration with 0.1N HCl until the colour changes from blue to light pink. A blank titration was also run with distilled water using the other chemicals in same proportion.

Total nitrogen was calculated by using the formula

$$\text{Total N, \%} = [(a - b) / (v \times S)] \times N(HCl) \times 1.4 \times V \quad (6)$$

where

a = ml of HCl acid required for titrating sample solution

b = ml of HCl acid required for titrating blank

N = Normality of acid solution

V = ml of total solution after digestion (= 100ml)

v = ml of digested solution taken for distillation (= 25ml)

S = Weight of the soil taken (10g)

2.4.8 Available phosphorus

Phosphorus in soils ranges from 0.01 to 0.03 % and occurs in several forms and combinations (Gupta, 2000). The total amount of phosphorus present in soil is not available to the plants, only a small fraction of it may be available which is of direct relevance in assessing the phosphorus fertility levels. Available phosphorus means the inorganic form of phosphorus, exclusively orthophosphate, which occurs in several forms and combinations present in soil. Both inorganic and organic forms of phosphorus occur in soils, both are important to plants as sources of this element and the relative amounts in the two forms vary greatly from soil to soil (Zhang and Karathanasis, 1997). Phosphate is a good indicator for P-supply capacity of a soil.

Phosphorus in soil is generally determined as available phosphorus, which can be extracted from soil with 0.002 N H_2SO_4. After extraction, phosphorus was estimated spectrophotometrically by Dickman and Bray (1940) method.

10 g of air-dry soil sample was taken in a 500 ml conical flask and 200 ml of 0.002 N H_2SO_4 was added. The suspension was shaken for about half an hour and filtered through Whatman No. 50 filter paper to get a clear solution. 2 ml of ammonium molybdate solution and 5 drops of stannous chloride reagent were added to 50 ml of the extract and a blue colour developed. The intensity of the blue colour was measured by using spectrophotometer (Perkin Elmer UV visible Lambda EZ 201) at 690 nm. A

standard curve was prepared with standard potassium hydrogen orthophosphate solution in the range of 0.0 to 10 mg/L following the same procedure.

The available phosphorus was calculated from the relation:

$$P, mg/kg = (mg\ P/dm^3 \text{ in soil extract} \times V)/ (S \times v) \quad (7)$$

where V = total volume of the soil extract prepared (200ml)

S = wt. of soil taken in gram

v = volume of the aliquot taken for analysis (50ml)

2.4.9 Soil Texture

The relative proportion of soil particles i.e. sand, clay and silt has profound effect upon the properties of soil including its water supplying power, rate of water intake, aeration, fertility, ease of tillage and susceptibility to erosion. Hydrometer method is used to estimate particle size distribution of soil as below

sand	2.0 to 0.05 mm diameter
silt	0.05 to 0.002 mm diameter
clay	< 0.002 mm diameter

40 g of air-dry soil was taken in a 500 ml conical flask to which 200 ml water was added followed by 8 ml 30 % H_2O_2 solution. The beaker, covered with a watch glass, was placed on a water bath at ~ 70.0 C to decompose organic matter. After 15 minutes, the flask was removed and allowed to cool. The above process was repeated three times and finally the beaker was put on the water bath again for two hours to remove the excess H_2O_2. The suspension was then transferred to a 1-litre cylinder and the volume was made up to 1 litre with distilled water. The mixture was agitated mechanically for one minute by a rubber stopper. After 4 minutes, the hydrometer reading was taken. The temperature of the suspension (t °C) was measured. The hydrometer was pre-calibrated. The suspension was kept undisturbed for 2 hours and hydrometer reading was taken again by dipping it in the suspension.

The sand, silt and clay percentages were then calculated from the following expressions:

$$\text{Sand \%} = 100 - P_4 \quad (8)$$

$$\text{Silt \%} = P_4 - P_{120} \quad (9)$$

$$\text{Clay \%} = P_{120} \quad (10)$$

where

P_4 = $[(R_4 \pm r) \times 100] / W$

P_{120} = $[(R120 \pm r) \times 100] / W$

R_4 = hydrometer reading at 4 min

R_{120} = hydrometer reading at 120 min

r = temperature correction $= \pm (t - 67) \times 0.2$

W = oven dry wt. of soil sample

t = temperature in ^0C at the time of measurement.

2.4.10. Oil and grease

Many aerobic and anaerobic processes are always present in soil and constituents like oil and grease may interfere with these. Oil and grease also form a very thin film on soil that reduces permeability and water holding capacity. Oil and grease also forms a very thin film reduces permeability and water holding capacity of soil (Devi, 1996). Fat, oil, and grease have a high C/N ratio (90:1) and, if applied to agricultural soils, may affect the availability of N to crops, due to soil N immobilization during its decomposition (Rashid and Voroney, 2004)

For determination of oil and grease, 1g of soil sample was taken in a cellulose extraction thimble. The thimble was filled with glass wool. Extraction of oil and grease was then done in a Soxhlet apparatus, using petroleum ether at a rate of 20 cycles / h for eight hours. The solvent from the extraction flask was then removed from the flask and taken in a pre-weighed beaker. The beaker was placed in a water bath at very low flame.

After removal of the solvent, the beaker was kept in a desiccator for one hour and weighed again. Oil and grease of air-dried soil is given by;

Oil and grease (mg/kg) = [(Wt gain by flask x 100) / weight of soil taken] x1000 (11)

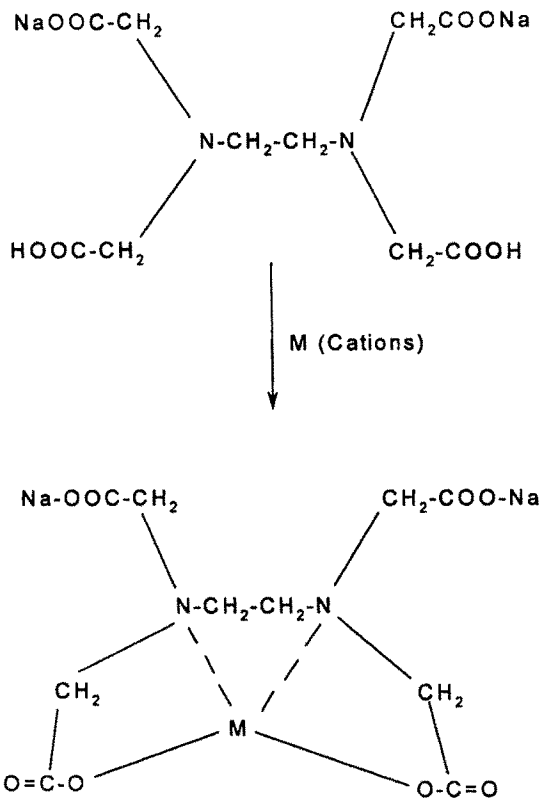
2.4.11. Exchangeable cations- Calcium, Magnesium, Sodium, Potassium

The exchangeable Ca^{2+} and Mg^{2+} ions in soil are extracted with a neutral 1.0 N NH_4OAc solution when the cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) are replaced with NH_4^+ ions. In the extracted solution, $Ca^{2+}$and Mg^{2+} ions were determined by the complexometric titration method using erhylenediaminetetracetic acid (EDTA), and Na^+ and K^+ were determined by the flame photometric method.

The most widely used salt of EDTA is the disodium salt with the formula Na_2H_2Y, $2H_2O$ where Y is the tetravalent anion of EDTA. When $Ca^{2+}$is treated with H_2Y^{2-} a very stable complex is formed. The generalized reaction of EDTA with Ca^{2+} ion is shown below:

$$Ca^{2+} + H_2Y^{2-} \longrightarrow CaY^{2-} + 2H^+$$

Mg^{2+} ion forms a similar complex, MgY^{2-}, which is far less stable than the Ca-complex. The characteristic reaction showing the complex formation of EDTA with a metal cation M is as follows (Hesse, 1971)



Preparation of the ammonium acetate extract: 50 g of the air-dried sample was treated with 40% alcohol and filtered through Whatman No. 50 filter paper. The soil was washed four times with 50 ml portion of 40 % alcohol. Then the soil was treated with 100 ml 1.0 N NH_4OAc solution and kept overnight. The suspension was filtered through Whatmann No.42 filter paper and the volume was made up to 500 ml with distilled water. A portion of the NH_4 acetate extract was evaporated to dryness to eliminate the interference of organic matter. The residue was dissolved in aqua regia. Again it was evaporated to dryness. Then residue was dissolved in distilled water to make up the original volume of the extract evaporated.

Calcium and magnesium: 50 ml of aliquot was taken in a conical flask with 1 ml of NH_4Cl – NH_4OH buffer solution and about 100 mg of Eriochrome Black T indicator. The solution becomes wine red and it was titrated with 0.01 N EDTA solution till the colour changes to blue.

Calcium: 50ml of the aliquot was taken in a conical flask with 2ml of 10% NaOH and about 100 mg murexide indicator. The pink colour solution was then titrated with 0.01 N EDTA solution until the pink colour changes to dark purple.

Calculation

$$Ca, meq/kg = (A \times 400.8 \times V) / (v \times 20.04 \times S) \quad (12)$$

$$Mg, meq/kg = [(B-A) \times 400.8 \times V] / [v \times S \times 1.645 \times 12.16] \quad (13)$$

where,

A = volume of EDTA (ml) used for Ca^{2+} determination

B = volume of EDTA (ml) used for Ca^{2+} - Mg^{2+} determination

V = volume of the soil extract prepared (500 ml)

v = volume of the soil extract titrated (50ml)

S = weight of the soil sample taken (50g).

Sodium and Potassium: Na^+ and K^+ in the filtrate of NH_4-acetate extract were determined by the flame photometric method (Elico Model CL 361).

2.4.12 Trace Metals

(a) Al, Cu, Fe, Mn and Zn: Some of these elements are essential for plant growth but they are utilized only in minute quantities in contrast to the macronutrients like N, P and K, which comprise a proportionally larger percentage of plant weight. When present in excess, these can also be toxic to plants.

(b) Heavy Metals: The effects of various heavy metals such as As, Cd, Cr, Hg, Ni, Pb, etc. in soil is governed by the nature and extent to which they are bound to clay minerals and soil organic matter.

These metals were extracted from soil as follows: Air-dried soil samples were ground to obtain a fine powder and screened through a 80 mesh sieve. The extraction was carried out as per procedure given by Pinta (1975). 1.0 g of the sieved sample was digested with 35 ml of acid mixture (consisting of 4 parts of conc. H_2SO_4, 2 parts of conc. HCl and 1 part of conc. HNO_3). The mixture was heated gently at first and then

more strongly until white fumes were no longer evolved. The residue was treated with 1:1 dil HCl, filtered through Whatman No. 42 and washed with distilled water several times. The final volume was made up to 100 ml with distilled water. The concentration of the metals was measured with the atomic absorption spectrophotometer (Varian SpectrAA 220). The metal content in the soil samples was found by using following formula:

$$\text{Metal Concentration, mg/kg} = (P \times Q \times R) / W \qquad (14)$$

Where, P = Concentration of metal in digested solution

Q = Final volume of digested solution (ml).

R = Dilution ratio

W = Amount of soil taken (1g).

The detailed experimental conditions for AAS analysis are given in Table 2.2

Table 2.2: Analytical conditions for atomic absorption spectroscopic analysis.

Element	Wavelength (nm)	Slit width (nm)	Working range (ppm)	Lamp current (mA)	Type of flame	Fuel gas flow rate (L/min)	Air flow rate (L/min)
Al	309.3	0.5	0.3 – 250.0	10	C_2H_2 -N_2O	1	3.5 (N_2O)
Cd	228.8	0.5	0.02 – 3.0	4	Air- C_2H_2	1	3.5
Cr	357.9	0.2	0.06 –15.0	7	Air – C_2H_2	1	3.5
Cu	324.7	0.5	0.03-10.0	4	Air- C_2H_2	1	3.5
Fe	248.3	0.2	0.06-15.0	5	Air-C2H2	1	3.5
Hg	253.7	0.5	2.00 - 400.0	4	Cold vapour	- -	3.5 (N_2)
Mn	279.5	0.2	0.02 – 5.0	5	Air -C_2H_2	1	3.5
Ni	232.0	0.2	0.1 –20.0	4	Air- C_2H_2	1	3.5
Pb	217.0	1.0	0.1 – 30.0	5	Air- C_2H_2	1	3.5
Zn	213.9	1.0	0.01 – 2.0	5	Air -C_2H_2	1	3.5

2.4.13 Major and Minor Oxides

X-ray fluorescence (XRF) spectrometer has been found to be a very efficient tool for measuring major and minor oxides in soil samples. For multi-element analysis of geochemical samples, it has become a proven technique and has been widely used as a rapid and accurate analysis method (Chen, 1985). Analysis of a group of elemental oxides in a single trial is possible in XRF.

Chemical composition of the soil samples with respect to major and minor oxides (SiO_2, Al_2O_3, Fe_2O_3, MnO, TiO_2, K_2O, Na_2O, MgO, CaO and P_2O_5) was determined by XRF measurement (Philips PW 1480 with Au-Cr dual anode system) at University Science instrumentation Centre, Gauhati University by applying pressed pellet technique. As soil standards are not available, rock standards were used for quantification of the results. Therefore, some discrepancies cannot be ruled out. **Sample preparation**: Soil sample for XRF measurement was prepared by the method of Thompson et al. (1996). The soil sample was ground to a fine powder and sieved with a 200-mesh sieve. 1.0 g of the sieved sample was mixed with a 0.5 g of boric acid and was thoroughly mixed in an agate mortar to get a fine homogeneous mixture. A deformable aluminium metal cup was filled with the mixture and was pressed in a cylindrical die of 40 mm diameter by means of a hydraulic press (AIMIL, Model 315) applying pressure in the range of 125 kN to 175 kN for about 5 minutes. A pressed pellet of circular size of 40 mm diameter with smooth face surface was obtained. The pellet was taken in a sample holder and inserted into the XRF instrument for analysis. This method was rapid and convenient, yielding high X-Ray intensity and facilitating matrix modification.

2.4.14 Identification of clay minerals with XRD analysis

XRD measurements were done to identify the clay fractions of the soil samples at the University Science instrumentation Centre, Gauhati University using Philips X –Ray spectrometer (PW 1710) using Cu anode. The scanning range was from 5.0 to 30.0 (2θ) in the continuous scan mode. The identification of clay minerals was done by using standard technique (Jackson, 1975; Moore and Reynolds Jr. 1989; Imam 1994).

Extraction of Clay Minerals from the Soil

About 25 g of soil sample was mixed with sodium acetate- acetic acid (pH 5.0) buffer and the suspension was allowed to stand for 30 minutes. The suspension was centrifuged and 50 ml of acetone was added. It was again centrifuged and the sample was transferred to a 500 ml beaker. 5 ml of 30 % H_2O_2 solution was added and the beaker was placed on a hot plate till the effervescence ceased. The process was repeated for three times. The sample was left overnight by adding 10 ml of 30% H_2O_2 solution. In the very next day, the suspension was digested for 2 hours on a hot water bath, washed with 1N sodium acetate solution, centrifuged and the supernatant liquid was discarded. 40 ml of 0.3 M sodium citrate and 0.125 M sodium bicarbonate (prepared by dissolving 88g of sodium citrate and 10.5g of sodium bicarbonate in 1 litre of distilled water) were added to the residue left and the mixture was placed on a water bath at a temperature of 70 – 80oC. 1.0 g of sodium dithionate ($Na_2S_2O_4$) was added to the mixture in small increments with constant stirring. The supernatant liquid was transferred to a 1000 ml measuring cylinder and the volume was made up with distilled water. The suspension was shaken vigorously and allowed to stand for about 6 hours. The top 10 cm of the suspension was collected at intervals and centrifuged to obtain the clay fraction. The clay minerals in this were identified from XRD measurements.

2.5 Selection of parameters for water analysis and methodology for determination

Water samples were collected in pre-cleaned plastic gallons filled as much as possible and tightly stoppered to avoid contact with air or to prevent agitation during transport. Drinking water samples were collected from tube wells and dug wells, surface water from the vast areas in the western side of the mill. After collection, proper labeling was made on each sample. pH and conductivity were measured immediately after collection of the sample. Storage and preservation of samples were done following standard procedure (APHA, 1995). For determination of metals in water, the samples after collection were acidified with conc. nitric acid and allowed to evaporate for some time. After the volume make-up was done with distilled water, the sample was finally kept in acid proof plastic bottle at ~ 4^0C in a refrigerator.

The parameters selected for monitoring were shown below:

(i) Aesthetic quality of water: Total hardness, total solids (TS), total suspended solids (TSS), total dissolved solids (TDS), conductance, pH, Cl^-, SO_4^{--}, PO_4^{---}, Na, K, Ca, Mg, Cu, Fe, Mn, Zn.

(ii) Inorganic constituents of significance to health: F^-, NO_3^-, Pb, Ni, Cr, As, Hg.

The analysis was carried out at the department of Chemistry, Gauhati University using standard methods (APHA, 1995).

2.5.1 pH

At a given temperature, the intensity of the acidic or basic character of water is indicated by pH or hydrogen ion activity. Measurement of pH is thus one of the most important and frequently used tests in water chemistry. It measures acid – base behavior of water system. Water pH in natural conditions is controlled by carbonate – bicarbonate equilibrium. The pH of drinking water lies generally between 6.5 and 8.5 (WHO,1995; BIS, 1981). Low pH causes corrosion in the distribution system and increases the metal contamination of drinking water (Trivedy and Goel, 1984).

All pH measurements were done using a digital pH meter (Model LI-127, ELICO). The instrument was calibrated for each set of measurement with standard buffer solutions.

2.5.2 Conductance

Conductivity is a numerical expression of the ability of an aqueous solution to carry an electrical current. It depends upon temperature, concentration and types of ions present (Hem, 1985). This ability depends on the presence of ions, their concentration and mobility. The extent of mineralization in water can be qualitatively measured by electrical conductance of water. It is an excellent indicator of dissolved solids present in water. EC measurement is an excellent indicator of TDS which is a measure of salinity that affects the taste of potable water (Unnisa and Khalillullah, 2004).

pH measurement was done using a digital pH meter (Model LI-127, ELICO). The instrument was calibrated for each set of measurement with standard buffer solutions.

2.5.3 **Solids**

Solids comprises amount of dissolved compounds and suspended particles present in water. It refers to matter suspended or dissolved in water. Solids may affect water or effluent quality adversely in a number of ways. The Total Dissolved Solids (TDS) normally consist of carbonates, chlorides, sulphates and nitrates of Na, K, Ca and Mg (Sudarshan and Reddy, 1991). Water with high dissolved solids generally is inferior in quality. TDS indicates the general nature of salinity of water (Singh, et al., 2004). Excessive TDS content gives an unpalatable mineral taste and has physiological and corrosive actions. It results in laxative action, affects cardiac patients, causes toxemia in pregnant woman (Trivedy, 1990). TDS corrodes and encrusts metal surfaces, damages water pipes, water heaters, toilet flushing system, clothes and dishwashers. Excessive TDS destroys aquatic plants, thus adversely affecting fish and other aquatic life (Alabaster, 1972) and water containing TDS in excess of 500 mg /L is not recommended for use in irrigation (Dierberg, 1991).

Insoluble particulate matter present in water is responsible for turbidity of water. These may be in organic or inorganic form, together known as Total Suspended Solids (TSS). TSS shelters micro organisms, reduces swimming efficiency of fishes and other aquatic life resulting in less growth and exposes aquatic life to micro organisms (Gower, 1980). The inorganic and biological particulate matter affects light penetration into water, thereby resulting in a decline of primary production, which cuts down food for fish (Joseph et al., 1984). If water with excessive TSS is used for irrigation, it leads to crust formation on topsoil preventing water and air penetration (Joy et al., 1990).

Total solids were determined by taking unfiltered water and evaporating it in a hot plate. 50 ml of water was taken in a pre-weighed (W1) clean 100 ml beaker. It was then allowed to evaporate carefully in a hot plate to dryness. The beaker was then allowed to cool for sometime and kept in a desiccator. The weight of the beaker was taken again (W2) and the total solids present in the water sample were measured as follows:

$$\text{Total Solids (TS), mg/L} = (W2 - W1) \times 1000 / V \qquad (15)$$

where, W2 = Final weight of the beaker and residue in g

W1 = Initial weight of the beaker in g

V = Volume of sample taken (50 ml)

For determining TDS of water samples, 50 ml of filtered water was taken in a 100 ml beaker. The weight of the empty beaker was taken (W1). The water was allowed to evaporate carefully on a hot plate. When no more water was there in the beaker it was allowed to cool for some time and kept in a desiccator and finally, the weight was taken (W2). TDS content was obtained from the relation

$$\text{TDS mg/L} = (W2 - W1) \times 1000/V \quad (16)$$

where, W1 = Final weight of the beaker and residue in g,

W2 = Initial weight of the beaker in g,

V = Volume of water sample taken (50 ml).

Total suspended solids present in a particular volume of water can be calculated as follows,

$$TSS = TS - TDS \quad (17)$$

2.5.4 Total Hardness

Hardness of water may be due to the presence of a number of dissolved polyvalent ions viz, Ca^{2+}, Mg^{2+}, Sr^{2+}, Fe^{2+}, Ba^{2+}, and Mn^{2+}. Amongst these, the first two are considered as the principal hardness causing ions in natural waters. The main source of these ions is sedimentary rocks, seepage and runoff from soils. Originally, water hardness was understood be a measure of the capacity of water to precipitate soap (Garg, 2003). Soap is precipitated chiefly by calcium and magnesium ions present. In conformity with the current practice, total hardness is defined as the sum of calcium and magnesium concentrations both expressed as calcium carbonate in mg/L. Hardness of water has a correlation with heart and kidney problem (Keller, 1979).

The total hardness of the water sample was measured by EDTA-complexometric method with Eriochrome Black T as an indicator:

Total hardness = mL EDTA used x 1000 / mL sample (18)

2.5.5 **Total Alkalinity**

Alkalinity of water is mainly due to the soluble carbonate and bicarbonate. The higher amount of alkalinity in groundwater imparts bitter taste to water and high values of alkalinity in surface water are indicative of the eutrophic nature of the water body (Kannan, 1991).

The total alkalinity is measured by acidimetric titration using different indicators that work in alkaline pH range (above 8.2) or in acidic pH range (below 6.0). For titration, the following reagents were prepared:

a) Phenolphthalein indicator – 0.25% solution in 60 % ethanol.
b) Methyl orange indicator – 0.5 % solution in 95 % alcohol.
c) Standard sulphuric acid - 0.02 N H_2SO_4

50 ml of water sample was taken in a beaker. To it, 2-3 drops of phenolphthalein indicator was added. Occurrence of pink colour indicates presence of carbonate and it was then titrated with standard 0.02 N H_2SO_4 until the colour just disappears. The volume of H_2SO_4 is noted. To this colourless solution, 1-2 drops of methyl orange indicator were added and the titration was continued till the colour changes from yellow to rose red. This corresponded to the total alkalinity. Final reading of H_2SO_4 volume was recorded.

Total Alkalinity, mg/L = (v x 0.02) x 1000/ mL of sample taken (i.e.50ml) (19)

where, v = ml of 0.02 N H_2SO_4 used with phenolphthalein and methyl orange indicators.

2.5.6 Sulphate

Sulphate is an indicator of hydrogeology and leaching of fertilizers into ground water (Madhuri et al., 2004). Water becomes rich with sulphate from different sources. A

large amount of SO_2 gas is released into atmosphere from coal and oil burning. It is a major component in air and highly soluble in water. SO_2 causes acid rain which damage plants and other aquatic systems and is ultimately transferred to water system through precipitation. When water is acidic, more sulphate content leads to corrosion of metals in the distribution system.

For determination of sulphate in water, the following reagents were required:

(i) Conditioning reagent: 75 mg of NaCl, 30 ml of conc. HCl, 100 ml 95% ethanol in 300 ml distilled water was taken together and to it 50 ml glycerol solution was added and mixed together

(ii) $BaCl_2$ dry crystals

(iii) Standard sulphate solution: 1479 g of anhydrous Na_2SO_4 was taken in 1 L of distilled water. This solution contained 100 mg/L of sulphate

100 ml of clear water sample was taken with 0.5ml of conditioning reagent. The sample was allowed to stir on a magnetic stirrer and a spoonful of $BaCl_2$ crystals were added and stirred for another 1 minute. After allowing the mixture to stand exactly for 4 minutes, optical density was measured on a spectrophotometer (Hitachi U3210) at 420 nm. A standard curve was prepared by the same procedure taking standard solutions of 5, 10, 15, 20, 30, and 40 mg/L. The sulphate content of the water sample was read from the calibration curve.

2.5.7 Nitrate

Nitrogen is present everywhere. Generally it comes to water as nitrate. Atmosphere N comes to earth as acid rain or is fixed in soil by bacteria. Most common sources of nitrate in water are domestic wastes, industrial effluents, fertilizers, decayed matter, sewage sludge, etc. Consumption of nitrate-rich water by infants causes methaemoglobinaemia. Nitrates can be readily converted to nitrite inside the body and the nitrites can give rise to the carcinogenic nitrosamines (Nawlakhe et al., 1995).

Nitrate was determined with the following reagents:

a) Standard nitrate solution: 0.7218g/L KNO_3 was dissolved in 1 L of distilled water (1.00 mL = 100 μg NO_3^--N)

b) Intermediate nitrate solution: 100 ml of stock nitrate solution diluted to 1000 ml with distilled water (1.00 ml= 10 μg NO_3^- - N)

c) 1 N HCl

50 ml of clear water sample was taken with 1 ml of HCl and was mixed thoroughly. Absorbance was read with a UV-Visible spectrophotometric (Hitachi U3210) at 220 nm to obtain NO_3^- reading and at 275 nm to determine interference due to dissolved organic matter. NO_3 calibration standards in the range 0 to 7 mg NO_3-N/L were prepared by diluting 50 ml of intermediate nitrate solution. The correction was applied for both sample and standard, by subtracting two times the absorbance reading at 275 nm from the reading at 220 nm to obtain absorbance due to NO_3. A standard curve was constructed for absorbances of NO_3-N of standard solutions.

2.5.8 Phosphate

Phosphorus remains in water as phosphate. Phosphorus is essential for the growth of organisms and can be the nutrient that limits the primary productivity of a body of water that stimulates the growth of photosynthetic aquatic micro and microorganisms in nuisance quantities. Soluble phosphorus can be lost in surface runoff waters, but is usually found adsorbed to soil particles transported by erosion. Phosphorus in runoff has been implicated in eutrophication (excessive algal growth) of lakes and streams.

The concentration of phosphate in water was measured spectrophotometrically. 100ml filtered water sample was taken with 4 ml ammonium molybdate solution and 5 drops of $SnCl_2$ solution. After 12 minutes optical density was measured spectrophotometrically at 690 nm ((Hitachi U3210). A standard curve was prepared by the same procedure taking blank and standard solutions of concentration 0.01, 0.02, 0.05, 0.1, 0.2, and 0.5 mg/L and the phosphate concentration of sample water was read from the curve.

2.5.9 Chloride

Chloride is a harmless constituent of all natural water and is generally not classified as a harmful constituent. In potable water, the salty taste produced by chloride concentration is variable and dependent on the chemical composition of water. Some waters containing 250 mg/L may have a detectable salty taste if the cation is sodium. On the other hand the typical salty taste may be absent in waters containing as much as 1000 mg/L when the predominant cations are Ca and Mg (Garg, 2003). Lochart et al. (1995) have reported that the taste threshold for chloride ion in water varies between 210 to 300 mg/L and also high concentration of chloride in water would cause unpleasant taste. In surface water, the high concentration of chloride is normally due to sewage and many of the soluble salts found in soil (Banerjee, 1994). Chloride may come to the water sources from animal and human waste. Chloride is the best indicator of pollution (Rai, 1975) and it is the most troublesome anion for irrigation in the sense that it is toxic to the plants.

Chloride was estimated by the argentometric titration method. 50 ml of sample was taken with 5-6 drops of 5% K_2CrO_4 and titrated with 0.02 M $AgNO_3$ till reddish brown precipitation was obtained. Chloride content is calculated as follows:

Chloride, mg/L = [(Titre reading x 0.02) x 1000 x 35.5] / Volume of sample (50 ml)

2.5.10 Fluoride

Fluoride comes to ground water from geological deposits, geochemistry of the location and the application of fertilizer like rock phosphate or fluorapatite. When water passes over or through fluoride bearing mineral deposits, a portion is dissolved and the water then contains a certain quantity of fluoride (Murali Krishna et al., 2003). Fluoride ions are likely to be leached out gradually, particularly on alkaline soils and move along with waterfront. Water with high fluoride content may cause serious health hazards including dental and skeletal fluorosis along with secondary neurological complications (Susheela, 1993). The water samples, which show higher concentration of fluoride, assume importance in view of the fact that fluorides in drinking water are responsible for human ailments, like dental anomalies and bone deformation (Sinha and Kant,

2003). More content of fluoride in surface water affects hatching of eggs in fish (Barik and Patel, 2004).

Fluoride was estimated spectophotometrically by the SPADNS method. Fluoride reacts with the coloured complex of zirconyl acid and SPADNS [Sodium-2-(parasulphopherylaze) 1,8-dihydroxy–3,6-naphthalene disulphonate] forming colorless $[Zr\ F_6\ ]^{-2}$ and releasing the dye. The decrease in intensity of the colour can be used to determine fluoride. The following reagents were prepared

a. SPADNS solution. 479 g of SPADNS was dissolved in 250ml distilled water.
b. 133 mg zirconyl chloride octahydride ($ZrOCl_2$, $8H_2O$) was dissolved in 25ml distilled water to which 350 ml of conc. HCl was added. The volume was made up by distilled water to 500 ml.
c. 221 mg of NaF was dissolved in 1 L of distilled water. 100 ml of the solution was made up to 1 L with distilled water to obtain a 100 ppm fluoride solution. A series of standard solutions containing 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 5.0, and 6.0 mg F/L was prepared.
d. Reference solution. 10ml of SPADNS solution was taken and the volume was made up to 100 ml with distilled water. To it, 7 ml conc. HCl and 3 ml distilled water were added. The resulting solution was used for setting the instrument reference point (zero).

To determine F^- in water samples, 50 ml of sample was taken and to it, 5 ml each of SPADNS and zirconyl acid reagents were added and mixed. After a few minutes, absorbance was measured at 570 nm (Hitachi U3210). Fluoride concentration was read directly by operating the instrument in photometry mode calibrating against a blank and standard solution.

2.5.11 Oil and grease

Oil and grease are used in domestic and industrial activities. These come to the environment as wastes in different forms with water or soil. If this waste is not managed

properly, it can cause major environmental problems. Animal and vegetable -based oil and grease often enter the wastewater collection system in the liquid form. An important property of oil and grease is its ability to separate and float on the water, in other words, they are hydrophobic compounds. Once in the wastewater collection system, these oil and grease cool and solidify. Grease will cling to sewer pipes and the surface causing a clog to form from the top of the pipe. These blockages and subsequent spills are unsightly, clean up is difficult, time consuming and costly (Fats, oil and grease manual, 2002). Again oil and grease present in surface water prevent O_2 from entering water. It also coats fish gills causing problems to aquatic biota even at low concentration.

To determine oil and grease, 250 ml water sample was taken in a separating funnel with of 10 ml. H_2SO_4 (1:2 mixture of H_2SO_4 , 50 ml conc. H_2SO_4 acid and 100 ml distill water) and 50 ml petroleum ether, and a little ethanol. The whole solution was shaken for a while and was allowed to stand for some time. The lower layer was discarded and the petroleum ether was drained out through a filter paper soaked in a pre-weighted (W1, g) glass beaker. Some more petroleum ether was allowed to pass through the filter paper so that no oil and grease remain stuck to the paper. The beaker was kept in a hot water bath so as to evaporate the ether. The weight of the beaker was recorded with the residue (W2, g) remaining. The oil and grease was calculated from the following relation:

Oil and grease, mg/L = [(W2 – W1) x 1000] / Volume of sample (50 ml)

2.5.12 Phenol

It is well known that phenol compounds enter pools with the sewage of woodworking enterprises, oil refining, and coal mining and chemical industries. However, a huge variety of phenol compounds are generated *in vivo*. Natural compounds in surface waters are encountered not only as free dissolved species; they also take part in condensation and polymerization reactions and produce humic complexes and polyaromatic compounds. The phenol concentration in aquatic ecosystems depends on the season (Tchaikovskaya et al., 2001). The phenol compounds differ by their toxic and organoleptic properties, chemical inertness, and sensitivity to

microbiological cleavage. Therefore, some of them are rapidly oxidized in the aquatic environment or are metabolized by microbial communities, whereas others remain unchanged for a long time or are accumulated in a pool, thereby bringing the actual threat to microorganisms (Kondratieva, 2000). The US Environmental Protection Agency (EPA) has decided that waters (lakes, streams) should be limited to 0.3 milligrams phenol per liter of water (0.3 mg/L) to protect human health from the possible harmful effects of exposure to phenol by drinking water and eating contaminated water plants and animals.

Phenol is determined spectrophotometrically. For this purpose, the following reagents were prepared

A. Stock phenol solution was prepared by taking 1 g phenol in freshly boiled and cooled 1 L distilled water.

B. Phenol solution of intermediate strength was prepared by taking 10 ml of the above solution in freshly boiled and cooled 1 L distilled water (1ml = 10μg phenol).

C. Standard phenol solution was prepared by taking 50 ml of the above solution in freshly boiled and cooled 1 L distilled water (1 ml = 1 μg phenol).

D. 0.5 N NH_4OH.

E. Phosphate buffer was prepared by taking 104.5 g K_2HPO_4 and 72.3 g KH_2PO_4 in 1 L distilled water.

F. 2 g of 4-aminoantipyrine was dissolved in 100 ml distilled water.

G. 8 g potassium ferricyanide, $K_3Fe(CN)_6$ was dissolved in 100 ml D/W.

100 ml of water sample was taken with 2.5 ml of NH_4OH and 2 ml of phosphate buffer. To this, 1 ml of 4-aminopyrine and 1 ml $K_3Fe(CN)_6$ were added and mixed well. After 15 min, absorbance was read at 500 nm spectrophotometrically (Hitachi U3210). A calibration curve was obtained with the standard solutions of phenol in the same way and with the help of this, the concentration of phenol in the various water samples was determined.

2.5.13 Common metals, Ca, Mg, Na, K

Ca, Mg, Na, and K are most common metals present in almost all sources of water. In drinking water, the presence of these elements may be beneficial for human being but toxic if concentration is more as well as used for a long period. The presence of calcium in water supplies results from passage through or over deposits of limestone, dolomite, gypsum and gypsiferous shale. It is an essential constituent of human being and low content causes rickets and defective teeth. It is also one of the nutrients required by different organisms. Ca in excess may increase the total hardness of water preventing lather with soap and increase the boiling point of water (Mohan et al. 2000). Increase in calcium ion concentration tends to cause precipitation of insoluble calcium phosphate. Calcium with chloride induces acidosis as the cation is not readily absorbed and so an excess Ca ion enters the blood and displaces the plasma bicarbonate resulting in clotting of blood (Bell et al. 1961).

The concentration of Mg in water is comparatively less than Ca. Excess Mg^{2+} causes scale formation in public distribution system (Singanan et al. 1996). Excessive consumption of magnesium acts as a depressant to the central nervous system, including narcosis. Too much magnesium reacts with carbonate causing belching and creates diarrhea. Calcium forms a double non-ionisable compound with magnesium and is therefore antidotal and leads to a cathartic action (Lohani, 2005). Magnesium hardness when exceeds ISI permissible limits (30-50 mg/L) may be cathartic and diuretic (Lalitha et al. 2004). Drinking water with high concentration of chloride may corrode the iron pipes in presence of Mg^{2+} ions used for ground water pumping (Jayashree, 2002). High salts like chloride, magnesium and calcium indicate a saline taste (Patil et al. 2003). Ca and Mg in water are responsible for scale formation in boilers, pipes and utensils.

Calcium was determined titrimetrically with EDTA solution using murexide as an indicator from the following formula:

Calcium, mg/L = (Volume of EDTA used x 400.8) / (Volume of sample taken)

Both calcium and magnesium form a complex of wine red colour with eriochrome black T at pH 10.0. The EDTA has got a strong affinity for Ca^{++} and Mg^{++} and

therefore, the complex with the dye breaks down and a new complex of blue colour is formed.

Magnesium, mg/L = [(y-x) x 400.8] / [ml of sample taken x 1.645]

where, y = EDTA used in hardness determination

x = EDTA used in calcium determination for the same volume of sample.

Sodium is the most common alkaline metal found in water. The ground and surface waters having high concentration of sodium are not good for consumption. It gives bitter taste to water and is dangerous for heart and kidney patients whereas high sodium in surface water is toxic for plants and aquatic life (Kellar, 1979). Persons affected with certain diseases require low sodium concentration. Intake of 100 mg/L of Na is known to raise blood pressure in children (Calabrese and Tuthill, 1977).

Potassium is another naturally occurring alkali metal found in natural sources of water. The concentration of this element is generally found low in comparison to sodium. Main source of this element in water is from weathering of rocks. It has similar chemistry with sodium. It has no adverse effect on human beings. For plants potassium is an essential element for growth.

Sodium and potassium were determined flame photometrically (Model CL 361) using standard calibration technique.

2.5.14 Trace metals, Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn

Aluminum. Al is the most abundant metal in the earth's crust (Storey and Masters, 1995; Glynn et al., 1999). Typically, a portion of the alum added to the raw water is not removed during treatment and remains as residual aluminum in treated water (Driscoll and Letterman, 1988; Van Benschoten and Edzwald, 1990). There is considerable concern throughout the world over the levels of aluminum found in drinking water sources (raw water) and treated drinking water (Srinivasan et al., 1999). A high (3.6 to 6 µg/L) concentration of aluminum may precipitate as aluminum hydroxide giving rise to

consumer complaints (Srinivasan et al., 1999; Lopez et al., 2002). Aluminum is also a suspected causative agent of neurological disorders such as Alzheimer's disease and presenile dementia (Srinivasan et al., 1999; Lopez et al., 2002; Gardner and Gunn, 1991; Jekel, 1991). The EPA drinking water standard for aluminum is 50 μg /L (Dezuane, 1997). Aluminium is acutely toxic to fish in acid waters (Chappell et al, 1991).

Arsenic. It is widely thought that naturally occurring arsenic dissolves out of certain rock formations when ground water levels drop significantly. Arsenic is ubiquitous in the environment, usually being present in small amounts in all rocks, soils, waters, air and biological tissues (Nriagu and Pacyna, 1988). Surface arsenic-related pollutants enter the ground water system by gradually moving with the flow of ground water from rains. Elevated concentrations were found in polluted environment (Nriagu and Azcue 1990). Prolonged exposure to arsenic can cause very serious health problems. Exposure to arsenic has been identified as a long-term cause of skin lesions, gangrene, cardiovascular disease, pulmonary disease, neurological disease, hypertension, peripheral vascular disease, diabetes mellitus, skin cancer, bladder cancer, lung cancer and cancer of the kidneys. In high concentrations, arsenic poisoning can also lead to an acute condition called arsenicosis (MAGC, 2001). The maximum permissible limit in drinking water is 0.01 mg/L (WHO, 2004).

Cadmium. Cd is found as natural deposits as ores. The greatest use of cadmium is primarily for metal plating and coating operations including pigment. Major industrial releases of cadmium are due to waste streams and leaching of landfills, and from a variety of operations that involve cadmium or zinc. In particular, cadmium can be released to drinking water from the corrosion of some galvanized plumbing and water main pipe materials. Some cadmium compounds are able to leach through soils to ground water. When cadmium compounds do bind to the sediments of rivers, they can be more easily bioaccumulated or re-dissolved when sediments are disturbed, such as during flooding. Its tendency to accumulate in aquatic life is high in some species, low in others. The cadmium-rich sludge can pollute surface waters as well as soils.

Chromium. Leaching from topsoil and rocks is the most important natural source of chromium entry into water. Cr can strongly attach to soil and only a small amount can dissolve in water and move deeper in the soil to underground water. It is recognized as an extremely significant pollutant due to its high toxicity and large solubility in water (Pinto et al., 2004). Chromium often accumulates in aquatic life, adding to the danger of eating fish that may have been exposed to high levels of chromium (Lenntech, 2006). The maximum permissible limit of chromium in drinking water as per WHO is 0.05 mg/L.

Chromium is used in metal alloys and pigments for paints, cement, paper, rubber, and other materials. Low-level exposure can irritate the skin and cause ulceration. Long-term exposure can cause kidney and liver damage, and also circulatory and nerve tissues. Electroplating, leather tanning, and textile industries release relatively large amounts of chromium in surface waters. Solid wastes from chromate-processing facilities, when disposed of improperly in landfills, can be sources of contamination for groundwater, where the chromium residence time might be several years

Copper. It is recognized as a harmless and essential element. Copper in our diet is necessary for good health. Drinking water normally contributes approximately 150 µg/day. The levels of copper in surface and groundwater are generally very low. High levels of copper may come from fertilizers, septic systems, animal feedlots, industrial waste, and food processing waste. Copper may occur in drinking water either from contaminated well water or corroded copper pipes. Corrosion of pipes is by far the greatest cause for concern (NSF, 2003). Copper salts are discharged through industrial wastewaters. Also they are used to control of biological growth in reservoirs and water transport lines.

Although copper is an essential micronutrient, but in high concentration causes taste and odor in water and also has physiological effects in humans. Presence of copper along with zinc, iron and lead is network corrosion suggestive (Zuan, 1997). In aquatic system large amount of Cu is harmful to organisms but its concentration is governed by other factors like total hardness and pH (Dixit and Witcomb, 1983). Immediate effects from

drinking water which contains elevated levels of copper include vomiting, diarrhea, stomach cramps, nausea. The seriousness of these effects can be expected to increase with increased copper levels or length of exposure (USEPA, 2003). Drinking water with high levels of copper for many years could cause liver or kidney damage (WHO 2004, Permissible limit 2.0 ppm). Abnormal accumulation of Cu is associated with a genetic defect known as hepato-lenticular degeneration (David et al. 1965).

Iron. The concentration of iron in most of surface water resources is high, due to the presence of iron salts in watersheds and as a constituent of riverbed. Increase of iron in water results in forming of suspended and colloidal particles in combination with organics or minerals. Iron in drinking water may be present as geological sources, industrial wastes and domestic discharges and also from mining products. Although the presence of iron has no health effects, but in high concentrations, it affects water quality, causes sediment agglomeration in distribution networks, accelerates iron bacteria growth, and consequently increases corrosion in network (Walter, 1981). The maximum permissible concentration of iron in drinking water is 0.3 mg /L (WHO, 2004). A low amount of this element is harmful. In presence oxygen or after chlorination, it is precipitable as oxide and forms a black sludge, which affects taste, odor and quality of water. Excess amount of iron (more than 10 ppm) causes rapid increase in respiration, pulse rate and coagulation of blood vessels (Garg, 2003).

Mercury. Mercury is or has been used, in electrical appliances (lamps, arc rectifiers, mercury cells), in industrial and control instruments (switches, thermometers, barometers) and in laboratory apparatus. Mercury can be released in ground water or in surface water by industrial wastewater discharge in rivers and land. The solubility of mercury compounds in water varies: elemental mercury vapour is insoluble, mercury (II) chloride is readily soluble, mercury (I) chloride is much less soluble and mercury sulfide has a very low solubility. Mercury can or cannot be toxic, depending on its chemical bonds. Fish and fish products account for most of the organic mercury in food. The average daily intake of mercury from food is in the range 2–20 μg, but may be much higher in regions where ambient waters have become contaminated with mercury and where

fish constitute a high proportion of the diet (Galal-Gorchev, 1991). Methylation of inorganic mercury is an important process in water and occurs in both fresh water and seawater (IPCS, 1989). Bacteria (*Pseudomonas* spp.) isolated from mucous material on the surface of fish and soil was able to methylate mercury under aerobic conditions. Some anaerobic bacteria that possess methane synthetase are also capable of mercury methylation (Wood & Wang, 1983). Once methylmercuryl is released from microbes, it enters the food chain as a consequence of rapid diffusion and tight binding to proteins in aquatic biota.

Manganese. Mn generally occurs with iron. It is an essential component of diet for normal humans but in excess, does not have any adverse effect (Lohani, 2005). It is involved in glucose utilization (Forstner and Wittmann, 1983). The maximum permissible limit for Mn in drinking water is 0.4 mg/L (WHO, 2004). Manganese accelerates bacterial growths (e.g. manengobacteria), which have taste and odor problems in drinking water (Maleki et al. 2005). At high concentrations in water, it will deposit on food during cooking, stains on sanitary ware, discolouration of laundry, deposits on plumbing fittings and cooking utensils. The presence of high level of Mn renders water unsuitable in certain industrial applications such as textile dyeing, food processing, distilling and brewing, paper, plastic and photographic plate industries.

Nickel. Small amounts of nickel are needed by the human body to produce red blood cells, however, in excessive amounts, it can become mildly toxic. Short-term over-exposure to nickel is not known to cause any health problems, but long-term exposure can cause decreased body weight, heart and liver damage, and skin irritation. The EPA does not currently regulate nickel levels in drinking water. There are no acceptable standards for nickel (Amman, 1995). Nickel can accumulate in aquatic life, but its presence is not magnified along food chains. Nickel salts enter surface waters through industrial wastewater. Nickel compounds have lower toxicity in comparison with other compounds. Presence of nickel inclined to carbonyl ions has remarkable toxicity. There are some reports on serious damages due to accidental drinking of water polluted by

nickel (WHO, 1991) through leaching from Ni containing pipes etc. Water-soluble Ni compounds have been known to cause nickel dermatitis on skin contact with humans and also have been responsible for causing respiratory tract irritation and asthma in industrial workers through inhalation (Fishbein, 1991).

Lead. Pb in the environment arises from both natural and anthropogenic sources. Exposure can occur through drinking water, food, air, soil and dust from old paint containing lead. In the general non-smoking, adult population the major exposure pathway is from food and water. Food, air, water and dust/soil are the major potential exposure pathways for infants and young children. For infants up to 4 or 5 months of age, air, milk formulae and water are the significant sources. In humans exposure to lead can result in a wide range of biological effects depending on the level and duration of exposure (Lenntech, 2006). The maximum permissible concentration of Pb in drinking water is 0.1 mg /L (WHO,2004).

Zinc. In natural surface waters, the concentration of zinc is usually below 10 µg/l, and in groundwater, 10–40 µg/l (Elinder, 1986). In tap water, the zinc concentration can be much higher as a result of the leaching of zinc from piping and fittings (Nriagu, 1980). Zn is required for human metabolism and growth. Drinking water usually makes a negligible contribution to zinc intake unless high concentrations of zinc occur as a result of corrosion of piping and fittings. Under certain circumstances, tap water can provide up to 10 % of the daily intake (Gillies and Paulin 1982; Lahermo, 1990). However, drinking water containing zinc at levels above 3 mg/litre tends to be opalescent, develops a greasy film when boiled, and has an undesirable astringent taste (WHO, 1996).

2.5.15 Extraction of the metals and Analysis

In this work, nitric acid digestion technique (APHA 1995) was used. For this purpose, a volume of 100 mL each of acid-preserved, well-mixed water samples was taken in a beaker, 5 mL of conc. HNO_3 was added and the mixture was slowly evaporated on a hot plate in a fume-hood to a volume of 10 – 20 mL of clear solution.

The beaker walls were washed with double-distilled water and the volume was remade to 100 mL in a volumetric flask.

The metals were estimated using AAS technique (Varian SpectrAA 220) with air acetylene flame and standards prepared in triple distilled water.

2.5.16 Extraction and determination of heavy metals in rice and husk

The collected rice grains were separated from husk. The husks and seeds were dried separately in an oven at ~50^0C and ground finely by a grinding machine. 1 g of finely ground rice grain and 1 g of husk were kept separately in crucibles and subsequently placed in a muffle furnace at a temperature 500 – 550 oC for a period of 4 hours. Thereafter, the crucibles were cooled and the residues were treated with an excess of 1N HNO_3 and evaporated to dryness on a hot plate. They were again placed in the muffle furnace at 500 ±10 oC for about 10 minutes. The perfectly clean white ash was then cooled. These were further treated with about 5 ml of 1N HNO_3 and swirled to dissolve the residue with addition of 5 ml of distilled water. The mixtures was filtered a number of times by washing the residue with small amounts of distilled water. It is collected in a volumetric flask and was made up to 50 ml by adding distilled water. The metals were determined with AAS using the formula:

$$\text{Metal, mg/L} = (\text{AAS reading} \times L \times M) / W$$

Where, L = Fill up volume in sample dissolution

M = Further dilution ratio.

W = The weighed amount of the sample.

The detailed experimental conditions used for AAS analysis are given in Table2.2