CHAPTER 3: METHODOLOGY

Water, like air, is one of the most important and most precious substances of natural resources and a regular and plentiful supply of clean water is essential for the survival and health of most living organisms. Water is commonly the mediator of interactions among the major divisions of our earth. These divisions are:

i. Exosphere
ii. Lithosphere
iii. Atmosphere
iv. Biosphere
v. Hydrosphere

The hydrological cycle is responsible for our weather and it makes our rivers run and balances the level of groundwater.

Methodology of the present work involves field work and laboratory work.

3.1 Field work

Field work mainly involves survey and sampling of potable water samples. Various sources of potable water were identified during the survey of study area. Further, in consultation with the people the suitable sites were selected for alternative source of potable water i.e. tuikhurs. The PHED sites were selected in order to procure samples evenly distributed over the area.

3.1.1 Survey and Selection of sampling sites

As a rule of nature, facility makes a man lenient and it is very true in case of environmental abuse, unscrupulous choice of fertilizers, insecticides, pesticides and poor farming practices that ultimately lead to soil pollution which in turn might be polluting our natural sources of surface &/ or an underground water. Nasty chemicals enter the food chain and cause a potential health hazard to the human body. Rainfall is an important factor and is the primary source of surface as well as groundwater on the earth. Level of groundwater table is always proportional to the rainfall. In the study area highest rainfall falls generally during June and July and on the contrary the month of January receives almost nil rainfall. Kolasib area of Mizoram is selected for the present study mainly because of the following facts:

1. Least or almost negligible information is available to the consumers regarding the water they consume for their domestic uses.
2. Usage of Tuikhur water for drinking and other domestic purposes as a supplementary resource of potable water is so far not assessed.

3. The poor awareness among masses for a cleaner environment. Such awareness to avoid the fixation of piggeries and other sanitary cabins near tuikhurs is observed to be alarmingly needed.

A detailed survey of sampling sites was performed before starting sampling and analysis of potable water samples. Townships in and around Kolasib, the district headquarter include Kolasib, Kawnpuir and Bilkhwathlir. All the three townships are at least connected through water connection from PHED as a basic source of potable water. However, the urbans also use tuikhurs and rain water as supplementary resources to cope up their requirement (Bharati et al., 2007). The need of supplementary resources arise due to the fact, that the water through PHED could not be regularly supplied and at the same time not enough. Moreover, the connection network of PHED does not cover the whole population. However, Population residing in the vicinity of the townships has to depend wholly on the tuikhur water for their domestic needs. As on May 12, 2009, the Kolasib town has only 1801 water connections for 19008 populations. According to the PHED, Kolasib itself, the population benefited by water connections is 11,317 leaving 7,691 people to procure water for their daily needs from tuikhurs. Similarly, Vairengte and Bilkhawthlir have 547 and 194 connections for 7715 and 4084 population respectively. Kawnpuir is a sub-division headquarters in the district but it has only 256 water connections.

Tuikhurs are widely distributed all through the areas in and around various townships. They are in fact water seepages mostly along the foot hills in the hilly terrains. Among the tuikhurs mostly are of the seasonal nature, where water diminishes during the non-monsoon periods. Still there are some tuikhurs which are perennial in nature therefore water is available throughout the year. Shortage of the potable water is to be fulfilled by the perennial tuikhurs fully for population out of PHED network and partly for urban localities. Few tuikhurs among all under public usage are having enough constructions to minimize the in-situ contaminations. The selected sites include renovated as well as raw tuikhurs.

Quite a good number of households are equipped with water harvesting facilities during rainy season and storing it for the usages of the same in relatively
dry periods. The construction of houses is typical Assam-type with tapering roofs. The channel surrounding roof-tops facilitate storage of water into tanks. This water can also be a source of potable water for the families deprived of PHED supply and situated at a distance from the tuikhurs.

Samples have been collected from all the three sources of potable water available to the citizens of the area in and around Kolasib, Mizoram. They are tuikhur water, PHED supply water and harvested rain water.

As a good chunk of population of the study area depends on tuikhurs for their water needs, 32 tuikhurs were selected from the proposed area of work. While selecting the tuikhurs, the opinion of local people was taken care of i.e. those perennial tuikhurs which are relatively more in usage than the others were selected for the present study. Twenty PHED supply households were also selected in such a way so that it covers almost all locations within the study area. Among the harvested rain water locations five were identified from different localities within Kolasib town.

### 3.1.2 Samples and Sample Code Plan

Detailed locations of tuikhurs, PHE points and rain water samples are given below with their codes to be used for ready reference (Plate II).

<table>
<thead>
<tr>
<th>Code</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>KT-1</td>
<td>Kolasib, Venglai- Convent road</td>
</tr>
<tr>
<td>KT-2</td>
<td>Kolasib, Venglai- St. John’s HS school</td>
</tr>
<tr>
<td>KT-3</td>
<td>Kolasib, Venglai- old UPC church</td>
</tr>
<tr>
<td>KT-4</td>
<td>Kolasib, Venglai - below P/S-III</td>
</tr>
<tr>
<td>KT-5</td>
<td>Kolasib, Banglakawn- Brahma Kumari’s off.</td>
</tr>
<tr>
<td>KT-6</td>
<td>Kolasib, lower electric veng</td>
</tr>
<tr>
<td>KT-7</td>
<td>Kolasib, Hmar veng- police station</td>
</tr>
<tr>
<td>KT-8</td>
<td>Kolasib, Saidan-I</td>
</tr>
<tr>
<td>KT-9</td>
<td>Kolasib, Saidan -II</td>
</tr>
<tr>
<td>KT-10</td>
<td>Kolasib, Diakkawn- petrol pump</td>
</tr>
<tr>
<td>KT-11</td>
<td>Kolasib, Diakkawn - football ground</td>
</tr>
<tr>
<td>KT-12</td>
<td>Kolasib, Diakkawn- Aizawl road I</td>
</tr>
<tr>
<td>KT-13</td>
<td>Kolasib, Diakkawn- Aizawl road II</td>
</tr>
<tr>
<td>KT-14</td>
<td>Kolasib, Vengthar- ICAR complex</td>
</tr>
<tr>
<td>KT-15</td>
<td>Kolasib, Project veng- Agriculture Guest House</td>
</tr>
</tbody>
</table>
Tuichhuahen has been divided into twelve well defined micro watersheds based on physiography. The presented results fall in the micro-watersheds identified as Number I, II, IV, VI and VII by Rai (2005).

Micro-Watershed number I: It expands over an area of 9.75 sq. km, with its stream length 5.00 km, perimeter 13.50 km and comprises of the southern most part of the study area i.e. Kawnpui. As many as 74 streams of different orders are pouring water to the micro-watershed which includes the analysed samples KT-27 to KT-30.

Micro-Watershed number II: It expands over an area of 9.38 sq. km, with its stream length 5.50 km, perimeter 15.50 km and comprises of the area known as Thingdawl situated in the immediate south of the Kolasib town under study area. As many as 60 streams of different orders are pouring water to the micro-watershed which includes the analysed samples KT-24 to KT-21.

Micro-Watershed number IV: It expands over an area of 8.04 sq. km, with its stream length 4.00 km, perimeter 15.90 km and comprises of the southern part of the Kolasib town under study area. As many as 69 streams of different orders are pouring water to the micro-watershed which includes the analysed samples KT-14 to KT-4.

Micro-Watershed number VI: It expands over an area of 7.33 sq. km, with its stream length 4.00 km, perimeter 11.00 km and comprises of the Kolasib town of the study area. As many as 59 streams of different orders are pouring water to the micro-watershed which includes the analysed samples KT-5 to KT-18.
Micro-Watershed number VII: It expands over an area of 7.46 sq. km, with its stream length 4.40 km, perimeter 12.00 km. and comprises of the northernmost part of the study area i.e. Bilkhawthlir. As many as 54 streams of different orders are pouring water to the micro-watershed which includes the analysed samples KT-19 to KT-20.

In the further chapters these tuikhur samples are arranged as they fall in the respective Micro-watersheds in the study area, established by Rai (2005).

<table>
<thead>
<tr>
<th>Micro water shed</th>
<th>Samples</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>water Shed I</td>
<td>KT-27</td>
<td>Kawnpui–Azl rd I</td>
</tr>
<tr>
<td></td>
<td>KT-26</td>
<td>Kawnpui–Azl rd I</td>
</tr>
<tr>
<td></td>
<td>KT-25</td>
<td>Kawnpui–police st</td>
</tr>
<tr>
<td></td>
<td>KT-28</td>
<td>Kawnpui–PWD</td>
</tr>
<tr>
<td></td>
<td>KT-29</td>
<td>Kawnpui–Mualvum rd</td>
</tr>
<tr>
<td></td>
<td>KT-32</td>
<td>Kawnpui – Hortoki III</td>
</tr>
<tr>
<td></td>
<td>KT-31</td>
<td>Kawnpui – Hortoki II</td>
</tr>
<tr>
<td></td>
<td>KT-30</td>
<td>Kawnpui – Hortoki I</td>
</tr>
<tr>
<td>Water shed II</td>
<td>KT-24</td>
<td>Bualpui BSNL</td>
</tr>
<tr>
<td></td>
<td>KT-23</td>
<td>Bualpui - below FCI</td>
</tr>
<tr>
<td></td>
<td>KT-22</td>
<td>Thingdawl pump st</td>
</tr>
<tr>
<td></td>
<td>KT-21</td>
<td>Thingdawl-Agri Park</td>
</tr>
<tr>
<td>Water shed IV</td>
<td>KT-14</td>
<td>Klb-ICAR complex</td>
</tr>
<tr>
<td></td>
<td>KT-11</td>
<td>Klb-Diakkawn ground</td>
</tr>
<tr>
<td></td>
<td>KT-13</td>
<td>Klb-Diakkawn- Azl rd II</td>
</tr>
<tr>
<td></td>
<td>KT-12</td>
<td>Klb, Diakkawn- Azl rd I</td>
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<tr>
<td></td>
<td>KT-16</td>
<td>Klb, Forest veng</td>
</tr>
<tr>
<td></td>
<td>KT-15</td>
<td>Klb, Project veng</td>
</tr>
<tr>
<td></td>
<td>KT-3</td>
<td>Klb-old UPC church</td>
</tr>
<tr>
<td></td>
<td>KT-1</td>
<td>Klb-Convent rd</td>
</tr>
<tr>
<td></td>
<td>KT-2</td>
<td>Klb, St. John’s school</td>
</tr>
<tr>
<td></td>
<td>KT-4</td>
<td>Klb- Venglai P/S-III</td>
</tr>
<tr>
<td>Water shed VI</td>
<td>KT-5</td>
<td>Klb-Banglakawn</td>
</tr>
<tr>
<td></td>
<td>KT-6</td>
<td>Klb-electric veng</td>
</tr>
<tr>
<td></td>
<td>KT-7</td>
<td>Klb, police st</td>
</tr>
<tr>
<td></td>
<td>KT-9</td>
<td>Klb-Saidan -II</td>
</tr>
<tr>
<td></td>
<td>KT-8</td>
<td>Klb- Saidan-I</td>
</tr>
<tr>
<td></td>
<td>KT-10</td>
<td>Klb-petrol pump</td>
</tr>
<tr>
<td></td>
<td>KT-17</td>
<td>Klb-Rengtekawn-I</td>
</tr>
<tr>
<td></td>
<td>KT-18</td>
<td>Klb-Rengtekawn-II</td>
</tr>
<tr>
<td>Water shed VII</td>
<td>KT-19</td>
<td>Bilkhawthlir-BSNL</td>
</tr>
<tr>
<td></td>
<td>KT-20</td>
<td>Bilkhawthlir-Post Off</td>
</tr>
</tbody>
</table>

### 3.1.2.2 Samples of PHE (supply) water (KP)

<table>
<thead>
<tr>
<th>KP-1 Kolasib, Venglai – Paster’s residence</th>
<th>KP-3 Kolasib, Venglai – Hospital</th>
</tr>
</thead>
<tbody>
<tr>
<td>KP-2 Kolasib, Venglai – Lalkunga’s house</td>
<td>KP-4 Kolasib, Banglakawn – Didi</td>
</tr>
<tr>
<td></td>
<td>restaurant</td>
</tr>
</tbody>
</table>
KP-5 Kolasib, Banglakawn – Post Office
KP-6 Kolasib, Project veng – BSNL office
KP-7 Kolasib, Project veng – Electric sub station
KP-8 Kolasib, Diakkawn – Paradise restaurant
KP-9 Kolasib, Diakkawn – Pu Hlua’s house
KP-10 Kolasib, Hmar veng- MST Bus stand
KP-11 Kolasib, Electric veng- near PHE office
KP-12 Kolasib, Rengtekawn- near Police check gate
KP-13 Thingdawl- near Post office
KP-14 Bualpui- Gorkha hotel
KP-15 Bualpui- FCI godown
KP-16 Kawnpui- near Govt. High school
KP-17 Kawnpui – near Hospital
KP-18 Kawnpui – near Mizoram Rural Bank Branch
KP-19 Bilkhawthlir – near Hospital
KP-20 Bilkhawthlir – PWD office

3.1.2.3 Samples of Stored Rain water

KR-1 Venglai, Kolasib
KR-2 Project veng, Kolasib
KR-3 Banglakawn, Kolasib
KR-4 Diakkawn, Kolasib
KR-5 Hmar veng, Kolasib

3.1.3 Sample Collection Scheme

Grab samples of Tuikhur waters (KT) and PHED supply waters (KP) were collected from 2005 to 2008 in pre monsoon, monsoon and post monsoon seasons consecutively. The collection of samples was started during post monsoon season of 2005. In this session various field works were conducted and 22 KT and 11 KP samples were collected. In the next session i.e. pre monsoon of 2006, 27 KT and 20 KP samples were procured. During the monsoon season of 2006, 24 KT and 14 KP samples along with 5 KR samples were collected. Since post monsoon, 2006 till pre monsoon of 2008 consistently 32 KT and 20 KP samples were collected. However, in monsoon 2007 number of KR samples remained 5 only, because of the fact that the limited number of houses equipped with the harvested rain water collection facilities.

Samples of potable water to be analyzed are representatives of the source from which water is drawn for different purposes. Through samples we aim to mimic the
entire source or get a scaled down model of the entire source. The integrity of the samples are maintained to ensure that the concentration of various water quality parameters do not change in the time that elapses between drawing the samples and analysis in the laboratory. Liquid samples are broadly classified into two major groups, i.e. the one called instantaneous/spot/snap or grab samples and the other continuous or composite samples. A grab sample is manually collected single portion of sample of water or waste water. When the grab samples of a particular water or waste water is collected at regular intervals for a specific period and mixed, then the integrated sample is known as ‘composite sample’.

For the present work, as the water samples were homogeneous, it was suffice to take the grab sample only. Water samples were collected in polythene bottles of 500 ml capacity fitted with airtight caps. Before collection of samples, polythene bottles were cleaned thoroughly and rinsed with distilled water. Samples for bacteriological examination were collected in clean and sterilized narrow mouthed neutral glass bottles of 500 ml capacity. The most convenient point for sampling potable waters is the consumers’ premises. Samples were possibly taken from a tap directly connected to the main in case of PHE supply water samples. Details regarding the position of the premises relative to the supply main and its possible proximity to a dead-end were noted while such samples were taken. Before collecting the samples, the inside and outside of the tap were thoroughly cleaned. The water being sampled was then allowed to waste for sometimes so that the sample was the representative of the whole supply.

### 3.1.4 Sample Collection Techniques

A proper record of potable water samples collected in suitable containers was maintained throughout the study period. The containers were labeled with:

1. Sample number
2. Date of collection of the sample
3. Time of collection of the sample
4. Name of the source of the sample

All these information were written on gummed papers and were pasted on the respective containers. After labeling, the samples were immediately brought to the laboratory for analysis to avoid any alteration or deterioration in their quality due to chemical or microbial activity.
No single method of preservation is entirely satisfactory and the preservative should be chosen with due regard to the determinations that are to be made. It should be noted that the preservative added for one constituent should not affect the determination of other constituent. Keeping the samples in the dark at low temperature is the best possible preservation. However, to avoid any change in quality parameters during delay in the analysis, suitable preservatives were added to the water samples.

3.2 Laboratory Work

Laboratory work involves analysis of physical, chemical and bacteriological parameters. Physical parameters include pH, electrical conductivity (EC), total dissolved solids (TDS), and turbidity. Chemical parameters selected for this work include total alkalinity (TA), total hardness (TH), carbonate (CO$_3^{2-}$), bicarbonate (HCO$_3^-$), sulphate (SO$_4^{2-}$), total chloride (TCl$^-$), fluoride (F$^-$), nitrate (NO$_3^-$), and metals and heavy metals like Na, K, Ca, Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and As. The bacteriological examination includes tests for total coliforms and the result is reported as most probable number (MPN).

3.2.1 Physical Parameters

The study of physical parameters of water is highly essential because the quality of water and ability to dissolve the chemicals in it totally depends on the physical characteristics of water. The physical properties of water is very important since the disposal of domestic sewage, more utilization of fertilizers to the soil for high yield of crops, industrial effluents discharged to the surface water and ever increasing human population have threatened the requisite standard of potable waters.

3.2.1.1 In Situ Physical Parameters

Physical parameters such as temperature, colour, odour, pH, EC and TDS were tested in situ. Temperature of the water samples was measured with the help of a stem thermometer in degree Celsius. Colour of the water samples was determined by the visual method while pH, EC and TDS were tested by portable pH, EC and TDS meters.

3.2.1.2 Laboratory

3.2.1.2.1 pH: pH represents the effective concentration (activity) of hydrogen ions (H$^+$) in water. This concentration could be expressed in the same kind of units as
other dissolved species, but \( H^+ \) concentrations are much smaller than other species in most waters. The activity of hydrogen ions can be expressed most conveniently in logarithmic units pH is defined as the negative logarithm of the activity of \( H^+ \) ions:

\[
pH = -\log [H^+]
\]

Where \([H^+]\) is the concentration of \( H^+ \) ions in moles per liter.

In water solution, variations in pH value from 7 are mainly due to hydrolysis of salts of strong bases and weak acids or vice versa. Dissolved gases such as carbon dioxide, hydrogen sulphide and ammonia also affect the pH of water. The overall pH range of natural water is generally between 6 and 8. Industrial wastes may be strongly acidic or basic and their effect on pH value of receiving water depends on the buffering capacity of water. pH lower than 4 will produce sour taste and higher value above 8.5 bitter tastes. Higher value of pH hastens the scale formation in water heating apparatus and reduces the germicidal potential of chlorine. pH below 6.5 starts corrosion in pipes, thereby releasing toxic metals such as Zn, Pb, Cd, Cu etc. Changes in pH can also affect aquatic life indirectly by altering other aspects of water chemistry. Low pH levels accelerate the release of metals from rocks or sediments in the stream. These metals can affect a fish’s metabolism and the fish’s ability to take water in through the gills, and can kill fish. pH measurements also provide a very quick and easy to obtain appraisal of the acid-base equilibrium in an ecological system. The pH measurements were done in situ on a portable pH meter (Eutech, Oakton).

3.2.1.2.2 EC: Electrical conductivity of a water sample is a measure of concentration of mineral constituents present in it. It is also a measure of the ability of the sample to carry electric current. It is an indicator of dissolved ions present in water samples. Electrical conductivity of the water samples was determined at the sampling sites itself by a portable conductivity meter (Eutech, Oakton). The EC values were recorded in \( \mu S/cm \).

3.2.1.2.3 TDS: Total dissolved solids (TDS) are the amount of solid substances dissolved in the water samples. In natural waters, the dissolved solids consist mainly of carbonates, bicarbonates, sulphates, nitrates and possibly phosphates of calcium, magnesium, sodium and potassium with traces of iron, manganese and other substances. The amount of dissolved solids present in water is a
consideration for the suitability for domestic use. The TDS values were also measured in situ with the help of a portable TDS meter (Eutech, Oakton).

3.2.1.2.4 Turbidity: Turbidity is a measure of the degree to which the water looses its transparency due to the presence of suspended particulates. The more total suspended solids in the water, the murkier it seems and the higher the turbidity. Turbidity is considered as a good measure of the quality of water. There are a number of parameters that influence the cloudiness of the water; however, it is generally caused by phytoplankton, sediments from erosion, waste discharge, algae growth, urban runoff etc. The suspended particles absorb heat from the sunlight, making turbid waters become warmer, and so reducing the concentration of oxygen in the water (oxygen dissolves better in colder water). Some organisms also can’t survive in warmer water. The suspended particles scatter the light, thus decreasing the photosynthetic activity of plants and algae, which contributes to lowering the oxygen concentration even more. Turbidity of the samples was determined by a Nepheloturbidimeter (Systronics Digital Nepheloturbidimeter-132) in NTU using hydrazine sulphate and hexamethylene tetramene as standards.

3.2.1.2.4.1 Preparation of Reagents and Standards
1 g of hydrazine sulphate was dissolved in distilled water to prepare 100 ml of solution (a). 10g of hexamethylene tetraamine was dissolved in 100 ml of distilled water to prepare 100 ml of solution (b). 5 ml of each of the solutions (a and b) were mixed in a 100 ml volumetric flask and was allowed to stand for 24 hours at 25°C. This solution was diluted with distilled water to the mark. This is a suspension having 400 NTU and can be stored for about a month. 10 ml of this stock solution was diluted to 100 ml with distilled water. This standard solution has 40 NTU and can be stored for about a week.

3.2.1.2.4.2 Procedure
i. The nephelometer was set at 100 using 40 NTU standard suspensions. Every per cent on the scale is equal to 0.4NTU turbidity.
ii. The sample was shaken thoroughly to let the air bubbles subside.
iii. The sample was taken in nephelometer sample tube and the value on the scale was recorded.

Calculation: \[ \text{Turbidity} = \text{Nephelometer reading} \times 0.4 \times \text{dilution factor} \]
3.2.2 Chemical Parameters

3.2.2.1 Total alkalinity

Alkalinity is a measure of the buffering capacity of water, or the capacity of bases to neutralize acids. Measuring alkalinity is important in determining a stream's ability to neutralize acidic pollution from rainfall or wastewater. Alkalinity does not refer to pH, but instead refers to the ability of water to resist change in pH. Alkalinity test is performed to determine bicarbonate (HCO$_3^-$), and carbonate (CO$_3^{2-}$) and occasionally hydroxide (OH$^-$) ions.

Total alkalinity was determined by titration with a standard solution of a strong acid indicated by means of colour. Phenolphthalein indicator enables the measurement of that alkalinity fraction that is contributed by the hydroxide and half that by carbonate. Indicators responding to the pH range 4.5 are used to measure the alkalinity contributed by hydroxide, carbonate and bicarbonate ions.

3.2.2.1.1 Reagents

Phenolphthalein indicator solution:

i. 5g of Phenolphthalein disodium salt dissolved in 1 litre of distilled water;
ii. Standard sulphuric acid of 0.02N strength;
iii. Methyl orange indicator solution: 0.05g of methyl orange dissolved in 1 litre of distilled water.

3.2.2.1.2 Procedure

Phenolphthalein alkalinity (P-Alkalinity)

i. 0.1 ml of phenolphthalein indicator was added to 50 ml of the water sample.
ii. It was titrated with 0.02N standard sulphuric acid till the colouration corresponding to the proper equivalence point of pH 8.3 develops.

Total alkalinity by methyl orange indicator method

i. 0.1 ml of methyl orange indicator was added to the solution in which phenolphthalein alkalinity had been determined.
ii. This solution was titrated with 0.02N standard acid to the proper equivalence point. The indicator changes to orange at pH 4.6 and pink at pH 4.0.

Calculation

Phenolphthalein alkalinity as mg/l CaCO$_3$ = \( \frac{A \times N \times 50000}{B \times N \times 50000} \)
Total alkalinity as mg/l CaCO$_3$ =
Where A = ml titrant required for sample to reach phenolphthalein end point
B = total ml titrant required to reach second end point
N = Normality of the acid

Calculation of alkalinity relationship

The results obtained from the phenolphthalein and total alkalinity determinations offer a means for the stoichiometric classification of the three principal forms of alkalinity present in the water samples.

Carbonate alkalinity is present when the phenolphthalein alkalinity is not zero but less than the total alkalinity.

Hydroxide alkalinity is present if the phenolphthalein alkalinity is more than half of the total alkalinity.

Bicarbonate alkalinity is present if the phenolphthalein alkalinity is less than half of the total alkalinity.

**Alkalinity relationship**

<table>
<thead>
<tr>
<th>Result of titration</th>
<th>Hydroxide alkalinity as CaCO$_3$</th>
<th>Carbonate alkalinity as CaCO$_3$</th>
<th>Bicarbonate alkalinity as CaCO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P= 0</td>
<td>0</td>
<td>0</td>
<td>T</td>
</tr>
<tr>
<td>P&lt; 1/2</td>
<td>0</td>
<td>2P</td>
<td>T- 2P</td>
</tr>
<tr>
<td>P= 1/2</td>
<td>0</td>
<td>2P</td>
<td>0</td>
</tr>
<tr>
<td>P&gt; 1/2</td>
<td>2P-T</td>
<td>2 (T-P)</td>
<td>0</td>
</tr>
<tr>
<td>P= T</td>
<td>T</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

P = Phenolphthalein alkalinity, T= Total alkalinity

**3.2.2.2 Total hardness**

Hardness is a measure of polyvalent cations (ions with a charge greater than +1) in water. It generally represents the concentration of calcium (Ca$^{2+}$) and magnesium (Mg$^{2+}$) ions, because these are the most common polyvalent cations. Other ions, such as iron (Fe$^{2+}$) and manganese (Mn$^{2+}$), may also contribute to the hardness of water, but are generally present in much lower concentrations.

Hardness affects the amount of soap that is needed to produce foam or lather. Total hardness of the samples was measured by the EDTA titrimetric method.

Principle of the titration
Ethylenediamine tetra acetic acid and its sodium salts form a chelated soluble complex when added to a solution of certain metal cations. If a small amount of Eriochrome Black T is added to an aqueous solution containing Ca\(^{2+}\) and Mg\(^{2+}\) ions at a pH of 10.0-10.2, the solution becomes wine red. If EDTA is then added as a titrant the Ca\(^{2+}\) and Mg\(^{2+}\) ions get complexed and after all the ions have been complexed the solutions turn from wine red to blue. This is the end point of the titration.

3.2.2.2.1 Reagents

i. Buffer solution: 1.179g of disodium salt of EDTA dehydrates and 0.78g of MgSO\(_4\).7H\(_2\)O was dissolved in 50 ml of distilled water. A mixture of 16.9g of NH\(_4\)Cl and 143 ml of conc.NH\(_4\)OH was added to this solution and diluted to 250 ml with distilled water.

ii. Inhibitor: 4.5g of hydroxyl amine hydrochloride was dissolved in 100 ml of ethyl alcohol. It acts as an inhibitor for interfering ions.

iii. Indicator: 0.5g of Eriochrome Black T dye was mixed with the inhibitor made above.

iv. Standard EDTA titrant of 0.01M: 3.723g of disodium ethylenediamine tetra acetate dehydrate (EDTA) was dissolved in distilled water and diluted to 1000 ml.

v. Standard calcium solution: 1.0g of anhydrous CaCO\(_3\) powder was transferred into 500 ml distilled water and added to it 1+1 HCl until all CaCO\(_3\) is dissolved. To this solution, 200 ml distilled water was added and boiled for few minutes. The solution so obtained is cooled and a few drops of methyl orange were added and adjusted to the intermediate orange colour by adding 1+1 HCl. The solution is transferred into a 1 litre volumetric flask and diluted to the mark with distilled water. This standard solution is equivalent to 1.0 mg CaCO\(_3\) per 1.0 ml.

3.2.2.2.2 Procedure

i. 25 ml of the sample was diluted to 50 ml with distilled water and 1-2 ml of buffer solution was added.

ii. 1-2 drops of Eriochrome Black T indicator was added to the above solution.

iii. Standard EDTA titrant was added slowly with constant stirring until the last reddish tinge disappears and the colour of the solution becomes blue.
Calculation
Hardness (EDTA) as mg/l CaCO₃ = (ml EDTA titrant x 1000 x N)/ ml sample
Where N = mg CaCO₃ equivalent to 1.0 ml EDTA.

3.2.2.3 Calcium

Calcium was determined by EDTA titrimetric method. When ethylenediamine tetra acetic acid is added to water samples containing both calcium and magnesium, it combines first with calcium that is present in the sample. Calcium is determined directly using EDTA when the pH is made sufficiently high so that magnesium largely precipitated as the hydroxide and an indicator is used which combines with calcium only.

3.2.2.3.1 Reagents

i. Sodium hydroxide 1N: 40g of NaOH is dissolved and diluted to 1 litre with distilled water.

ii. Murexide indicator: It is prepared by mixing 0.20g of murexide with 100g of solid NaCl.

iii. Standard EDTA titrant 0.01M: It is prepared by dissolving 3.723g of disodium ethylenediamine tetra acetic acid dehydrate salt in 1000 ml distilled water.

3.2.2.3.2 Procedure

i. 20 ml of water sample was taken in a conical flask.

ii. 2 ml of 1N- NaOH was added to the conical flask.

iii. To the above solution 1 drop of murexide indicator was added and titrated with EDTA titrant with continuous stirring till a purple colour persists. This is the end point.

Calculation
Ca (mg/l) = ml EDTA titrant x 400.80/ ml sample

3.2.2.4 Magnesium

Magnesium ions were calculated from the total hardness obtained by the EDTA titrimetric method and the calcium ions estimated by using the formula,

Mg (mg/l) = \( \frac{TH - (2.497 \times Ca)}{} \)

Where TH= Total hardness
Ca= Amount of calcium estimated by EDTA titration

3.2.2.5 Sulphate

Estimation of sulphate ions was done by turbidimetric method. Sulphate ions are precipitated in a hydrochloric acid medium with barium chloride in such a manner so as to form barium sulphate. The absorbance of sulphate suspension is measured by spectrophotometer and sulphate ion concentration is determined by comparison with a standard curve.

3.2.2.5.1 Reagents

i. Conditioning reagent: 50 ml of glycerol was mixed with a solution containing 30 ml HCl, 300 ml distilled water, 100 ml 95% ethyl alcohol and 75g sodium chloride.

ii. Barium chloride crystals

iii. Standard sulphate solution: 0.1479g of sodium sulphate was dissolved in distilled water and diluted to 1000 ml. This solution contains 100ppm of SO₄

3.2.2.5.2 Procedure

i. 100 ml of the sample was taken in a 250 ml flask. 5.0 ml of the conditioning reagent was added to this and mixed well.

ii. A pinch of BaCl₂ crystals was added to the above solution and stirred for one minute.

iii. Immediately after stirring some of the solution was poured into the spectrophotometer at 420nm and turbidity was measured. Readings were taken at an interval of 30 seconds for 4 minutes. The highest reading was considered as the main reading.

iv. The sulphate concentration in the sample was estimated by comparing the turbidity reading with a standard curve made by comparing with standard sulphate solution.

Calculation

Sulphate (SO₄²⁻) mg/l = mg SO₄ x 1000/ml sample

3.2.2.6 Total Chloride

Chloride is invariably present in small quantity in almost all natural waters and its content goes up appreciably with increasing salinity. Chloride mainly reaches to the water bodies from the leaching of chloride-containing rocks and
soils with which the water comes in contact. It may impart salty taste to water depending on the nature of the cation constituents. High chloride concentrations may harm metallic pipes structures. Its higher concentrations in irrigation waters may be harmful to many plant species.

Chloride was estimated by volumetric titration of neutral or slightly alkaline sample against silver nitrate solution using potassium chromate as an indicator. On adding silver nitrate to the water sample it reacts with chloride ions of the sample to form silver chloride which gets precipitated. When all the chloride ions have been converted to silver chloride, the titrant reacts with potassium chromate to form silver chromate. The red colour of silver chromate changes to pinkish yellow colour at the end point.

3.2.2.6.1 Reagents

i. Standard silver nitrate titrant, 0.0141N: 2.396g of AgNO₃ was dissolved in distilled water and diluted to 1000 ml. It was stored in a brown bottle.

ii. Standard sodium chloride solution, 0.0141N: 0.8241g of NaCl was dissolved in distilled water and diluted to 1000 ml.

iii. Potassium chromate indicator solution: 50g of K₂CrO₄ was dissolved in little distilled water and added to it silver nitrate solution until a definite red precipitate is formed. The above solution was allowed to stand for 12 hours, filtered and diluted the filtrate to 1000 ml with distilled water.

3.2.2.6.2 Procedure

i. 100 ml of the sample was taken in a conical flask.

ii. 1 ml of K₂CrO₄ indicator solution was added to the sample.

iii. The above solution was titrated with standard silver nitrate solution till a pinkish red colour persists. This is the end point.

iv. Similar experiment was performed for blank also.

Calculation

\[ \text{Cl}^-(\text{mg/l}) = (A-B) \times N \times 35.45 \times 1000 / \text{ml sample} \]

Where A= ml AgNO₃ for sample,
B= ml AgNO₃ for blank, 
N= normality of AgNO₃ solution

3.2.2.7 Fluoride

Fluoride is one of the very few chemicals that have been shown to cause significant effects in people through drinking-water. Fluoride has beneficial effects on teeth at low concentrations in drinking-water, but excessive exposure to fluoride in drinking-water, or in combination with exposure to fluoride from other sources, can give rise to a number of adverse effects. These range from mild dental fluorosis to crippling skeletal fluorosis as the level and period of exposure increases. Crippling skeletal fluorosis is significant course of morbidity in number of regions of the world. Fluoride is known to occur at elevated concentration in a number of parts of the world and in such circumstances can have, and often has, a significant adverse impact on public health and well being.

Most people associate fluoride with the practice of intentionally adding fluoride to public drinking water supplies for the prevention of tooth decay. However, fluoride can also enter public water systems from natural sources, including runoff from the weathering of fluoride-containing rocks and soils and leaching from soil into groundwater.

Fluoride contents in drinking water samples were determined using expandable Ion-Analyzer Model EA 940 with fluoride ion selective electrode (Orion Ion Selective Electrode Model 96-09) at IIT Mumbai.

3.2.2.7.1 Principle of Operation of the Fluoride ISE

In the case of the F⁻ ISE, the ion-selective membrane is a single crystal of Lanthanum Fluoride (LaF₃) doped with Europium Fluoride (EuF₂) which produces holes in the crystal lattice through which F⁻ ions can pass. When immersed in a fluoride solution and connected via a voltmeter to an AgCl/KCl external reference electrode immersed in the same solution, the negative F ions in the solution pass through the crystal membrane by normal diffusion from high concentration to low concentration until there is an equilibrium between the force of diffusion and the reverse electrostatic force due to repulsion between particles of similar charge. On the other side of the membrane there is a corresponding build-up of positive ions.
The buildup of negative F⁻ ions on the inside of the membrane is compensated for by Cl⁻ ions in the internal reference solution becoming neutralized by combining with the Ag/AgCl wire, and electrons are thus forced through the external wire to the voltage measuring device (ion meter or computer interface). The other terminal of the voltmeter is connected to the Ag/AgCl wire of the external reference electrode. Here, the influx of electrons causes Ag ions in the filling solution to accept electrons and deposit on the silver wire and, consequently, Cl⁻ ions to flow out into the sample solution.

Note that, in general, depending on the concentrations inside and outside the membrane and which ion is being measured, all the reactions described above could occur in the opposite direction.

3.2.2.8 Nitrate

Though nitrate is an essential element in the life processes of plants and animals, it is potentially hazardous when present in drinking water at sufficiently high concentrations. Numerous sources in the environment contribute to the total nitrate content of natural waters viz. atmosphere, geological sources, soils, atmospheric nitrogen fixation and anthropogenic sources that include industrial wastes containing N- compounds, human and animal wastes and agricultural activities. Nitrate (NO₃⁻) is highly soluble (dissolves easily) in water and is stable over a wide range of environmental conditions. It is easily transported in streams and groundwater. Nitrate itself is relatively non-toxic but when ingested with food or water, it may be reduced to nitrite by bacteria in the mouth or gut. This reduced nitrite is a potential threat to human health when found in excess quantity in drinking water. Methemoglobinemia, commonly known as ‘blue baby’ disease in infants is closely related to nitrate concentration in drinking water. Infants are most prone to nitrate concentration because they have underdeveloped metallic enzyme, relatively small blood volume and greater reactivity of fetal haemoglobin.

The determination of nitrate concentration in the samples was done by ultraviolet spectrophotometric method. Measurement of UV absorption at 220 nm enables rapid determination of NO₃⁻. Since dissolved organic matter also may absorb at 220 nm and NO₃⁻ does not absorb at 275 nm, a second measurement made at 275 nm is used to correct the NO₃⁻ value. Acidification with 1N HCl is
designed to prevent interference from hydroxide or carbonate concentrations up to 1000 mg CaCO$_3$/l.

3.2.2.8.1 Reagents

i. Stock nitrate solution: Potassium nitrate (KNO$_3$) is dried in an oven at 105°C for 24 hours. 0.7218g of dry KNO$_3$ was dissolved in distilled water and diluted to 1000 ml. This solution is stable for about a period of six months.

ii. Intermediate nitrate solution: 100 ml of stock nitrate solution was diluted to 1000 ml with distilled water. This solution is also stable for about six months.

iii. Hydrochloric acid solution, HCl, 1N.

3.2.2.8.2 Procedure

i. Treatment of sample: 1ml of HCl solution was added to 50 ml of sample and mixed thoroughly.

ii. Preparation of standard curve: NO$_3^-$ calibration standards were prepared in the range of 0 to 7 mg NO$_3^-$ -N/l by diluting to 50 ml the following volumes of intermediate nitrate solution: 0, 1.00, 2.00, 4.00, 7.00, …35.00ml. NO$_3^-$ standard was treated in the same manner as sample.

iii. Spectrophotometric measurement: A wavelength of 220 nm was used to obtain NO$_3^-$ reading and a wavelength of 275 nm was used to determine interference due to dissolved organic matter.

Calculation

Two times of the absorbance reading at 275 nm was subtracted from the reading at 220 nm for samples and standards to absorbance due to NO$_3^-$. A standard curve was constructed by plotting absorbance due to NO$_3^-$ against NO$_3^-$ - N concentration of standard.

3.2.2.9 Metals and Heavy Metals

All the metals and heavy metals were measured on ICP-AES (Horiba Jobin Vyon ULTIMA-2) at IIT Mumbai.

3.2.2.9.1 Principle

ICP emission spectrometry is a comparatively new technique with enormous potential in geochemistry. In principle the method is capable of measuring most elements in the periodic table with low detection limits and good precision over several orders of magnitude. Elements are measured simultaneously and a
complete analysis can be made in the space of about two minutes, making it an extremely rapid analytical method.

ICP emission spectrometry is a ‘flame’ technique with a flame temperature in the range of 6000-10000K. It is also a solution technique and standard silicate dissolution methods are employed. The sample solution is passed as an aerosol from a nebulizer into argon plasma. The inductively coupled plasma is a stream of argon atoms, heated by the inductive heating of a radio-frequency coil and ignited by a high frequency Tesla spark. The sample dissociates in the argon plasma and a large number of atomic and ionic spectral lines are excited. The spectral lines are detected by a range of photomultipliers, they are compared with calibration lines and their intensities are converted into concentrations.

3.2.3 Bacteriological Parameters

3.2.3.1 Total Coliform

The total coliform group includes the aerobic and the facultative anaerobic, gram-negative, non-spore- forming, rod- shaped bacteria that ferment lactose with gas production within 48 hours at 35°C (APHA, 2005). This group includes the Escherichia coli, Enterobacter, Klebsiella and Citobacter. These coliforms are discharged in high numbers (2 x 10^9 coliforms per day per capita) in human and animal feces, but not all of them are fecal origin. These indicators are useful for determining the potable water, shellfish- harvesting waters and recreational waters (Bitton, 1999). In water treatment plants, total coliforms are one of the best indicators of treatment efficiency of the plant. This group has also been found useful assessing the safety of reclaimed wastewater in the Windhoek reclamation plant in Namibia (Grabow, 1990)

3.2.3.1.1 Test Procedure to determine Most Probable Number (MPN)

The multiple tube fermentation technique was used to enumerate positive presumption and confirmed coliform test.

3.2.3.1.1.1 Presumptive Test

Dilution above 1:1000 was prepared; five fermentation tubes previously filled with 9 ml of Mac Conkey broth were prepared for each dilution. Now one Durham’s vial was put in an inverted condition inside each fermentation tube. The tubes were plugged with cotton and sterilized in an autoclave. Now sample was added to each test tube with the help of a sterilized pipette. The tubes were vigorously shaken and
incubated at 35-37°C for 48 hours. Each test tube was examined for gas production. The tubes showing gas in the Durham’s vial were recorded as positive. The tubes showing positive results were now subjected to the confirmatory test.

3.2.3.1.1.2 Confirmatory Test

The fermentative tube was filled with 10 ml Brilliant Green Lactose Bile (BGLB) broth and Durham’s vial was put in an inverted position in each fermentation tube. The positive tubes were shaken gently and one loopful of sample was transferred to each fermentative tube having BGLB broth. These tubes were incubated at 35-37°C for 48 hours.

The tubes producing gas were recorded as positive and MPN/100 ml was calculated.

\[
\text{MPN/100 ml} = \text{MPN table value} \times 10 \div \text{Starting value}
\]