CHAPTER - 2

MATERIAL AND METHODS

2.1 DESCRIPTION OF THE SAMPLING SITES:

Nagaon paper mill (NPM) site is about 6 KM from river Kopili. The effluent from the mill after treatment in ETP plant is discharged into drain which comes through several beels (big water reservoirs) such as Elenga, Taranga, Eyang, Italiapara and ultimately it falls to river Kolong, a tributary of the mighty river Brahmaputra, after traversing a zigzag course of 25 Km. The average effluent generation, which was discharged to the beel was 46089 kl per day (range-35110 to 51290, kl/day) during August 1996 to July 1997.

The maximum-recorded flow of this river Kolong is around 2000 m³/s and minimum of about 25 m³/s.

2.2 SAMPLING STATION AND FREQUENCY OF COLLECTION OF WATER AND EFFLUENT SAMPLES.

Water samples were collected monthly from all sampling station for a period of one year from August 1996 to July 1997. Selections of the sampling sites were decided keeping in mind the overall objectives of the study. The present study included eight locations starting from Junction box before ETP to confluence point. The sampling stations for collection of samples were chosen one at junction box (JB) to know the characteristic of the effluent before the
treatment and one sampling station - 1 at the outlet, ETP just after the treatment of the effluent and sampling stations 2,3,4,5, and 6 at natural beel water system. The sampling station - 7 was at the up stream of the river Kopili, at a distance of 6 km from mill site and was not polluted by the paper mill effluent. The different sampling stations were shown in Fig.2.1. The sampling stations were tabulated in the Table no.2.1 with the approximate distance from NPM. For comparison purpose water samples from sampling station - 7 were collected and analyzed.

Table no.2.1:

Location of sampling stations for water, effluent and bed sediments.

<table>
<thead>
<tr>
<th>Sampling station no.</th>
<th>Name of sampling stations</th>
<th>Approximate distance From NPM in km</th>
</tr>
</thead>
<tbody>
<tr>
<td>J.B.</td>
<td>Junction Box</td>
<td>0</td>
</tr>
<tr>
<td>1.</td>
<td>Outlet of lagoon</td>
<td>0</td>
</tr>
<tr>
<td>2.</td>
<td>Elenga beel</td>
<td>3</td>
</tr>
<tr>
<td>3.</td>
<td>Chakomako</td>
<td>6</td>
</tr>
<tr>
<td>4.</td>
<td>Ajuri</td>
<td>11</td>
</tr>
<tr>
<td>5.</td>
<td>Malobari</td>
<td>18</td>
</tr>
<tr>
<td>6.</td>
<td>Italapar (confluent point)</td>
<td>25</td>
</tr>
<tr>
<td>7.</td>
<td>Up stream of river Kolong (Haliamukh)</td>
<td>6</td>
</tr>
</tbody>
</table>

The analysis of water samples for all other parameters excepting heavy metals were collected once in every month for a period of one year starting from August 1996 to July 1997. However, the measurement of heavy metals for water samples had been done quarterly for a
period of one year starting from September 1996 to June 1997. (i.e. September, December, March and June).

2.3 SAMPLING STATIONS AND FREQUENCY OF COLLECTION OF BED SEDIMENT SAMPLES

Bed sediment samples were collected from the bed of the effluent-receiving stream from sampling station - 1 to the river, Kolong and Kopili. The sediment samples were also collected from the same sampling stations (except from sampling station JB) from where water samples were drawn. The samples were collected quarterly for a period of one year from September 1996 to July 1997, on the first week of each month during 7.00 am to 9.00 am. The bed sediment samples with an average depth of 0-15 cm were collected from the course of beel bed to the river bed. The samples of sediments were collected with the help of Eckman dredge.

The bed sediment were collected and analyzed as per standard procedures. The sampling stations for collection of bed sediment were also shown in Fig.2.1. The sampling stations were tabulated in the Table no.2.1 with the approximate distance from NPM.

2.4 SAMPLING STATIONS AND FREQUENCY OF COLLECTION OF GROUNDWATER SAMPLES

Nagaon paper mill is surrounded by hills and villages. Seven villages around the Nagaon paper mill were considered for collection of groundwater samples. The samples were collected
from deep wells. The sampling stations of groundwater around Nagaon paper mill are shown in fig.2.2. The location of sampling stations for groundwater samples were given in Table 2.2 with the approximate distance from Nagaon paper mill.

Table 2.2:

<table>
<thead>
<tr>
<th>Sampling station no.</th>
<th>Name of location</th>
<th>Approximate distance from NPM (km)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Amlighat</td>
<td>3-4</td>
</tr>
<tr>
<td>2.</td>
<td>Sindhikhar</td>
<td>6-7</td>
</tr>
<tr>
<td>3.</td>
<td>Deosal</td>
<td>1-2</td>
</tr>
<tr>
<td>4.</td>
<td>Nakhola</td>
<td>0.5-1</td>
</tr>
<tr>
<td>5.</td>
<td>Tegheria</td>
<td>1-2</td>
</tr>
<tr>
<td>6.</td>
<td>Ajiuri</td>
<td>10-11</td>
</tr>
<tr>
<td>7.</td>
<td>Chakomako</td>
<td>6-7</td>
</tr>
</tbody>
</table>

Water samples were collected during December 1996 and June 1997 from deep wells, used by the local inhabitants for drinking / domestic purposes. Water samples were collected in the sample containers, which were washed and rinsed with distilled water.
FIG. 2.1: SAMPLING STATIONS ON EFFLUENT DISPOSAL ROUTE AND UPTAKE RIVER WATER OF NAGAON PAPER MILL.
FIG. 2.2: SAMPLING STATIONS OF GROUND WATER, AROUND NAGAON PAPER MILL.
2.5. METHODOLOGY FOR WATER, EFFLUENT AND BED SEDIMENT SAMPLES

The analysis of the beel water, effluent and bed sediment samples were done as per the standard procedures\textsuperscript{1-5}. The methods selected in this investigation often dependent upon the availability of particular equipments in the laboratory. The chemicals used were mostly of analytical grade. The determination of heavy metals in water and bed sediment samples were done with the help of Shimadzu AA-680, Atomic Absorption spectrophotometer by atomizing aqueous samples in air acetylene flame. The determination of mercury in effluent, water and sediment samples was carried out with the help of mercury analyzer (ECL-2). Metals like sodium and potassium were determined with the help of flame photometer (Systronic-121).

Parameters like PH, and turbidity of water, effluent samples were determined immediately, after collection of samples. For all other parameters analysis were completed as soon as possible in the laboratory after preservation of samples as per the procedure describe\textsuperscript{1}.

The numbers of parameters that have been used now a days to measure water, effluent and bed sediments quality are very large. In the present work the parameters chosen were given in 1.5.3 for effluent and water samples, 1.5.4 for bed sediment samples and 1.5.5 for groundwater samples.

The collection of sample of sediment was not easy because of several factors, viz - creeping of sediments of the beel and river bed, variation in the quality of sediments according to seasonal variation, disturbances caused in the original distribution pattern due to agricultural activities, such as irrigation the water from the beel system to the agricultural field, fishing of
becl etc. The soil samples were kept in a wide mouth plastic container, which was washed and dried and brought to the laboratory for further processing prior to analysis.

The samples were kept scattered under the sun on a plain paper for about 3 hours. The air-dried samples were crushed with a wooden pestle in a wooden mortar and sieved through a 2 mm screen. The 2 mm sieved soil is suitable for determination of water-soluble parameters. The 0.5 mm sieved soil samples were used in the determination of organic matter. For estimation of heavy metals nylon sieve was used. Generally a conventional ratio of 1:5 (soil: water) is adopted for determination of soluble salts. For determination of heavy metals, the dried soil samples weighing 1g were digested in concentrated nitric and perchloric acid (5:1) to destroy organic matters. The residue was dissolved in dilute HCl and heavy metals were analyzed as usual.

2.6. NATURE, SIGNIFICANCE, PRINCIPLE AND PROCEDURE OF MEASUREMENT OF DIFFERENT PARAMETERS

2.6.1. PH.

The PH is one of the most characteristic features of water quality, which controls the aquatic environment. PH is the measure of the intensity of alkalinity and measures the concentration of hydrogen ions in water. It does not measure total acidity or alkalinity. All chemical and biological reactions are directly dependent upon the hydrogen ion concentration. The principal sources that regulate the PH in natural water are carbon dioxide, carbonic acid, bicarbonate ion and carbonate ion. PH of water gets drastically changed with time due to the exposure to air, biological activity and temperature changes. Significant changes in PH of natural water occur due to disposal of industrial wastes, acid mine drainage etc.
Further, it can also be argued that due to high turbidity on elevated water temperature, the photosynthetic process by the green aquatic flora may be stopped leading to accumulation of free CO₂, which ultimately lower the PH of water. The PH of the sewage water shows alkalinity due to the presence of sufficient carbonates variation in PH, and shows no relationship with DO⁶. Under natural conditions the value of PH in surface water range from around 5.0 to 8.6. PH is the most important variable in raw water that will affect the process of coagulation⁹. It is an important parameters in water quality study as it influences the degree of toxicity of many pollutants and also determines the solubility of metals from bottom sediments¹⁰.

PH of effluent, surface water, groundwater and sediment samples was measured with the help of digital PH meter, with temperature compensation arrangement.

In soil, PH is a very important property because, it determines the growth of the plants availability of nutrients, bacterial activity and its physical conditions. If soil is strongly acidic or alkaline, nothing may grow. For each species of plant, there is a PH range favorable for the growth of plants. PH of soil is the measure of hydrogen ion activity and depends in relative amounts of the absorbed hydrogen and metallic ions. It is a good measure of acidity and alkalinity of soil water suspension and provides a good identification of the soil chemical nature. PH of soil suspension highly depends on the soil to water ratio and increases with dilution.

The PH of bed sediments was determined as such, and as air-dry samples (soil: water = 1: 2.5 and soil: water = 1: 5). 20 grams of sediments was dissolved in 100 ml – distilled water. It was stirred with the help of glass rod for about an hour at regular intervals. The PH was determined with digital PH meter. (Systronic-335).
2.6.2 SUSPENDED SOLIDS (SS)

All contaminants of water other than dissolved gases contribute to the solid load, which may be classified by their size, state, chemical characteristics and size distribution. Suspended matter can be inorganic or organic including soil and mineral particles. Inert inorganic materials like clay, talc, titanium oxide and calcium carbide etc have no specific polluting effect. However, due to presence of suspended matters and colloidal particles, it imparts turbidity to natural waters. It will also reduce the sunlight affecting the photosynthetic activity essential to maintain healthy condition in a stream. In natural waters the suspended solids are less than sewage or industrial effluents. No specific limit has been described for suspended solids in water used for domestic and industrial purposes, but it is indirectly controlled by the limits on turbidity (5 units). The major part of the suspended solids in the paper mill effluent usually consists of fibers and fiber particles. Fiber are detrimental because they tend to settle in the receiving water, which will change the nature of the bed and affect fauna and flora, exert BOD on the water. In case of high organics in it, putrefaction may occur and stream be devoid of dissolved oxygen. Mineral and suspended matter can lead to silting and if the streambed is blanketed destruction of plant and animals life may occur. The Indian standard Institution has specified a maximum limit of 30 mg/l for suspended solids in wastewater discharged into watercourse. So the suspended solids are very objectionable in natural water. It has been reported that low concentrations below 25 mg/l of suspended matter is not harmful to fish life.

According to Shishkim, a river, receiving water from a paper mill indicated the water quality in the river to vary during the year with the largest seasonal variations in suspended solid.
A well-mixed sample of effluent and surface water was filtered through a standard glass-fiber filter prepared as per procedure. The residue retained on the filter was dried in an oven at 103 - 105 °C.

Suspended solids, mg/l = \[(A - B) \times 1000 / \text{sample volume, ml}\]

A = weight of the filter + dried residue, mg; B = weight of filter, mg

2.6.3. TOTAL DISSOLVED SOLIDS (TDS)

Dissolved solids include inorganic as well as organic matter and can affect various uses of water resources, if present in high concentration. The dissolved solids consist mainly of carbonates, chlorides, sulphates and nitrate as also sodium, potassium, calcium and magnesium with traces of iron, manganese and other substances. Excess dissolved solids impart physiological effects and unpalatable minerals taste on water and have corrosive properties. The physiological effects include laxative action due to sodium sulphate and magnesium sulphate. Fish and other aquatic animals have a large degree of tolerance, but they are indirectly affected due to elimination of desirable food plants by excess of dissolved salts. With the exception of lignin most of the dissolved materials are relatively rapidly degraded in the wastewater. In 1958 W.H.O. international standards set the permissible limits for dissolved solids as 500 mg/l and excessive limits as 1500 mg/l. Water with dissolved salts content more than 500 mg/l is not recommended for use in irrigation.

TDS of effluent, surface water and groundwater was determined as given in APHA. It is the portion of solid residue left after evaporation of filtered sample. 100 ml of filtered sample was evaporated in a pre-weighed evaporating dish prepared as per procedure (platinum for water...
sample and porcelain for effluent), on a water bath. The residue left after evaporation was dried at 103 – 105°C till a constant weight was obtained.

CALCULATION:

Total dissolved solids, mg/l = \( \frac{(W_1 - W_2) \times 1000 \times 10^0}{V} \)

Where, 
- \( W_1 \) = Final weight of the dish (in mg).
- \( W_2 \) = Initial weight of the evaporating dish (in mg).
- \( V \) = Volume of sample taken.

2.6.4 TEMPERATURE

Temperature is very important quality parameters. Measurement of temperature of water is basically important for its effects on the chemical, biochemical and biological activities, vapour pressure and the saturation values of solids and gases. The variety and distribution of aquatic organisms and other life forms greatly depend on water temperature\(^{14-16}\). An increase in temperature water leads to the speeding up of the chemical and biological activities in water, reduces the solubility of gases and amplifies the taste and odour. The biological activity is enhanced by higher temperature up to about 60° C. Similarly anaerobic decomposition is also largely affected by temperature change. At temperature above normal oxygen solubility in water is reduced appreciably leading to the obnoxious septic conditions and as temperature range of 7°
C to 11° C has a pleasant taste and is refreshing. Temperature of effluent, beel water and groundwater was recorded using a thermo probe at the site of collection.

2.6.5. ELECTRICAL CONDUCTIVITY (EC)

The electrical conductivity of water is based on the presence of ions. Conductivity is used to characterize the gross chemical characteristics of water and is measure of the ability to conduct an electric current. The electric current is transported by the ions in the solution, which increase as the concentrations of ions measure. The conductivity test is important as a guide in the determination of total dissolved salts and can be made by measuring the electrical conductance of water, sewage on effluents samples. The conductivity measurement of water samples is now regarded as the standard procedure for evaluating the salt content of natural waters.

The evaluation of the effects of salinity on the basis of conductivity measurements, which provides better estimates of osmotic pressure, is more reliable than based on salt concentrations expressed in percentage or ppm. There is a close relationship between plant growth and the osmotic pressure of soil solutions. An increase in the osmotic pressure of a soil solution result in a decrease in the water uptake by plant roots. Soluble salts decrease the availability of water by contributing osmotic pressure to the integrated total moisture stress. That is, the sum of the soil moisture tension on molecular attraction of the surface soil particles for water on the osmotic pressure of soil solution. Water having electrical conductivity of 5,000-20,000 micromhos/cm had been successfully used on light textured soils by Durad in Algeria. Water with EC 5,000-8000 micromhos/cm has no adverse effect on crop growth and germination of barley and wheat, when used on loamy sand to sandy soils.
The EC of effluent, beel water, groundwater and bed sediment was measured using digital conductivity meter. The EC of the soil was measured by preparing a saturated extract from a saturated soil paste.

2.6.6 TURBIDITY

Turbidity is a measure of the extent to which light is either absorbed or scattered by suspended materials in water. Suspended matter of various kinds is responsible for turbidity of water. Colloidal matter microscopic organisms, silt, clay etc. that does not settle readily are responsible for turbidity of water. Industrial wastes may add large amounts of organic and inorganic substances that produce turbidity. A high turbidity in water also indicates the presence of pathogenic organism or toxic substance and are, therefore a cause for concern. Suspended particulate matters causing turbidity may provide a safe habitat for various kinds of microscopic organisms and interferes with the effective disinfections by chlorine. The maximum turbidity limit prescribed by ISI is 10 NTU for domestic supply water. Turbidity caused by concern, since it has been found to be carcinogenic.

Turbidity of effluent, beel water and groundwater samples was measured using Nephelo turbidity meter 131-systromics.

2.6.7 ALKALINITY
Alkalinity of both natural and wastewater is an important parameter, because its value help in ascertaining addition of proper doses of chemicals in water and wastewater treatment processes. The alkalinity of natural or treated water is normally due to the presence of bicarbonates, carbonates, hydroxide, borates, phosphates, silicate and other bases.

The values have direct effect on organisms and on toxicity of certain pollutants. Alkalinity due to natural carbonates and bicarbonates is not a health hazards unless the value exceeds 400mg/l as calcium carbonates. Natural alkalinity helps to buffer PH change and is thus important for fish and other aquatic life. A minimum alkalinity of 20mg/l is recommended for this purpose. Excessive alkalinity causes eye irritation and damage to plant and soil.

Total alkalinity of effluent, beel water and ground was directly determined by titrating the samples with a standard sulphuric acid first to PH 8.3 using phenolphthalein indicator. This will show complete neutralization of 'OH and half of CO$_3^{2-}$. This is followed by another titration of same sample until the PH drops to 4.6 with methyl orange as an indicator. This will correspond to the total alkalinity e.g. OH$, C0_3^{2-}$, and HCO$_3^{-}$.

\[
\text{Total alkalinity, mg/l as calcium carbonate} = \frac{A \times T \times 1000}{\text{ml of sample}}
\]

A = ml of H$_2$SO$_4$ used

T = titer of standard acid, mg CaCO$_3$/ml
Like water total alkalinity, soluble carbonates and bicarbonates can be determined by the direct titration of the sediment solution with a strong acid (HCl) using methyl orange and phenolphthalein indicators.

1: 5 sediment suspensions was prepared by dissolving 20gm of soil in 100 ml of distilled water stirred mechanically for about an hour at regular interval. The suspension was filtered through whatman filter paper No 50 using Buchner funnel and vacuum pump.

The total alkalinity, carbonate and bicarbonate were analyzed in 100ml of soil solution following the procedure described for water sample.

2.6.8. TOTAL HARDNESS

The hardness of water is not a pollution parameter, but indicates water quality, mainly in terms of Ca$^{2+}$ and Mg$^{2+}$ ions, expressed as calcium carbonate. Polyvalent ions of some other metals like strontium; iron, aluminum, zinc and manganese etc. are also capable of precipitating the soap and thus contributing to hardness but to a little extent or to negligible amount. When hardness numerically is greater than the sum of carbonate and bicarbonate alkalinity, that amount of hardness equivalent to the total alkalinity is called "carbonate hardness". The amount of hardness in excess of this is called non-carbonate hardness. The carbonate hardness is due to bicarbonate and carbonate of calcium and magnesium while non-carbonate hardness is usually understood be the hardness produce by the equivalent proportions of chloride and sulfide to magnesium, calcium and strontium. The so-called non-carbonate hardness is ascertained purely by calculation, by subtracting the carbonate hardness from the total hardness. There are cases where the carbonate hardness is higher than the non-carbonate hardness.
The hardness of water reflects the nature of the geological formation with which the water is in contact. Generally surface waters are softer than groundwater. Soft water having hardness less than 30 mg/l is likely to be corrosive. Waters about 150 mg/l are reported to cause no harmful effects upon health of consumers. It is reported that sewage water carbonate hardness may be utilized for irrigation.

Total hardness of effluent, beel water and groundwater was determined by the EDTA titration method, using Eriochrome black-T as indicator. For wastewater preliminary treatment of samples were done as per the procedure given.\(^1\)

50 ml of effluent or water sample was taken in a 200ml conical flask. 1 ml of buffer solution was added. The solution became wine red after dissolving 100-200 mg of Eriochrome Black-T indicator. The content was nitrated with EDTA solution until red colour changed into blue.

\[
\text{Hardness as CaCO}_3 (\text{mg/l}) = \frac{\text{ml EDTA titrated} \times E \times 1000}{\text{ml of sample taken}}
\]

where, \(E = \text{mg of CaCO}_3 \text{ equivalent to 0.1 ml of EDTA}\)

2.6.9. CALCIUM

Calcium is one of the most abundant elements in natural waters. Calcium is reduced at higher PH due to precipitation as calcium carbonate.\(^2^3\) Calcium is an essential element and human body requires approximately 0.7 to 2.0 gm of calcium per day as a food element, which cannot be supplied even by hard water. Most common nutritional lack in many parts of the world...
is calcium deficiency. But high calcium content waters cause more soap consumption and other cleaning agents for washing, bathing and laundering. Lehr et al 1980 24 pointed out that concentration up to 1800 mg/l is not hazardous for any physiological reaction in man. Calcium is an important nutrient for plants as well as crops.

The interaction between calcium and hardness showed that under the impact of environment, a traditional sewage water structures might change its function and roles maintaining itself in the process. It would be wrong however to interpret the sewage water in terms of pollution process as calcium has its influence both in plants and animal life 25. By decreasing, calcium into its competitive structure, this find its base in the water regularly and by subjecting itself to the rules of competitive action both calcium hardness has its own characteristics. It is beneficial in reducing the corrosion of the sewage water pipes due to the formation of a thin layer of scale. It has also been found to antagonize the toxicity of various substances such as lead, zinc aluminum

Calcium of effluent, beel water and sediment samples was determined by EDTA titration method. Preliminary treatment of water and wastewater samples were done as per the procedure given in APHA.1

In case of bed sediment samples organic matters were removed from soil extract prior to titration with EDTA. Calcium in soil samples was determined by leaching the soil with ammonium acetate solution.

Calcium in soil samples were determined as per the procedure 2.

\[
\text{Calcium, (mg/l)} = \frac{A \times B \times 400.8}{\text{ml of sample}}
\]
A = ml titrant for sample, B = mg CaCO₃ equivalent to 1.0 ml EDTA titrant at the calcium indicator end point.

2.6.10. MAGNESIUM

Magnesium is an important parameters for evaluating the physico-chemical characteristics of effluent water. It is relatively non-toxic to man and is an essential element for human being. The total hardness of water depends upon the concentration of calcium and magnesium. Magnesium occurs in all kinds of natural waters with calcium, but its concentration remains generally lower than the calcium. Sewage waters are also important contributors of magnesium, which depends upon exchange equilibria and presence of the ions like sodium. Magnesium in industrial water is undesirable since it is the major scale forming substance. The recommended value of magnesium content in domestic water supply is 30.0 mg/l.

Magnesium contributes about 2.1 % of the earth’s crust. Magnesium deficiency may induce cardiac necrosis. The daily magnesium requirement of an average person is 300 to 500mg. In presence of sulphate it acts as a laxative.

Magnesium in effluent, beel water, groundwater and sediment samples was estimated as the difference between total hardness and calcium as calcium carbonate. Magnesium in soil samples was determined by leaching the soil with ammonium acetate solution. Magnesium in soil samples was determined as per the procedure.
Mg as CaCO₃, mg/l = (Total hardness (as CaCO₃, mg/l) - calcium hardness (as CaCO₃, mg/l) x 0.243

2.6.11. DISSOLVED OXYGEN (DO)

It is important index for the purity of the water resources. Dissolved oxygen in natural and wastewater depend on the physico-chemical and biochemical activities in the water body. It is key factor in water pollution and waste treatment process control. The high concentration of organic matter deplete the dissolved oxygen and there by upset the oxygen balance. Besides the solubility of oxygen, dissolved oxygen determination is vital for ensuring aerobic conditions in waters that receives polluting matter in the form of sewage, industrial waste. In the control of stream pollution, it is necessary to maintain conditions satisfactory for the growth and reproduction of fish and other aquatic life. This requires the maintenance of dissolved oxygen concentrations that will support aquatic life in a healthy condition.

Solubility of oxygen depends on temperature, pressure and salinity of water. It is essential to the life of fish and other aquatic organism. Dissolved oxygen in industrial water is undesirable, as it induces corrosion reactions.

In liquid wastes, dissolved oxygen (DO) is the most important factor in determining whether aerobic or anaerobic organism carry out biological change. If sufficient DO is available, aerobic organisms oxidize the wastes to innumerous products. If DO is deficient, anaerobes take part in the conversion and reduce the waste often to obnoxious end products.
DO of effluent, beel water and groundwater was determined with the help of a DO meter immediately after collection (El-801E). This method is suitable as the effluent was coloured and all cases the calibration was done using distilled water.

2.6.12. BIOCHEMICAL OXYGEN DEMAND (BOD)

The biochemical oxygen demand is the amount of oxygen required by microorganisms engaged in the utilization of organic matter present in wastewater under defined conditions and within a defined period of time. This test is one of the most important tests made to determine the strength or polluting power of sewage, industrial wastes, effluents and polluted water. Hence it is important in stream pollution control activities and surveys designed to evaluate the purification capacity of receiving bodies of water.

The BOD exerted by organic matter in pulp and paper mill effluent is derived mostly from carbohydrates material of the wood substance, salts of fatty acids, alcohol and other substance present in dissolved state. Some volatile compounds like alcohols, ketones, phenols, mercaptants terpenes present in foul condensate and pulp washing water account for about one third of the total BOD load in combined wastes. The mixed populations of microbes that are found in biological wastewater treatment plants readily degrade the above organics. Spent liquor also contains other organics like lignin and its derivatives, which are highly resistant to microbial degradation, and do not contribute to BOD, but exert COD. Although, these appear to be non-biodegradable, a major portion of them may biologically stabilize after proper acclimatization of seed used in BOD test. A considerable part of the wood components dissolved in the pulping and bleaching process, is easily biodegradable. Examples of such compounds are low molecular
hemicelluloses, methanol, acetic acid, formic acid, sugar etc. The content of easily biodegradable compounds is usually measured by the BOD test. The chemical compound in pulp mill effluents responsible for causing environmental impacts at the community and population in the aquatic environment have been greatly complicated by the presence of environmental pollutants such as BOD\textsuperscript{30-31}. The BIS standard for BOD value of surface water is 3mg/l. It was suggested that a BOD level of 2.0 mg/l be accepted as the maximum permissible limits for unpolluted water.

BOD of effluent and beel water was determined immediately after collection of samples. The effluent samples were neutralized to PH 6.5 to 7.5 with sulphuric acid. In order to determine the BOD the bacterial degradation process was allowed to prove under controlled conditions in test flasks and the quantity of oxygen consumed was determined. The test was carried out by adding diluting water having no oxygen demand to the sample and determining its DO content after dilution. The sample was then incubated for five days at 20\degree C, after which the DO content was again obtained. The difference in two values indicated the amount of oxygen used up by the sample during this period and represents the five day BOD.

The free residual chlorine from the effluent was removed prior to the measurement of BOD\textsuperscript{2}.

\[ \text{BOD, mg/l} = (D_0 - D_5) \times \text{dilution factor} \]

Where, \( D_0 \) = Initial DO in the sample

\( D_5 \) = DO after five days

2.6.13. CHEMICAL OXYGEN DEMAND (COD)

The chemical oxygen demand test is widely used as a measure of the pollution strength of domestic sewage as well as industrial wastes. The test is designed to measure the oxygen
required for the oxidation of organic and oxidizable inorganic matter, corrected for the influence of chlorides in the sample. The organic matter includes both biodegradable as well as non-biodegradable substances. The non-biodegradable and slowly biodegradable compounds in the effluent mainly consists of tannic and lignic acids, cellulose, phenols, polysaccharides, benzene, pesticides chlorohydrocarbon etc. Generally, the pulp and paper mills, wastewater is characterized by high COD load and COD cannot be removed in the absence of a techno-economic solution as on date.

The dichromate test is useful in analysis of sewage, effluents, polluted waters most trade wastes. Another important advantage of this test is the short time. COD is always greater than BOD. BOD, measuring the biodegradable organics is about 50 to 70% of COD and the difference (COD-BOD), gives a rough estimate of the non-biodegradable part. The lower the ratio of BOD/COD, the higher is the fraction of slowly biodegradable compounds.

The dichromate reflux method has been selected for COD determination, because it has advantages over other oxidants in oxidizability, applicability to a wide variety of sample. COD measurement of the sample was carried out immediately after collection. For beel water and groundwater 50 ml of sample was taken. However, for effluent a diluted sample was taken.

Chemical oxygen demand was determined by refluxing the effluent, beel water and groundwater sample with an excess of potassium dichromate in a strongly acidic medium in the presence of a catalyst (Ag₂SO₄). The excess of potassium dichromate remaining after reaction is
titrated against a standard ferrous ammonium sulphate, using ferroin as an indicator. The procedure was repeated for a blank. The COD values are given by,

\[
\text{COD, mg/l} = \frac{(A - B) \times N \times \text{of ferrous ammonium sulfate} \times 1000 \times 8}{\text{Sample volume (ml)}}
\]

Where,

- \(A\) = volume (ml) of titrant required for blank
- \(B\) = volume (ml) of titrant required for sample
- \(N\) = strength in normality of the titrant.

\(8 \times 1000 = \text{milli equivalent wt. of } O_2 \times 1000 \text{ ml/l}\)

2.6.14 RESIDUAL CHLORINE

Bleaching operations in paper industries contribute chlorine. Residual chlorine can exist in the water in various forms, e.g. as chlorine, as hypochlorite ion, or as hypochlorous acid. Residual chlorine reacts readily with any nitrogen compounds, which may be present in the water to form the chloramines, monochloramine, dichloramine and nitrogen trichloride and also displays an oxidizing effect. The chlorinated industrial effluents normally contain only combined chlorine.

In pure water, residual chlorine concentrations as high as 2.0 mg/l have not been found to cause objectionable tastes and odours, but if any organic substances such as phenol are present even in very small concentrations, chlorine produces undesirable tastes and odours. Large concentrations of chlorine can accelerate corrosion particularly when oxygen is present.
The determination of total chlorine in samples containing organic matter presents special problems. Because of the presence of ammonia, amine and organic compounds, particularly organic nitrogen, residual chlorine exists in a combined state. A considerable residual may exist in this form, but at the same time there may be appreciable unsatisfied chlorine demand. Addition of reagents in the determination may change their relationships, so that residual chlorine is lost during the analysis. In wastewater, the differentiation between free chlorine and combined chlorine ordinarily is not made, because wastewater chlorination seldom is carried for enough to produce free chlorine. Since the sample water contains significant amounts of organic matter. The iodometric back titration method was adopted. This method is suitable for measuring total chlorine concentration greater than 1mg/l.

Residual chlorine in the effluent and beel water sample was determined by iodometric method of titration in which iodine liberated after addition of potassium iodide is titrated with standard sodium thio-sulphate solution using starch indicator. The sodium thiosulphate solution was standardized against standard K$_2$Cr$_2$O$_7$ solution. 100 ml of water sample was taken for each determination. The PH of the sample was maintained at around 4, prior to titration by adding 5.0ml glacial acetic acid.

The residual chlorine is calculated.

\[
\text{Residual Cl}_2, \text{ ml/l} = \frac{V \times N \times 1000 \times 35.5}{100\text{ml}}
\]

\[V = \text{volume of titrant. } N = \text{Normality of titrant.}\]
### 2.6.15. CHLORIDE

Chloride is one of the common anions in water and wastewater, which occurs in all natural waters in varying concentration. The chloride content normally increases as the mineral content increases.

Man and other animals excrete containing very high quantities of chlorides. The human body discharges 8 to 15 grams of sodium chloride per day. Higher concentration of chloride in natural waters may also be due to the contamination by seawater, brines from caustic and chlorine plant. Although chloride is not classified as harmful constituents, excessive chloride concentration of more than 250mg/l may damage metallic pipes and structures. A high chloride content is not desirable for domestic, industrial and irrigation purpose. In irrigation it exerts a deleterious effect on the plants. Different plants are more or less sensitive to chlorides. At concentrations below 140 mg/l no problems are to be expected. Problems increase between 140-350 mg/l and severe problems should be expected above 350mg/l. According to BIS standard for effluent discharge in surface water, chloride concentration of 600 mg/l is harmless.

Chloride in effluent and beel water was determined by silver nitrate method. Silver nitrate reacts with chloride ions to form silver chloride during titration, using potassium chromate as an indicator. 100ml of the sample, after adjusting PH to the range 7 - 9.5, was titrated against standard silver nitrate solution using 1 ml of potassium chromate solution as indicator, until a slightest perceptible reddish colouration persists. A blank titration of 100 ml chloride free distilled water was carried out. Since the effluent was coloured 3ml of Al(OH)₃ suspension was added. To the filtrate 1 ml of H₂O₂ was added to remove interfering substance.
Chloride, mg/l = \frac{(A-B) \times N \times 35.45 \times 1000}{ml \text{ sample taken}}

Where, 
\begin{align*}
A &= \text{ml AgNO}_3 \text{ solution consumed for sample} \\
B &= \text{ml AgNO}_3 \text{ solution consumed for blank} \\
N &= \text{Normality of AgNO}_3 \text{ solution (of the titrant)}. \\
\end{align*}

Most of the chloride in the soil is soluble in the water and determined directly by titration method with AgNO\textsubscript{3} using K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} as indicator.

\% Chloride = \frac{ml \times N \text{ of AgNO}_3 \times 35.5}{ml \text{ soil solution} \times 2}

The percentage of chloride was converted to mg/kg.

2.6.16. SULPHATE

Sulphate ions are relative abundant in natural waters ranging from a few to several thousands mg/l. Sulphate as magnesium sulphate causes laxative effects to children particularly in hot weather or climate. High amounts of sulphate impart a bitter taste to the water.

Sulphate in industrial waters causes potential scaling problems. Sulphates have no detrimental effect on the corrosion of brass filling in domestic water and to increase the corrosiveness towards concrete. Regarding irrigations above 200 mg/l are undesirable.
Sulphates are reduced under anaerobic conditions to hydrogen sulphide, which causes odour and is oxidized to sulphuric acid and corrode sewers. At PH values of 8 and above, most of the reduced sulphur exists in solution only as HS⁻ and S²⁻ ions and the amount of free H₂S is negligible and odour problem do not occur. At PH 7, the equilibrium shifts towards the formation of H₂S and serious odour problem occur. When sulphides are present in high concentration in industrial water, it attacks the resistant alloys, such as brass and stainless steel and causes deterioration.

Sulphate in effluent, beel water, groundwater and sediment was estimated as per standard methods.¹ ² Like chlorides, most of the sulphates are soluble in water and can directly be determined in the soil solution, by gravimetric method.

200ml sample was diluted with distilled water. PH was adjusted to 4.5 to 5.0 with HCl using methyl red indicator (to orange colour). After boiling for about one minute, hot barium-chloride solution was slowly added, and kept the beaker for more than 2 hours at 80-90 °C. The contents were filtered through an ashless filter paper (Whatman no.40). The content on the filter paper was ignited at 800 °C, cooled and weighed.

\[ \text{Sulphate, mg/l} = \frac{\text{mg BaSO}_4}{\text{Vol. Sample in ml.}} \times 411.5 \]

In case bed sediment, 1: 5 sediment soil samples was prepared. The filtered solution was used for determination of sulphate as done in case of water sample.

\[ \text{Sulphate, % as SO}_4^{2-} = \frac{\text{mg/l sulphate of soil solution} \times 411.6}{2000 \times \text{ml of soil solution}} \]

The percentage of sulphate was converted to mg/kg
2.6.17: OIL AND GREASE

A large number of organic compounds originating from petroleum constitute the oil and grease content. These organics may be volatile or non-volatile, soluble or insoluble, persistent or biodegradable and their physical, chemical or toxicological properties may be widely variant for oil and grease as water quality parameters. Oil and grease enter natural water bodies from several sources like industrial effluents, petrochemical plants and oil refineries, storage tanks and automobile waste. These makes a significant contribution to pollution of the aquatic environment by preventing transfer of oxygen from the atmosphere and lead to very low level dissolved oxygen in the water due to microbial oxidative attack on the hydrocarbon molecule. It is generally recommended that domestic water supplies should be free from oil and grease, particularly from the tastes and odour associated with petroleum products. Fresh water or marine species are highly susceptible to oil and petroleum chemicals and a concentration of as low as 0.1 mg/l may be fatal. Jacobsen and Boylan 1973 showed that aquatic life can be harmed at concentration of 1 µg/l. Thus the chemicals enter human food chain through these species. The bacterial degradation of oil is very slow and oil products persist for long periods in bottom sediments.

Oil and grease in the effluent water and soil samples were estimated by solvent extraction with petroleum ether followed by evaporation of the solvent and weighing of the residue. The solvent is evaporated over a water bath at 70°C. For preservation, samples were acidifying with 1:1 HCl. The oil and grease content was obtained as follows.

\[
\text{Oil and grease, mg/l} = \frac{(A - B) \times 1000000}{\text{Sample volume in ml.}}
\]
Where, \( A = \) Final weight of dish in gm

\( B = \) Initial weight of dish in gm.

2.6.18. TANNIN AND LIGNIN

Tannin and lignin are the plant constituents that often enter the surface water through the wastes of pulp and paper mill. The paper industry produces huge quantities of coloured wastewaters. The characteristic dark brown colour of paper industry wastewater is due to the presence of polymeric, chlorinated products of lignin.\(^{37}\) The wastewater containing lignins as colouring materials are discharge mainly from the bleaching and recovery sections. Several bacterial, algal species have been found to degrade the polymeric lignin derivatives\(^{38-39}\). Lignin and its derivatives are in general difficult to degrade by physical, chemical and biological methods. Lignin breakdown involves multiple biochemical reactions that have to take place more or less simultaneously. In chemical pulping about 5-10 % of the lignin remains in the pulp which is subsequently depolymerised and removed in multi stage bleaching. The lignin is converted to alkaline soluble compounds by treatment with oxidizing agents. After bleaching wastewaters mainly contain degradation products of lignin. The principal constituents of chemithermo mechanical pulping effluents are polysaccharides (10-15 %), organic acids (35-40 %), and lignin (30-40 %)\(^{40}\)

The tannin and lignin in effluent and beel water samples were determined by colorimetric method. Both tannin and lignin react with Folin phenol reagent (tungstophosphoric and
molybdophosphoric acids) to form blue colour compounds. The concentration of which was measured by using spectrophotometer at a wavelength of 700 nm.

2.6.19. MERCURY

Although mercury is not an abundant chemical element in nature, it has became so widespread, as a result of many industrial and agricultural applications that it is at present an almost normal component in trace concentration of water, soil, plants animals and even the human organism. Liquid effluent and solid waste from the chloro alkali plant in general and paper mill in particular have been known to discharge mercury into the environment. The continuous ingestion of mercury over long periods of time can cause the accumulation of a concentration high enough for its serious toxic effects to appear. In recent years, therefore, increasing attention has been paid to the analysis of mercury in the air, water, soil, plants and food. The toxic forms of mercury produced by oxidation are soluble in water and this can enter aquatic and terrestrial ecosystem by wet deposition. Many lakes have been rendered useless for fishing because of mercury pollution. Mercury migrates in the surface water in the form of salts, inorganic complex, organometallic complex or chelates. Mercury metal soluble to the extent of 60 ppb under natural conditions. It is precipitated by adsorption on inorganic sediments and humic constituents or can also precipitate as sulphide during decay of organic matter. It can be released again as the relative by soluble methyl mercury, due to the action of micro-organism. The mercury found in lakes, rivers and currents does not normally exceed 0.1 μg/l, but in some local areas close to natural sources of mercury, the concentration can rise to over 80 μg/l.

The normal concentration of mercury in soils is 20 to 150 ppb, average 70 ppb, except near mercury deposits where it go up to 250 ppb. The quality of soil and sediment is of interest,
as mercury often accumulate in great quantities on sediments and in overlying water. Given their capacity to incorporate organic and inorganic elements during transport and precipitation, the study of sediments is important.

Mercury content of effluent, beel water and soil sediment samples was determined using mercury Analyzer (ECIL, India). The methodology is the detection of Hg, by absorption spectrophotometer of flameless atom. The Hg is reduced to elemental state and then volatilized by simple aeration with air. The volatile Hg vapours pass through a cell in the light path radiation at 253.7 nm (by Hg cathode lamp). The deflection reading is converted to mg/l of Hg from the deflection vs. mg/l of Hg.

2.6.20. SODIUM

Sodium is one of the most abundant element in natural waters which vary from less than 1.0mg/l to more than 500mg/l. It is of importance when salinity and total dissolved solids are a consideration in the use of the water. Sodium has important considerations with regard to irrigation waters only. An excessive amount of sodium in drinking water is harmful to persons suffering from cardiac, renal and circulatory diseases. Sodium present as sodium chloride in concentrations more than 500 mg/l makes the water unpalatable and causes appetites disturbances.

If the concentration of sodium and potassium in boiler exceeds 50mg/l, foaming troubles may occur. The percent sodium (ratio of sodium to total cations) is important in agriculture and human pathology. The percent sodium exceeds 60, the water is considered to be unsuitable for irrigation purposes. Soil permeability has also been found to be affected by high sodium ratio.
Calcium and magnesium in the proper proportions maintain soil in good condition. Sodium has a direct toxic effect on many plants.

The sodium absorption ratio (SAR) value has been used to estimate the quality of sodium absorbed into the soil complex,

\[
SAR = \frac{[\text{Na}^+]}{\sqrt{((\text{Ca}^{2+} + \text{Mg}^{2+})/2)}
\]

Sodium is required in limited amounts for most plant growth and high concentrations are toxic to plants.

The flame photometric (ELICO- CL 22D) method was used to determine sodium content of the effluent, beel water, groundwater and sediment samples. The preliminary treatment of the effluent and water samples were done as per standard method\(^1\) and samples were preserved in polythene bottle. Sodium in soil samples was determined by leaching the soil with ammonium acetate solution.

2.6.21. POTASSIUM

Potassium is an essential nutritional element, but in excessive amounts it acts as a cathartic. It is reported that foaming may be caused in boilers by more than 50 mg/l of potassium and sodium in water. Low concentrations of potassium in irrigation water are essential for plant nutrition with other mineral nutrients.
The flame photometric method was used to determine potassium content of the effluent, beel water, groundwater and sediment samples. Potassium in soil samples was determined by leaching the soil with ammonium acetate solution.

2.6.22. COLOUR

Pure water is colourless. But water in nature is often coloured due to the presence of natural metallic ions (iron or manganese), humus and peat materials, plankton, weeds and industrial wastes. Industrial wastes from textiles and dying operations, pulp and paper production, food production etc. add substantial colouration to water in receiving streams. Hence, coloured industrial wastewater may require colour removal before discharge into natural water systems, as coloured water is not aesthetically acceptable to the general public. Highly coloured water is unsuitable for laundering, dyeing, papermaking, beverage manufacturing etc.

Intense brown colour associated with pulp and paper mill effluent is caused by lignin and its derivates \(^{51-55}\) which are relatively stable compounds that degrade very slowly in receiving water. The wastewater containing lignin as colouring material is discharged mainly from pulp washing, bleaching and chemical recovering section of pulp and paper mill. These compounds absorb light at wavelength 400 and 500nm. Tannins and other pigments present in the wood also contribute to colour in the effluents to a certain degree. A relationship exists between the lignin content of the pulp mill effluent and its COD value particularly in kraft mill waste. Therefore, COD reduction in the effluent is dependent on colour reduction. The method employed for colour removal from pulp and paper mill effluent included chemical treatment, massive lime treatment, activated carbon, resin adsorption or Ozonation.
The colour value of water is extremely pH dependent. It increases as the pH of the water is raised. For research purposes, it is necessary to determine the colour response of given water over a wide range of pH values.

As turbidity interferes with the colour determination by increasing the colour intensity, therefore, the turbidity was removed by centrifugation of water sample before analysis. For determination of colour, samples were collected in clean glass bottles and analysis was done immediately after collection.

Colour of the effluent and beel water samples were measured by visual comparison of the samples with known concentration of coloured solution. The platinum-cobalt method of measuring colour is the standard method.\textsuperscript{1}

\[
\text{Colour units (Hazen) = Estimated colour } \times \text{ dilution factor.}
\]

A series of working colour standards were prepared to cover the range 5 to 70 Hazen. 50 ml of the sample in a Nessler tube was compared with that of the working standards.

2.6.23. LEAD

Lead is a physiologically unessential and potentially harmful metal, which contaminates our environment. It can accumulate in many biological system units it reaches toxic levels\textsuperscript{56} and tends to deposit in the bones as a cumulative poison. Detrimental effects associated with lead have been recognized for a long time and it exerts, its most significant toxic effects on the
nervous system, the kidney etc. In animals including man, gastro-intestinal absorption of lead ranges between 5-15 percent of the total amount ingested. However, children have been shown to absorb much more, about 40 per cent of it. More than 90% of the lead absorbed goes to blood, where it can be detected in red blood cell associated with its membrane and hemoglobin. Later it is distributed to liver, kidney and bones including teeth.

Plants growing near busy highways are regularly exposed to fume and smoke discharged from automobiles containing plenty of lead. It has been estimated that almost 450 tons of lead are emitted annually into the atmosphere in the Bombay along through automobile exhaust. Pb in effluent, beel water and soil was determined with the help of atomic absorption spectrophotometer after pretreatment of the samples. The soil samples were prepared as per the procedure described given in 2.5.

2.6.24. CADMIUM

Cadmium is now considered as a significant environmental pollutant with profound toxic effects on aquatic animals. The main sources of cadmium contamination into the environment from mining and metallurgical operations, electroplating industry, units manufacturing polyvinyl chloride, plastics, nickel-cadmium batteries, paints, pigments and combustion of fossil fuels. Cadmium contamination of water may also come from use of metallic and plastic pipes. There is a progressive accumulation of cadmium in soft tissues of the body, particularly in kidney and liver. Due to its potential for gradual accumulation much concern has been expressed about the regularly growing levels of cadmium in cereals, vegetables and other materials. The metal can
exert a number of detrimental effects on health. The WHO European standard for cadmium in water is 0.5 mg/l.

Cd in effluent, beel water and soil was determined with the help of atomic absorption spectrophotometer after pretreatment of the samples. The soil samples were prepared as per the procedure described in 2.5.

2.6.25. COPPER

Copper contamination of the environment is largely due to its release by industrial units producing non-ferrous metals, fertilizers, disposal of tailings or the solid wastes from mines and from fly ash produced by combustion of coal and organic matter. Copper, an essential metal that is found in all living organisms and its deficiency is characterized by hypochoronic microlytic anemia. Most of all other foods of animal origin contained between 2 to 4 ppm. The recommended daily intake of copper ranges from 2.0 to 3.0 mg in humans. It is mainly through food and water that human's take up copper. Soluble copper concentration in drinking water ranges between 1.5 to 2.4 mg/ per liter in urban areas, while in rural areas it is usually well below 1 mg per liter. The concentrations of copper found in natural waters are not known to have adverse effect on humans, though copper in excess of 1 mg/l may impart some taste to water.

In plants, low levels of copper are essential for normal activity of a number of enzymes and for chlorophyll synthesis. However, at a slightly higher concentration copper is the most toxic element after mercury. Inhibition of growth occurs at concentration less than 0.1 ppm in majority of plant species. Uptake of copper by plants is accelerated in presence of calcium and magnesium ions, but diminishes with fall in PH. A higher concentration of copper is injurious to blue and green algae, since then metal tends to suppress nitrogen fixation.
Cu in effluent, beel water and soil was determined with the help of atomic absorption spectrophotometer after pretreatment of the samples. The soil samples were prepared as per the procedure described in 2.5.

2.6.26. ZINC

Zinc is essential trace elements for both plants and animals. However, an excessive level of the metals is considered problematic, primarily in connection with toxic effects on flora and fauna. Effects are most marked when low pH and lack of soil binding sites combine to enhance the availability of the metal in sensitive plant systems. In recent years, extensive use of Zinc has been made in many industrial processes, which include welding and smelting or fabrication of molten metals. Above 40-ppm level this metal imparts a faint but definite metallic taste and milky appearance to fresh water. High concentration (above 5mg/l) of Zinc in domestic water is undesirable from aesthetic consideration.

Zn in effluent, beel water and soil was determined with the help of atomic absorption spectrophotometer after pretreatment of the samples. The soil samples were prepared as per the procedure described in 2.5.

2.6.27. ARSENIC

The occurrence of Arsenic in natural water is rare. In lime-stones and siliceous deposits its concentration ranges between 0.5 to 2.0 ppm while in volcanic rocks as much as 20 ppm of arsenic could be found. Natural processes such as weathering and degradation of rocks annually release about 80,000 tons of arsenic into the environment. Global emission of this metal due to
human activity has been estimated to be about 240,000 tons per year. The WHO international standard for drinking water is 0.01 mg/l$^{63}$ and recommended a maximum daily intake of 0.05 mg/kg of body weight. It is a cumulative poison. A number of proteins and enzymes containing sulpha-hydral groups have been found to be altered by exposure to arsenic. Mitochondria enzyme systems are particularly affected which disturbs tissue respiration. A general feeling of weakness, nausea, loss of appetite, often vomiting and diarrhea characterize chronic arsenic poisoning. Nerves of limbs are affected and loss of sensation in hands and feet occurs. Small concentrations of arsenic are known to stimulate plant growth; large concentrations present in irrigation water may cause reduction in overall yield of crop plants.

Soil contaminated with arsenic has arisen as a result of the mining and smelting of the metal arsenic concentration in soils average 5-6 mg/kg, but vary considerably according to region with some Dantmoor soils reaching 250 mg/kg. Arsenic in effluent, beel water and soil was determined with the help of atomic absorption spectrophotometer after pretreatment of the samples. The soil samples were prepared as per the procedure described in 2.5.

### 2.6.28. WATER HOLDING CAPACITY

Water holding capacity of bed sediment is the capacity of the sediment to retain the water amount and depends upon the soil structure, and constituent components. The loamy and clayey soils have more capacity of water holding than sandy soil. It was determined using the following formula $^{5}$.

\[
\text{Water holding capacity (%) = } \frac{c - (b + m) \times 100}{b - a}
\]

\[
b - a
\]
Where,  
\[ a = \text{Weight of the box + filter paper (gm).} \]
\[ b = \text{Weight of the box + filter paper + dry soil (gm).} \]
\[ c = \text{Weight of the box + wet filter paper + saturated soil after 24 hrs retention (gm).} \]
\[ m = \text{moisture content of the filter paper (gm).} \]

2.6.29. PERCENTAGE WATER

The bed sediment contains water depending upon the structure and composition of bed sediment. The following equation was used to determine the percentage of water content:

\[
\text{Water content (\%)} = \frac{\text{Diff of mass in wet and dry state represent fine soil samples} \times 100}{\text{Mass of representative soil samples}}
\]

The percent of water content was determined by using the following formula.

\[
\% W = \frac{W_2 - W_3 \times 100}{W_3 - W_1}
\]

Where,  
\[ W_1 = \text{Mass of container with lid (gm).} \]
\[ W_2 = \text{Mass of container with lid + Wet soil (gm).} \]
\[ W_3 = \text{Mass of container with lid + dry soil (gm).} \]

The bed sediment sample was dried in oven at a temperature of \( 110 \pm 5^0 \) C for 24 hours.

2.6.30. BULK DENSITY

In nature, soils of different textures tend to have different densities. Clay, clay loam and silt loam soils may have densities ranging from 1.00 to 1.60 gm/ cm\(^3\) and sands and sandy loams
from 1.2 to 1.8 gm/cm³. Soil bulk density is a very good indicator of soil structural quality. Soil bulk density is simply the dry mass of soil per unit volume. This is not the same as the specific gravity of the soil. Bulk density of bed sediment is the weight of the wet soil per unit volume. Bulk density of soil depends upon the nature of the soil and its constituents. Bulk density was determined using the following formula:\(^5\)

$$\text{Bulk density, gm/cm}^3 = \frac{W_s - W_c}{V_c}$$

Where, \(W_s = \text{weight of soil and container (gm)}\)
\(W_c = \text{wet of empty container (gm)}\)
\(V_c = \text{volume of container (cm}^3\)"

2.6.31. ORGANIC CARBON

The soil productivity is determined primarily by organic matter, which constitutes less than 5% of the soil. The organic matter provides food for microorganisms. Takes part in chemical reactions such as ion exchange, governs the physical properties of soil and contributes to the weathering of mineral matter. The biologically active components of organic matter consist of polysaccharides, amino sugars, nucleotides, organic sulphur and phosphorous compounds.

The method adopted for determination was Walkley and Black’s method (modified). The elementary carbon present as graphite, charcoal etc. is not attacked in this method and only organic carbon is determined. The recovery of the carbon in this method is not 100 percent. Only about 60 - 90 % of the total organic matter is recovered.
The dried bed sediment sample was screened through 0.5 mm non-ferrous screen. 10 gm dried sample was taken in a conical flask, added 10 ml 1N, \(K_2\text{Cr}_2\text{O}_7\) solution plus 20 ml conc. \(\text{H}_2\text{SO}_4\), mixed by swirling. After about 30 minutes, diluted with 200 ml distilled water. Added 10 ml phosphoric acid, then 1 ml of diphenylamine indicator, and titrated against 0.4 N ferrous ammonium sulphate, to the end point of brilliant green. A blank with same quantity of the chemicals without soil was carried out.

\[
\% C = \frac{3.951}{W} \left( 1 - \frac{T}{S} \right)
\]

Where

- \(W\) = weight of sample (gm)
- \(S\) = ml of the ferrous solution with the blank titration.
- \(T\) = ml ferrous solution with sample titration.

The factor average recovery of about 75 % organic matter by this method has been taken into consideration in the above formula.

2.6.32. ORGANIC MATTER

Organic matter in bed sediment sample was determined by Walkley and black method. Soil sample was digested with excess of potassium dichromate and sulphuric acid and the residual unutilized dichromate was then titrated with ferrous ammonium sulphate, as stated in 2.5.31.

Organic matter is calculated by this formula,

\[
\% \text{ organic matter} = \% \text{ organic carbon} \times 1.724
\]
The factor 1.724 is based on the assumption that carbon is only 58% of the organic matter (88).

2.6.33. IRON

Iron ranks next to aluminum in abundance of metals in the earth's crust. Natural waters contain only minor amounts of iron. Iron oxides FeO (OH) and magnetite Fe₃O₄ constitute a major mineral fraction of many soils. Iron usually exists in natural water both in ferric and ferrous forms. The form of iron may be altered as a result of oxidation, or reduction, or due to the growth of bacteria. Usually the ferric form is predominant in most of the natural water. Iron in water may be either in true solution, or in colloidal state or in the form of relatively coarse suspended particles. The iron content of some deep wells and industrially contaminated streams may be very high.

In 1958 WHO international standards for drinking water specifies a permissible limit of 0.3 mg/l and an excessive limit of 1.0 mg/l iron. It is well known fact that both iron and manganese are essential to the human body. So it is reported that the low limit placed upon the metal standards has no health significance and the limits are based on aesthetic and taste considerations. Iron imparts a bittersweet astringent taste to water, which is detectable at very low concentrations (1 or 2 mg/l).

Iron in sediment sample was determined by spectrophotometric method. The iron chelates with 1-10 phenanthroline at PH 3.2-3.4 to form complex of orange-red colour. The intensity of this colour is proportional to the concentration of iron and can be determined colorimetrically.
REFERENCES:

1. APHA Standard methods for examination of water and wastewater, 20th Ed.
   APHA, AWWA, WPCF. (1998)


3. Indian standard: Method of sampling and test for industrial effluents IS: 2488 (part III), (1968); IS: 2488 (part IV), (1974); IS: 2488 (part V), (1976).


61. Vallee, B.L., Zinc and its biological significance, Arch. Indust. Hlth. 16:147 (1957)
