

CHAPTER 5

ASSESEMNT OF
THE QUALITY OF GROUND WATER
AND
SOIL CONTAMINATED
WITH SUGAR FACTORY EFFLUENT

5.1 INTRODUCTION

Air, water and soil pollution has been recognized as one of the major problems of the modern world. The increasing demand for water and dwindling supply has made the treatment and reuse of industrial effluents an attractive option. The problem of environmental pollution on account of essential industrial growth is practical terms, the problem of disposal of industrial water, whether solid, liquid or gaseous. All the three types of wastes have the potential to pollute water and soil ecosystem (Kisku et al, 2000). Use of industrial effluent and sewage sludge on agricultural land has become a common practice in India as a result of which contaminants present in effluent can be transferred and concentrated into water bodies and soil (Bouwer, 2000). Industrial effluents containing various metallic and nonmetallic elements act as nutrients but at the higher concentration they show toxic effects on seed germination and seedling growth, ultimately adversely affecting plant growth and yield in cultivated land (Sen et al, 2011).

Watercourses and aquatic habitats can be polluted by agrochemicals and sediments due to both sugarcane cultivation and downstream sugarcane processing. Groundwater can be contaminated by leaching of nutrients from fertilizers especially when applied to sandy soils that can extend to downstream coastal zone ecosystems (WWF 2003). Pollution of rivers by industrial effluent has in the past been a major problem at some mills in India for example, in the Abu drainage area at Meerut in Uttar Pradesh (Rajendra Singh 2000). They examined soil and water pollution levels and identified indiscriminate discharge of effluents from a wide range of industries including sugar mills resulting in serious effects on the local flora and fauna, and water was found to be unsuitable for human consumption, domestic use and irrigation purposes.

The soil is a living, dynamic system made up of different mineral particles, organic matter and a extremely diverse community of living and interacting microorganisms that is referred to as the soil ecosystem or the soil food web. Soil not only provides mankind with food and renewable energy sources, but also produces living space and food for billions of microorganisms. Conservation of this ecosystem is seen as vital for maintaining the physical, chemical and biological integrity of the soil and the sustainable cultivation of sugar crops (e.g. Morgan 1986; Meyer and Wood (2000).

Ramalho *et al.* (2001) analyzed soil samples treated with sugarcane industrial residues. Anil kumar *et al.* (2003) studied the effect of distillery spentwash on some soil characteristics and water. Roy *et al.* (2007) studied the effect of irrigation by sugar factory effluent (spentwash) and the well water from adjoining area in Wardha district, Maharashtra. Siddiqui and Waseem (2012) made attempts to study the influence of sugar mill treated and untreated effluent on seed germination and seedling growth of cereal crops.

Doke *et al.* (2011) assessed physico-chemical parameters of treated waste water effluents from a sugar industry and determined the effect of various concentrations (0%, 20%, 40%, 60%, 80 % and 100%) of effluent on seed germination, germination speed, peak value and the germination value of Mung (*Vigna angularis*), Chavali (*Vigna cylindrical*) and Jowar (*Sorghum cernum*) seeds. Ajamal and Khan (1983) evaluated the effects of sugar mill effluent on soil and crop plants. Baskaran *et al.* (2009) evaluated impact of sugar mill effluent polluted soil and its effect of green gram.

Nunes *et al.* (1981) reported that increasing levels of spentwash application did not alter total N, organic carbon and exchangeable Na contents but exchangeable K, Ca, Mg contents were increased whereas, exchangeable aluminium, available phosphorus and nitrate nitrogen contents decreased. Devarajan and Oblisamy (1995) studied the effect of distillery effluent on soil properties, yield and quality of sugarcane. They studied physical soil characteristics influenced by application distillery effluent and noticed better soil aggregation and water permeability. The available nutrients were also increased with effluent irrigations, the available N from 276 to 412, available P from 21.0 to 34.0 and available K from 700 to 2400 kg ha⁻¹. The mineralization of organic materials and the nutrients present in the effluent were responsible for the increase in the availability of plant nutrients (Somashekar *et al.*, 1984).

Mattiazio and Ada Gloria (1985) found that organic matter oxidation brought out by microbial activity was responsible for increased pH when soil was treated with distillery effluent. The electrical conductivity of the soils also increased significantly with effluent irrigation. The organic carbon content of the soils increased significantly with effluent irrigations, which might be because the effluent contains high organic load. The available N, P, K, Ca, Mg and micronutrient contents of the soils, in both the seasons, were significantly increased due to effluent irrigations. Scandaliaris *et al.*, (1987) pointed out that application

of spentwash to soil increased soil NO₃ availability, EC and interchangeable potassium. Chang and Li (1988) found that application of vinasse to the main crop of cane increased the available K content of the surface soil and remained high even after the harvest of first ratoon. The available K was increased by 4 to 5 times due to effluent irrigations. This is due to the fact that K is one of the components supplied in large quantities (11500 ppm) by distillery effluent (Betranou *et al.*, 1989).

Taluk and Medeiros (1989) also observed increased soil pH, available N, P, K, Ca and Mg due to the application of 80m³ vinasse per hectare. Irrigation to cane field with distillery effluent had a tendency to increase exchangeable calcium. Mbagwu and Ekwealor (1990) stated that increased levels of distillery effluent application resulted in increased mean weight diameter water stable aggregates (1.6 to 2.2 mm), moisture retention (17.2 to 20.3 per cent) as well as available water holding capacity of soil (14.7 to 18.3 per cent).

Sweeney and Graetz (1991) reported that the digested distillery effluent application increased concentrations of most elements particularly K in soil. The decreasing trend of infiltration rate (IR) was noticed with effluent irrigations. However, the drop in IR was marginal at 50 and 40 times dilutions (33.4 and 31.2 cm/hr) when compared with water (33.8 cm/hr). The infiltration rate of the soils was significantly reduced with effluent irrigations, in both the seasons. The reduction was marginal (5.2 per cent) at 50 times dilution and appreciable (54.5 per cent) at 10 times dilution.

Shinde *et al.* (1993) observed increased EC of saturation paste extract and available K in soil when applied with spentwash solids. Further, noted increase in available N, P and DTPA extractable Fe, Mn and Zn in the soil at the harvest of sorghum. Zalawadia and Raman (1994) studied the effect of effluent on changes in fertility status of clay soil of Gujarat. They recorded higher values of electrolyte conductivity, organic carbon, available N, P and K with the usage of effluent water than with normal water at the same level of fertilizer application.

Irrigation with treated distillery effluent to sugarcane soil under varying dilutions significantly altered the microbial load in the rhizosphere. The population varied with period

under effluent irrigation and the peak was recorded in the fifth month. The microbial population was found to be high in the soil that was irrigated with 50 times diluted effluent (Lakshmanan and Gopal, 1996).

Singh and Raj Bahadur (1997) stated that effluent irrigation decreased the rate of infiltration and bulk density of soils, which are favorable traits for sandy soils. Whereas, Pathak *et al.*, (1999) noticed improved saturated hydraulic conductivity, bulk density and volumetric water content of soils with effluent application. Application of diluted distillery effluent in 1:10 and 1:20 ratio recorded higher cane yield of 129.5 and 122.3 tonnes per ha, respectively over 1:30, 1:40 and 1:50 dilutions at sugarcane research station, Cuddalore. There was general build up of organic carbon, soil available N, P, K, Ca, Mg, Na, Fe, Mn, Zn, Cu nutrients including the sodium. There was remarkable addition of 170 and 155 kg of K per ha due to the application of effluent 1:10 and 1:20 dilution, respectively. There was an increase in organic carbon (0.14 per cent), N (48 kg), P (4.4 kg) and K (170 kg) in sugarcane crop receiving 1:10 diluted effluent irrigation (Natarajan, 1999).

A field experiment on pineapple crop (cv. smooth caenne) was conducted on a reddish yellow latosol in trespontas of Brazil by Paula *et al.* (1999). The crop was irrigated with 0, 100, 200 and 400 m³ha⁻¹ vinasse as potassium source. Soil analysis after harvest of crop indicated that vinasse increased K, Ca and Mg contents in soil. A significant increase in the uptake of N, P and K nutrient by the addition of spentwash @ 50 m³ ha⁻¹ was observed over control, 12.5 and 37.5 m³ ha⁻¹ treatments and also there after decreasing trend was noticed in 75.0 and 87.5 m³ ha⁻¹. The pH values of soil decreased with increased levels of spentwash but EC values increased with increased levels of spentwash. Decreased calcium and increased EC values leading to adverse effects on structure and hydraulic conductivity of soil were noticed by Patil *et al.* (2000).

Eco-friendly utilization of distillery effluent in agriculture may serve as one of the nutrient management practices for enhancing crop yields besides reducing the costs of fertilizers. But, it has to be used judiciously and cautiously on a limited scale because of very high organic load. Distillery effluent has excessive BOD (45000 - 55000 mg/l), COD (90000 - 110000 mg/l) and EC (16 - 29 dS/m). These problems can be overcome either by the application of distillery effluent after proper dilution (1:10 to 1:50) with irrigation water or by pre-plant application (40 to 60 days before planting) to give sufficient time for the

oxidation of organic matter. The untreated distillery spentwash also known as raw spentwash is acidic in nature (pH 3.5 - 4.0) and can be effectively used for the reclamation of non-saline soil. Addition of effluent significantly increased the EC, organic carbon, available N, P, K, Ca and Mg contents as well as micronutrients in soil as reported by Baskar *et al.* (2003).

Sugar Industry being an important role in the Indian economy as well as in the foreign exchange earnings and also plays a very vital part in polluting the environment with its waste discharge. With expansion of Sugar plants, pollution due to inadequate pretreatment methods and release of effluents in water or soil threaten the environment. Jadhav *et al* (2013) studied four Sugar Industries for its potential as the primary source of water pollution. There are reports indicating that farmers who had used sugar factory effluents consistently for irrigation, found that the growth and yield of the crop and soil health were reduced (Swamy, 2001; Deshmukh 2001).

Pertaining to the available literature, the study related to impact of Chopda sugar factory effluent on quality of water and soil was severely lacking and hence it was considered worth to undertake the present part of investigation in which efforts were in direction to study quality of ground water and soil in the vicinity of Chopda sugar factory since adjoining some of the farmers use sugar industry effluents for irrigation.

5.2 MATERIALS AND METHODS

To evaluate the impact of wastewater of Chopda sugar factory on quality of ground water and soil, the study was conducted as follows:

A) Study of ground water quality

The ground water samples collected in the vicinity of Chopda Sugar Factory, which is situated near village Chahardi in Chopda tahshil of Jalgaon district in Maharashtra. Six ground water resources (Bore well water) established as sampling stations (W1 to W6) for collection of ground water samples within the periphery of six kilometers of Chopda Sugar factory (Figure 5.1 and Table 5.1). All the sampling sites were visited in the morning to collect water samples, which brought to the laboratory through airtight polythene bags or cans, and

will be stored at 4⁰C. Ground water samples were analyzed by the standard methods for examinations of water and wastewater. (APHA, 1995).

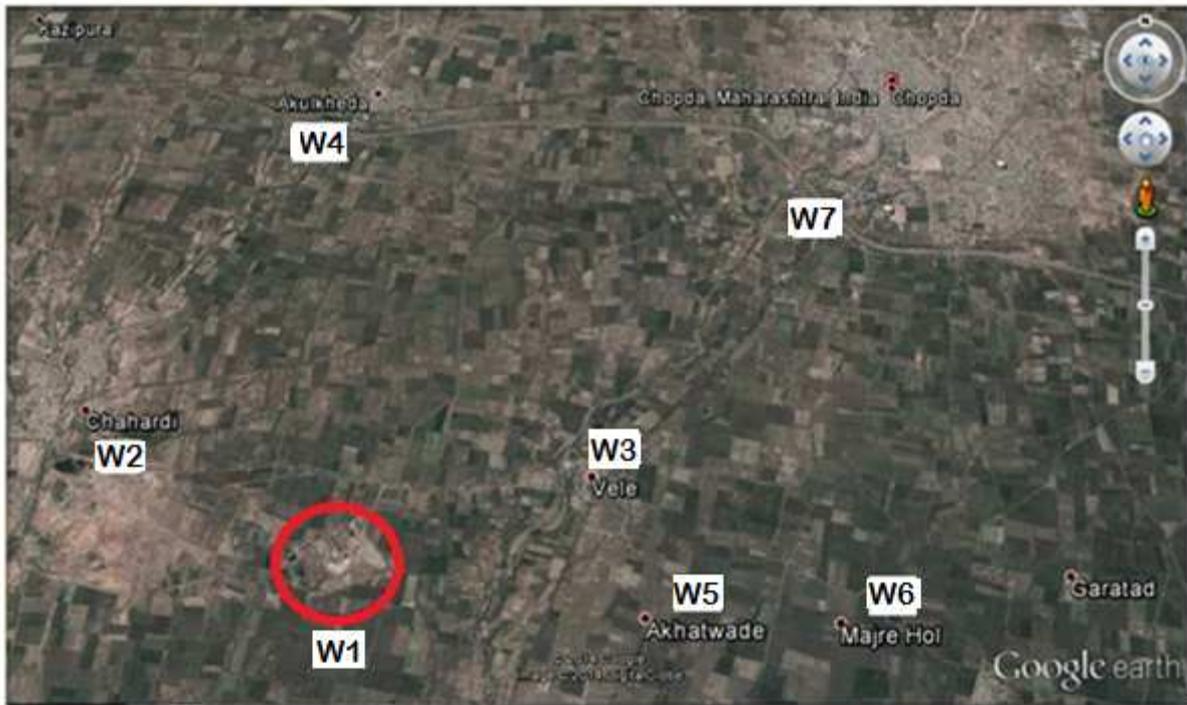


Figure 5.1 Satellite Image of Chopda Sugar Factory (shown in red circle), seven sampling sites within 6 km area (Source: Google Earth)

Table 5.1 Details of ground water sampling stations in the vicinity of Chopda sugar factory.

Sampling station code	Name of the sampling station	Distance from sugar factory (Km)
W1	Project site	--
W2	Chahardi	1.5
W3	Vele	2
W4	Akulkheda	4
W5	Akhatwade	3
W6	Majarehole	5
W7	Chopda	6

W1 to W7 = Water samples from bore well (except W4 = open well)

The common and essential ground water quality parameters like water temperature, pH, EC, Turbidity, hardness, DO, BOD, COD, TDS, total alkalinity, inorganic phosphorus, sulphates, chlorides, nitrates, and magnesium were estimated as per APHA (1996), and Aqua-analyzer (IAAB). The results were analyzed statistically as per the methods exemplified by Gurumani (2005). With the help of a mobile mini laboratory (Aqua-analyzer) there was ‘on the spot’ analysis of direct (temperature, and pH) and titrimetric (alkalinity, salinity, DO, and hardness) parameters. For analysis of Turbidity, BOD, COD,

TDS, inorganic phosphorus, sulphates, chlorides, nitrates, and magnesium, water samples were brought to the laboratory (Table 5.2).

Table 5.2 Ground water quality parameters and method used for their analysis:

No.	Parameter	Method used
1	Temperature	Thermometric
2	pH	PH metric
3	Electric conductance	Conductometer
4	Turbidity	Nephelometric
5	DO	Winkler's iodometric titration
6	BOD	Winkler's iodometric titration
7	COD	Dichromate oxidation
8	Hardness	EDTA titrometric
9	TDS	Evaporation of Filtrate
10	Alkalinity	Titrometric
11	Inorganic phosphorus	Spectrophotometric
12	Sulphates	Gravimetric
13	Chlorides	Titrometric
14	Magnesium	EDTA titrometric
15	Nitrates	Calorimetric

Water is a vital essential commodity necessary for the survival of vegetation, animals and human beings and for proper balance of ecosystem itself. Six ground water (Bore well water) samples were collected in the study area and analyzed for various parameters describing the baseline water environment in the vicinity of Chopda sugar factory. The estimating methods were same as that of spentwash analysis. The details of additional methods are as follows:

TURBIDITY

Nephelometric Method

PRINCIPLE

When light passes through a sample having suspended turbidity, some of the light is scattered by the particles. The scattering of the light is generally proportional to the turbidity. The turbidity of a sample is thus measured of the amount of light scattered by the sample taking a reference with standard turbidity suspension.

The determination of turbidity is interfered by the presence of debris and other rapidly settleable matter; the true colour in the sample reduces the values of turbidity.

APPARATUS AND REAGENTS

A. Nephelometer (Turbidimeter)

It measures the scattered light at the right angle of the path of incident light.

B. Sample tubes

The clean and colorless glass tubes free of any scratch or etching were used.

C. Stock turbidity suspension

a) 1.0 g of hydrazine sulphate $(\text{NH}_2)_2\text{H}_2\text{SO}_4$ was dissolved in distilled water to prepare 100 ml solution.

b) 10.0 g hexamethylene tetramine $(\text{CH}_2)_6\text{N}_4$ was dissolved in distilled water to prepare 100 ml solution. 5 ml of each of the solutions (a and b) were mixed in a 100 ml volumetric flask and allowed to stand for 24 hours at 25°C . It was then diluted to 100 ml mark. This was 400 NTU (Nephelometric Turbidity Units) suspension. This solution can be kept for about a month.

D. Standard turbidity suspension

40 NTU solution was prepared by diluting 10 ml of stock solution to 100ml. This solution was prepared every week.

PROCEDURE

1. For handling the Nephelometer, the instructions supplied by the manufacturer were followed.
2. The instrument was set at 100 with 40 NTU standard suspension. In this case, every division on the scale was equal to 0.4 NTU turbidity.
3. The sample was shaken thoroughly and kept for sometime to eliminate the air bubbles.
4. The sample was put in the Nephelometer sample tube and the value on the scale was noted.
5. If sample was suspected to have more turbidity (more than 40 NTU), it was diluted to that turbidity values to come below 40 NTU, and the readings were noted.

CALCULATION

Turbidity, NTU = Nephelometer reading \times 0.4 \times dilution factor.

HARDNESS (EDTA METHOD) (Calcium, Magnesium & Total Hardness):

Hardness to water is mainly imparted by alkaline earth metallic cations, mainly calcium and magnesium present in it. However, to lesser extent cations like iron, manganese and strontium are also responsible for hardness. Generally, an aquatic ecosystem receives calcium from lime stone, dolomite and gypsum deposits in the catchments and its level may range between zero to several hundred mg/L. Hardness when caused because of carbonates (HCO_3) and bicarbonates is called temporary hardness since it can be removed by boiling the water. Sulphates and chlorides of these cations cause permanent hardness, which is not removed by simple boiling of water. Ecologically, temporary hardness plays a key role in buffering capacity thus neutralizing an off set in pH due to addition of acidic products. This has a great effect on biotic diversity and biomass in an ecosystem. Hardness also restricts water use, hard water is unsuitable for cooking, washing and bathing due to high boiling point in the first, while poor lather forming capacity in the latter two uses.

PRINCIPLE

Hardness is generally caused by the calcium and magnesium ions present in water. 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 the hardness. However, the concentrations of these ions is very low in natural waters, therefore hardness is generally measured as concentration of only calcium and magnesium (as calcium carbonate), which are far higher in quantities over other hardness producing ions.

Calcium and magnesium form a complex of wine red colour with Erichrome Black T at pH of 10.0 = 0.1 The EDTA (Ethylene Di-amine Tetra Acetic Acid) has got a stronger affinity towards Ca^{++} and Mg^{++} and, therefore, by addition of EDTA, the former complex is broken down and a new complex of blue colour is formed.

REAGENTS

EDTA solution, 0.01 M

3.723g of disodium salt of EDTA was dissolved in distilled water to prepare 1 litre of solution. It was stored in polythene or pyrex bottle.

Buffer solution

a) 16.9 g ammonium chloride (NH_4Cl) was dissolved in 143 ml of concentrated ammonium hydroxide (NH_4OH).

b) 1.179 g of disodium EDTA and 0.780.7H₂O were dissolved in 50 ml distilled water. Both (a) and (b) solutions were mixed and diluted to 250 ml with distilled water.

A. Erichrome Black T (Solochrome Black T) indicator

0.40 g of Erichrome Black T mixed with 100g NaCl (A.R.) and grinded.

B. Sodium sulphide solution

5.0 g of Na₂S, 9H₂O dissolved in 100ml of distilled water. The bottle was tightly closed to prevent oxidation.

PROCEDURE

- 1) 50 ml sample was taken in a conical flask.
- 2) 1 ml of buffer solution was added to the sample.
- 3) If the sample was with higher amounts of heavy metals, 1 ml of Na₂S solution was added.
- 4) 100-200 mg of Erichrome Black T indicator was added to the solution, as result solution turned wine red.
- 5) The contents were titrated against EDTA solution; at the end point color changed from wine red to blue.

CALCULATION

$$\text{Hardness as mg/L CaCO}_3 = \frac{\text{ml EDTA used} \times 1000}{\text{ml of sample}}$$

TOTAL ALKALINITY, CARBONATES AND BICARBONATES

Alkalinity is important for fish and aquatic life because it protects or buffers against pH changes (keeps the pH fairly constant) and makes water less vulnerable to acid rain. The main sources of natural alkalinity are rocks, which contain carbonate, bicarbonate, and hydroxide compounds. Borates, silicates, and phosphates may also contribute to alkalinity.

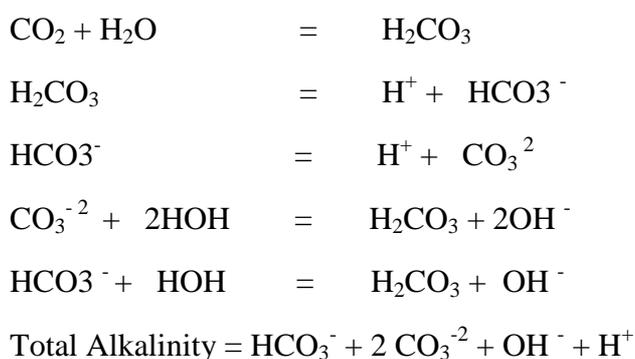
Table 5.3 Some recommended alkalinity values	
Industry and Process	Recommended Maximum Total Alkalinity (in mg/L CaCO ₃)
Carbonated beverages	85
Food products (canning)	300
Fruit juice	100
Washing diapers	60
Pulp and paper making	150
Rayon manufacture	50
Tanning hides	135
Textile mill products	50-200
Petroleum refining	500

Limestone is rich in carbonates, so waters flowing through limestone regions generally high alkalinity — hence its good buffering capacity. Conversely, granite does not have minerals that contribute to alkalinity. Therefore, areas rich in granite have low alkalinity and poor buffering capacity. Some recommended alkalinity values are given in above Table 5.3.

PRINCIPLE:

Alkalinity of the water is its capacity to neutralize a strong acid and is characterized by the presence of all hydroxyl ions capable of combining with the hydrogen ions. Alkalinity in neutral waters is due to free hydroxyl ions and hydrolysis of salts by weak acids and strong bases. When a salt of weak acid and strong base is hydrolyzed, it forms the weak acids and the strong bases. The weak acid is unable to dissociate more, and when the titration is carried out with a strong acid the equilibrium is shifted to the right and all the salt is hydrolyzed. The number of milliequivalents of acid used in the titration to combine all the hydroxyl ions is called as *total alkalinity*.

Most of the alkalinity in the neutral waters is formed due to the dissolution of CO₂ in water. Carbonates and bicarbonates thus formed are dissociated to yield hydroxyl ions. Carbonate salts produce double the hydroxyl ions than the bicarbonates. Therefore the total alkalinity caused by CO₂–H₂O system can be represented by the following equations



Total Alkalinity can be estimated by titrating the sample with a strong acid (HCl or H₂SO₄), first to pH 8.3 using phenolphthalein as an indicator and then further to pH between 4.2 and 5.4 with methyl orange or mixed indicator. In first case, the value is called as phenolphthalein alkalinity (PA) and in second case; it is total alkalinity (TA). Values of carbonates, bicarbonates and hydroxyl ions can be computed from these two types of alkalinities.

REAGENTS:

a) Hydrochloric acid, 0.1 N

12N concentrated HCl (sp.gr.1.18) diluted to 12 times (8.43 ml to 100 ml) to prepare 1.0N. It was further make 0.1 N HCl (100 to 1000ml). The solution was standardized against sodium carbonate solution.

b) Methyl orange indicator, 0.05%

0.5 g of methyl orange was dissolved in 100 ml of distilled water.

c) **Phenolphthalein indicator** 0.5 g of phenolphthalein was dissolved in 50 ml of 90% ethanol and 50 ml of distilled water. 0.05 N CO₂ free NaOH solution was added dropwise, until the solution turns faintly pink.

d) Sodium carbonate, 0.1N

5.300 g of Na₂CO₃ previously dried at 250⁰C for about 4 hours was dissolved in distilled water to prepare 1 liter of solution.

PROCEDURE

1. 100 ml of sample was taken in a conical flask and 2 drops of phenolphthalein indicator added to the sample.
2. When the solution remained colourless, PA= 0, and the total alkalinity was determined as described in step 4.
3. When the color changed to pink after addition of phenolphthalein, it was titrated with 0.1 N HCl until the color disappeared at end point. This was phenolphthalein alkalinity (PA).
4. 2-3 drops of methyl orange were added to the same sample and continued the titration further, until the yellow color changed to pink at the end point. This was total alkalinity (TA).

CALCULATION

$$\text{PA as CaCO}_3, \text{ mg /L} = \frac{(\text{A} \times \text{Normality}) \text{ of HCl} \times 1000 \times 50}{\text{ml of sample}}$$

$$\text{TA as CaCO}_3, \text{ mg /L} = \frac{(\text{B} \times \text{Normality}) \text{ of HCl} \times 1000 \times 50}{\text{ml of sample}}$$

Where, A = ml of HCl used with only phenolphthalein

B = ml of total HCl used with only phenolphthalein and methyl orange

PA = Phenolphthalein alkalinity

TA = Total alkalinity.

B) Study of Soil quality parameters

Collection of soil samples for its physico-chemical analysis:

Ideally, a soil should be tested without disturbing or altering it chemically or mechanically in the process of sample preparation. This would require testing *in situ*, which is not technically feasible today. Soil samples were collected from seven sampling sites, which were having details as given in Table 5.4. The temperatures of each soil samples were noted and then samples were brought to laboratory in paper bags with tags having detailed information. Soil samples were then dried, pulverized, weighed and processed for analysis of their physico-chemical parameters.

Table 5.4 Details of soil sampling stations in the vicinity of Chopda sugar factory

Sampling station code	Name of the sampling station	Distance from sugar factory (Km)	Soil irrigation
S1	Project site	--	Spentwash
S2	Chahardi	1.5	Spentwash
S3	Vele	2	Spentwash
S4	Akulkheda	4	Open well water
S5	Akhatwade	3	Bore well water
S6	Majarehole	5	Bore well water
S7	Chopda	6	Bore well water

Before bringing the soil samples to the laboratory for physico-chemical analysis, collection and preparation of soil sample was done with perfection. Equipments used to collect soil samples: Spade, Polythene bags, 12 inches scale, a sheet of thick paper, Polythene sheet (2ft x 2ft), tags, etc.

Procedure

Sampling station was visited and soil unit (or plot) was determined. The site was cleaned with spade from where soil sample was collected. The spade was inserted into soil. Standing on opposite side, again the spade was inserted into soil. A lump of subsoil was removed from a pit of vee (V) shape formed in the soil. At the depth of about 12", the temperature of soil was noted.

The soil samples were collected separately from each sampling site during the operation period of Chopda Sugar factory in 2011-12, 2012-13 and 2013-14. The soil sample were transferred to polythene bags and tagged with the information related to date, time and location of sampling station. The detailed information related to following point was noted in the notebook:

- Name and address of the farmer (or farm owner).
- Soil texture (sandy/clay/loam).
- Availability of irrigation facilities.
- Upland/Mediumland/Lowland.
- Information of the previous crop.
- Name and variety of the crop cultivated.
- Dose of organic manure, if applied.
- Dose of fertilizers, if applied.
- Yield.
- Problem, if any.
- Date of sample collection.
- Signature of the farmer (or farm owner).

B) Physico-chemical analysis of soil samples from following point of view:

- 1) Soil pH and EC were measured in 1:5 solution of soil and water extract after shaking for 30 min. (Hesse, 1971).
- 2) Organic carbon (OC) was analyzed by digestion of soil in dichromate solution as explained by Schollenberger method (1945).
- 3) An available Nitrogen, Phosphorous, Potassium were detected by chemical analytical methods as described by Delavalle (1992).
- 4) Iron, Zinc, Copper, Manganese and Lead in soil were determined by Aqua Regia extractant methods as described in ISO 11466 (1995) .

1. Soil pH

It was measured potentiometrically in a slurry using an electronic pH meter. Soil pH was normally measured in soil/water slurry. The presence of soluble salts in a soil sample may affect pH. For that reason, some analysts prefer to measure pH in a mixture of soil and 0.01 M CaCl₂. The excess salt in this solution masked the effects of differential soluble salt concentrations in individual samples.

Soil pH is a measure of hydronium ion (H_3O^+ or, more commonly, H^+) activity in a soil suspension. This property influences many aspects of crop production and soil chemistry, including availability of nutrients and toxic substances, activity and diversity of microbial populations, and activity of certain pesticides.

Soil pH is defined as the negative logarithm (base 10) of the H^+ activity (moles per liter) in the soil solution. As the activity of H^+ in the soil solution increases, the soil pH value decreases. Soils with pH values below 7 are referred to as “acid”; pH values above 7 are referred to as “alkaline”; soils at pH 7 are referred to as “neutral.”

2. Determination of Electric conductivity of soil

The categories of soils with respect to conductivity (total soluble salts) in mmhos/cm (dS/m) followed are given in Table 5.5.

Table 5.5 Categories of soil as per their EC values

Conductivity	Category of soil
Below 1	Normal
1-2	Critical for germination
2-3	Critical for growth of salt sensitive plants
Above 3	Injurious to most plants

3. Determination of Organic Carbon Content in the soil

Principle

The carbon present in the soil is oxidised to carbon dioxide (CO_2) by heating the soil to at least $900\text{ }^\circ\text{C}$ in a flow of oxygen-containing gas that is free from carbon dioxide. The amount of carbon dioxide released is then measured by titrimetry, gravimetry, conductometry, gas chromatography or using an infrared detection method, depending on the apparatus used. When the soil is heated to a temperature of at least $900\text{ }^\circ\text{C}$, any carbonates present are completely decomposed. The second method, a modification of the Schollenberger method (1945), relies upon outside heat to drive the organic C oxidation by chromic acid. Two digestion alternatives are presented and the amount of Cr reduction is estimated colorimetrically.

Reagents

Digestion solution (0.5 M $\text{Na}_2\text{Cr}_2\text{O}_7$ in 5 M H_2SO_4): 140 g $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ dissolved in 600 mL of distilled water. 278 mL of concentrated H_2SO_4 slowly added to it and allowed to cool and diluted to 1 L.

Procedure

- 1) Scoop 1 g of soil sample transferred into a 50 mL Erlenmeyer flask.
- 2) 10 mL of dichromate-sulfuric acid digestion solution was added to it. A reagent blank without soil was prepared.
- 3) Erlenmeyer flasks were covered with glass marbles, which act as reflux condensers, to minimize loss of chromic acid.
- 4) Flasks were placed in oven and heat to 90°C for 90 minutes for digestion.
- 5) After removing and cooling the contents for 5 to 10 minutes, remove the glass marble caps were removed and 25 mL of water was added.
- 6) The suspension was mixed thoroughly by blowing air through the suspension via the 25 mL pipettes or by mechanical shaking.
- 7) The reaction mixture was allowed to stand three hours or overnight.
- 8) 5 mL of clear supernatant was transferred into a colorimeter tube. Care was taken not to disturb the sediment on the bottom of the flasks.
- 9) The blue color intensity of the supernatant was read on a colorimeter at 645 nm, with the reagent blank set to give 100 percent transmittance (or 0 absorbance). The instrument was calibrated to read percentage OM (or tons/acre) from a standard curve prepared from soils of known OM content.

5) Determination of available nitrogen in soil samples

Nitrogen is one of the major elements required for life. It will stimulate above ground growth, and produces the rich green colour that is the characteristic of healthy plants, because of this Nitrogen is essential for plant life. 78% of the atmosphere is covered by molecular Nitrogen (N_2); animals cannot use this form of nitrogen. This molecular Nitrogen must first combine with Oxygen or Hydrogen to produce compounds such as Ammonia or Nitrate, or some other organic form of Nitrogen. This is called Nitrogen Fixation. Some Nitrogen Fixation occurs by lightning and some other by blue green algae. However, the bulk of Nitrogen Fixation is preferred by bacteria living in the soil. Some of the Nitrogen Fixation bacteria were living free in the soil, while the others were living within the root nodules of leguminous plants such as soya bean, peanut, beans, clover, alfalfa, etc. Because

of Ammonia or Ammonium is produced by the decomposition process, the decomposition of materials in the forest is also a source of Nitrogen. The movement of Nitrogen from the atmosphere into inorganic forms, followed by the incorporation of Nitrogen into plant matter is represented as the Nitrogen Cycle.

The rate of plant growth is proportional to the rate of nitrogen supply. If the soil is deficient in Nitrogen, the plants become stunted and pale. However, an excess of Nitrogen can damage the plants just as over-fertilizing the lawn can burn and damage the grass.

Apparatus: Kjeldahl Digestion Assembly, Ammonia Distillation Assembly.

Principle:

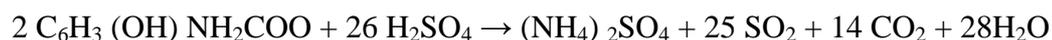
The Kjeldahl method permits the available nitrogen to be precisely determined in the plant and in the soil. The method of determination involves three successive phases which are,

- 1) Digestion of the organic material to convert nitrogen into HNO_3 .
- 2) Distillation of the released Ammonia into an absorbing surface or medium.
- 3) Volumetric analysis of the Ammonia formed during the digestion process.

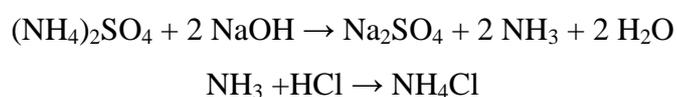
Digestion: Digestion of the organic material is carried out by digesting the sample with Con. H_2SO_4 in the presence of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ as a catalyst and K_2SO_4 which raise the digestion temperature. The organic material decomposes into several components i.e.,



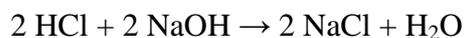
In the organic matter, some nitrates are present, most of which are lost during the digestion. The loss may be disregarded for most soils. Since the amount of $\text{NO}_3^- - \text{N}$ is far lesser than the Organic Nitrogen.



Distillation: The Ammonia content of the digest is determined by distillation with excess NaOH and absorption of the evolved NH_3 is in standard HCl .



Volumetric Analysis: The excess of standard HCl is titrated against standard NaOH using Methyl Red as an indicator. The decrease in the multi equivalence of acid is determined by acid-base titration, which gives a measure of the N content of the sample. The end point is determined by a change of colour from pink to yellow.



Significance: The chemical analysis of the soil for nitrogen is less precise when the requirement for this element needs to be forecast over a longer period of time, as they vary not only with species, but with the phase of growth and season as well. Therefore the chemical test for NO_3^- and NH_4^+ signifies the momentary status when the sample is taken and measures must be taken instantaneously.

5) Estimation of Available Soil Phosphorus

This method estimates the relative bioavailability of ortho-phosphate($\text{PO}_4\text{-P}$) using 0.5N NaHCO_3 adjusted to pH 8.5 and is based on the method developed by Olsen et al.,1954. In the process of extraction, CO_2 from bicarbonate is driven off, pH increases and bicarbonate converts to carbonate. Thus there is lower calcium activity as calcium carbonate is formed increasing the quantity of phosphates in solution. Phosphorus content is determined spectrophotometrically at 882nm at an acidity of 0.24 MH_2SO_4 (Rodriguezetal.,1994) by reacting with ammonium molybdate using ascorbic acid as a reductant in the presence of antimony (Murphy and Riley, 1962) using manual or automated techniques. The method has shown to be well correlated to crop response phosphorus fertilization on neutral to alkaline soils. The method has a phosphorus detection limit of approximately 2.0 mg kg⁻¹ (on a dry soil basis) and is generally reproducible to within $\pm 12\%$.

Equipment

1. Analytical balance, resolution ± 0.01 g.
2. Oscillating mechanical shaker, capable of 180 oscillations per minute (opm).
3. Repipette dispenser, calibrated to 40.0 ± 0.4 mL, 9.0 ± 0.1 mL.
4. 125-mL plastic extraction Erlenmeyer and associated filtration labware.
5. Whatman No. 1, No. 2, filter paper or equivalent.
6. Pipettes: 0.250 ± 0.005 mL, 0.500 ± 0.005 mL, 1.00 ± 0.01 mL, 2.00 ± 0.02 mL, 3.00 ± 0.03 mL, 4.00 ± 0.04 mL.

7. Spectrophotometer wavelength 882 nm and 2.5 cm matching spectrophotometer cuvette or automated Flow Injection Analysis system instrumentation.

Reagents

- 1) Deionized water, ASTM Type I grade.
- 2) Sodium bicarbonate extracting solution (0.5 N NaHCO₃ @ pH- 8.50). Dissolve 42.01g of NaHCO₃ in about 900mL of deionized water. Adjust the pH to 8.50 ±0.05 with 2.0 N NaOH before diluting with deionized water to 1,000 mL. This solution is unstable with regard to pH and should be prepared as required.
- 3) Modified Reagent A (Watanabe and Olsen, 1965).
 - Ammonium Molybdate: Dissolve 12.0 g. of A.R. [(NH₄)₆Mo₇O₂₄ · 4H₂O] in 250 mL of deionized water.
 - Antimony Potassium Tartrate: Dissolve 0.291 g. of A.R. antimony potassium tartrate [K(SbO)C₄H₄O₆ · ½ H₂O] in 100 mL of deionized water.Add both of the dissolved reagents to 1,000 mL of 5.76 N H₂SO₄ (160mL of concentrated sulfuric acid per liter, Self and Rodriguez, 1996) mix thoroughly and make to 2,000mL. Modified Reagent A (mixed reagent) last at least four months if it is stored in an opaque plastic bottle.
- 4) Reagent B, ascorbic/molybdate reagent (Watanabe and Olsen, 1965). Dissolve 1.32g. of A.R. ascorbic acid (C₆H₄O₆) in 250 mL of modified Reagent A and mix well. This reagent should be prepared as required.
- 5) Phosphorus Calibrations Standards. From a standard solution containing 1,000mg/L PO₄-P, prepare 100 mL of standard in 0.5N NaHCO₃ containing 100mg/L PO₄-P. Then, using the 100 mg/ L PO₄-P standard, prepare seven calibration solutions of 100 mL each in 0.5 N NaHCO₃ with PO₄-P concentrations of 0.00, 0.25, 0.50, 0.75, 1.00, 2.00, and 4.00 mg/ L.

Extracting Procedure

- 1) Weigh 2.00 ± 0.02 g of air dried soil pulverized to pass 10 mesh sieve (< 2.0 mm) in a 125-mL plastic extraction erlenmeyer.
- 2) Add 40.0 mL of 0.5 N NaHCO₃ extraction solution
- 3) Include a method blank and standard quality control samples.
- 4) Place extraction vessels on oscillating mechanical shaker for thirty (30) minutes.
- 5) Filter suspension immediately - within 1 minute (refilter if filtrate is cloudy).

Phosphorus Analysis

- 1) Pipette a 3.0 mL aliquot of standard or soil extract into a 2.5 cm matching spectrometer tube.
- 2) Add 9.0 mL of deionized water.
- 3) Add 3.0 mL of Reagent B (ascorbic/molybdate reagent).
- 4) Adjust and operate spectrophotometer in accordance with manufacture's instructions. Read absorbance at a wavelength of 882 nm after 10 minutes of adding the Reagent B. Adjust the 0.000 absorbance using the 0.00 standard. Determine absorbance of a method blank, standards and unknown samples. Calculate phosphorus concentration for blank and unknown samples from standard curve and record phosphorus to the nearest 0.01 mg/ L PO₄-P in extract solution.

Calculations

Report soil bicarbonate available phosphorus to the nearest 0.1 mg/ kg

$$\text{Soil PO}_4\text{-P mg/kg} = (\text{PO}_4\text{-P mg/ L in extract} - \text{blank}) \times 20$$

6) The Determination of available Potassium in soils

Soil is a complex mixture of mineral particles, organic matter, water and air. The mineral particles come from the breakdown of rocks. As rocks break down into the particles of sand, silt and clay that make up soil, potassium and other elements are released and may become available to plants. It is important to assess the quantity of potassium in the soil solution and the readily available pool to ascertain whether or not to apply potassium fertilizer.

Principle:

Potassium is extracted from air-dried soil samples by shaking with 0.5M ammonium acetate/acetic acid solution for 30 minutes. This effectively displaces the potentially available K⁺ ions. The potassium content of the filtered extract is then determined using a Jenway PFP7 Flame Photometer.

Materials required

a. Ammonium Acetate/Acetic Acid

Aqueous solution: 0.5M with respect to both reagents (38.55g ammonium acetate and 29ml of glacial acetic acid, diluted to 1 litre with deionised water).

b. Standard Potassium Solution: 2000ppm

Accurately weigh 1.907g of potassium chloride previously dried for 2 hours at 105°C.

- c. Dissolve in about 50ml of the ammonium acetate/acetic acid solution.
- d. Transfer to a 500ml volumetric flask and dilute to 500ml with the ammonium acetate/acetic acid solution.

Procedure

- 1) Pass the sample of air-dried soil through a 2mm sieve. Using a scoop, measure out 10ml of the sieved soil without tapping to avoid compacting. Transfer to a 100ml polyethylene bottle, together with 50ml of the ammonium acetate/acetic acid solution.
- 2) Stopper the bottle, transfer to a shaker and shake for 30 minutes (275 strokes per min, 25mm travel).
- 3) Removed from the shaker, allowed to stand for several minutes and then decanted the supernatant liquid through a dry Whatman No. 2 filter paper.
- 4) Potassium standard solutions were prepared to cover the range 0 to 100 ppm potassium
- 5) Flame Photometer was set at 100 using the 100ppm potassium solution.
- 6) 20, 40, 60 and 80 ppm potassium standard solutions were to prepare a calibration graph.
- 7) Determine the potassium content of the soil extract by aspirating the solution, diluting as necessary in ammonium acetate/acetic acid solution. Calculate the concentration by reference to the calibration graph, taking into account any dilution factors.

Preparation of potassium standard dilutions

- 1) Transfer 25 ml of the 2000ppm potassium standard solution to a 100 ml volumetric flask and dilute to 100 ml with the ammonium acetate/acetic acid solution. This solution contains 500ppm potassium.
- 2) Transfer 10ml, 20 ml, 30 ml, 40 ml and 50 ml aliquots of the 500 ppm potassium solution to 250ml volumetric flasks. Dilute to 250 ml with the ammonium acetate/acetic acid solution and mix well. These solutions contain 20, 40, 60, 80 and 100 ppm potassium respectively.

7) Determinations of Zn, Fe, Cu, Pb and Mn in soli samples using aqua regia

Principle

The dried Sample is extracted with a hydrochloric/nitric acid mixture by standing for 16 h at room temperature, followed by boiling under reflux for 2 h. The extract is then clarified and made up to volume with nitric acid. Elements are determined by spectrometry.

Reagents

Hydrochloric acid (HCl) concentration 12 mol/l, $\rho \approx 1.19$ g/ml

Nitric acid (HNO₃) concentration 15.8 mol/l, $\rho \approx 1.42$ g/ml

Nitric acid (HNO₃) concentration 0.5 mol/l

Procedure

Laboratory sample

Weigh 3,000 g air-dried soil (particle size < 2 mm) of known moisture content in the 250 ml reaction vessel.

Aqua regia extraction

Moisten with about 0.5 ml to 1.0 ml of water and add, while mixing, 21 ml of hydrochloric acid followed by 7 ml of nitric acid (15.8 mol/l), drop by drop if necessary, to reduce foaming. Connect the condenser (and the absorption vessel) to the reaction vessel, and allow to stand for 16 h at room temperature to allow for slow oxidation of the organic matter in the soil.

The amount of aqua regia is sufficient only for oxidation of about 0.5 g of organic carbon. If there is more than 0.5 g of organic carbon in the 3 g subsample, proceed as follows. Allow the first reaction with the aqua regia to subside. Then add an extra 1 ml of nitric acid (15.8 mol/l) only to every 0.1 g of organic carbon above 0.5 g. Do not add more than 10 ml of nitric acid at any time, and allow any reaction to subside before proceeding further.

Raise the temperature of the reaction mixture slowly until reflux conditions are reached and maintain for 2 h, ensuring that the condensation zone is lower than 1/3 of the height of the condenser, then allow to cool.

Allow the reaction vessel to stand so that most of any insoluble residue settles out of suspension. (Add the contents of the absorption vessel to the reaction vessel, via the condenser, rinsing both the absorption vessel and condenser with a further 10 ml of nitric acid (0.5mol/l)). Decant the relatively sediment-free supernatant carefully onto a filter paper, collecting the filtrate in a 100 ml volumetric flask. Allow all the initial filtrate to pass through the filter paper, and then wash the insoluble residue onto the filter paper with a minimum of nitric acid (0.5mol/l). Collect this filtrate with the first before proceeding further. The extract thus prepared is ready for the determination of trace elements, by an appropriate method.

Determination of Elements:

Measure the elements cations (Zn, Fe, Cu, Pb and Mn) in the extract using one of the spectrometric determination methods and calculate according to apparatus.

5.3 RESULTS AND DISCUSSION

A) Quality of Ground water samples collected in the vicinity of Chopda sugar factory:

The result of analysis of the physico-chemical parameters of the ground water samples collected within six km area of Chopda sugar factory are discussed below:

Temperature: The fluctuations in temperature of ground water samples collected from sampling stations W1 to W7 are graphically represented in Figure 5.1. The minimum and maximum temperature of ground water samples were 22.2 ± 1.2 °C and 26.4 ± 0.7 °C respectively. There was not significant relationship between the temperature of water samples and distance of sampling station from the project site. Somewhat higher temperatures were noted in the samples collected from W4 site indicated that openness of well water and impact of environmental temperature on the well water. The highest temperature recorded in each water sample during year 2012-13 might be attributed to scorching heat effect on water bodies contrary to the more and continuous rainfall during 2013-14 might be lowered the temperatures of water samples.

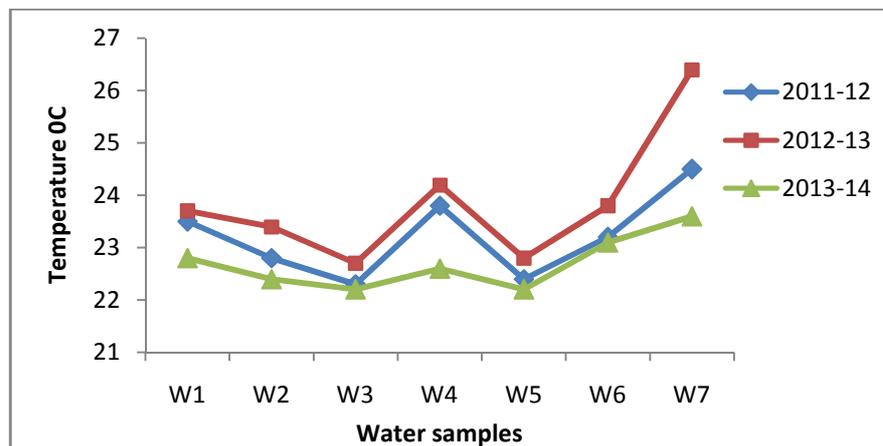


Figure 5.1 Fluctuations in temperature (°C) of water samples during three years of study

pH : The variations in pH of ground water samples collected from sampling stations W1 to W7 are graphically represented in Figure 5.2. The minimum and maximum pH values of ground water samples were 6.3 ± 0.2 and 7.4 ± 0.3 respectively. Pertaining to observed data,

it became clear that due to impact of acidic nature of the effluent of Chopda sugar factory that percolated through soil and contaminated the water bodies might caused to lower the pH water collected from W1 and distance of sampling station from project site might played a role in normalizing the water pH to near about 7. Statistical analysis of recorded data related to fluctuations in pH of ground water samples collected from W1 to W7 during three years of study revealed that a change in pH from acidic to neutral was observed, as there is increase in the distance of sampling station from Chopda sugar factory.

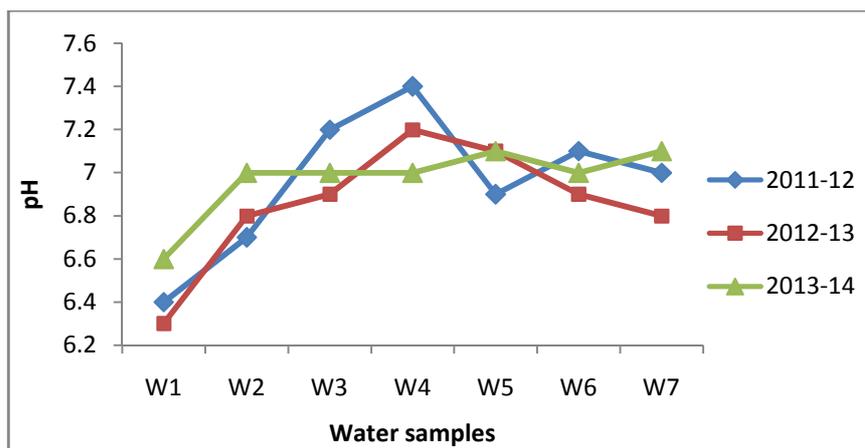


Figure 5.2 Variations in pH of water samples during three years of study

Electric conductance (EC): The result of analysis of EC values of ground water samples collected from W1 to W7 is graphically represented in Figure 5.3. The lowest and highest EC values of ground water samples recorded during the study were $0.39 \pm 0.03 \text{ dS}\cdot\text{m}^{-1}$ and $0.79 \pm 0.02 \text{ dS}\cdot\text{m}^{-1}$ respectively.

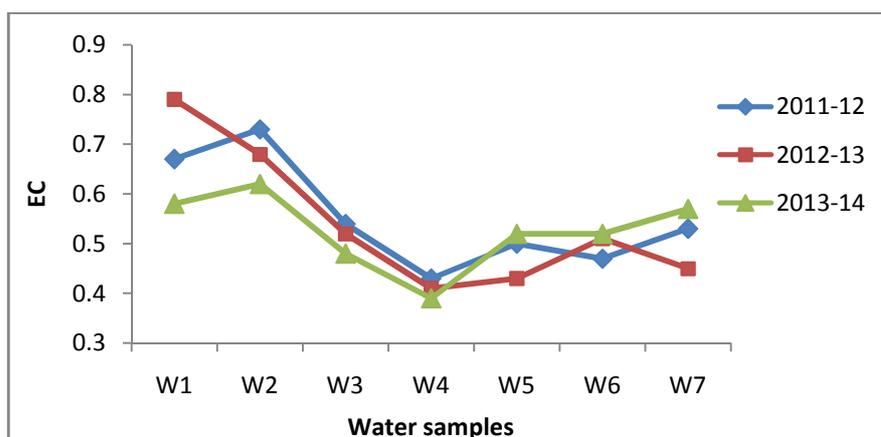


Figure 5.3 Variations in EC values of water samples during three years of study

Comparatively higher values of EC were noted in water samples collected from W1 (project site) and W2 sampling sites that might be due to closeness of spentwash dregs of Chopda

sugar factory form where the wastewater percolated and contaminated the water bodies and increased the amount of dissolved salts leading higher EC than that of other ground water samples.

Increase in the distance of sampling site from Chopda sugar factory might caused the lowering effect of EC values in water samples. Comparatively lower EC values in all water samples collected during year 2012-13 and higher EC values in all water samples collected during year 2013-14 were recorded in the present study which might be due to drought like conditions during 2012-13 and more and continuous rainfall during 2013-14 that may decreased and increased the water volumes respectively.

Turbidity: The variations in turbidity of ground water samples collected from sampling stations W1 to W7 are graphically represented in Figure 5.4. The minimum and maximum values of turbidity of ground water samples were 1.6 ± 0.4 NTU and 3.7 ± 0.2 NTU respectively. Pertaining to noted observations, it became clear that near the sampling site more was the turbidity in water sample. Thus, the distance affected the turbidity values of each ground water samples in the vicinity of Chopda sugar factory. The wastewater percolated through soil and contaminated the water bodies might cause to increase turbidity of water samples.

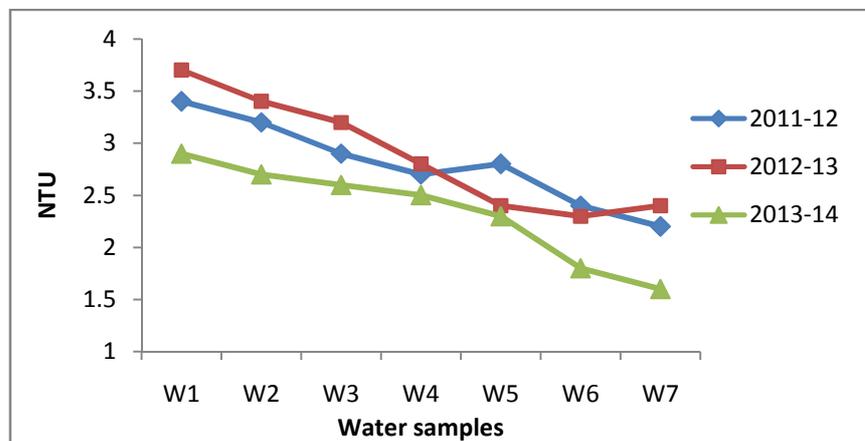


Figure 5.4 Variations in Turbidity (NTU) values of water samples during study period

Dissolved Oxygen (DO): The result of DO analysis of ground water samples collected from W1 to W7 is graphically shown in Figure 5.5. The lowest and highest DO values of ground water samples recorded during the study were 5.2 ± 0.3 mg/L and 6.9 ± 0.4 mg/L respectively. Lower DO values in water samples during year 2012-13 and higher DO values in water samples during year 2013-14 were related to higher temperatures during year 2012-

13 and lower temperatures during year 2013-14 since there is inverse relation in DO and temperature.

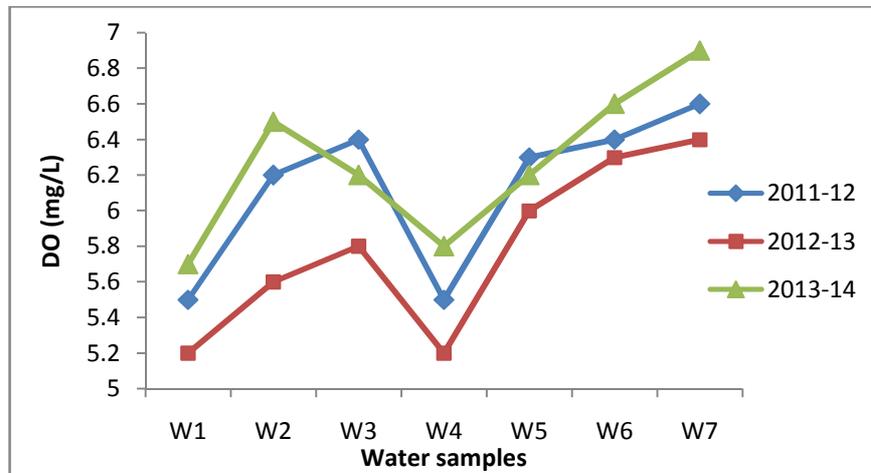


Figure 5.5 Variations in dissolved oxygen (mg/L) values of water samples during three years of study period.

Biological Oxygen Demand (BOD): The variations in BOD values of ground water samples collected from sampling stations W1 to W7 are graphically represented in Figure 5.6. The minimum and maximum values of BOD of ground water samples were 5.0 ± 0.3 mg/L and 14.9 ± 0.7 mg/L respectively during three years of study.

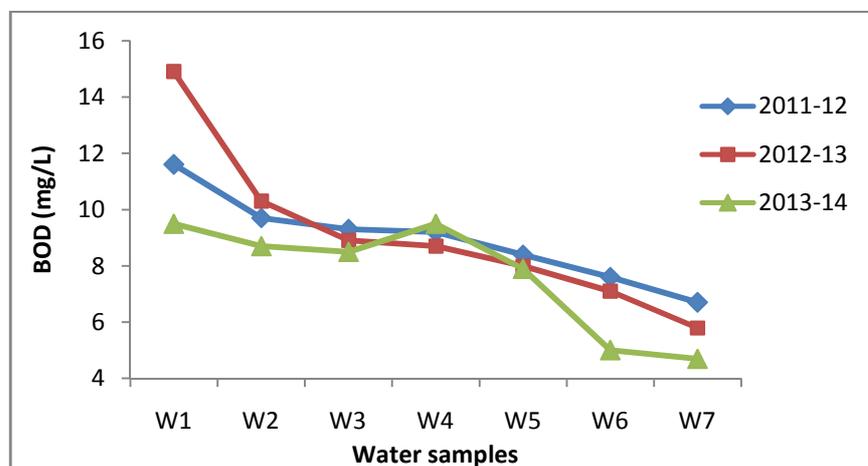


Figure 5.6 Variations in Biological oxygen demand (mg/L) of water samples during three years of study period.

The observations noted in present investigation indicated that near the sampling site more was the BOD in water sample and vice-versa. The wastewater of Chopda sugar factory percolated through soil and contaminated the water bodies that might cause to increase

demand of more oxygen for oxidation of organic pollutants to be oxidized by certain microorganisms.

Chemical oxygen demand (COD): The result of analysis of COD values of ground water samples collected from W1 to W7 is graphically shown in Figure 5.7. The lowest and highest COD values of ground water samples recorded during the study were 57.0 ± 3.4 mg/L and 4.7 ± 0.8 mg/L respectively. There was a statistically significant relationship between the COD values of water samples and distance of sampling sites ie. less is distance between sampling site from Chopda sugar factory more was COD value in water sample. This finding supported that contamination of water resources due to percolated wastewater from Chopda sugar factory added organic contaminants that required more oxygen.

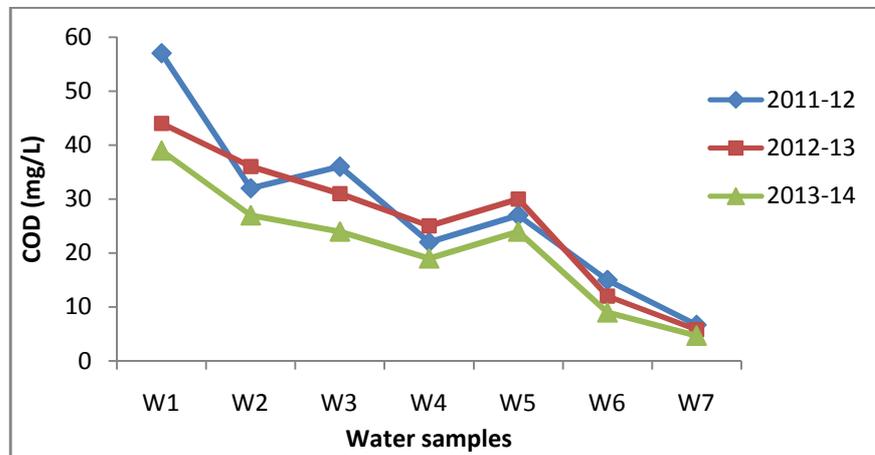


Figure 5.7 Variations in Chemical oxygen demand (mg/L) of water samples during three years of study period.

Hardness: Analysis of hardness due to presence of calcium and magnesium ions in water samples collected from W1 to W7 during three years of study is represented in the form of histograms in Figure 5.8. The lowest and highest hardness values of ground water samples recorded during the study were 136.2 ± 11.5 mg/L and 57.4 ± 6.4 mg/L respectively. Hardness due to calcium in each ground water sample was more than that of magnesium. There was a statistically inverse relation between the hardness values of each ground water samples and distance of sampling sites ie. Less is distance between sampling site from Chopda sugar factory more was hardness in water sample. This finding indicated that the ground water resources might be contaminated with wastewater percolated from spentwater storage digs from Chopda sugar factory.

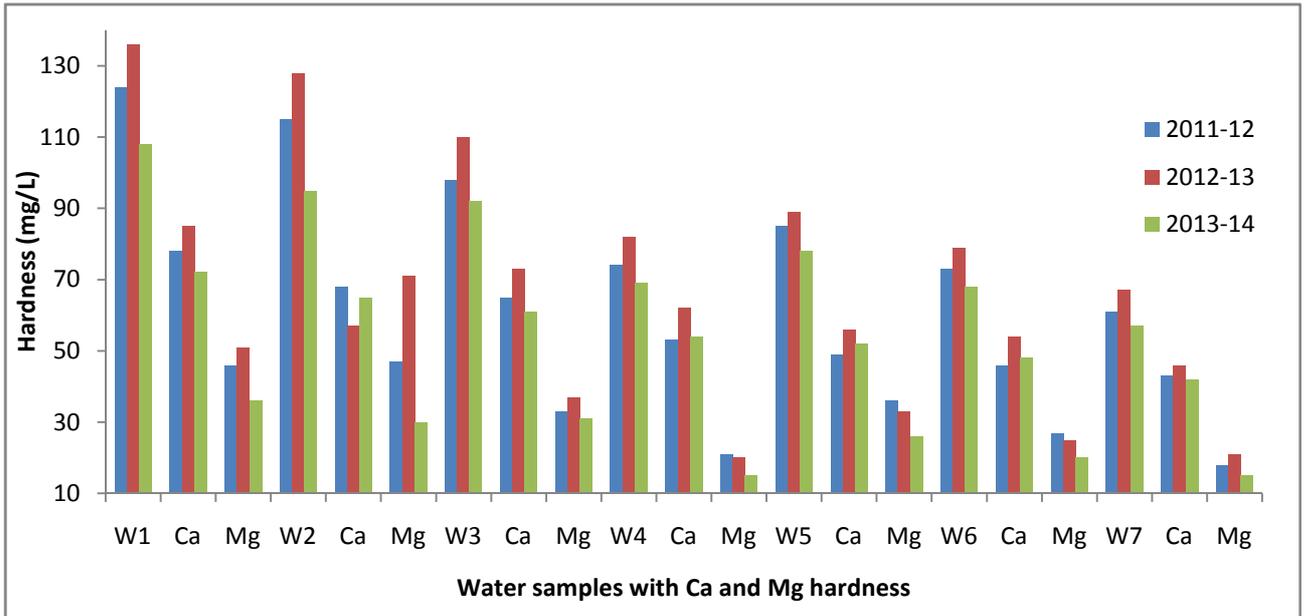


Figure 5.8 Histogram showing variations in Hardness (due to Ca and Mg in mg/L) of water samples during three years of study period.

Total Dissolved Solids (TDS): The variations in TDS values of ground water samples collected from sampling stations W1 to W7 are graphically represented in Figure 5.9. The minimum and maximum values of TDS values of ground water samples were 256.5 ± 14.6 mg/L and 69.4 ± 5.7 mg/L respectively.

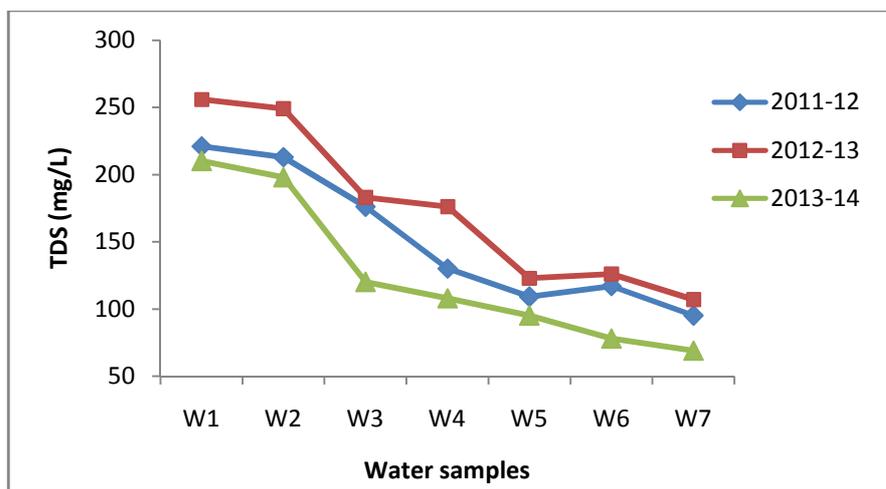


Figure 5.9 Variations in Total dissolved solids (mg/L) in water samples during three years of study period.

It was observed during the present part of investigation that more is the distance of sampling station from Chopda sugar factory less was the TDS values in water samples throughout the

study period. This might be due to more contamination of water resources due to wastewater percolated from digs made in the Chopda sugar factory to store spentwash. Comparatively lower TDS values in water samples collected during year 2013-14 were might be due to drought like conditions while more and continuous rainfall during year 2012-13 might be increased TDS values in water resources in the vicinity of Chopda sugar factory.

Alkalinity: The estimated values of alkalinity of ground water samples collected from seven sampling station in 6 km area around Chopda sugar factory are shown graphically in Figure 5.10. The alkalinity of water samples fluctuated between 62.3 ± 4.5 mg/L to 96.2 ± 7.9 mg/L during the period of study. The observed data revealed that alkalinity of ground water was directly proportional to the distance of sampling station from the Chopda sugar factory i.e. more is the distance higher was the alkalinity. In addition, the well water samples collected from sampling site W4 shown lower alkalinity values than that of other sampling stations. This might be due to presence of the large volume of water in a well which was more diluted due to neutral rain water that reduced its alkalinity. It was also supported by the fact that more and continuous rainfall during year 2013-14 might cause reduction in alkalinity of each water resources.

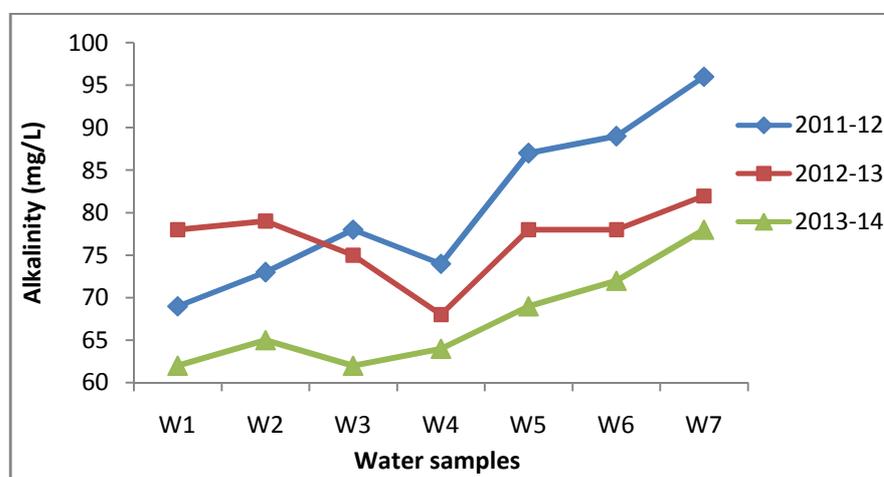


Figure 5.10 Fluctuations in Alkalinity (mg/L) of water samples during three years of study period.

Phosphates: The result of analysis of phosphate values of ground water samples collected from W1 to W7 is graphically shown in Figure 5.11. The lowest and highest phosphate values of ground water samples recorded during the study were 0.07 ± 0.01 mg/L and 0.16 ± 0.02 mg/L respectively. The water samples collected from W1, W2 and W3 shown

progressively lower presence of phosphates while the well water samples (W4) shown lowest values of phosphates. Whereas, water samples collected from W5 to W6 showed progressive increase in phosphate concentration and again increase in phosphate content was noted in water samples collected from sampling site W7. These observations may not be linked in any ways to percolation of wastewater form Chopda sugar factory.

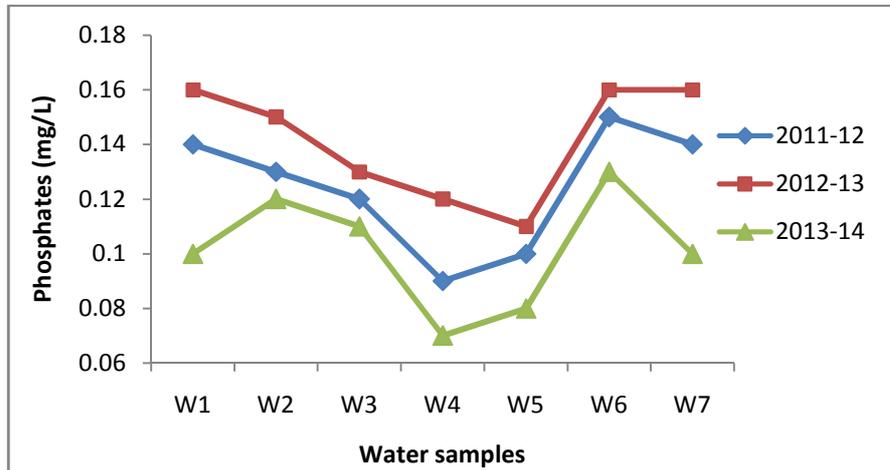


Figure 5.11 Variations in Phosphates content (mg/L) in water samples during three years of study period.

Sulphate: Analysis of water samples collected from W1 to W7 for its Sulphate content is shown Figure 5.12. The maximum value of sulphate content (170.7 ± 12.6 mg/L) was found at W1 and the minimum value (92.4 ± 7.3 mg/L) was recorded at W7. Pertaining to recorded observation, it may concluded that there was statistically significant reciprocal relation between the phosphate content in ground water samples and the distance of the sampling sites form Chopda sugar factory.

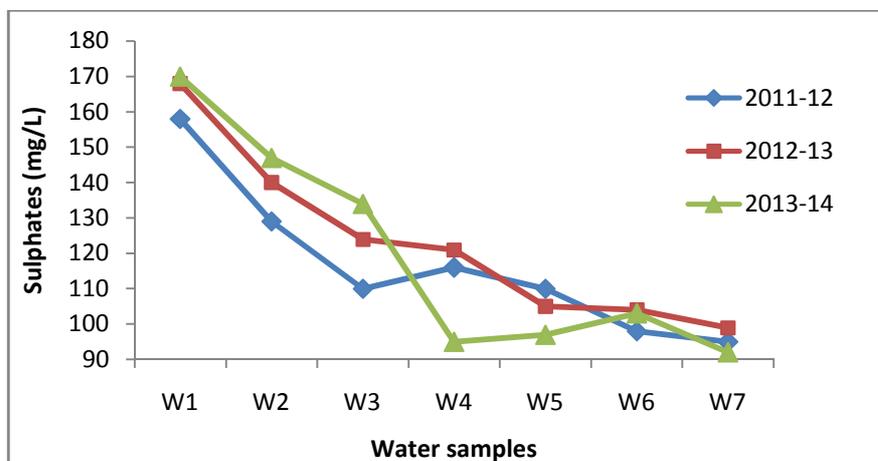


Figure 5.12 Variations in Phosphates content (mg/L) in water samples during three years of study period.

Chlorides: The estimated values of chloride content in water samples collected from W1 to W7 within six km area of Chopda sugar factory during three years of study is graphically shown Figure 5.13. Except in the higher chloride values (maximum of 45.3 ± 3.8 mg/L in three years) in water sample collected from bore well at the sampling site W1 (very near to project site of Chopda sugar factory), there was not a statistically significant fluctuations in the chloride values of water samples collected from W2 to W7. The minimum values of chloride content (19.4 ± 2.3 mg/L) were noted in water samples that were collected from sampling site W6.

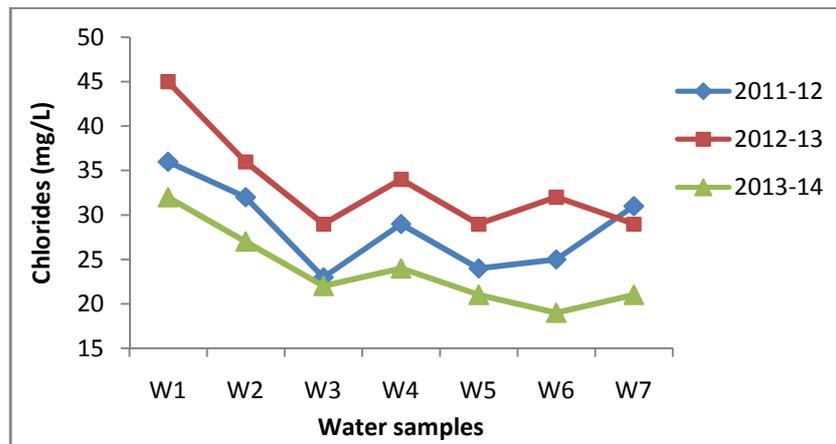


Figure 5.13 Fluctuations in Chloride content (mg/L) in water samples during three years of study period.

Nitrate: The result of analysis of nitrate content in ground water samples collected from W1 to W7 is graphically shown in Figure 5.14. The lowest and highest nitrate values of ground water samples recorded during the study were 0.62 ± 0.03 mg/L (at W5 and W7) and 2.1 ± 0.05 mg/L (at W4) respectively.

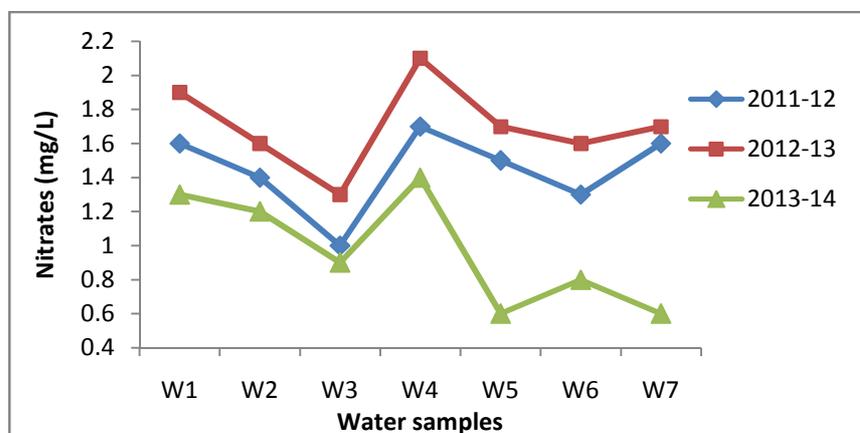


Figure 5.14 Fluctuations in Nitrate content (mg/L) in water samples during three years of study period.

Over all there was not significant alterations in nitrate content of ground water samples collected from W1 to W7 except that of W4. An open well water (W4) might be charged with agriculture runoff containing nitrogen fertilizers and hence these water samples showed comparatively higher nitrogen content.

Magnesium: The estimated values of Magnesium content in water samples collected from W1 to W7 within six km area of Chopda sugar factory during three years of study is graphically shown Figure 5.15. The higher magnesium values (maximum of 24.5 ± 4.4 mg/L in three years) were noted in water sample collected from bore well at the sampling site W1 (very near to project site of Chopda sugar factory) whereas lower values of Magnesium (12.5 ± 1.2 mg/L) were recorded in well water samples collected from W4. From W1 to W4, the ground water samples shown downward trend in its Magnesium content and later on there was no such specific relation between concentration of Magnesium in water sample and the distance of sampling site from Chopda sugar factory..

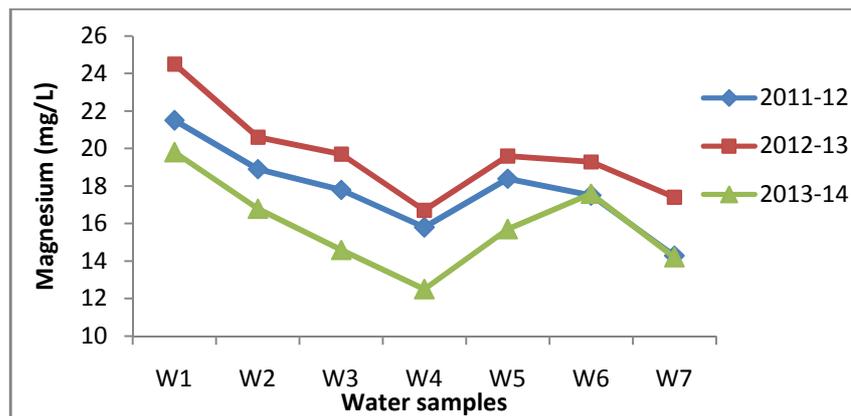


Figure 5.15 Variations in Magnesium content (mg/L) in water samples during three years of study period.

Resembling to above results, Anil kumar *et al.* (2003) noted the effect of distillery spentwash on water and soil characteristics. Comparison of the water and soil characteristics revealed that the spentwash was highly polluted with very high (far more than ISS standards) BOD, COD and dissolved suspended solids which were diluted after mixing with river water. Ajamal and Khan (1983) and Doke *et al* (2011) also reported very high TDS, COD, BOD, Chloride, Sulphates and low DO in sugar factory effluent.

B) Quality of soil samples collected in the vicinity of Chopda sugar factory:

Data pertaining to the survey of agricultural soils irrigated with spentwash and irrigated with ground water resources within six km area of Chopda sugar factory for different periods to evaluate the effect of spentwash irrigation on physico-chemical properties of soil are presented in Table 5.6. Each figure in the table is Mean \pm SD of six observations. During the operational periods of Chopda sugar factory in the year 2011-12, 2012-13 and 2013-14, analysis of each parameter was performed twice. The soil in the six km area of Chopda sugar factory is shallow to very deep black soils, loamy soils, lateritic soils and is suitable for agriculture and horticulture crops.

Soil pH

The pH of the soil samples collected from S1 to S7 shown variations from 5.5 to 7.6 within three years of study. The soil samples collected at S1, S2 and S3 where the soil plots were irrigated with spentwash in general recorded lower pH values than the soils, which did not receive spentwash. The data on soil pH indicated that all soil profiles irrigated with spentwash were slightly acidic in nature. The highest pH of 7.6 was recorded in the surface (0-12 cm) depth of S7 (soil irrigated with ground water located near Chopda city) and lowest pH of 5.5 was recorded in the surface (0-12 cm) depth of S1 site (100 m from Chopda sugar factory) where soil was irrigated with spentwash. In general, the pH of the soil increased as the distance between sampling site and sugar factory had increased. Spentwash irrigated soil with slightly acidic pH was also noted by Samuel and Muthukkaruppan (2011).

Electrical conductivity (EC)

In the present part of analysis, EC values fluctuated within 0.88 ± 0.07 dS/m to 3.11 ± 0.04 dS/m during three years of study in the soil samples collected from S1 to S7 within six km area of Chopda sugar factory. The data indicated that EC values of all soil samples were low indicating the nonsaline nature. The highest EC (3.11 dS/m) was recorded at S1, followed by moderate EC (3.07 dS/m) at W3 and then lower EC (3.02 dS/m) at W2. In all three plots (S1, S2 and S3), the soil was irrigated with spentwash for >6 years. Whereas the lowest EC (0.88 dS/m) in 0-12 cm depth at S6 (not irrigated with spentwash). The observed data indicated that spentwash irrigated soil tend to show increase in EC values of soils; whereas soils irrigated with open well or bore well water shown comparatively lower EC values.

Table 5.6 Physico-chemical properties of soil irrigated with spentwash (at S1 to S3) and ground water (at S4 to S7) within six km area of Chopda sugar factory during study period.

Sr. No	Parameter	S1 (Project site)	S2 (Chahardi)	S3 (Vele)	S4 (Akul-kheda)	S5 (Akhat-wade)	S6 (Majare-hole)	S7 (Near Chopda City)
1	pH	5.5 ±0.3	5.8 ±0.2	5.7 ±0.4	6.2 ±0.3	6.6 ±0.2	7.1 ±0.2	7.6 ±0.2
2	EC (dS/m)	3.11 ± 0.04	3.02 ±0.06	3.07 ±0.03	2.42 ±0.05	2.75 ±0.03	0.88 ±0.07	1.56 ±0.07
3	Organic Carbon (g/kg)	9.72 ±0.4	8.82 ±0.3	8.54 ±0.3	6.41 ±0.2	5.53 ±0.2	5.84 ±0.4	6.23 ±0.6
4	Available N (kg/h)	102.4 ± 8.3	128.3 ± 9.6	112.2 ± 8.6	87.4 ± 7.3	83.9 ± 6.3	90.6 ± 8.4	79.8 ± 6.7
5	Available P (kg/h)	59.4 ±4.7	54.8 ±5.9	62.6 ±5.8	45.5 ± 3.4	42.8 ± 3.8	38.9 ± 4.2	51.2 ± 4.9
6	Available K (kg/h)	621.2 ± 12.6	424.3 ± 8.4	580.4 ± 6.9	85.5 ± 4.2	72.6 ± 2.3	98.2 ± 5.7	67.7 ± 6.2
7	Iron (mg/kg)	14.39 ± 0.7	10.32 ± 1.2	9.29 ± 0.9	6.44 ±0.52	7.23 ±0.26	5.91 ±0.31	5.35 ±0.48
8	Zinc (mg/kg)	9.77 ±0.43	7.23 ±0.21	11.19 ±0.34	3.41 ±0.2	4.23 ±0.1	5.35 ±0.3	3.95 ±0.2
9	Cu (mg/kg)	3.72 ± 0.04	2.69 ± 0.02	2.88 ± 0.05	0.48 ± 0.03	0.34 ± 0.03	0.28 ± 0.02	0.31 ± 0.04
10	Mn (mg/kg)	13.6 ±1.9	21.9 ±2.2	16.2 ± 1.4	4.12 ±0.3	3.24 ±0.2	4.32 ±0.4	3.95 ±0.4
11	Pb (mg/kg)	1.05 ±0.04	1.21 ±0.03	0.98 ± 0.04	1.42 ±0.02	1.32 ±0.02	0.89 ± 0.03	1.24 ± 0.02

Each value is Mean ± SD of 6 observations

Organic Carbon

Perusal of data indicated that organic carbon content varied from low (5.53±0.2 g/kg) to high (9.72±0.4 g/kg) in these soils. The highest organic carbon (9.72 g/kg) was recorded at 0-12 cm depth at S1, followed by 8.82 ±0.3 g/kg at S2 and 8.54 ±0.3 g/kg at S3; soil at these sites were irrigated with spentwash. The soil irrigated with ground water resources shown organic contents 6.41 ±0.2 g/kg at S4, 5.53±0.2 g/kg at S5, 5.84 ±0.4 g/kg at S6 and 6.23±0.6 g/kg at S7. The observed revealed that soil organic carbon increased due to application of spentwash of Chopda sugar factory for irrigation.

Similar to above results, Pathak *et al.* (1999) also noted significant increase in soil pH, EC and organic carbon when irrigated with distillery effluent.

Available Nitrogen (N)

The result of analysis indicated that available N was higher in soil which was irrigated with spentwash than that of soil irrigated with ground water resources. The available N content fluctuated between 79.8 ± 6.7 kg/h to 128.3 ± 9.6 kg/h in soil samples during three successive operational periods of Chopda sugar factory. Comparatively higher available N content were found in soil samples in a decreasing order of 128.3 ± 9.6 kg/h (at S2), 112.2 ± 8.6 kg/h (at S3) and 102.4 ± 8.3 kg/h (at S1), whereas soil plots which were not irrigated with spentwash showed available N content in an increasing order of 79.8 ± 6.7 kg/h, 83.9 ± 6.3 kg/h, 87.4 ± 7.3 kg/h and 90.6 ± 8.4 kg/h at S7, S5, S4 and S6 respectively. Scandaliaris *et al.*, (1987) and Baskar *et al.* (2003) support the finding that spentwash irrigated soil had more available N.

Available Phosphorus (P)

The soils collected from S1 to S7 sites recorded low to high available P. The highest available P (62.6 kg/ha) was recorded in 0-12 cm depth at S3 (spentwash irrigated soil) and lowest available P (22.1 kg/ha) at S6 (soil not irrigated with spentwash). Comparatively much higher available P values were noted in the soil samples collected from S1, S2 and S3 (irrigated with spentwash of Chopda sugar factory) than that of S4 to S7 where the soils irrigated with ground water resources. The observed data clearly indicated that there was increase in available P in soils which were irrigated with spentwash.

Available Potassium (K)

The observations recorded during analysis of available K in soils showed drastic differences in its estimated values. The highest available K (621.2 kg/ha) was recorded in 0-12 cm depth the soil in the vicinity of Chopda sugar factory (S1) which was irrigated with spentwash and lowest available K (67.7 kg/ha) was noted in soil irrigated with bore well water near Chopda city (S7). The range of available K in spentwash irrigated soil was 424.3 ± 8.4 kg/h to 621.2 ± 12.6 kg/h and it varied from 67.7 ± 6.2 kg/h to 98.2 ± 5.7 kg/h in soil irrigated with ground water resources. Pertaining to results of available K analysis in soil samples collected in six km area of Chopda sugar factory indicated that the spentwash increased the content of available K in the soil profile. Findings of Sweeney and Graetz (1991) and Shinde *et al.* (1993) support the present investigation.

Available Iron (Fe)

Available Fe recorded in soils of different profiles at S1 to S7 sampling sites was above the critical level (2.5 mg/kg). The highest available Fe (14.39 mg/kg) was recorded in 0-12 cm depth at S1 (spentwash irrigated soil) and lowest available Fe (5.3 mg/kg) in soil sample collected from S7 (ground water irrigated soil). There is considerable differences in the available Fe in soils that were irrigated that that of soil which were not irrigated spentwash of Chopda sugar factory. The available Fe was fluctuated from 9.29 ± 0.9 mg/kg to 14.39 ± 0.7 mg/kg in soil irrigated with spentwash (S1, S2 and S3) whereas available Fe was lesser as compared to above mentioned values and it varied from 5.35 ± 0.48 mg/kg to 7.23 ± 0.26 mg/kg in soil irrigated with open or bore well water (S4 to S7). Thus, it can be inferred that spentwash might increased the available Fe in soil.

Available Zinc (Zn)

The available Zn was above critical level (0.6 mg/kg) in all profile soil samples. The highest available Zn (11.19 mg/kg) was recorded in 0-12 cm depth at S3 (spentwash irrigated soil) and lowest available Zn (3.4 mg/kg) in soil sample collected from S4 (not irrigated with spentwash). Spentwash irrigated soil samples collected from S1, S2 and S3 showed available Zinc 9.77 ± 0.43 mg/kg, 7.23 ± 0.21 mg/kg, 11.19 ± 0.34 mg/kg respectively whereas comparatively lower values of available Zn were found as 3.41 ± 0.2 mg/kg, 4.23 ± 0.1 mg/kg, 5.35 ± 0.3 mg/kg and 3.95 ± 0.2 mg/kg in S4, S5, S6 and S7 soil samples respectively. From observed that it might become clear that the available Zn increased due to spentwash irrigation.

Available Copper (Cu)

In all the soil samples collected from S1 to S7 the available Cu was found above the critical level (0.2 mg/kg). The highest available Cu (3.72 mg/kg) was recorded in 0-12 cm depth at S1, followed by 2.69 mg/kg at S2 and 2.88 mg/kg at S3. These soils were irrigated with spentwash during three years of study whereas lowest available Cu (0.28 mg/kg) was found at S6 site, where soil was not irrigated with spentwash. The open or bore well was used for irrigation at S4 to S7 and their soil samples showed comparatively lower available Cu as 0.48 ± 0.03 , 0.34 ± 0.03 , 0.28 ± 0.02 and 0.31 ± 0.04 mg/kg at S4, S5, S6 and S7 respectively. Pertaining to observed data it became clear that spentwash irrigation might cause to increase available Cu in soils.

Available Manganese (Mn)

The data indicated that soils of different profiles recorded Mn above critical level (1.0mg/kg). The highest available Mn (21.9 mg/kg) was recorded in 0-12 cm depth at S2 (spentwash irrigated soil) and lowest (3.24 mg/kg) at S5 (not irrigated with spentwash). The available Mn increased with the use of spentwash for irrigation (at S1, S2 and S3) and it was become clear from the differences in observed values of available Mn in soils which were irrigated with ground water resources. Soils at S4 to S7 were shown lesser amount of available Mn as 4.12, 3.24, 4.32 and 3.95 mg/kg respectively due the fact that they were not irrigated with spentwash.

Available Lead (Pb)

The observed data indicated that soils of different profiles recorded Pb slightly above critical level (1.0mg/kg) at the sampling sites S1, S2 and S3 where farmers used spentwash for irrigation. But surprisingly at sampling sites S4 to S7 where ground water resources were used to irrigate the soil showed variation in available Pb in the range of 0.89 to 1.42 mg/kg. Overall, in relation to available Pb in S1 to S7, there was no significant difference in their values. The irrigation of soil with spentwash could not alter the available Pb values as compared to the soils irrigated with ground water resources.

Somewhat similar results were noted by Ramalho *et al.* (2001) who analyzed soil samples treated with sugarcane industrial residues for available Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn and found that all heavy metals increased significantly with the exceptions of Zn and Mn. Roy *et al.* (2007) also noted the effect of irrigation by sugar factory effluent (spentwash) and the well water with high TDS (422-608 mg/L), COD (1152-17680 mg/L) and BOD(380-650 mg/L) than well water (TDS 240 mg/L), COD (3.8 mg/L) and BOD 1.2 mg/L). They also reported presence of some nutrients, viz. N, P, K, Zn, Cu, Fe, Mn in surface layer of soil in different seasons, but contrary to present investigation they reported heavy metals (Cd, Co, Cr, Ni, Pb) within the permissible limits. Resembling to results of present investigation, Siddiqui and Waseem (2012) reported high contents of COD, BOD, TSS, TDS, and low contents of DO in sugar mill effluent and noted inhibitory effect of high concentration of distillery effluents on fertility of soil.

5.4 CONCLUSION

In the present part of investigation, it was found that the ground water quality of bore wells at W1 (at Chopda sugar factory), W2 (at Chahardi), W3 (at Vele) adversely affected due the fact that these sampling stations are within 2 km of area Chopda sugar factory. While the water quality at W4 to W7 was also affected to some extent so far its physico-chemical properties were concerned. The water quality of bore wells in the vicinity of Chopda sugar factory was deteriorated might be due to contamination of organic content present in spentwash that percolated through soil layers and polluted the ground water resources. Soil quality is a complex concept, involving a wide range of biological, chemical and physical variables. Irrigation of soil with Chopda sugar factory effluent significantly altered physico-chemical parameters mainly at the sampling sites at S1, S2 and S3.

Since Chopda sugar factory is playing significant role in socio-economical sector of Chopda tehsil and Jalgaon district as well. There is tendency of farmers in the vicinity of Sugar factory to rely upon the spentwash for irrigating their agricultural land in spite of several reports indicating that farmers, who had used sugar factory effluents consistently for irrigation, found that the growth and yield of the crop and soil health were reduced. The power supply failure, continuous load shading and drought like condition during year 2012-13 might divert most of farmers in the vicinity of Chopda sugar factory to use spentwash for irrigation using manual ways.

Although the physico-chemical properties of spentwash irrigated agricultural soil showed increase in available N, P, K and other constituents yet its continuous application to the soil may be harmful and can cause potential pollution hazards because anything in excess is hazardous. Hence, a suitable management system needs to be evolved for the application of effluent to the soil without causing deterioration in the quality of the environment. There must be strict legislation on judicial use of spentwash that must be pretreated to remove pollution load.