Chapter-II

MATERIAL AND METHODS

In order to get reliable and useable data in water and soil quality monitoring investigation, the important points to be considered are the analytical and other methods employed, the type of investigation, the purpose of study, what data are needed and how it can be useful in a proposed study. Keeping the above points in view, the field and laboratory procedure were adopted to fulfill the objectives of study. The following steps were undertaken for the present investigation.

1. Selection of suitable groundwater and soil sampling stations,
2. Collection of water, effluent and soil samples,
3. Laboratory analysis of collected samples by suitable method, &
4. Evaluation of water and soil chemistry data obtained.

2.1 Groundwater:

Selection of sampling sites:

As stated in previous chapter, the stream carrying effluent from sugar mill flows through the study area. The loss of some effluent is envisaged due to percolation through soil zone. This wastewater is therefore expected to reach the ground water table. Hence, it was essential to have the sampling sites near the streams and
few meters away from the effluent stream. Accordingly, a grid method of sampling in the study area has adopted for collecting the groundwater (Trivedy and Goel, 1986). The groundwater composition in this particular case is likely to vary from place to place and time to time. Therefore, representative dug wells were selected for water samples collection. Some selected dug wells were close the effluent stream and some were progressively away from it. Thus dug wells as well as some bore wells in the study area were selected for their inventory and collection of water sample (Fig. 7, 8 & 9). This sampling station was broadly falls into three categories as.

a. The areas serving the source of water supply for drinking purpose.

b. The agricultural area, used mainly for irrigation, and

c. The wells, which are contaminated by, sugar factory effluent.

**Collection of Samples:**

In view of the fact that water is susceptible to change in the composition because of its powerful solvent properties and evaporation (De, 1986) some of the points were considered during collection of water samples such as homogeneity and size of samples. Similarly, by considering the operational period (October to January) of Gajanan sugar factory, the groundwater samples were collected monthly from October to December in 2007 and January to April in
Fig- 7: Bore well point about 4.5 km away from the sugar factory.
Fig- 08: Ground water pollution in the nearby dug well water approximately 750 mts away.

Fig- 08: Ground water pollution in the nearby dug well water approximately 750 mts away.
Fig. 09: Ground water pollution in the nearby dug well water approximately 3.0 km. mts away.

Fig. 09: Ground water pollution in the nearby dug well water approximately 4.5 km. mts away.
Fig- 09 : Ground water pollution in the nearby dug well water approximately 4.7 km mts away.
2008. The samples were collected after pumping the well for half an hour. The collected water samples were labeled properly and a record was made, such as water depth, lithologies and operating condition of the well. The effluent sample was collected twice during running period (in December 2007 and in January 2008) of factory from the effluent carrying stream while flowing through study area. While the soil samples were collected only once in the month of March 2008.

The collected water, soil and effluent samples were brought to the laboratory for further analysis. The analysis was carried out with the help of suitable laboratory analytical or instrumental methods available (Pondhe, 2005).

**Laboratory analytical methods:**

The collected groundwater samples were brought to laboratory to carry out the chemical analysis of the constituents. These samples were filtered through Whatman No. 42 filter paper. Chemical analysis of filtered water samples was carried out to estimate/determine pH, Electrical conductivity (EC), Sodium (Na$^{2+}$), Potassium (K$^+$), Calcium (Ca$^{2+}$) Magnesium (Mg$^{2+}$), Chloride (Cl$^-$), Total alkalinity (as CaCO$_3$), Total hardness (as CaCO$_3$), Sulphate (SO$_4^{2-}$), Phosphate (PO$_4^{3-}$), Nitrate (NO$_3^-$), Dissolved Oxygen (DO), Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) etc. The methods used for this analysis were standardized
according to the procedure given in standard method or examination of water and wastewater by APHA-AWWA and WPCF (1975; Trividy and Goel, 1986; Gaines, 1993; Kodarkar et.al. 1998 Pondhe, 2005). The results are reported in parts per million (ppm). For diagramatic representation the data in ppm were converted to equivalent per million (epm). Analytical methods used for the chemical analysis of water are briefly outlined below.

**Cationic constituents:**

**Calcium:**

Volumetric determination of calcium was carried out with the help of EDTA method (IS: 3025, 1964). In this the EDTA combine first with calcium. When pH is made sufficiently high, the magnesium is precipitated as hydroxide and the indicator murexide combines with calcium only to give pink colour to calcium containing solution. With EDTA, this color turn to violet at pH 12 to 13. The concentration of calcium was determined using following formula.

\[
\text{Ca}^{2+} \text{ (mg/l)} = \frac{\text{ml of EDTA used} \times 400.8}{\text{ml of sample used}}
\]

**Magnesium:**

The method of calculation suggested by ISI (ISI: 3025, 1964) was used for estimation of magnesium. The concentration of \(\text{Mg}^{2+}\) ion was calculated by using following equation.
\[ \text{Mg}^{2+} \text{(mg/l)} = \frac{(A-B \times 400.8)}{\text{ml of sample} \times 1.645} \]

Where,

A= is the ml of EDTA used in hardness determination and

B= is the ml of EDTA used in calcium determination

**Sodium and Potassium:**

The estimation of sodium and potassium was carried on flame photometer. The instrument was calibrated by running the set of standards each time followed by unknown samples. The results were calculated by preparing calibration curve for standard solutions and concentrations of unknown samples were found out from the graph.

**Total hardness:**

The hardness is normally expressed in terms of \( \text{CaCO}_3 \). The EDTA method (Goetz, 1950, 1959; Trivedy and Goel, 1986) was used to measure the concentration of calcium and magnesium ions in the water as a means of determining the total hardness of water. This method is based on the principle that Ethylene Diamine Tetra Acetic acid (EDTA) and its sodium salts form chelate stable soluble complex when added in the solution of certain metal contains.

\[ \text{M + EDTA} \rightarrow \text{M EDTA Complex}. \]
A small amount of Erichome black T is added to an aqueous solution containing calcium and magnesium ions at the pH of 10. As a result, calcium and magnesium ion get complexed and the solution become wine red. Since EDTA has strong affinity towards calcium and magnesium ions, on the addition of sufficient amount of regent a new complex of blue color is formed at the end of titration (Snoeyink and Jenkins, 1980). The total hardness was calculated by using following formula.

\[
\text{Total hardness (mg/l) = } \frac{\text{ml of EDTA used}}{\text{ml of sample used}} \times 1000
\]

**Anionic constituents:**

**Chloride:**

The chloride in the water can be determined by several methods viz. argentometric of Mohr’s method, mercuric nitrate method and potentiometric method. In the present study argentometric method (Trivedy and Goel, 1986) was considered suitable for the determination of chloride. In natural or alkaline solution, potassium chromate can indicate the end point of titration of chloride. AgNO\(_3\) react with the chloride ion to form very slightly soluble white precipitate of silver chloride. After all chloride is removed, indicator changes its color to radish brown of silver
chromate. The concentration of chloride was determined by using the following relation.

\[
\text{Cl (mg/l)} = \frac{N \times \text{ml of AgNO}_3 \times 35.5 \times 1000}{\text{ml of sample used}}
\]

Where \( N \) is the Normality of \( \text{AgNO}_3 \)

**Sulphate:**

The sulphate was determined by the turbidimetric method (HMSO, 1972). In this method, the sulphate ion is precipitated in the form of barium chloride in hydrochloride acid medium. The concentration of sulphate was determined from the absorbance of light by barium sulphate and then by comparing it with a standard curve, using spectrophotometer at 420nm wavelength.

**Total Alkalinity:**

Several authors (Larsen and Henely, 1955), (Thomos and Lynch, 1960) have suggested different methods for the determination of alkalinity in natural waters in terms of equivalent \( \text{CaCO}_3 \). The hydroxyl ions present in the sample as a result of dissociation or hydrolysis is determined by titration with hydrochloric acid by using phenolphthalein and methyl orange as an indicator. The pink color appears with phenolphthalein indicator, referred to as phenolphthalein alkalinity. The yellow color appears with methyl orange indicator and is called as methyl orange alkalinity. The total of both reading gives
the total alkalinity present in the water sample. Formula used for measurement of alkalinity was,

\[
\text{PA as CaCO}_3 \text{ (mg/l)} = \frac{A \times \text{Normality of HCl} \times 1000 \times 50}{\text{ml of sample}}
\]

\[
\text{TA as CaCO}_3 \text{ (mg/l)} = \frac{A \times \text{Normality of HCl} \times 1000 \times 50}{\text{ml of sample}}
\]

Where,

A= MI of HCl used with phenolphthalein.

B= MI of HCl used with phenolphthalein and methyl orange.

PA= Phenolphthalein alkalinity.

TA= Total alkalinity.

**Minor constituents:**

**Phosphate:**

There are several methods available for the determination of orthophosphate viz. vanadomolybdate method, stannous chloride method and ascorbic acid method. Out of this method stannous chloride method was chosen in the present work, as this method is more sensitive than other two.

The principle of this method is that the phosphate ion combines with ammonium molybdate under acidic condition to form a complex known as ammonium phosphomolybdate. The excess of ammonium molybdate is reduced with stannous chloride, which gives
the blue color of molybdenum. The intensity of blue color was measured by spectrophotometer at 690nm wavelength. The results were calculated by preparing calibration curve for standards solutions and concentrations of unknown samples were found out from the graph.

**Nitrate:**

There are two methods of determination of nitrate in water viz. Phenol disulphonic method and brucin method. Phenol disulphonic method was used in the present study. The nitrate react with Phenol disulphonic acid to form nitro derivative in alkaline medium and develops yellow color. The intensity of this color was measured by colorimeter at 410 nm wavelength. The results were calculated by preparing calibration curve for standard solutions and concentration of unknown samples were found out from the graph.

**Indicator parameters:**

**Dissolved Oxygen:**

The dissolved oxygen in water was determined with the help of Winkler method (Winklers Idometric Azide modification method) by APHA-AWWA and WPCF, (1975). In this method addition of divalent manganese solution, followed by strong alkali to the water sample, oxidizes rapidly an equivalent amount of dissolved oxygen present in it. This in presence of iodide ions on acidification,
the oxides of manganese revert to divalent state with the liberation of iodine equivalent to original dissolved oxygen content in the sample. The iodine is then titrated with a standard solution of sodium thiosulphate. The dissolved oxygen present in the sample was determined using the following relation.

\[
DO \text{ (mg/l)} = \frac{N \times \text{ml of Na}_2\text{S}_2\text{O}_3 \times 8 \times 1000}{V2 \times (V1-V)} \times \frac{1}{V1}
\]

Where,

- \(V1=\) volume of sample titrated
- \(V2=\) total volume of sample, \(V=\) volume of reagent added.

**Chemical Oxygen Demand:**

Moore *et.al.* (1949) Suggested dichromate refluxing method for the determination of the oxygen consumed. In this method, the sample is refluxed with a known amount of potassium dichromate and strong sulfuric acid, followed by silver sulphate and mercuric sulphate. After cooling and dilution up to 140 ml with distilled water, the excess of dichromate is titrated with ferrous sulphate with the help of ferroin indicator, which changes its color from blue green to radish brown. The COD was estimated by using the following formula.

\[
COD \text{ (mg/l)} = \frac{\text{ml of FAS} \times N \times 8 \times 1000}{\text{ml of sample titrated}}
\]
Where FAS is Ferrous Ammonium Sulphate

N is the normality of FAS.

**Biochemical Oxygen Demand:**

Hemmer, (1977), Sawyer and McCarty (1985) and Trivedy and Goel (1986) has given the method for determination of the BOD. This is based on the determination of oxygen. In this method addition of divalent compound followed at high pH, oxidizes rapidly equivalent amount of dissolved oxygen present in the form of divalent compound precipitate. For the long period of incubation at room temperature (up to 5 days) in the presence of iodine ions and in acidic medium all divalent compound reverts to CO$_2$, H$_2$O, ammonia etc. that can be measured. The excess of divalent compound is then titrated with sodium thiosulphate after 5 days.

** Irrigation quality parameters:**

The parameters for irrigation of water quality were also calculated with the help of some formulae given by (USDA, 1956, Goel, 1997, Mahida, 1981). For this purpose the result obtained after determination/estimation of Sodium (Na$^{2+}$), Potassium (K$^+$), Calcium (Ca$^{2+}$), Magnesium (Mg$^{2+}$), Chloride (Cl$^-$), and Total alkalinity (as CaCO$_3$) in mg/l were converted in milliequivalent per liter (meq/l). These values of respected cation and or anions were used in following
calculations of respective parameter of irrigation quality for getting its index or ratios.

**Sodium Absorption Ratio (SAR):**

The index is used for predicting the sodium hazard of water in agricultural use. It is the concentration of sodium and proportion of sodium to calcium and magnesium. SAR was calculated as,

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

**Residual Sodium Carbonate (RSC):**

If the water contains carbonate and bicarbonate in excess of calcium and magnesium then this excess is denoted as RSC and was calculated by following formula.

\[
RSC \text{ (meq/l)} = (\text{HCO}_3^- \text{ CO}_3^-) - (\text{Ca}^{2+} + \text{Mg}^{2+})
\]

**Kellys Ratio or Kellys Index (KR/KI):**

It represent alkali hazard of water. KR is nothing but the proportion of sodium to calcium and magnesium and was calculated as,

\[
KI \text{ (meq/l)} = \frac{\text{Na}^{2+}}{\text{Ca}^{2+} + \text{Mg}^{2+}}
\]
Soluble Sodium Percentage (SSP):

It is the percentage of sodium concentration to sodium, calcium and magnesium concentration and was calculated by following formula.

$$\text{SSP (meq/l)} = \frac{\text{Na}^+}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+}$$

Schollers Index (SCI):

This is the proportion of excess concentration of chloride to sodium and potassium to chloride and was calculated with following formula.

$$\text{SSP (meq/l)} = \frac{\text{Cl}^- (\text{Na}^+ \text{K}^+)}{\text{Cl}^-}$$

The result obtained for all above water analysis and calculation during study are presented in table number 1 to 20. The average data was made and presented in table 8 (Monthly average) and 9 (Entire average). The data is also subdivided for easy understanding into off season (i.e. February 2007 to March 2004) and operational period (season i.e. October 2003 to January 2004) of the industry and are presented in Table 10 and 11.
2.2 Soil:

**Selection of the sampling stations:**

In order to get an idea about development of salinity and or alkalinity as well as for variation in soil chemistry, the sampling stations were established along the length of stream and also across it. In all eleven sampling locations were selected for the collection of soil samples.

**Laboratory analysis of soil samples:**

The collected soil samples were analyzed for determination of pH, EC exchangeable cations etc.

**EC and pH:**

For this, 1:5 soil: water suspension (in distilled water) was made and EC and pH of this suspension were determined with the help of digital EC and pH meter (Trivedy and Goel, 1986).

**Exchangeable Cations:**

In the laboratory, the exchangeable cations were determined by taking 25 gram of air dried soil and adding to it 100ml of 40% alcohol and shaking the system. After fifteen minutes this suspension was filtered through ordinary filter paper and washed with 40% alcohol, twice. The scarped soil from the filter paper was taken in another beaker and 100 ml ammonium acetate was added to it and kept overnight. This suspension was filtered using an ordinary filter
paper and washing it with ammonium acetate solution to make the final volume of 100 ml. Then the filtrate was used in determination of the exchangeable cations viz. \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \), \( \text{Na}^+ \), and \( \text{K}^+ \) with the help of method described under water analysis with different formula which are given here as,

\[
\text{Ca}^{2+} \text{ in meq/100g} = \frac{A \times 400.8 \times V}{v \times 20.04 \times 10 \times S}
\]

\[
\text{Mg}^{2+} \text{ in meq/100g} = \frac{B - A \times 400.8 \times V}{v \times 1.645 \times 10 \times S \times 12.16}
\]

\[
\text{Na}^+ \text{ in meq/100g} = \frac{\text{mg Na}^+/ \text{of soil extract} \times V}{10 \times S \times 23}
\]

\[
\text{K}^+ \text{ in meq/100g} = \frac{\text{mg K}^+ \text{ of soil extract} \times v}{10 \times S \times 29}
\]

Where,

A = Volume of EDTA used for \( \text{Ca}^{2+} \) determination in ml

B = Volume of EDTA used for \( \text{Ca}^{2+} + \text{Mg}^{2+} \) determination in ml.

V = Total volume of soil extract prepared.

S = Weight of soil taken.

V = Volume of extract titrated.

**Cation Exchange Capacity (CEC):**

It is the degree at which soil can absorb and exchange cations (positively charged ions). Hence, this test measures the soils ability to hold cation by electrical attraction. The CEC was calculated by following formula (Daji, 1985).
CEC (meq/100g) = Na concentration of extract of soil x 100
Weight of soil in grams

**Exchangeable Sodium Percentage (ESP):**

The ESP of the soil is the percentage of exchangeable sodium ions to the total exchangeable cations in the soil sample. It was calculated from the formula as given below (USDA, 1954).

\[
\text{ESP (meq/100g)} = 100 \left( -0.0126 + 0.01475 \times \text{SAR} \right) \\
1 + \left( -0.126 + 0.01475 \times \text{SAR} \right)
\]

Similarly the **SAR** and **SSP** for soil were also calculated as formulae described under water analysis.

The results obtained after analysis of soil are presented in table 21 to 24. The correlation matrix was obtained within different properties of well water [well waters (Table 22) which is used to irrigate the soil (Table 23) in study area] and soil and is presented in table 24. The elaborated and subsequent discussion on result of soil and water analysis is described in next chapters.