Assessment of Groundwater Quality in Malwa Region of Punjab

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INFRASTRUCTURE ENGINEERING

Submitted by

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DECLARATION

I hereby declare that this work is being presented in the thesis entitled **"Assessment of Groundwater Quality in Malwa Region of Punjab"** in partial fulfillment of the requirement for the award of degree of **Master of Engineering in field of Civil Engineering** with specialization in Infrastructure Engineering submitted at Thapar Institute of Engineering and Technology (Patiala) is an authentic record of my own work carried out during the period from 26-12-2018 to 15-7-2019 under the guidance of **Dr. Dwarikanath Ratha, Associate Professor,** Department of Civil Engineering and **Dr. B.R. Yadav, Assistant Professor,** School of Energy and Environment.

The matter embodied under this thesis has not submitted by me for the award of any other degree or diploma.

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It is to certify that above statement made by the student concerned is correct and true to the best of our knowledge and belief.

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ABSTRACT

Quality of drinking water is the major issue which creates most of the health problems in the living organisms. The limited drinking water sources create a huge problem in different areas of world where fresh drinking water is very expensive and less available. This study highlights the groundwater quality status of six districts of the Malwa region of Punjab i.e. Patiala, SAS Nagar (Mohali), Sangrur, Mansa, Mukatsar and Bathinda. One hundred and thirty (130) samples were taken from the selected districts of Malwa region of the Punjab from different land-use i.e. Industrial sector, Agriculture Sector and Domestic sector. The sampling of the groundwater was done one time in each months of February to June 2019.

The physical and chemical analysis of samples of study area executed as per APHA guidelines. The major parameters of the pysico-chemical properties were calculated i.e. pH, EC, TDS, Total Hardness, major anions and cations. Results indicate that the salt concentration determined through Electrical Conductivity testing is the maximum in Mukatsar, Bathinda and Mansa districts. Also the major dominance of the salts concentration is found in order of $SO_4^{2-} > Mg^{2+} > NO_3^- > Ca^{2+}$.

The correlation analysis of the results calculated from laboratory testing shows that the strong correlation of Electrical Conductivity (EC) existed with TDS, Alkalinity, TH, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, and NO_3^- at significant levels of $p<0.01$. The nitrate shows a negative trend with the depth of the groundwater table. Groundwater Quality Index (GQI) of the study area varies from medium to marginal level in the entire study area. The results tabulated from the calculations of Magnesium Absorption Ratio (MAR) shows that the groundwater in the study area is unsuitable for agriculture purpose.

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ABBREVATIONS AND NOTATIONS

1	**U.S.G.S.**	United States Geological Survey
2	**C.W.C.**	Central Water Commission of India
3	**N.W.A.**	National Water Academy
4	**C.G.W.B.**	Central Ground Water Board of India
5	**E.P.A.**	Environment Protection Agency
6	**W.H.O.**	World Health Organization
7	**B.I.S.**	Bureau of Indian Standards
8	**A.P.H.A.**	American Public Health Association
9	**MAR**	Magnesium Absorption Ratio
10	**TH**	Total Hardness
11	**GQI**	Groundwater Quality Index
12	**WQI**	Water Quality Index
13	**EC**	Electrical Conductivity
14	**TDS**	Total Dissolved Solids
15	**TSS**	Total Soluble Solids
16	**TS**	Total Solids
17	**NTU**	Nephelometric Turbidity Unit
18	**mg/l**	Milligram per Liters
19	**µS/cm**	Micro Siemen per Centimeter
21	**r**	Coefficient of Correlation
22	**p**	Probability
23	**I.S.**	Indian Standards

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Quality of drinking water is the major issue which creates most of the health problems in the living organisms. The limited drinking water sources create a huge problem in different areas of world where fresh drinking water is very expensive and less available. Water is an important need of all living organisms at our planet which is lifeline of the earth. Although 2/3rd part of the earth is filled with water but there are many countries facing shortage of the pure drinking water. As per the statistics available, 94% of the water available in world is brackish and only 6% of the water is fresh drinking water. Also it is reported in literature that 27% of water is flowing water and the rest of the water is available in the form of groundwater (USGS).

Only 4% of the total world water sources are available in India for 18% of the world population. India also has an extensive river network. The large Indus-Ganga-Brahmaputra in the North region of India, the Narmada-Tapi- Mahanadi in Central region of the country and Godavari-Krishna-Cauvery of South India has been the source of the water for our country. Most of the people of India are depending on groundwater for their daily life (CWC,NWA 2017). Groundwater development is to be under in safe condition if the rate of withdrawal of groundwater is not exceeding the natural recharge of the groundwater (Alley et al. USGS 2013).

The rate of the groundwater development is about 61% in India. In the states like Delhi, Haryana, Punjab & Rajasthan the rate of ground water development is in unsafe condition which means in these states the groundwater consumption is more than the rate of groundwater recharge. On the other side in the states like Tamil Nadu, Uttar Pradesh and UT's of Daman & Diu and Pondicherry, the scenario of the groundwater development exceeds 70 % (CWC, NWA 2017).

The Punjab state has an area of 50362 sq. km and which is 1.6% of total area of India. Besides that it contributes 42% rice, 55% wheat and 24 % cotton production in the country

(CGWB 2014). Due to the vast agriculture network of state, the consumption of the fertilizers and the pesticides in agriculture is at higher rate. The Malwa region consumes 75% of the pesticides in the state (CGWB 2014). On the other hand the waste from the industrial activities also led to pollute the groundwater through the discharging effluent in the drains.

The polluted groundwater affects the domestic water supply systems and the pond water systems as it is unsafe for human as well as for wildlife. The major sources of groundwater pollutions are sanitations system on site, landfills and effluents generated from the wastewater treatment plants.

If the drinking water contains bacteria and viruses it creates serious health problems like learning disabilities, pregnancy risks, liver and kidneys problems etc. (EPA)

Similarly in the Industrial sector, some physic-chemical parameters give its impact on the industrial operations related with water sources. The foaming and the scaling is one of the major problems. To prevent this problem, the continuous study on the chemical properties of groundwater is required.

Groundwater quality for irrigation purpose is essential with respect to concentration of the elements. Concentration of dissolved mineral in groundwater affects the plant growth and physic-chemical properties of soil (Ehya et al. 2017). The quality of irrigation groundwater is based on three major components a) soluble salts content in groundwater that creates its impact on crops through osmotic action b) The ionic concentrations and boron content which have an adverse impacts on crops quality c) The cations of sodium which splits the clay minerals which leads permeability(Karnth et al. 1987).

Since the rapid industrialization, urbanization and agriculture action contaminates the groundwater with time, the regular assessment of the groundwater quality is necessary for ecosystem health and domestic use.

As per the report entitled by Central Ground water board, most of the physic-chemical properties of the groundwater of the Punjab state specially in Malwa region of Punjab (South west region of the Punjab) are beyond its permissible limits It is reported in the

CGWB report that, The physico-chemical parameters i.e. Total Hardness, Chlorides, fluoride, nitrate, and heavy metals concentrations are beyond permissible limits.

1.2 ORIGIN OF THE STUDY

The rapid industrialization, urbanization and agriculture action contaminates the groundwater with time. Since most of the people of our country use the groundwater for their daily needs, the quality of the groundwater should be as per guidelines. The consumption of contaminated water creates a number of health issues. In order to check the quality of the drinking water, BIS as well as WHO prepared a guidelines and mentioned the permissible limits of various physico-chemical parameter. Table 1.1 shows the guidelines for each parameter and their impact on health if present in drinking water beyond permissible limits.

Table1.1 *Different parameters guidelines and its health implications*

S.No	**Parameter**	**Units**	**Permissible limits (IS 10500-2012) (DL-PL)**	**WHO Guidelines**	**Health Implications (Kumar et al. 2017)**
1	pH		6.5-8.5	7-8.5, PL=9	Gives acidic and basic nature of groundwater
2	Turbidity	NTU	0-1	-	Presence of bacteria and dissolved solids
3	EC	µS/cm	500-1000	500-1400	Salinity content & Gastro intestinal Irritation
4	TDS	mg/l	500-2000	-	Dissolved solids which imparts hardness
5	TH	mg/l	200-600	100-500	Scale formations
6	Calcium	mg/l	75-200	75-200	Essential for Bones development
7	Magnesium	mg/l	30-100	50-150	Indicate suitability for irrigations purpose MAR

S.No	Parameter	Units	Permissible limits (IS 10500-2012) (DL-PL)	WHO Guidelines	Health Implications (Kumar et al. 2017)
8	Alkalinity	mg/l	200-600		Scale formations
9	Sulphate	mg/l	200-400	200-400	Laxative Effect in human body
10	Chlorides	mg/l	250-1000	200-600	Disinfection purpose for bacteria
11	Fluoride	mg/l	1.0-1.5	1.5	Dental caries, Fluorosis diseases
12	Nitrate	mg/l	45	45	Blue baby disease

The present study analyzes the status of the present scenario of groundwater with respect to quality.

1.3 NEED OF THE STUDY

As the report entitled by the Central Ground Water Board (2014) India, it states that the groundwater quality of the Punjab state specially in southwest belt of the Punjab state is not fit for the drinking. Table 1.2 shows the various location of Punjab in which the certain water quality parameters are found beyond permissible limits by CGWB, 2014.

Table 1.2 *Affected districts from different chemicals in groundwater of Punjab as per ‘Central Ground Water Board.*

Sr.No	Parameter	Affected Districts
1	Salinity (EC>3000μS/cm at 25°C)	Faridkot, **Bathinda**, Ferozepur, **Mansa, Mukatsar**
2	Fluoride (>1.5mg/l)	**Mukatsar, Bathinda,** Ropar, **Mansa,** Ferozepur & Faridkot.
3	Arsenic (>0.05mg/l)	**Mansa**, Tarantaran, Amritsar, Kapurthala, Ropar

Sr.No	Parameter	Affected Districts
4	Iron (>1.0mg/l)	Nawashahr, Sangrur, Patiala, Amritsar, Ropar, Bathinda, Gurdaspur, Hoshiarpur, Jallandhar, Ludhiana & Mansa
5	Nitrate(>45mg/l)	Gurdaspur, **Bathinda,** Ferozepur, Ludhiana, **Mansa,** Jallandhar, Faridkot, **SAS Nagar & Patiala**
6	Heavy Metals Lead(>0.01mg/l) Cadmium(>0.03mg/l) Chromium(>0.05mg/l)	Lead:- Kapurthala, **Patiala**, Ropar, Fatehgarh Sahib, **Bathinda,** Faridkot, Ferozpur, Ludhiana, **Mansa**, Nawashahr, Gurdaspur, **Patiala & Mukatsar.** Cadmium:- **Sangrur,** Fatehgarh Sahib, Nawashahr, Amritsar & Ludhiana Chromium:- **Sangrur, Mansa**, Amritsar, Ropar, Gurdaspur & Amritsar

Table 1.2 shows the districts are in bold formats which are covered under the study area of the present work.

The present work access the various water quality parameters of the groundwater of Malwa region of the Punjab state (i.e. southwest region of Punjab). The water quality includes the basic physico-chemical properties of the groundwater samples like as pH, Total dissolved Solids (TDS), Total Solids (TS), Electrical Conductivity (EC), Total Hardness (TH), major ions and anions. Since the study on the physico-chemical analysis and WQI for Punjab south west region is limited, there is need of analyzing the status of the physico-chemical parameters as well as WQI in the study area.

1.4 SCOPE OF THE STUDY

The present study has following scopes.

The impact on groundwater quality is analyzed by measuring the various physico-chemical parameters. The co-relation between the various physico-chemical parameters and the location of sample needs to be established. The impact of various activities like agriculture, industrial and domestic etc on the quality of groundwater is monitored. The water quality index needs to be calculated using various physico-chemical parameters of the samples collected from the study area.

1.5 ORGANIZATION OF THE THESIS

This thesis highlights the groundwater scenario in the southwest region of the Punjab state i.e. Malwa region of Punjab. In the chapter 1 the brief introduction of the world water availability scenario including the physico-chemical analysis and the information about the WQI of the study area. Ongoing in the chapter 2 the brief literature review of the physico-chemical analysis and WQI performed by the different authors. The condition of the study area is defined in the chapter 3 including the methodology of the sampling etc. In chapter 4 the testing standards and the protocols are used during the performance of all the tests are confined. The result and analysis discussion with the graphs and other diagrams are shown in the chapter 5. The GQI of the study area is determined in the chapter 6 along with its methodology. The conclusions as we concluded from all the study is described in the chapter 7.

1.6 CONCLUDING REMARKS

In this chapter the introductory information regarding the status of groundwater availability and issues related to poor quality of drinking water have compiled. The information about impact of various physico-chemical parameters on groundwater in Punjab state is discussed. The impact of various parameters on groundwater quality was also discussed.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTORY COMMENTS

The previous chapter describes the introduction on groundwater quality study, requirement of the study in Malwa region Punjab and Scope of the present study. The present chapter discusses the previous similar work carried out nationally as well as internationally. The present literature review is made on two different components such as literature review on groundwater quality and Literature review on water quality index.

2.2 LITERATURE REVIEW ON GROUNDWATER QUALITY

Water requirements for the daily purposes is mainly depends on the source of its generation i.e. groundwater, rainwater and water comes in the rivers are generally as we found in our daily life. The groundwater is one of the important nonrenewable sources on our planet which exploited from different polluting agencies and its steady rise in its usage in agriculture activities about 70% in many regions of the world (Taylor 2014). Rise in the usage of the groundwater leads to the deterioration of its physico-chemical quality which further creates it impact on our daily life.

The main concerns also generated as there are more than 200 million peoples in the world (including India) suffering from dental and skeleton fluorisis which due to the rich in fluorides in the groundwater (Brinda et al., 2011).

Gowrisankar et al. (2017) studied groundwater recharge from the check dam which creates its impact on the physico-chemical properties of the groundwater at the Krishnanagar district of Tamilnadu state. They were obtained water samples from 15 wells having depth from 10m to 50m periodically and studied the physico-chemical properties of the ground water like TDS (225mg/l-1834mg/l), Total Hardness (TH) varies between 114mg/l-614mg/l, pH varies 7-9.1 which shows alkaline nature of groundwater, Electrical Conductivity varies in 330-2866µS/cm, and also verified the major anions and cations presented in the sampled groundwater and the values were got from testing were examined with BIS 10500-2012.

From these physico-chemical properties they found that the groundwater in study region was very hard in nature and moderately hard as per according to classification of Sawyer and McCarty. The fitness of groundwater being considered for agriculture was determined by Electrical Conductance (EC), Sodium Absorption Ratio (SAR), and Permeability Index (PI) and for drinking water the results were generated from testing of physico-chemical parameters were compared with the classification on the basis of the Sawyer & McCarty (1967). They concluded that due the presence of check dam at the study area is acceptable for agriculture as well as for domestic basis. The groundwater away from the check dam site has high concentrations of the ions as compared to the area near the check dam site.

Thakur et al. (2016) assessed the groundwater qualities of three administrative blocks of the Rupnagar district of Punjab state, the two blocks from these exploitation of the groundwater reached near about 200%. They collected sixty groundwater samples from the tubewells at shallow depth under the pre-monsoon season in May of 2013 and these samples were assessed with the major chemical parameters and they concluded that each parameter was perfectly fall under the permissible limits as per Indian Standards, but the Electrical Conductivity (EC) 458-1126 µS/cm, Total Dissolved Salts (TDS) 293-633 mg/l, Ca content (26.9-77.4mg/l) and Mg content (11.7-63.4 mg/l) were exceeds from its permissible limits. The data showed on the diagram of US Salinity Laboratory showed the most of the samples fall under C_2S_1 and C_3S_1 which gave the prove of the groundwater is fit for agriculture purposes of that study area in all types of soils. The other chemical properties like %sodium (%Na), Sodium Absorption Ratio ranges 0.07 meq/l to 1.26 meq/l. (SAR), Residual Sodium Carbonate (RSC) ranges from -3.16 meq/l to 1.45 meq/l also showed the groundwater of the given study area useable for irrigation purpose. They also computed the Permeability Index (PI) varied from 7 % to 14 % and fall under Class I(Domenico & Schwartz 1990) category i.e. 100% permeability of the soil. At last they concluded that the chlorides, sulfate, nitrate and fluoride in under permissible limits as per BIS 2012. The major cation & anion are in under order of Mg^{2+}> Ca^{2+}> Na^{+}> K^{+} and anion concentrations followed by HCO_3^-> Cl^-> SO_4^{2-}> NO_3^-.Finally they concluded that the groundwater quality studied under given area good for domestic and irrigation purposes. Best usage made by taken the preventive and precautionary measures.

Garg et al. 2014 they studied the physico-chemical properties of the groundwater specially fluoride and nitrate in the southwestern region of the Punjab state. The parameters were analyzed by them during observation study were pH (range 6.24 to 8.67), Total Dissolved Solids (mean 1511.9 mg/l), Electrical Conductivity (173 to 12270µS/cm), Fluoride Concentration (range 0.27 to 10.6 mg/l), Nitrate Concentration (range 0 to 90 mg/l) and Depth (0 to 300 feet) of source also. They also noted that the occurrence of fluoride in groundwater from fluoride bearing minerals like fluorite, fluorapatite, topaz, quartz and mica in bed rock. They also did the correlation analysis of fluoride and nitrate with pH, EC and depth. They realized that in the correlation analysis that the pH shows a positive correlation with fluoride (R^2= 0.8214) and pH with nitrate shows a negative correlation (R^2=0.935). The fluoride is generally occurred by the hydro-geological strata i.e. sellaite (MgF_2), fluorspar (CaF_2), cryolite (Na_3AlF_6) and fluorapatite [$3Ca_3$ $(PO_4)_2$ Ca (F, Cl_2)]. It also creates in the sedimentary rocks & Igneous rocks in the form of fluorspar and cryolite. Fluoride is also affected by the pH value of the groundwater (Sharma et al.2014), higher value of the pH contribute in enrichment of the Fluoride ion content in groundwater. OH^- ions with high pH value and same charge, radius can replace the exchangeable F^- ions from fluoride containing minerals (micas/muscovite, illite, chlorite and amphiboles) which increase the concentration of fluoride in groundwater (S. Gupta et al., 2012).

The mechanism of F^- ion replacement in muscovite with hydroxyl ion as shown in following reaction (Sharma et al., 2014)

$$KAl_2 [AlSi_3O_{10}] F_2 + 2OH^- \rightarrow KAl_2 [AlSi_3O_{10}][OH]_2 + 2F^- \qquad (2.1)$$

The hydrolysis of alumino-silicates minerals from sandstone aquifers creates bicarbonate ion which also helps dissolution of fluoride ions a given below:-

$$CaF_2 + 2HCO_3^- \rightarrow CaCO_3 + 2F^- + H_2O+ CO_2 \qquad (2.2)$$

The factors like rock type, geological strata formation, contact time of circulating groundwater with rock crates its direct impact the fluoride concentration in groundwater

(Frencken et al. 1992). In the presence of the different ions i.e. bicarbonates and calcium also give its impact in the fluoride concentration in groundwater (M. Pahwa et al., 2004).

The occurrence of the fluoride content in the groundwater is also from the anthropogenic activities like phosphatic fertilizers, ceramic industries, clays used in bricks & burning of the coal which also leads to formation of fluoride in the groundwater (Jacks et al. 2002).

These minerals are also insoluble in water. Therefore fluoride is also present in the fluoride bearing effluents are mixed with the groundwater from industries (Mohapatra et al., 2009). They also say that the positive correlation between pH and fluoride occurs due to the dissolution of fluoride bearing minerals in ground water.

$$CaF_2 + CO_3^{2-} \rightarrow CaCO_3 + 2F^- \qquad (2.3)$$

$$CaF_2 + 2HCO_3^{2-} \rightarrow CaCO_3 + 2F^- + H_2O + CO_2 \qquad (2.4)$$

Nitrate mix with groundwater from the leaching action of the soil generally in the sandy soils, well drained soils at shallow water levels. In the shallow aquifer aerobic conditions crates the high nitrate (NO_3^-) concentration for longer period of time. According to Mr. Sondhi (A. Bhardwaj et al., 2012) anthropogenic activities, the increase in the consumption of the artificial fertilizers, MSW sites and land use activities leads to increase the nitrate content in the groundwater of the India (Bhardwaj et al., 2012)(Behera et al., 2003).

Usually the ammonia in nitrogen in fertilizer converts in nitrate with the process of biological nitrification and the reactions takes place as shown in the fig below:-

$$NH_3 + 2O_2 \rightarrow NO_3^- + H^+ + H_2O \qquad (2.5)$$

The adverse impact of high nitrate is to be recorded in the drinking water (Walton 1951). The higher the nitrate levels leads to the occurring cancer in human beings (Clark et al.1997).These two parameters are in the major consideration in this area of the Punjab state which also crates the health effect on the population

The negative correlation exist between nitrate and pH due to reduction of alkaline medium towards nitrate which results decreasing in pH and increase in nitrate content. EC shows a positive trend with the fluoride and nitrate whereas the correlation of fluoride and nitrate with depth gives the negative trend (R^2=0.95002 & R^2= 0.4321). Higher fluoride and nitrate content observed at shallow depth 100 to 150 feet and maximum observed at the depth of 0 to 50 feet. At last they concluded that the rural areas of the southwest Punjab passing from that problem of fluoride and nitrate at the water at depth of 0 to 100 feet with occurrence of fluoride with geogenic sources.

Kumar et al. 2007 This paper highlights the existed physico-chemical properties of the two most cultivated areas of the southwest districts of the Punjab state i.e. Patiala and Muktsar. They collect the groundwater samples during the pre-monsoon and post monsoon seasons. They studied the physico-chemical parameters i.e. all major anions and cations, total hardness (116.3-715 mg/l in Patiala and 358-1250 in Mukatsar), EC varies as 430-1960 μS/cm in Patiala and 530-7580 μS/cm in Mukatsar district, Sulphate content (SO_4^{2-} varies in Patiala 4.50mg/l -202.7 mg/l and in Mukatsar district 22mg/l – 3050mg/l). These properties are determined in comparison of the chemical composition of the existed concentrations. They resulted that the groundwater in Patiala district is better for the irrigation purposes but in future it may be deteriorate whereas in case of the Mukatsar district the groundwater of that region is not acceptable for drinking and irrigation. With the monsoon impact the groundwater of the Patiala region becomes flushing and dilution but on the other hand the impacts of monsoon on the groundwater of the Mukatsar district show generation of the anions and cations in the groundwater of that region.

Jagadeshan et al. 2015 In this paper the author shows ion signature which are responsible for geogenic sources in Vaniyar river basin in Dharampuri district of the Tamilnadu state. This study taken with the objective of the release of fluoride from the rocks and its mechanism, which creates its impact on human health, along with the status of physico-chemical parameters. The samples are collected by them June 2011 to August 2014 and they collect 569 samples from wells. They check all the physico-chemical parameters under which they observed that the pH of the given study area 6 to 8.49, total dissolved solids (TDS) varied under 234mg/l to 2646mg/l. The variations in various cationic ions were in under 31mg/l to 496mg/l. Calcium and Magnesium content ranged under 19 to 211mg/l and 11 to 148mg/l respectively. Similarly the variations in other parameters like Chloride content, bicarbonate and sulphate were recorded as 62 to 784mg/l, 78 to 610mg/l and 6 to 346mg/l respectively. They noticed that the fluoride concentration in 396 samples out of 569 found above the permissible limit of drinking water as per BIS i.e. 1.5mg/l and it is varies from 0.15mg/l to 6.14 mg/l. They also found that the concentration of the fluoride higher in the deep well. They also analyzed that the source of the fluoride in groundwater is due to presence of the fluoride bearing minerals. Fluoride dissolved through the leaching action of fluoride wit groundwater. They found that the geochemical reaction takes place with groundwater and fluoride bearing minerals (biotite & hornblende mineral) which further leads to release fluoride in groundwater.

Magesh et al. 2016 They undergone under the study of an occurrence of fluoride along with its physico-chemical properties in groundwater and its distribution in the region of the Tamiraparani river basin of the south India. They collected total 124 groundwater samples for their analysis in time of post monsoon season (Jan-2016) from hilly areas of the Western Ghats. They collected the samples from wells which are situated at the shallow depth ranges from 0.5m to 14m deep. They measured the physico-chemical properties like Temperature, pH(6.45-8.8), EC(340-3688µS/cm), TDS(218-2360 mg/l) and major anions i.e. HCO_3^-, SO_4^{2-}, Cl^-, and NO_3^- and major cations like Ca^{2+}, Mg^{2+}, Na^+ and K^+ as per the protocol of APHA. They measured fluoride (F^-) by ion selective electrode (0.01- 1.6725mg/l). They also calculate Total Hardness by EDTA titration method (87.11- 1597.97mg/l).At last they found that the concentration of the fluoride ions varies from 0.1mg/l to 1.67mg/l as lies with its higher concentration showed in the northern and central part of the study area. They also found that the generation of the fluoride from the natural conditions (Geogenic & Geochemical inferences).They observed that the fluoride generation mainly origin from geogenic sources (calcite and fluorite).

Brindha et al. (2016) In this paper they studied the groundwater quality at three regions i.e. Nalgonda District of Telangana, river basin of Vaniyar & Pambar River basin in Tamilnadu of South India. They collected total 484 samples from which they collected 36 samples from Nalgonda, 193 from Pambar and at last 255 from Vaniyar river basin. They analyzed the basic water quality parameters like EC(144-5030µS/cm in Nalgonda, 150-6000µS/cm in Pambar and 366-4129µS/cm in Vaniyar), TDS(92.2-3219.2 mg/l in Nalgonda, 96-3840 mg/l in Pambar and 234.2-2642.6 mg/l in Vaniyar), pH(6.1-9.3 in Nalgonda,6-9.5 in Pambar and 6.1-8.5 in Vaniyar), Carbonate, Bicarbonate & Fluoride(0.1-8.8 mg/l in Nalgonda, 0.1-4.3mg/l in Pambar and 0.2-6.9 mg/l in Vaniyar) at given study area and they found that the EC and TDS vary like in Nalgonda district as a fresh (1000mg/l) whereas in Pambar and

Vaniyar the groundwater is brackish. Similarly pH and alkalinity showed the basic nature of groundwater which is controlled with its bicarbonate content (Arya et al. 2011). Groundwater show more basic nature in Pambar region i.e. pH about 9.5 and average bicarbonate was about 323.8 mg/l whereas groundwater in Nalgonda and Vaniyar basin less alkaline as compared to Pambar region. As the results founds about fluoride in given study region were above from permissible level i.e. 1.5mg/l, they recorded maximum concentration of the fluoride as 4mg/l. They noticed that the 35% of samples were above the permissible limits of fluoride. They found the generation of the fluoride in the given study area due to the fluoride bearing minerals i.e. fluorite, flurapatite, biotite & hornblende. The correlation gave the signs of fluoride generation through geochemical process i.e. rock water interaction and weathering.

Mohan et al. (2005) This paper highlights the ground water quality scenario in the Bhasta and Kalu river basin which is situated about 50km from northeast of Mumbai in the Thane district of Maharashtra. The groundwater quality assessed during their study and they noticed the groundwater higher content of calcium and magnesium as in basaltic region of study area. The TDS value in both region below its permissible limit i.e. TDS<1000mg/l. Similarly they also noticed the presence of the calcium and magnesium ions which produce hardness which is recorded in pre monsoon in bhatsa and kalu 218-326 ppm and 240ppm-680ppm and for post monsoon 178ppm-326ppm and 80-350ppm. The Chloride content was within the permissible limit as per BIS and WHO. At last they conclude that the groundwater quality falls under permissible limits.

Jagadeshan G et al. (2014) This study present the hydro geochemistry of the Vaniyar river basin's groundwater for monitoring the concentration of fluoride in that region. They collected 357groundwater samples one time each of two month. They analyzed the hydrochemistry analysis under which they covered the physico-chemical properties of the groundwater and the concentration of fluoride in groundwater analyzed. They observed the pH of groundwater of given study area ranged between 6 to 8.49, EC is varied by 366 to 4129 μS/cm. Similarly chlorides were varied from 62 to 784 mg/l. the concentration of sulphate was also recorded as 6 to 346 mg/l. The fluoride concentration varied 0.1 mg/l to 6.48 mg/l. They concluded that the changes occurred in bicarbonate concentration leads to vary the concentration of fluoride ions, which shows that the increase in the alkalinity, the increment in the fluoride ions with leaching. They also concluded that where the concentration of the Calcium and Magnesium lowest the concentration of fluoride increases. The peoples living in this area also suffered from fluorosis disease. They also found that the concentration of the fluoride is higher at deeper well which is due to presence of the epidot hornblende rock mineral.

Elango L et al. (2015) The leading intension of this paper to identify the fluoride content in groundwater. They chose the study area in Vaniyar river basin in Dharampuri district of the Tamilnadu State. They collect 650 groundwater samples for analyze. They calculate all the physico-chemical parameters for analyzed the basic hydro chemical properties. They found majority of the groundwater samples that were fall under the Na- Cl type and Ca-Mg-Cl-SO_4. Few of the water samples were Na- HCO_3 and Na- HCO_3-Cl types. They also found the out of the 650 samples in 446 samples had fluoride content above its permissible limit as per the BIS 2013 i.e. 1.5mg/l. The fluoride content varied from 0.14mg/l to 6.48mg/l. Similarly the other physico-chemical properties of the groundwater were pH ranges between its permissible limit. The total hardness varied from 81mg/l to 1008mg/l. the calcium content range from 11mg/l to 175 mg/l which is less than maximum permissible limit as per BIS 2013. On the other hand the concentration of magnesium ranges between 19mg/l to 164 mg/l. 8% of the samples exceeds the permissible limit of magnesium i.e. 100mg/l as per BIS 2013. They found that the fluoride in the groundwater produced from the percolation and disintegration of fluoride bearing minerals like charnockite and epidot hornblende biotite genesis. Biotite $K(Mg,Fe)_3(AlSi_3O_{10})(F,OH)_2$ and the hornblende$(Ca_2(Mg,Fe,Al)_5(Al,Si)_8O_{22}(OH,F)_2$ were fluoride rich minerals.

Brindha et al. (2010) This paper highlights the groundwater status for many parts in Nalgonda district, in Andhra Pradesh, India. The intension of this study is finding the causes of higher concentration of fluoride and nitrate in groundwater. They considered 240 wells for field survey and the selected the 46 wells for their study purpose. The samples were collected in the period of one year in March 2008 to January 2009. They also noticed that the fluoride concentration is varied from 0.1mg/l to 8.8 mg/l. The pH varies from the 6.9-8.5. Due to the higher alkalinity the leaching of fluoride, from that the concentration of fluoride increases (Wodeyar and Sreenivasan, 1996; Subba Rao, 2003; Jacks et al.,2005;Kodata et al., 2007). They concluded that the main source of generation of fluoride from weathering action of the granitic rock. The evapotranspiration, coal and clay produced from brick kilns also lead the fluoride concentration in the groundwater. The reason behind the increased level of nitrate in given study area is seepage of animal waste along rain water.

2.3 LITERATURE REVIEW OF GROUNDWATER QUALITY INDEX

Jain et al. (2010) They studied the groundwater condition of the Nainital district, Uttarakhand, India. They collected forty samples also including 28 spring samples in the pre-monsoon and post-monsoon season. On that samples they performed the physico-chemical analysis from which they concluded that the pH of given water samples varied between 5.9 to 8.1 in pre-monsoon and 6.3 to 7.9 in post-monsoon. The EC varied by 210 to 970 µS/cm in pre- monsoon and 203 – 900 µS/cm. The TDS varied from 134mg/l to 621mg/l and 203mg/l to 900mg/l is pre and post monsoon respectively. They also noticed that the TDS level at depth below 40m lies in the permissible limits. The alkalinity varied from 76 to 380 mg/l to 71- 354 mg/l in pre and post monsoon seasons. Chloride in the given study area became much low concentration varied from 2.2 to 13mg/l and 2.0 to 11mg/l pre and post monsoon respectively. The sulphate content present in the form of soluble salt in groundwater which was varies from in the pre and post monsoon 2.5 to 140mg/l and 2.3to112mg/l. They concluded that the value of various constituents in spring water low as related to water from hand-pump and tube-well.

Suthar et al. (2017) This study aims to inspect the fluoride content and its health hazard in groundwater of Malwa region of the Punjab, India. They collected 76 samples from 14 districts of southwest region of Punjab state i.e. Malwa region. The physico-chemical analysis performed on these samples from that they found that the fluoride content changes from 0.60 to 5.07 mg/l. They also found that the most of the samples above its permissible limit of fluoride content as per WHO. On the basis of that they found the chronic daily intake (CDI) and Hazard Quotient (HQ). They calculate the HQ in the ranges of 0.29-2.41 for adults and 0.67- 5.63 for children. On the basis of these HQ’s they categorized the high risk zone for fluoride related problems. Due to this there were significant needs of attention.

Ramesh et al.(2010) studies the water quality index studies which is done on the atleast 22 different parameters. They collected 24 groundwater samples on that they analysed the physico-chemical properties on it. They categorized the parameters and different sub-indexes were formed foe different physico-chemical properties. They compared the suggested drinking water quality index (DWQI) with the Geometric DWQI and arithmetic DWQI. At the end they results the Arithmetic DWQI scores higher than the proposed DWQI and geometric DWQI. They check also the correlation on all indices at $r \geq +0.98$ between all indices. The comparison shows that the DWQI which is proposed was most reliable index and it reduced the sensitivity of conventional WQI.

Ehya et al.(2018) studied the groundwater hydrochemistry at Basht Plain in SW Iran. The motive of this study the groundwater quality parameters for different purpose i.e. irrigation, livestock, drinking and irrigation. They selected 28 wells for collecting the groundwater sample for analyzing the physico-chemical properties. The analysis showed that the groundwater of given study area had a major dominance of HCO_3^-, SO_4^{2-}, Ca^{2+}& Mg^{2+}. They also noticed that the groundwater of given study area also acceptable irrigation purposes from parameters like %Na, SAR, MAR, PI, RSC and KR. The LSI and FC parameters were also calculated for corrosive and Foaming action properties for all water samples. At last they concluded that TDS of the groundwater samples shows that there were no restrictions of water use for drinking for domestic purposes.

2.4 GAP ANALYSIS

From the above literature review it is found that limited study has been conducted for the physico-chemical analysis and WQI for the southwest region of the Punjab state. The water quality of the Punjab state is deteriorated due to recent development in industrial sector as well as extensive use of the pesticides and fertilizers in agriculture sectors. Therefore, it is essentially need to investigate the groundwater quality of the Punjab state continuously.

2.5 OBJECTIVES:-

The research includes the following specific objectives:-

1) To study the variation of the physico-chemical properties of groundwater in different season.

2) To formulate the correlation between the different physico-chemical properties of groundwater and its variations with the different parameters.

3) To study the variations of the physico-chemical property of the groundwater for different sectors.

4) To access the groundwater quality through water quality index.

2.6 CONCLUDING REMARKS:-

From the above literature review we conclude that the areas under which the physico-chemical parameters above its permissible levels such as fluoride and nitrate, then there is need of significant attention regarding its controlling activities and declared as high risk zone. There is also a need for making the preventive actions like defluorination techniques to meet permissible concentration levels. On the other hand the physico-chemical parameters like nitrate, due to excess use of fertilization and other sanitary leakages action of underground pipe lines leads to the rise in nitrate levels in groundwater. Astute and cautious approach shall be taken to prevent the contamination of groundwater.

CHAPTER 3

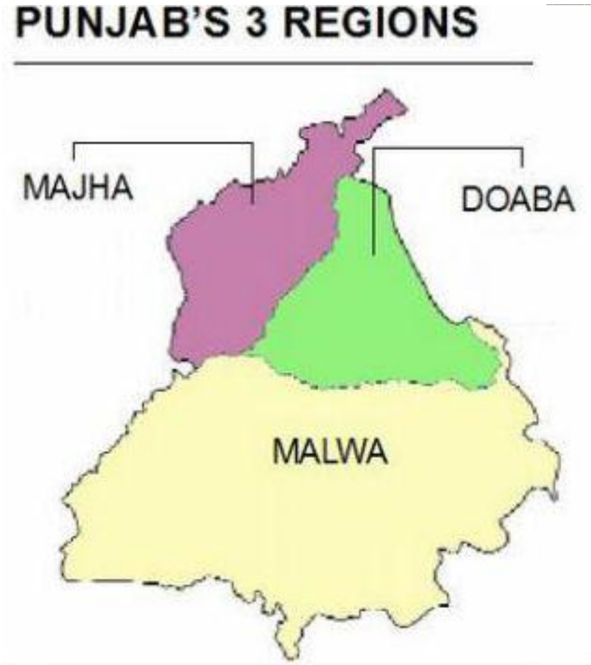
STUDY AREA

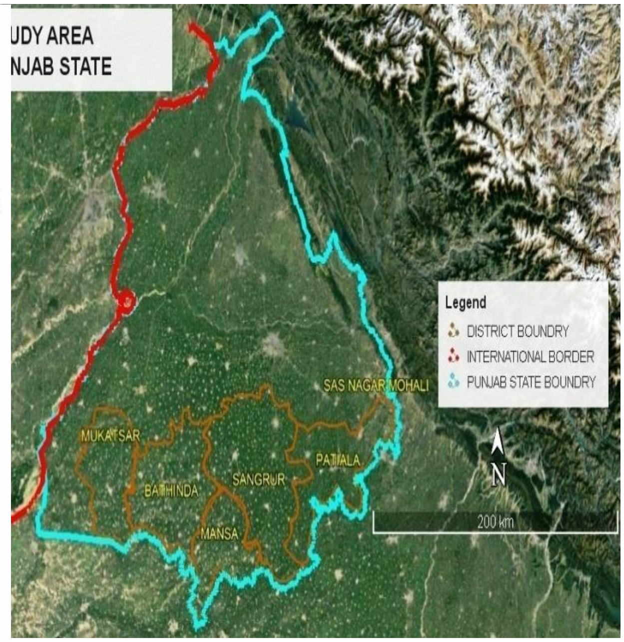
3.1 INTRODUCTORY COMMENTS

In previous chapter, extensive literature review of the proposed study has been conducted. The present chapter considers the detailed information about the study area, sampling of the groundwater samples, methodology of the sampling etc.

3.2 STUDY AREA

The Punjab state has three regions based on the boundary of the three major rivers of the state i.e. Sutlej River, Beas River and Ravi River. The area between the Beas River and Ravi River is known as the Majha Area, similarly area between River Beas and Sutlej known as the Doaba Area and the remaining area below the river Sutlej is known as Malwa Area as shown in Figure 3.1(a). The Punjab state is the north- west state of India having North Latitude 30° 4’ and East Longitude 75° 5’. The Malwa region is situated in the south part of Punjab which covers major part of the Punjab state. Ludhiana, Patiala, Sangrur, Moga, Faridkot, Ferozpur, Ropar, Fatehgarh Sahib, Mansa, Bathinda, Mukatsar & SAS Nagar (Mohali) are the major districts of the Malwa region of the Punjab State. The present study considers 6 districts of the Malwa region i.e. Patiala (30°2’N, & 76°25’E), SAS Nagar (Mohali) (30° 42' 16.7364" N & 76° 43' 4.3428" E), Sangrur (30°12’N & 75°53’E), Mansa (29° 59' 17.6820" N & 75° 22' 45.3252" E), Bathinda (30° 11' N & 75° 00' E)& Mukatsar (30° 28' 48.1512" N&74° 31' 5.5344" E). Figure 3.1b shows the detailed study area. The people living in t these districts of Malwa region of Punjab are highly dependent on agriculture sector. Also the growth of the industrial sector is taking place from last also take place in Malwa region from last 10 to 15 years. Due to the dependency on agricultural sector and growing industrialization the ground water in these districts are generally extracted over the permissible limits. The water table of Bathinda, Mukatsar, & Mansa is at shallow depth whereas the water table the other districts in study area available at larger depths.





(a) **(b)**

Source: Punjab Blogs.com

Figure 3.1 Majha, Malwa & Doaba region of the Punjab state. (a) Regional Area View (b) Study Area View

The climatic conditions of study area are continuously varied in throughout the whole year i.e. Winter, Summer & Monsoon. The winter season lies between the Dec to March, similarly the summer season continue from the April upto the monsoon onset. The monsoon seasons also stay between the last weeks of June to the first week of the September. The study area also suffers from the winter drizzling days in the months of December and January. The average annual rainfall in given study area is 775.6mm within the period of July to September. The temperature gradient also changes throughout the year. The annual temperature of the study area varies from 2°C to 45°C (Thakur et al., 2016).

3.3 TOPOGRAPHY

The topography of the given study area majorly comprised with clay, silt & sand which is the alluvial type depositions of soil minerals. The soils of the given study area have polyhalites, anhydrites (gypsum), shale, dolomite etc. which have some fluoride content (Sidhu et al., 1977). Major source of groundwater of the study area is due to recharge of the groundwater through rainfall or irrigation water. The abstraction of the groundwater in

Malwa region mainly from the hand pumps. The Water table of Sangrur and some area of the Patiala district lie below 40m whereas SAS Nagar (Mohali), Mansa, Bathina and remaining area of the Patiala & Sangrur district are lies between 20 – 40m below ground level. In Mukatsar District the depth of water table is 0-10 m below ground level (CGWB 2014).

3.4 METHODOLOGY OF SAMPLING

Samples of the groundwater were taken from grab sampling technique with submersible pumps and handpumps (if available).The field visit were carried out for collection of all samples from a particular selected points as shown in Table 3.1. The samples were collected after the pumping of water at least 5 min because the water stayed in pipeline is pumped out. The samples collection technique is considered on the basis of the land-use application i.e. domestic, industrial & agriculture sector. All the samples were collected in 1L polyethene bottles and kept in cold room at 4°C. The collection of samples were collected in each month from February 2019 to June 2019. Table 3.1 shows the detailed information regarding the locations from where the samples were collected. Figure 3.2 shows the location of sampling sites in the study area.

Table 3.1 *Sampling Sites and Land-use.*

Sr.No	Sample ID	Sample Name/Land-use	North Latitude	East Longitude	Depth(m)
1	**PTAD1**	Patiala Domestic	30°20'26.43"N	76°25'35.49"E	39.624
2	**PTAD2**	Patiala Domestic	30°22'7.66"N	76°22'20.16"E	42.67
3	**PTAI1**	Patiala Industrial	30°22'29.65"N	76°25'6.67"E	50.29
4	**PTAI2**	Patiala Industrial	30°22'13.88"N	76°24'41.35"E	45.72
5	**PTAA1**	Patiala Agriculture	30°16'44.99"N	76°24'58.53"E	48.77

Sr.No	Sample ID	Sample Name/Land-use	North Latitude	East Longitude	Depth(m)
6	**PTAA2**	Patiala Agriculture	30°22'41.46"N	76°23'26.68"E	42.67
7	**SAND1**	Sangrur Domestic	30°14'0.01"N	75°50'22.68"E	45.72
8	**SAND2**	Sangrur Domestic	30°15'44.7"N	76°23'01"E	39.62
9	**SANI1**	Sangrur Industrial	30°13'17.48"N	75°50'35.56"E	41.15
10	**SANI2**	Sangrur Industrial	30°13'49.06"N	75°50'23.32"E	44.20
11	**SANA1**	Sangrur Agriculture	30°16'11.74"N	76°10'12.29"E	42.67
12	**SANA2**	Sangrur Agriculture	30° 9'10.81"N	75°50'1.03"E	45.72
13	**MAND1**	Mansa Domestic	30° 0'1.99"N	75°23'30.94"E	18.28
14	**MANI1**	Mansa Industrial	30° 2'8.55"N	75°24'9.71"E	30.48
15	**MANA1**	Mansa Agriculture	30° 5'11.06"N	75°36'51.39"E	91.44
16	**BATD1**	Bathinda Domestic	30°11'21.08"N	74°57'23.45"E	7.62
17	**BATI1**	Bathinda Industrial	30°14'12.94"N	74°55'16.91"E	15.24
18	**BATA1**	Bathinda Agriculture	30° 8'47.70"N	74°59'15.99"E	24.38
19	**BATA2**	Bathinda Agriculture	30° 16'31"N	74°56'22"E	22

Sr.No	Sample ID	Sample Name/Land-use	North Latitude	East Longitude	Depth(m)
19	**MUKD1**	Mukatsar Domestic	30°11'35.52"N	74°30'34.30"E	40
20	**MUKI1**	Mukatsar Industrial	30°10'16.90"N	74°30'45.68"E	10.67
21	**MUKA1**	Mukatsar Agriculture	30° 8'57.09"N	74°23'18.73"E	18.28
22	**MUKD2**	Mukatsar Domestic	30° 27'51"N	74°31'05"E	12
22	**MOHD1**	Mohali Domestic	30°41'24.56"N	76°42'14.29"E	15.24
23	**MOHD2**	Mohali Domestic	30°41'40.41"N	76°41'11.82"E	33.52
24	**MOHA1**	Mohali Agriculture	30°43'57.88"N	76°36'59.56"E	36.57
25	**MOHA2**	Mohali Agriculture	30°40'58.49"N	76°37'8.49"E	39.624

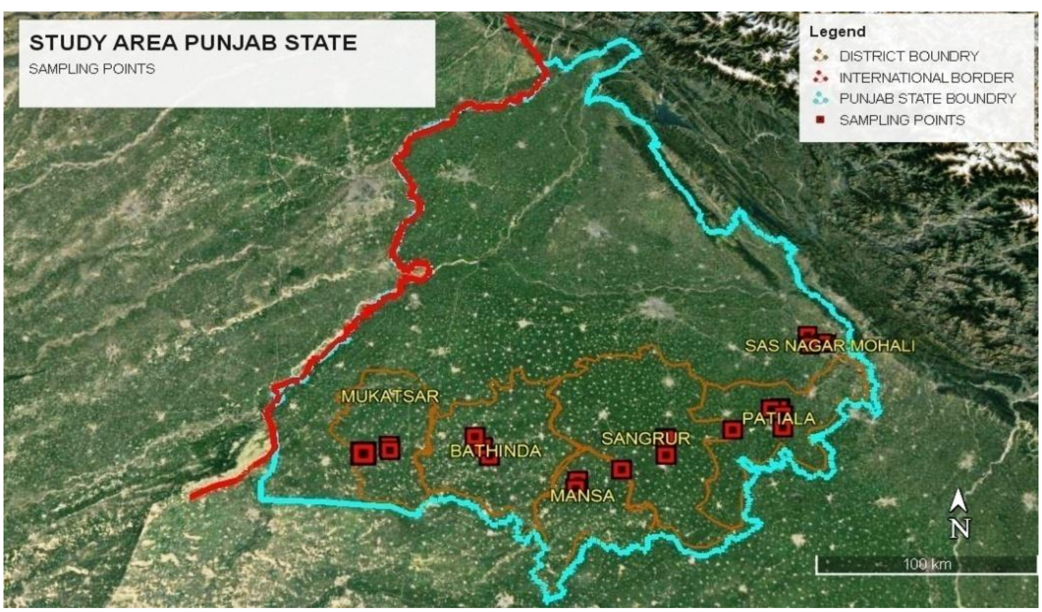


Figure 3.2 Sampling Site Location

The Table 3.2 shows the number of the samples collected in each month from each sector of each district of the study area.

Table 3.2 *Sampling Methodology*

Sr.No	District	Landuse	No. of Sample taken
1	Patiala	2 Agriculture,2 Domestic & 2 Industrial	6
2	Sangrur	Same as 1	6
3	SAS Nagar Mohali	2 Domestic and 2 Agriculture	4
4	Mukatsar	1 from each Domestic, Agriculture & Industrial area	3
5	Mansa	Same as 4 Sr.No	3
6	Bathinda	Same as 4 Sr.No	3
	Total		**25**

Figure 3.3 shows the percentage of the samples collected from various sectors. There are 25numbers of the total samples collected from the study area in each month out of which there were36 % of samples collected from each domestic and agriculture sector whereas 28% of total samples collected from Industrial sector.

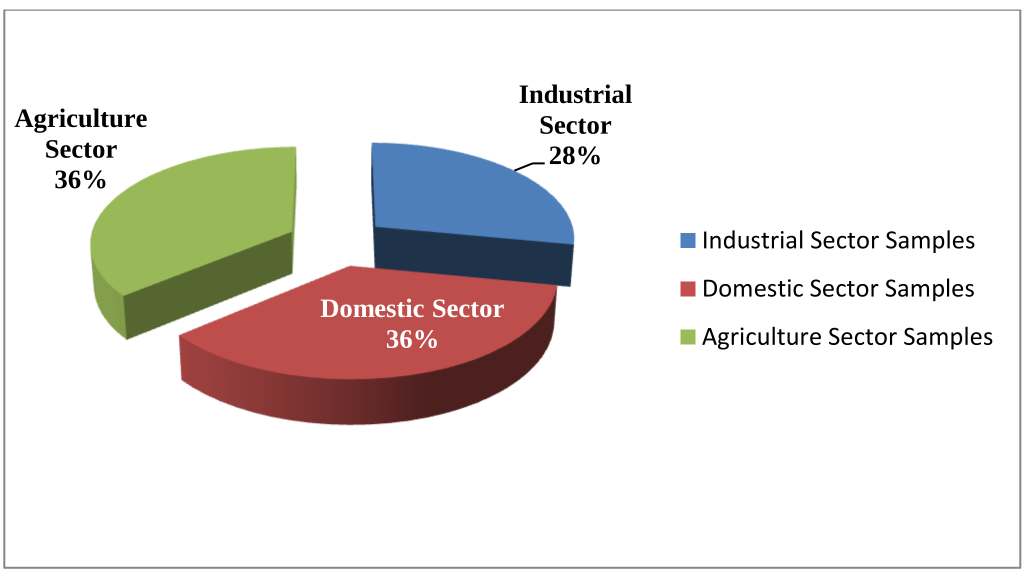


Figure 3.3 Percentage of the sample collected from various sectors

3.5 CONCLUDING REMARKS

In the above chapter we discussed the salient features of the given study area, its topography and the general geographic conditions. In the next chapter, we have discussed about the methodology for testing parameters and its guidelines from the specified protocols.

CHAPTER 4

INSTRUMENTATION & TESTING

4.1 INTRODUCTORY COMMENTS

In previous chapter, the discussion regarding study area, sampling sites and their location is made. Also the procedure followed in the sampling of groundwater is discussed. The present chapter discuss about the testing methodology of all the physico-chemical parameters required for groundwater quality analysis.

The groundwater quality for the present study is analyzed for Physical and Chemical characteristics and the following parameters are tested in the lab in order to determine the overall quality of groundwater of the study area. Table 4.1 shows the various tests and their methodology adopted for measurement of various physico-chemical parameters.

Table 4.1 *Testing Methods and Specifications*

Sr.No	**Parameter Tested**	**Standard Methods**
1	pH	Glass Electrode Method (APHA Standard Manual 4500-H+ PH VALUE)
2	Turbidity	Glass Electrode Method (APHA Standard Manual 2130 TURBIDITY)
3	Electrical Conductivity	HANNA Conductivity Meter (APHA Standard Manual 2510 CONDUCTIVITY)
4	Temperature	Laboratory and Field Methods (APHA Standard Manual 2550 B. Laboratory and Field Methods)
5	Total Solids	Gravimetric Method (2540 B. Total Solids Dried at 103–105°C)
6	TDS	Glass Electrode Method (APHA Standard Manual 2540 C. Total Dissolved Solids Dried at 180°C)
7	TSS	Gravimetric Method (APHA Standard Manual 2540 D. Total Suspended Solids Dried at 103–105°C)
8	Total Hardness	EDTA Titration Method (APHA Standard Manual 2340

Sr.No	Parameter Tested	Standard Methods
		HARDNESS
9	Calcium Content	EDTA Titration Method (APHA Standard Manual 3500-Ca B. EDTA Titration Method)
10	Magnesium Content	Calculation Method (APHA Standard Manual 3500-Mg B. Calculation Method)
11	Chloride Content	Argentometric Method (APHA Standard Manual 4500-Cl– B. Argentometric Method)
12	Sulphate Content	Gravimetric Method with Drying of Residue(APHA Standard Manual 4500-SO_4^{2-} D. Gravimetric Method with Drying of Residue)
13	Potassium	3120 B. Inductively Coupled Plasma (ICP) Method (APHA Standard Manual 3120 B. Inductively Coupled Plasma (ICP) Method)
14	Sodium	3120 B. Inductively Coupled Plasma (ICP) Method (APHA Standard Manual 3120 B. Inductively Coupled Plasma (ICP) Method)
15	Fluoride Content	SPADNS Method (APHA Standard Manual 4500-F^- D. SPADNS Method)
16	Nitrate Content	Ultraviolet Spectrophotometric Screening Method (APHA Standard Manual 4500-NO_3^- B. Ultraviolet Spectrophotometric Screening Method)
17	Lead	3120 B. Inductively Coupled Plasma (ICP) Method (APHA Standard Manual 3120 B. Inductively Coupled Plasma (ICP) Method)
18	Chromium	3120 B. Inductively Coupled Plasma (ICP) Method (APHA Standard Manual 3120 B. Inductively Coupled Plasma (ICP) Method)
19	Cadmium	3120 B. Inductively Coupled Plasma (ICP) Method (APHA Standard Manual 3120 B. Inductively Coupled Plasma (ICP) Method)

4.2 TESTING & CALCULATIONS

4.2.1 PH & TEMPERATURE

pH and temperature was measured by the pH meter by Glass Electrode Method as per APHA manual specifications in clause 4500-H+ PH VALUE in APHA for pH and clause 2550 B for temperature measurement. In this method the experiment was conducted with glass electrode with the process of the emf generated which exist a linear relation with the pH. The instrument is calibrated with the different pH values of buffer solution i.e. 4.01, 7.01 & 10.01.

Similarly for temperature measurement the above pH meter shows a temperature readings also.

4.2.2 TURBIDITY

This parameter of groundwater samples is an important parameter for physico-chemical properties considerations and it indicates the clarity of the water & wastewater samples. This parameter is also applicable for the analysis of the groundwater clarity. This test is performed with APHA specification clause number 2130 Turbidity.

The Turbidity of the all the samples measured by the nephelometric method as mentioned in the APHA. The nephelometer was caliberated with different standard solutions of calibration 10NTU, 20NTU, 100NTU and 800 NTU solutions.

The nephelometer works based on the principle of the light scattering. If intensity of the light scattered is higher the turbidity of the water sample is higher.

Procedure: - Initially a sample cells was taken and washed with distilled water. The sample cell was filled by water sample and tightened. Then the sample cell was cleaned with smooth piece of cloth and put it in the sample cell holder. The result will be shown on the turbidity meter screen after clicking on read button.

Precautions:- a)The sample was well shaken before transferred to sample cell holder.

b) Water bubble was removed if it was appearing in sample cell.

c) All moisture from outside the sample was removed before insertion of sample cell in sample holder.

4.2.3 ELECTRICAL CONDUCTIVITY

It is the one of the important property of groundwater to analyze its ability to carry the current. Its SI Unit is the reciprocal of ohm which is called as Siemens (S). The representation of the conductivity is in millisiemen per meter (mS/cm).

Procedure: - Initially a beaker of 100ml was taken and washed it with distilled water. The water sample used for testing was shaking well. The water sample was stirred and inserted in the beaker. the conductivity meter (HANNA) kept in Switch ON condition and washed the electrode with the distilled water from that the value of the conductivity on the conductivity meter's screen shows "0 mS/cm" and "stable". The electrode was dipped in the sample placed in the beaker and take reading of conductivity on the screen.

Precautions: - a) The beaker was washed well with distilled water properly before use.

b) The sample was well shaken before testing.

c) The instrument was calibrated carefully.

4.2.4 TOTAL SOLIDS (TS)

In this test the water sample is evaporate in weighing dish and further proceeds to drying at the constant weight in an oven at 103°C to 105°C. The gain in the weight observed in the weight over the empty dishes represents the presence of total solids in a given sample.

Procedure: - The evaporating dish of 100 ml was taken and washed it with distilled water then drying it in oven before use. The dish from oven was removed and placed them in the desiccators for some time. The evaporating dish was taken out from desiccators and weights it (B). The evaporating dish was filled with water sample and placed in the microwave oven at temperature of 103 °C to 105°C. After 24 hours the dish was taken from the microwave oven and insert in desecrator for 10 to 15 minutes. Note the weight of empty dish with dry residue (A) with equation 4.1 given below.

Weight of the Dish + Dry residue (mg) = A

Weight of the Dish (mg) = B

$$\text{Total Solids} = \frac{(A-B)\times 1000}{\text{Sample Volume}} \qquad (4.1)$$

Precautions:- a) Read the observations of weight of beaker very carefully.

b) The sample inserted in the beaker after well shaking the sample.

c) After taking the beaker out of the microwave oven insert that sample in desiccators at least for 15 min.

4.2.5 TOTAL DISSOLVED SOLIDS (TDS)

TDS is an essential parameter of physico-chemical properties of water and waste water from quality point of view. TDS is calculated with the help of HANNA conductivity meter by Glass Electrode method. There is also some relations which gives the value of TDS w.r.t. EC as shown in equation 4.2 suggested by (Carrol 1962) given below: -

$$\text{TDS}\left(\frac{\text{mg}}{\text{l}}\right) = 0.64 \times \text{EC} \qquad (4.2)$$

Procedure: - In this test a beaker of 100ml was taken and washed it with the distilled water or rinsed with the sample water. The beaker was filled by 100ml of the water sample. Note down the reading from TDS meter by inserting the electrode in beaker.

Precautions:-a) the sample taken for experiment from bottle after well shaking the water sample.

b) The electrode was washed properly with distilled water and cleaned it.

c) Set the reading of the instrument at 0 before dip in water sample.

4.2.6 TOTAL SUSPENDED SOLIDS (TSS)

The total suspended solids are calculated by the calculation methods from equation 4.3 as shown below:-

$$TSS\ \left(\frac{mg}{l}\right) = TS - TDS \qquad (4.3)$$

The TSS is calculated from calculation method as shown above in equation 4.3.

4.2.7 TOTAL HARDNESS (TH)

The sum of the calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations is known as the total hardness. It is expressed as the calcium carbonate in milligrams per liter (mg/l).

As per APHA if the total hardness is equal to or less than the sum of the alkalinity due to carbonate and bicarbonate, then all the total hardness is due to the presence of the carbonate hardness and the bicarbonate hardness is absent.

According to the APHA there are two methods of the calculation of total hardness of the water as given below: -

1) Total hardness by calculation: - It is used when the mineral analysis is to be performed. This method is also applicable for the all the waters and gives higher accuracy. In this method the total hardness is to be calculated by the following equation 4.4

Total Hardness (mg/L) equivalent to $CaCO_3$ /L

$$= 2.497(Ca, mg/L) + 4.118\ (Mg^{2+}, mg/L) \qquad (4.4)$$

2) Total hardness by EDTA Titrimetric Method: - In this method Ethylenediaminetetra-acetic acid and sodium salts from a single complex bond when added to the certain metal ion solution. If a certain small content of Eriochrome Black T or Calmagite added to solution having some calcium and magnesium content at a pH of 10.0 ∓ 0.1, then the solution turn its color towards wine red. After that if the same solution titerate with the EDTA solution as a titrant the calcium and magnesium ions in solution is complexes. When all the Calcium and magnesium ions are complexed, the color of solution changes from wine red to blue.

Procedure: - In this a flask was taken and washed it with distilled water. 50ml of the water sample was taken in beaker. 2ml of ammonia buffer solution added in that water sample. With ammonia buffer solution some small quantity of the EBT indicator also added in it, which forms the color of solution of wine red. Solution was titrated with EDTA as titerant. The total hardness is to be calculated b the equation number 4.5 given below: -

$$\text{Total hardness (EDTA) as mg/L of } CaCO_3 = \frac{(A-B)\times 1000}{\text{ml of sample}} \tag{4.5}$$

A= Final reading in burette

B = Intial reading in burette

A-B= Vol. consumed of EDTA

Precautions:-a) Use the sample for test after shaking it as well.

b) Titrate with slowly speed like drop wise as the sample tends to go towards its end pont.

4.2.8 CALCIUM CONTENT AND CALCIUM HARDNESS

The calcium content is found with the EDTA titrimetric method in which the EDTA when added to water, it firstly combine with the calcium. Calcium is easily detected when pH is sufficiently high that the magnesium is largely precipitated as the hydroxides and an indicator used that combines with the calcium. All the different indicators give color change when it titerate with EDTA at the pH of 12 to 13.

Procedure: - The conical flask was taken and washed it with the distilled water. 50ml of water sample was filled in flask and 0.1 to 0.2 g or 1 or 2 drop of indicator was added in it i.e. murexide or calcium tablets. After dissolving the indicator, 2ml of 1N NaOH was added and then titrate upto the end point. The color changes from pink to blue which shows the end point of titeration.

The calcium content and Calcium Hardness calculated from equation 4.6 and 4.7 given below:-

$$\text{Ca mg/l} = \frac{A\times B\times 400.8}{\text{ml of sample}} \tag{4.6}$$

$$\text{Calcium Hardness as } CaCO_3/L = \frac{A \times B \times 1000}{\text{ml of sample}} \qquad (4.7)$$

A= ml of titrant for sample

B= mg of $CaCO_3$ equivalent to 1.00 ml of EDTA titrant at the calcium indicator end point.

Precautions: -a) The indicator in water sample dissolved completely.

b) Stir the sample upto the end time of titration process as the color changes from light pink to blue in color.

c) Wash the flasks and other components carefully.

4.2.9 MAGNESIUM CONTENT

The magnesium is the second element of GROUP IIA in the periodic table. The occurrence of the magnesium is the earth's crust is 2.1%, similarly in solids its average abundance 0.03 to 0.084 %, in steams it lies about 4mg/l and in the groundwater the abundance is greater than 5mg/l (APHA 20th Edition). It commonly exists in the minerals like dolomite. It is also used as an alloy, fertilizers, dying operations and so many more.

Magnesium salts disintegrate down heated forms a scaling in the boilers. The processes like reverse osmosis, chemical softening decreases the magnesium and leads hardness to the acceptable limits.

Procedure: - The magnesium content is calculated from the Calculation Method from Calcium hardness and calcium content as given in APHA protocol as mentioned in article no 4.1.8 in this report. The magnesium content is calculated from equation 4.8 given below:-

$$\text{Mg mg/l} = [\text{Total Hardness (as mg } CaCO_3/L) - \text{Calcium Hardness (as mg } CaCO_3/L)] \times 0.243 \qquad (4.8)$$

The other methods for determination of magnesium as per APHA are given below: -

a) Atomic Absorption Spectrometric Method

b) Inductively Coupled Plasma Method

c) Inductively Coupled Plasma Mass Spectrometric Method (used at lower detection limits)

d) Calculation Method

4.2.10 CHLORIDE CONTENT

The chloride is present in the Water and wastewater in the form of the Chloride (Cl^-) ion, which is one of the major anion. The salty taste of the water signifies the presence of the chloride in the water when its concentration exceeds 250mg/L. At that much concentration the chloride is easily detectable with taste if cation is sodium. On another side the salty taste is absent if the water having 1000mg/L as much when the most of the cations are calcium and magnesium.

There are following six methods for determination of the chloride content as given below: -

a) Argentometric Method

b) Mercuric Nitrate Method

c) Ptentiometric Method

d) Ferricyanide Method

e) Flow Injection Analysis

f) Capillary Ion Electrophoresis Methods

In the present work to calculate the chloride content the Argentometric Method was used.

Procedure: -In this test flask was taken and wash it with distilled water. 50ml of the water sample poured in flask and burette was filled with 35N silver nitrate ($AgNO_3$). 1ml of Potassium Chromate as an indicator was added in sample .Titrate the sample upto the end point as the color changes from yellow to Brick Red which indicate the end point of the titration. The calculation for the determination of chloride content is done with note the initial and final reading from burette of the use of silver nitrate solution in titration process using equation 4.9 given below:-

$$\text{Chloride (mg/L)} = \frac{(A-B)\times 1000}{\text{ml of sample}} \tag{4.9}$$

A = ml titration for sample

B = ml titration for blank

Precautions: - a) for new sample wash the flask as it is used with distilled water.

b) Note the reading in the burette upto the lower meniscus level.

4.2.11 SULPHATE CONTENT

Sulphate concentrations ranging in groundwater generally varies from a few to several hundred per liter. Drainage of Mines are plays a dominant role in contribution of sulphate in water with pyrite oxidation.

There are following methods are available for determination of the sulphate content as follows: -

a) Ion Chromatographc Method

b) Ion Electrophoresis Method

c) Gravimetric Method

d) Turbidmetric Method

e) Automated Methylthyemol blue Method

In present work to calculate the sulphate content the Gravimetric method with drying residue.

Procedure: - In this test a flask was taken and washed it with distilled water. 100ml of sample water added in it and also 2ml of 6N HCL added in it and boiled until the bubbles area formed due to boiling. Sudden after the boiling, 15 ml of $BaCl_2$ sol added in that boiled sample. Cool it for some time. On the other hand Whattman Filter paper was taken, having pore size 0.45 μm and note its weight. When the water samples become cool then these water samples were filtered by Whattman Filter paper. The filter paper was placed in microwave for 24 hrs. The filter paper placed in microwave was taken out and immediately placed in the desecrator for some time. Then take the final weight of that filter paper. The determination of the sulphate is to be done as per equation 4.10 as follows.

Te reaction takes place when the $Bacl_2$ is added in the water sample treated with 6N HCL as follows: -

$$SO_4^{2-}\ (mg/L) = \frac{BaSO4\ \times 411.6}{ml\ of\ sample} \qquad (4.10)$$

4.2.12 FLUORIDE CONTENT

The fluoride content in the drinking water is approximately 1.0mg/L is effectively control the dental caries without any health impacts. If the fluoride above its permissible limits i.e. 1.5 mg/L as per IS10500:2012 and WHO recommendations it creates fluorosis disease. In some cases if fluoride content above 10mg/L then that water is subjected to the defluoridated.

There are so many methods for determination of the fluoride as given below: -

a) Ion – Selective Electrode Method

b) SPADNS Method

c) Complexone Method

d) Ion – Selective Electrode Flow Injection Analysis.

In present work SPADNS method used for the determination of the fluoride content. This method is based on the calibration curve within the range of 0 to 1.4 mg/L Fkuoride concentration. The Acid-zincroyle SPADNS reagent is used to detect the fluoride concentrations in the given samples. The reference solution is to be made for setting the spectrophotometer at Zero.

Procedure: - The nesslier tubes used for testing and wash it with the distilled water. 50ml of the water sample filled in nesseller tube and 10ml of Acid-zincronyl- SPADNS reagent added in it. A cuvette was taken and washed with distilled water. The cuvette was filled by the reference solution upto the 3/4th portion. Set the Spectrphotometer at the wavelength of 570nm. The cuvette is placed in spectrophotometer and set the instrument at Zero. Cuvette was taken out from spectrophotometer and washed by distilled water. Washed cuvette filled with the sample treated with the Acid-zincronyle- SPADNS reagent. The cuvette was placed in the spectrophotometer and the reading of Absorbance was taken. From that absorbance reading determine the fluoride content from calibration curve graph determined. If the absorbance not lies in calibration limits dilute the sample and take absorbance under the calibration limits, then that fluoride content is multiplied by the dilution factor which gives the actual value of fluoride content.

The fluoride content is measured by the following equation 4.11

$$\text{mg/L of } F^- = \frac{A}{\text{ml of Sample}} \times B/C \qquad (4.11)$$

A = µg F^- determined from graph

B/C= only when sample is diluted, B is distilled volume collected, C portion taken for color development.

Precautions: - a) Wash the nesseller tube and cuvette thoroughly before used for experiment.

b) The sample was diluted with pure distilled water free from impurities.

c) Clean cuvette before placing in cuvette holder in spectrophotometer with tissue.

4.2.13 NITRATE CONTENT

Nitrate is also the one of the major chemical under the physico-chemical analysis of the water and waste water. This is generally used in the fertilizers that we provide to the agriculture activities. It also impacts the soil properties of the ground. There are following methods are available for determination of the nitrate content in the water.

a) UV Spectrometric Screening Method

b) Ion Chromatography Method or Capillary Ion Electrophoresis

c) Nitrate Electrode Methods

d) Cadmium Reduction Method

e) Automated Cadmium Reduction Method

The methods i.e. UV spectrometric Screening Method was used which is applicable for the range of the nitrate concentration of 0 to 7 mg/L. Prepare the calibration curve in the range of 0 to 7 mg/l nitrate content at 220nm wavelength. For higher nitrate content of the water samples, the samples are diluted due which they come under the range of 0 to 7 mg/l.

Procedure: - A nesseller tube was taken and washes it with the distilled water. 50ml of the water sample was filled and 1ml of 1N HCl added in it. On the other hand the wavelength of the UV Spectrophotometer setted at 220nm. The two cuvettes were taken and washed it with the distilled water. Cuvettes were filled by water sample and placed in the cuvette holder of the UV spectrophotometer and the instrument set at auto-zero. Take out one cuvete and wash with distilled water then fill the 50ml water sample treated with the HCl in it. Take the Absorbance reading of the sample. From that absorbance reading find the nitrate content from the calibration curve.

Precautions:- a) Readings of the absorbance was taken carefully.

b) The cuvettes were washed again when the sample is changed with distilled water.

c) All the absorbance readings were taken at a single wavelength of 220nm.

4.3 INSTRUMENTATIONS

There are various instruments are used for some physico-chemical properties such as pH, Temperature, Electrical Conductivity, Turbidity and TDS etc.

4.3.1 pH METER

The pH of the groundwater samples were measured with the HANNA HI5221 pH meter with single input channel using the glass electrode methods. This instrument works in range of measurement of pH from pH value of -2.0 to 20.0 and has an accuracy of ±0.1pH. It also has a capacity to store 10000 reading points during its working. The reading is shown on the LCD display. the electrode cap was removed from the electrode and washed it with the distilled water. 100 ml of water sample was taken in beaker and that electrode was dipped in it the reading of the sample is shown on the screen as shown in Figure 4.1 below:-

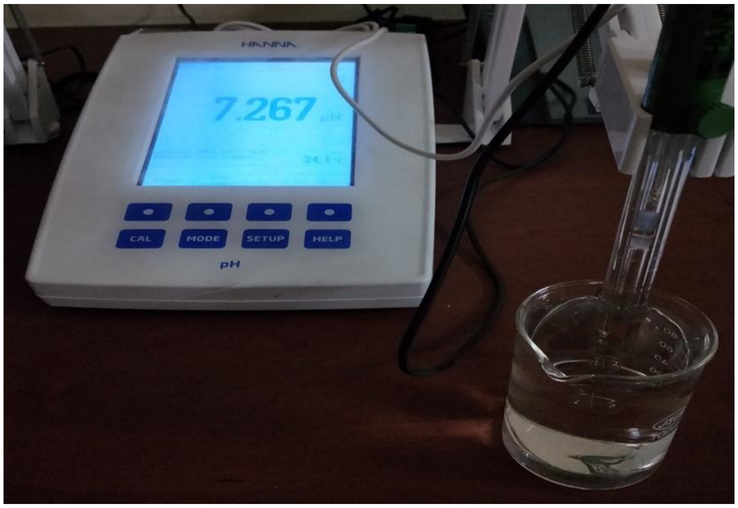


Figure 4.1 pH Meter (HANNA 5521)

4.3.2 ELECTRICAL CONDUCTIVITY METER

The Electrical Conductivity of the groundwater sample is measured by the HANNA HI 5321 conductivity meter. The range of this conductivity meter is 0µS/cm to 1000mS/cm with an accuracy of the ±0.001 µS/cm. The cell constant of the conductivity meter is 0.0500 to 200.00 / cm and the temperature coefficient are 0.00 to 10.00 % /°C. The conductivity of the groundwater sample is to be measured by wash the glass electrode first with the distilled water and clean it with the tissue paper. 100ml groundwater sample was taken in the glass beaker of 100ml. The glass electrode inserted in that groundwater sample. The reading of the conductivity is shown on the display as shown in the Figure 4.2 below in units of µS/cm and mS/cm. This instrument has ability to record 100000 data points and easily worked in the environment having temperature 0 to 50°C.

Precautions:- a) the electrode washedd with the distilled water properly.

b) Note the reading from the screen showing the 'Stable' on the right top of the screen.

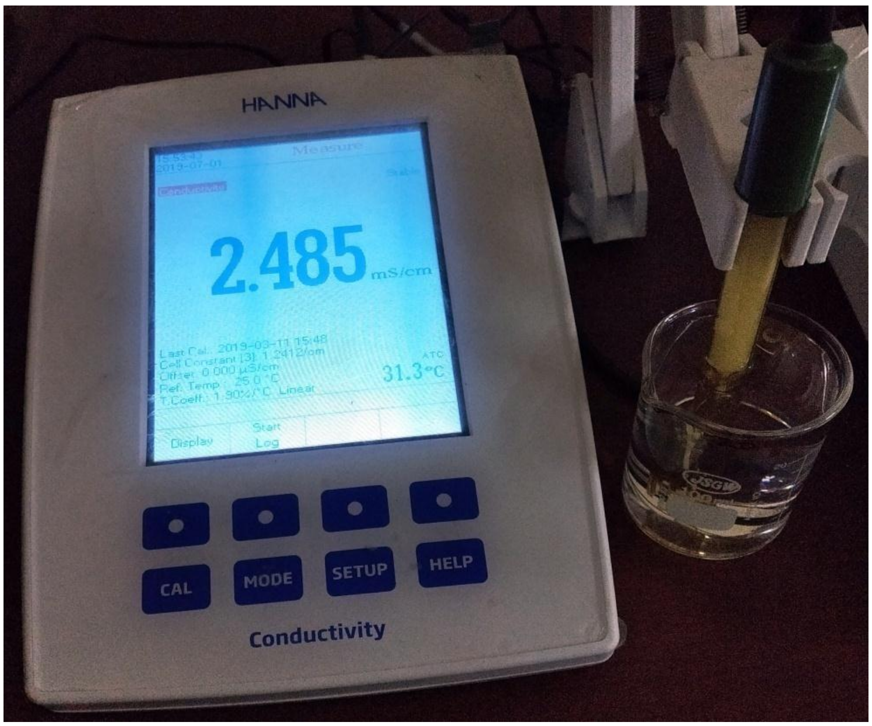


Figure 4.2 Conductivity Meter HANNA HI 53221

4.3.3 TURBIDITY METER

The turbidity of the samples is measured by the HACH 2100Q portable turbidity meter. Before testing the turbidity test firstly calibrated with solution of 10NTU, 20NTU, 100NTU and 800NTU.In this test wash the sample tube with the distilled water and rinsed with the sample water. Then fill the sample upto the mark of the sample tube then clean it with the smooth cloth. Now put that sample tube in the Turbidity meter and note down the reading shown on the screen of Turbidity Meter. During starting of test shake the sample thoroughly for collecting accurate results.

4.3.4 TDS METER

It is determined with HANNA HI5321 conductivity meter after note down the reading of the EC from Conductivity meter and click on the MODE tab as shown in Figure 4.3 below and then select the TDS option. The value of the TDS shown on the screen in ppm(parts per million) and ppt (parts per thousand). The range of this instrument for measurement is from 0.00ppm to 400ppt with accuracy of ±0.001ppm. It also has a data storage capacity of 100000 data points. It easily worked under the temperature range of 0 to 50°C.

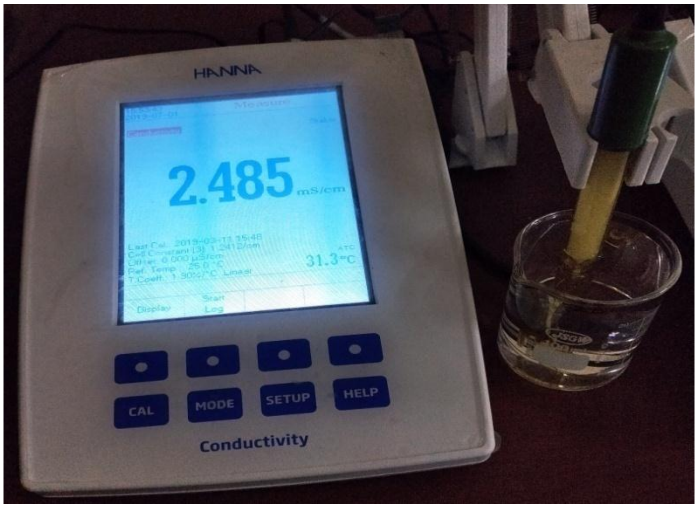


Figure 4.3 TDS Meter

The TDS parameter also measured in the Conductivity meter as described procedure in Clause 4.3.4.

Precautions:- a) Wash the electrode properly before used in another sample with distilled water.

b) Note the reading when the 'Stable' appeared on the right top of the screen.

4.4 CONCLUDING REMARKS

In this chapter it is found that the methodology of the practical testing and analyzing the practical work as used in the statistical analysis. We also found the how to perform the practical tests with higher accuracy. With this chapter in the next chapter we study how to analyze these results with statistical methods.

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 INTRODUCTORY COMMENTS

The previous chapter describes the different instruments and testing methods used for determinations of the physico-chemical properties of groundwater samples collected at various places of study area. The present chapter analyses and discusses the results obtained after the testing of samples. There are total 130 groundwater samples collected from study area and tested in laboratory for determining its physico-chemical properties. The data obtained from laboratory are analyzed through different statistical software (SPSS20, Origin 8 and MS Excel). The correlations between various groundwater quality parameters have been checked.

5.2RESULTS AND DISCUSSIONS

The groundwater samples were collected from six different districts of Malwa region once in each month from February to June. The samples collected were tested in laboratory. Statistical analysis was made from the data obtained.

5.3PHYSICO-CHEMICAL RESULTS

The various statistical parameters i.e. mean and standard deviation for each groundwater quality parameter for Malwa region were obtained from the testing data. Also mean and standard deviation for each groundwater quality parameter for each district were calculated. Table 5.1 shows the various statistical analysis determined by the obtained data for Malwa region in which the whole data were combined for all six districts. The full physic-chemical results in month wise and district wise are attached in Annexure 1.

Table 5.1 *Descriptive Statistics analysis of all 130 samples of study area*

Parameter	Units	Min	Max	Mean	Std. Deviation	No. of samples
pH		7.12	8.8	7.74	0.27	130
Turbidity	NTU	0.19	30.2	2.62	4.71	130

Parameter	Units	Min	Max	Mean	Std. Deviation	No. of samples
EC	µS/cm	294	11640	2092.51	2357.92	130
TDS	mg/l	110	5820	1038.33	1176.63	130
ALKALINITY	mg/l	160	920	510.47	165.13	130
TH	mg/l	125	2445	585.52	381.89	130
CALCIUM (Ca^{2+})	mg/l	20	424	91.01	61.41	130
MAGNESIUM (Mg^{2+})	mg/l	3.16	364.19	87.04	63.36	130
CHLORIDE (Cl^{-})	mg/l	22	2594	347.49	418.06	130
SULPHATE (SO_4^{2-})	mg/l	0	4601	672.28	862.86	130
FLUORIDE (F^{-})	mg/l	0.17	0.98	0.49	0.17	130
NITRATE (NO_3^{-})	mg/l	0.35	108.69	22.75	27.88	130

The above descriptive statistics analysis are compared with the IS10500-2012 and WHO guidelines as given below in Table 5.2 From that it is found that the mean values of some parameters is above its permissible limits and unfit for drinking purpose.

Table 5.2 *Water quality of present study area with respect to IS 10500-2012 and WHO Guidelines*

Parameter	**Units**	**IS 10500-2012**		**WHO Guidelines(1994,2004)**		**Percent of samples above Permissible Limit (IS 10500-2012) (WHO- 2017)**	**Health Implications(Kumar et al. 2007)**
		Desirable Limit (DL)	**Permissible Limit(PL)**	**Desirable Limit (DL)**	**Permissible Limit(PL)**		
pH		6.5-8.5	No relaxation	7-8.5	9.2	0.77	Taste
Turbidity	NTU	1	5	-	-	15.38	
EC	µS/cm			500	1400	47.94	Gastro-intestinal irritation
TDS	mg/l	500	2000	-	-	10	Scale formation
Alkalinity	mg/l	200	600			21.54	Scale formation
TH	mg/l	200	600	100	500	30	Scale formations
Calcium ($Ca^{2+)}$)	mg/l	75	200	75	200	3.85	Scale formations
Magnesium ($Mg^{2+)}$)	mg/l	30	100	50	150	26.92	Encrustation in sanitation system
Chloride ($Cl^{-)}$)	mg/l	250	1000	200	600	4.62	Salty Taste
Sulphate (SO_4^{2-})	mg/l	200	400	200	400	40.77	Laxative effect
Fluoride (F^-)	mg/l	1	1.5	-	1.5	Above PL=0 Below 0.5 mg/l= 60	Fluorosis and skeletal imperfections
Nitrate (NO_3^-)	mg/l	45	No relaxation	-	45	20.77	Methaemoglobinemea

The parameters like TH, Alkalinity, TDS and SO_4^{2-} above its desirable limits as compared with IS10500-2012. From Table 5.2, it is found that the some of the places of Malwa region have concentrations of salts beyond permissible limit. The parameter EC, Ca^{2+} ,Mg^{2+} , Cl^- and SO_4^{2-}, NO_3^-have higher concentrations at certain location which exceeds the permissible limits as per IS10500-2012. The pH of the one sample belongs to Bathinda region is at boundary of permissible limit i.e. (pH=8.5). It is also found from Table 5.2 that, 47.94% of the samples have higher value of EC which indicates there must be higher alkalinity and TH in groundwater of those areas. It is confirmed from the testing that, 21.54% of samples have Alkalinity more than its permissible limits and the 30% of samples have TH above its permissible limits. From this data it is concluded that the most of the area of the southwest belt of Punjab state has salt dominance in order of $SO_4^{2-} > Mg^{2+} > NO_3^- > Ca^{2+}$.

The concentrations of all the parameters of the groundwater quality of Malwa region is shown in the Table 5.3 which shows the concentrations in all 5 months from February to June with maximum and minimum content . The graphical representation of concentrations for all parameters is shown subsequently in this chapter.

The statistical summary of all the data variations in all the districts in study area is shown in Table 5.3. It is seen from Table 5.3 that the Districts like Bathinda , Mukatsar and Mansa have poor drinking quality.

Table 5.3 *Variation in concentrations of various parameters in all districts of study area*

Sr. No	**Parameter**	**District**	**Mean**	**Standard Deviations**	**Permissible limits (IS 10500-2012)**	**Remarks**
1	pH	Patiala	7.59	0.28	6.5-8.5	Indicates the Acidic and Basic nature of groundwater.
		Sangrur	7.65	0.13		
		Mohali	7.71	0.19		
		Mansa	7.89	0.22		
		Mukatsar	7.77	0.23		
		Bathinda	8.01	0.36		
2	Turbidity (NTU)	Patiala	0.18	1.56	1-5 NTU	It identifies the presence of dissolved solids and
		Sangrur	0.74	0.74		
		Mohali	4.25	8.13		
		Mansa	3.25	4.38		

Sr. No	Parameter	District	Mean	Standard Deviations	Permissible limits (IS 10500-2012)	Remarks
		Mukatsar	3.7	3.39		bacterial presence.
		Bathinda	5.04	6.68		
3	EC(μS/cm)	Patiala	965.03	405.64	500-1400 μS/cm As per WHO Guidelines	It gives the salinity content of groundwater and Identifies suitability for Irrigation purpose
		Sangrur	1154.06	516.34		
		Mohali	1132.68	422.22		
		Mansa	1803.38	641.98		
		Mukatsar	6087.67	4024.18		
		Bathinda	2839.12	1720.82		
4	TH(mg/l)	Patiala	422.77	96.08	200-600mg/l	The presence of salts of Calcium and magnesium and hardness status of groundwater identified
		Sangrur	510.57	135.92		
		Mohali	496.20	179.64		
		Mansa	498.53	248.46		
		Mukatsar	1081.06	730.61		
		Bathinda	684.53	387.41		
5	Alkalinity(mg/l)	Patiala	426.57	104.85	200-600 mg/l	Alkalinity gives us the bicarbonates and carbonates ions in groundwater and it responsible for Scale formations
		Sangrur	431.50	63.32		
		Mohali	517.00	89.99		
		Mansa	580.20	94.16		
		Mukatsar	560.65	201.47		
		Bathinda	609.12	179.16		
6	Calcium(mg/l)	Patiala	83.04	26.39	75-200 mg/l	It also imparts in hardness and then responsible for scale formation.
		Sangrur	82.95	32.00		
		Mohali	85.49	39.23		
		Mansa	62.80	27.74		
		Mukatsar	162.54	126.55		
		Bathinda	79.54	46.53		
7	Magnesium(mg/l)	Patiala	52.31	17.62	30-100 mg/l	It also indicate the suitability of groundwater for Irrigation purposes MAR.
		Sangrur	73.71	25.52		
		Mohali	68.68	31.17		
		Mansa	83.03	51.92		
		Mukatsar	164.03	109.12		
		Bathinda	118.08	69.17		
8	Chloride(mg/l)	Patiala	161.80	66.46	250-1000 mg/l	It helps in disinfection activity of groundwater.
		Sangrur	242.17	127.40		
		Mohali	170.25	68.81		
		Mansa	287.50	98.33		

Sr. No	Parameter	District	Mean	Standard Deviations	Permissible limits (IS 10500-2012)	Remarks
		Mukatsar	1033.84	795.52		
		Bathinda	405.29	258.38		
9	Sulphate(mg/l)	Patiala	433.14	543.98	200-400 mg/l	It creates laxative effect in human body when above its permissible limits
		Sangrur	274.91	439.28		
		Mohali	163.87	384.11		
		Mansa	858.88	906.86		
		Mukatsar	1614.68	1365.86		
		Bathinda	947.41	711.63		
10	Fluoride(mg/l)	Patiala	0.55	0.20	0.5-1.0 mg/l (WHO 2017)	Fluoride more than 1.0 mg/l causes bone decay and below 0.5mg/l causes dental fluorosis and skeletal imperfections
		Sangrur	0.40	0.10		
		Mohali	0.41	0.09		
		Mansa	0.47	0.14		
		Mukatsar	0.56	0.13		
		Bathinda	0.56	0.21		
11	Nitrate (mg/l)	Patiala	4.53	1.93	45mg/l	More than 45mg/l causes blue baby disease.
		Sangrur	4.02	1.55		
		Mohali	11.47	9.24		
		Mansa	41.65	27.63		
		Mukatsar	58.78	22.67		
		Bathinda	43.45	29.86		
12	TDS (mg/l)	Patiala	504.15	229.59	500-2000 mg/l	It also causes Scale formations.
		Sangrur	576.62	261.00		
		Mohali	562.12	214.05		
		Mansa	984.29	217.82		
		Mukatsar	2927.44	2134.16		
		Bathinda	1369.92	888.94		

5.4 VARIATIONS IN PYSICO-CHEMICAL PROPERTIES

5.4.1 pH

This parameter of groundwater samples in the study area varies from 7.12 to 8.8. The least value was recorded at Patiala Industrial sector (PTAI2) in the month of February and the maximum was recorded in the month of June at Industrial area of Bathinda district (BTAI1). The monthly variation of pH is given in Figure 5.1. It is observed that the groundwater in the study area is basic in nature and it is lying within the permissible limits given by BIS 10500-

2012 and World Health Organization (WHO). The mean pH is 7.14 which also lie within the permissible limits.

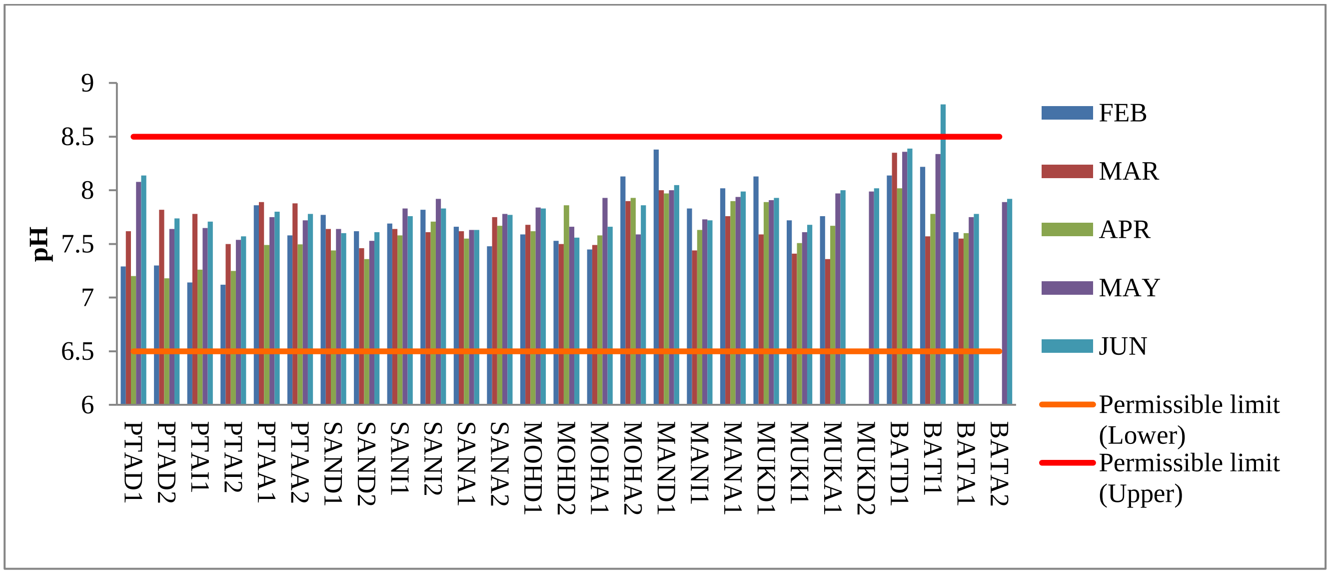


Figure 5.1 Distribution of pH in different sampling sites

The pH value of groundwater in both domestic and industrial area of Bathinda was higher side in all the months and it was beyond the permissible limit in the month of June for the sample collected from industrial area.

5.4.2 TURBIDITY

The turbidity of groundwater of the present study varies between 0.19 to 30.2 NTU. The monthly variation of turbidity is shown in Figure 5.2. The minimum (0.19NTU) and maximum (30.2 NTU) turbidity was recorded in Mansa industrial sector in March and SAS Nagar (Mohall) agriculture sector in May respectively. Higher the turbidity in the groundwater is responsible for presence of bacteria, viruses and disease born organisms which were gives symptoms of nausea, diarrhea and cramps (Memon et al.2016).

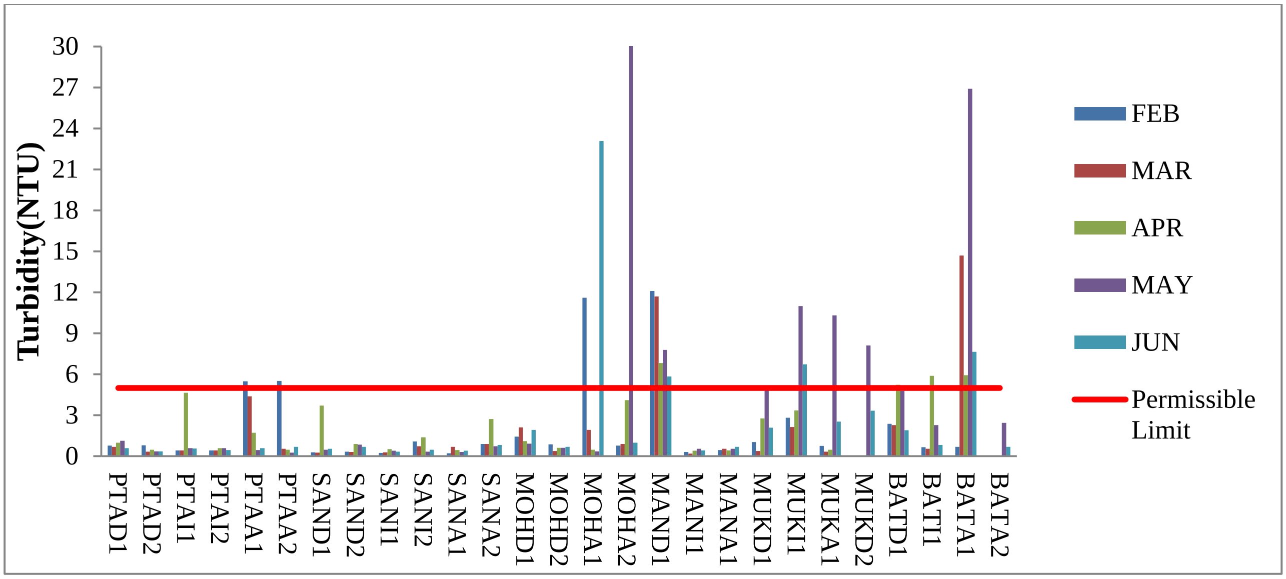


Figure 5.2 Distribution of Turbidity in different sampling sites

It was found that there is strong relation between turbidity with hardness and salt concentration. MUKI1, MUKA1 and MUKD2 are the sites having higher concentration of turbidity and hardness.

5.4.3 ELECTRICAL CONDUCTIVITY (EC)

EC is the main parameter of identifying the total salt concentrations in soil. The variations of EC in all five months are shown in Figure 5.3.

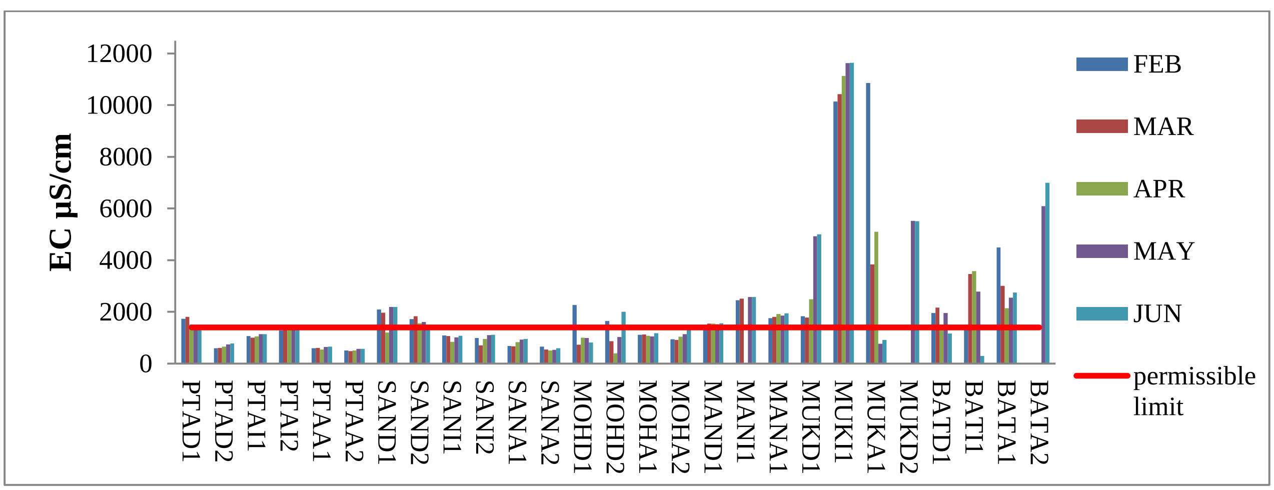


Figure 5.3 Variations of EC in different sampling sites

It also affects the crop yield. The large variations of EC were noticed which varies from 294 µS/cm to 11640 µS/cm at Bathinda Industrial sector in June (BATI1) and Mukatsar Industrial sector in June respectively. It is observed that the maximum EC was recorded in Mukatsar district in both agriculture and industrial area of the district. In the period of the five months from February to June, it is observed that the EC in Agriculture area of Patiala District is lying within the permissible limits (483.3 to 569.7µS/cm).

The classification of the groundwater on the basis of EC is compared with IS 11624-1986 which classify the quality of irrigation water based on the value of EC. The Table 5.4 shows the classification of quality of irrigation water given by Wilcox, 1955. The results of EC obtained in groundwater samples of present study are compared with classification given by Wilcox, 1955. The recommend permissible value of the EC varies from 500 to 1400 µS/cm as per WHO guidelines. It is found from present analysis that, 48% samples are above the permissible limits according to WHO guidelines. It is also observed that as per IS 11264-1986, the groundwater of of the Mukatsar and Bathinda district is unfit for both drinking and agriculture purposes. Figure 5.3 shows that the groundwater in these districts has the EC value more than 6000 µS/cm. More concentration of salinity (EC) decrease the osmotic activities of plants which leads the interruption of absorption of soil nutrient and water from soil.

Table5. 4 *EC Classification based on Wilcox 1955, IS 11264-1986 and WHO Guidelines*

Parameter	**Range**	**Classification**	**Districts under this criteria**
EC µS/cm (Wilcox 1955)	Less than 250 µS/cm	Excellent	No District fall under this criteria
For Drinking Water Quality	250-750	Good	Patiala & Sangrur
	750-2000	Permissible	Sangur & Mohali
	2000- 3000	Doubtful	Mansa & Bathinda
	>3000	Unsuitable	Mukatsar, Mansa & Bathinda
EC µS/cm (IS	Less than 1500	Low	Patiala, Sangrur &

Parameter	Range	Classification	Districts under this criteria
11264-1986)			Mohali
For Irrigation Water Quality	1500-3000	Medium	Mansa , Bathinda & Mohali
	3000-6000	High	Mansa & Bathinda
	>6000	Very High	Mukatsar
EC µS/cm (WHO Guidelines) For Drinking Water Quality	500-1400	>1400 not fit for drinking	Patiala, Sangrur & Mohali

5.4.4 TOTAL DISSOLVED SOLIDS (TDS), TOTAL HARDNESS (TH) & ALKALINITY

TH, Alkalinity and TDS are the most important parameter for classifying the quality of groundwater for both drinking and Irrigation purpose. Figure 5.4 and 5.5 and 5.6 represents the variations of TH, alkalinity and TDS in study area respectively.

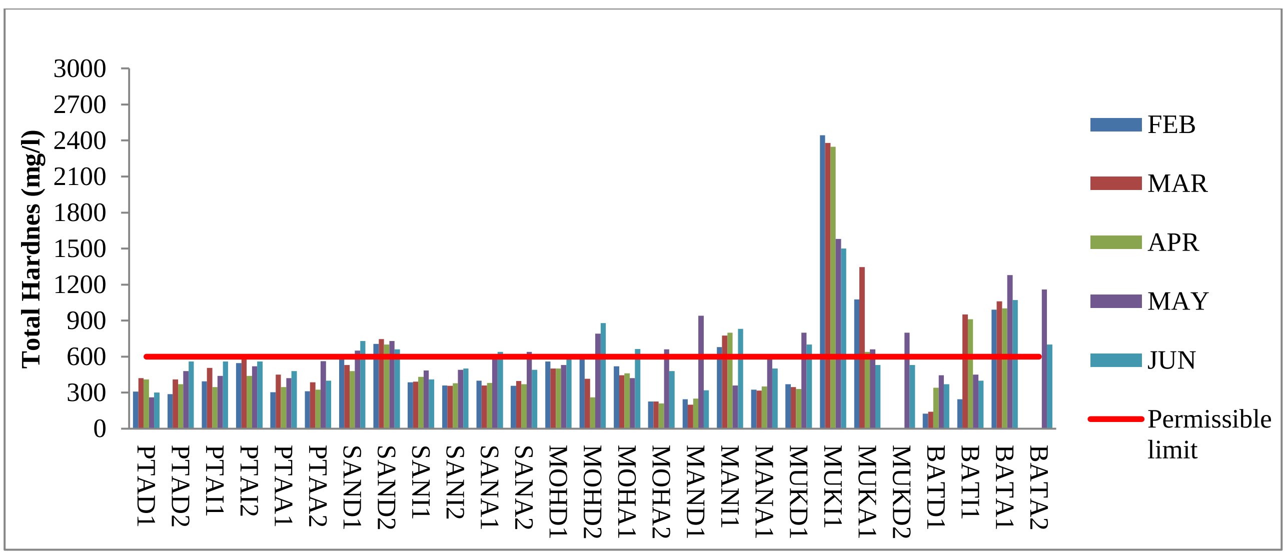


Figure 5.4 Variation of total hardness in different sampling sites

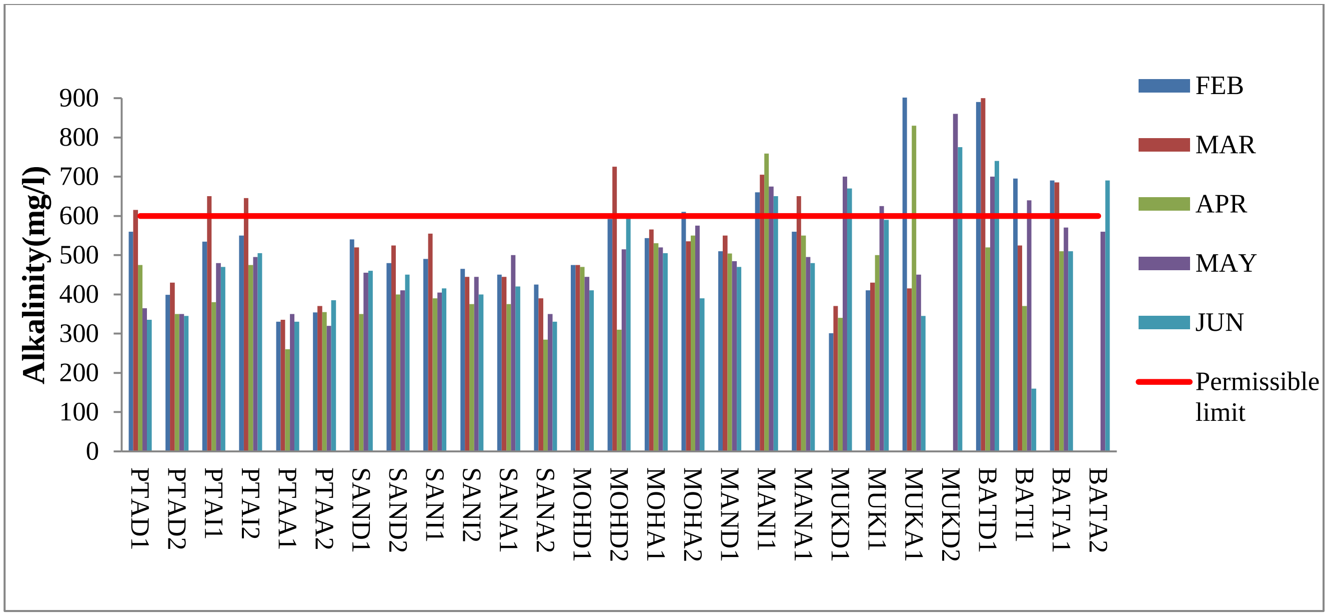


Figure 5.5 Variation of Alkalinity in different sampling sites

The TDS of the groundwater in study area varies from 110mg/l to 5820mg/l. The Total Hardness (TH) and Alkalinity of groundwater in study area varies from 125-2445mg/l and 160-1475 mg/l respectively.

It is observed that the 10% of total samples have TDS beyond permissible limits as per BIS 10500-2012 and WHO guidelines. Similarly, It is observed that, 21.54% and 30% samples contain the Alkalinity and TH respectively beyond its permissible limits. Higher value of TDS (5820mg/l) was recorded in the Mukatsar industrial sector and the lowest (110mg/l) was recorded in the Bathinda Industrial sector. The groundwater of study area was hard in nature which shows that there is higher the salt concentrations of calcium, magnesium, sulphates and chlorides etc which contributes to the hardness as well as alkalinity of the groundwater. The classification criteria of the groundwater are shown in the Table 5.5 on the basis of TDS and TH. Groundwater in the Mukatsar and Bathinda district was much hard and containing higher salt concentration as shown in Figure 5.4. Groundwater with high hardness produces the scaling effect on the surfaces of metals. The alkalinity of the study area shown in the Figure 5.5 which shows that the groundwater was alkaline in nature and the pH of all the groundwater samples lie above 7.

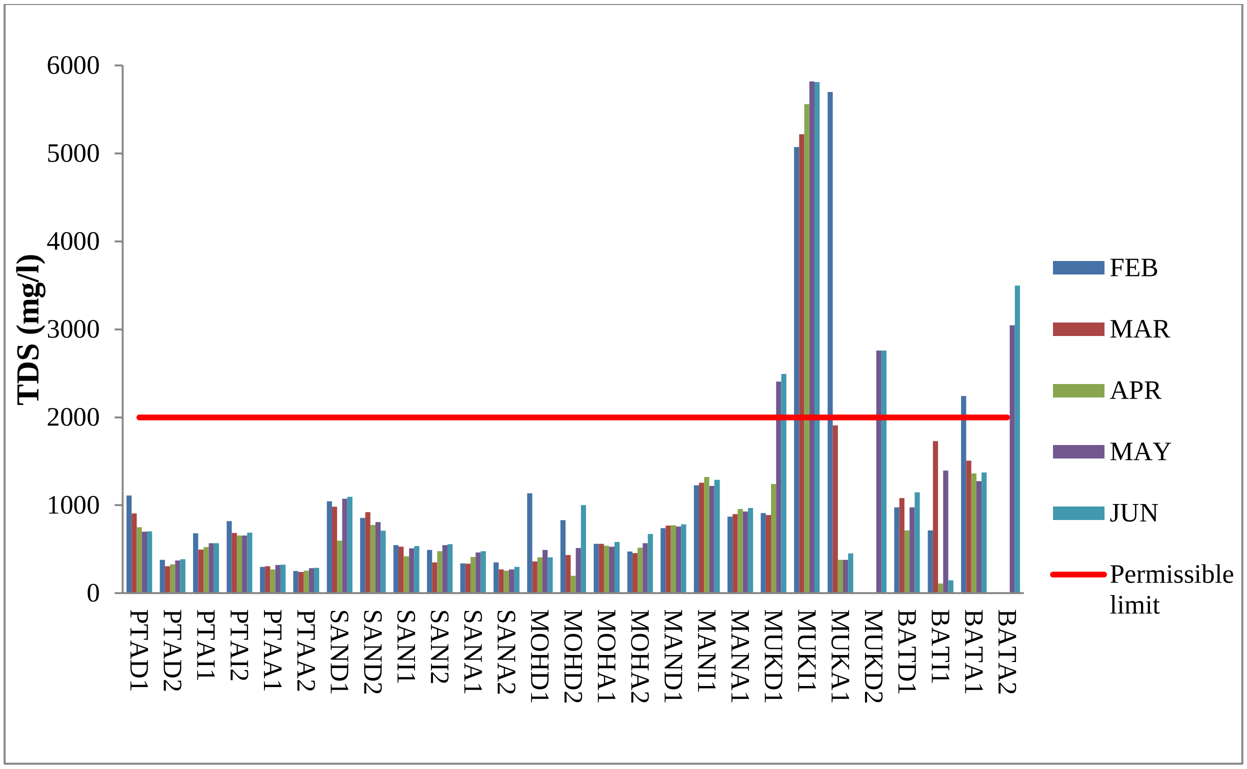


Figure 5.6 Variation of TDS in different sampling sites

The Figure 5.6 shows the variation of TDS in study area. It is found from Figure 5.6 that, the TDS value of the groundwater in Mukatsar and Bathinda districts are above the permissible limits as mentioned in BIS 10500-2012. The higher TDS occurs due to the more salts concentrations present in groundwater from soil minerals and other anthropogenic activities.

The alkalinity and TH concentration both are above its permissible limit as described by IS 10500-2012, which means that the groundwater of study area have higher alkalinity due to excess presence of calcium and magnesium salts and their carbonates and bicarbonates. Both the TH and Alkalinity if excess in groundwater then the scale formations are formed on metal surfaces. Classification of groundwater on the basis of TDS and TH are shown in Table 5.5 given below:-

Table 5.5 *Classification of groundwater with Davies et al. (1966), Sawyer et al (1967) and IS 10500-2012*

Parameter	**Range**	**Class of water**	**No of samples under range (percent of samples), Districts.**
TDS (Davies et al. 1966)	<500	Desirable for drinking	43(33.09) Patiala & Sangrur
	500-1000	Permissible for drinking	55(42.30) Sangrur, Mohali & Patiala
	<3000	Useful for irrigation	24(18.46)Mansa , Mukatsar & Bathinda
	>3000	Unfit for drinking and irrigation	8(6.15), Mukatsar
TH (Sawyer et al. 1967)	<75	Soft	0(0)
	75-150	Moderately Hard	2(1.53)
	150-300	Hard	10(7.69)Patiala, Mohali
	>300	Very Hard	118(90.76)Mansa, Patiala, Mukatsar, Bathinda, Sangrur Mohali
TH (IS 10500-2012)	More than 600	Above permissible limit Not use for drinking	39(30)Mansa, Bathinda & Mukatsar

The TH of the study area is higher due to the strata of the soil in study area is calcareous soil which have a higher content of calcium in this type of soil. That may be a valid reason behind the excess in TH of groundwater in study area.

5.4.5 CALCIUM (Ca^{2+}) AND MAGNESIUM (Mg^{2+})

The calcium and magnesium ions in the groundwater of study area were more dominance for excess hardness of a groundwater. The higher concentration of the calcium (424mg/l) content was found in Industrial area of the Mukatsar District in industrial sector in March whereas the lowest concentration was recorded in Bathinda district in month of March and June. The permissible value of the calcium and magnesium as per IS 10500-2012 is 200mg/l for calcium and 100mg/l for magnesium. The variation of calcium and magnesium ions had shown in Figure 5.7 and 5.8 respectively.

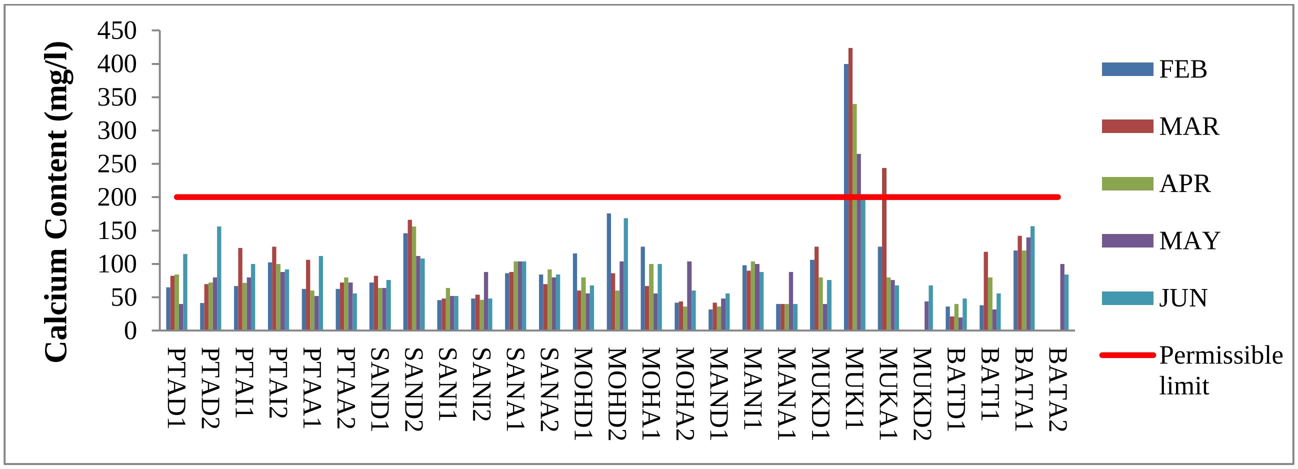


Figure 5.7 Variation of calcium in different sampling sites

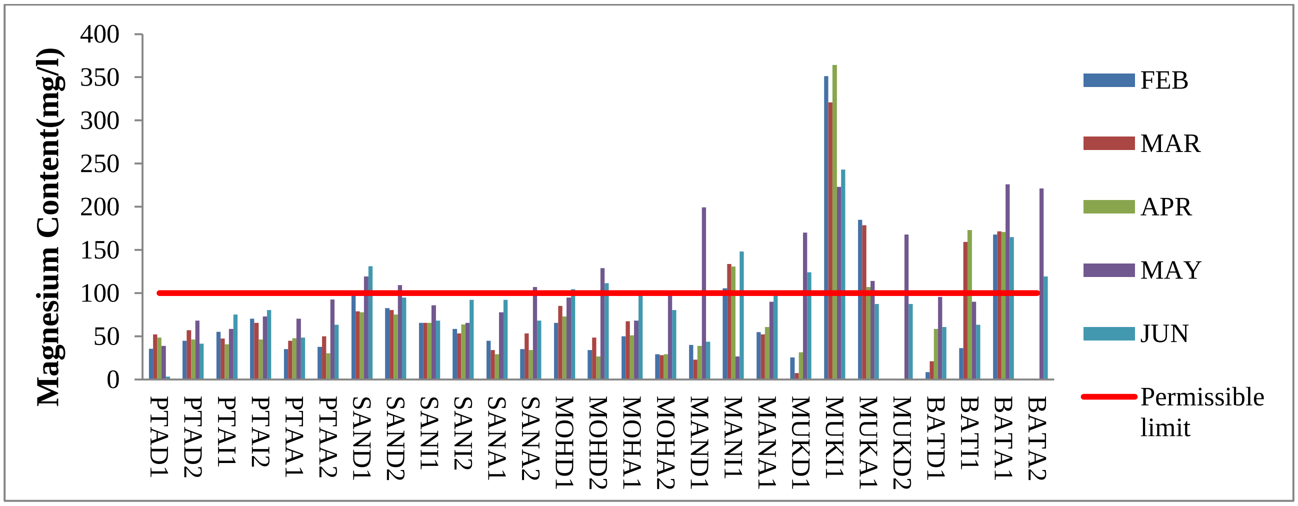


Figure 5.8 Variation of Magnesium content in different sampling sites

The maximum (364.19) and minimum (3.16) magnesium content was recorded in district Mukatsar(MUKI1) district in April and Patiala district(PTAD1) in June. There were 3.85% samples of calcium content above its permissible limits i.e.200mg/l as per IS 10500-2012 whereas 26.92% samples of magnesium content above its permissible limit (100mg/l).Therefore these two ions calcium and magnesium also contribute in making of groundwater alkaline in nature. Also the presence of calcium and Magnesium depends on the type of soil present in an area.

5.4.6 CHLORIDE (Cl^-) & SULPHATE (SO_4^{2-}) CONTENT:-

The chloride content in the study area is varies from 22 to 2594mg/l. The mean of the chloride content in study area was recorded 347.49 mg/l which is above the desirable limit (250mg/l) as per IS10500-2012 and WHO guidelines. The monthly variation of chloride shown in the Figure 5.9.

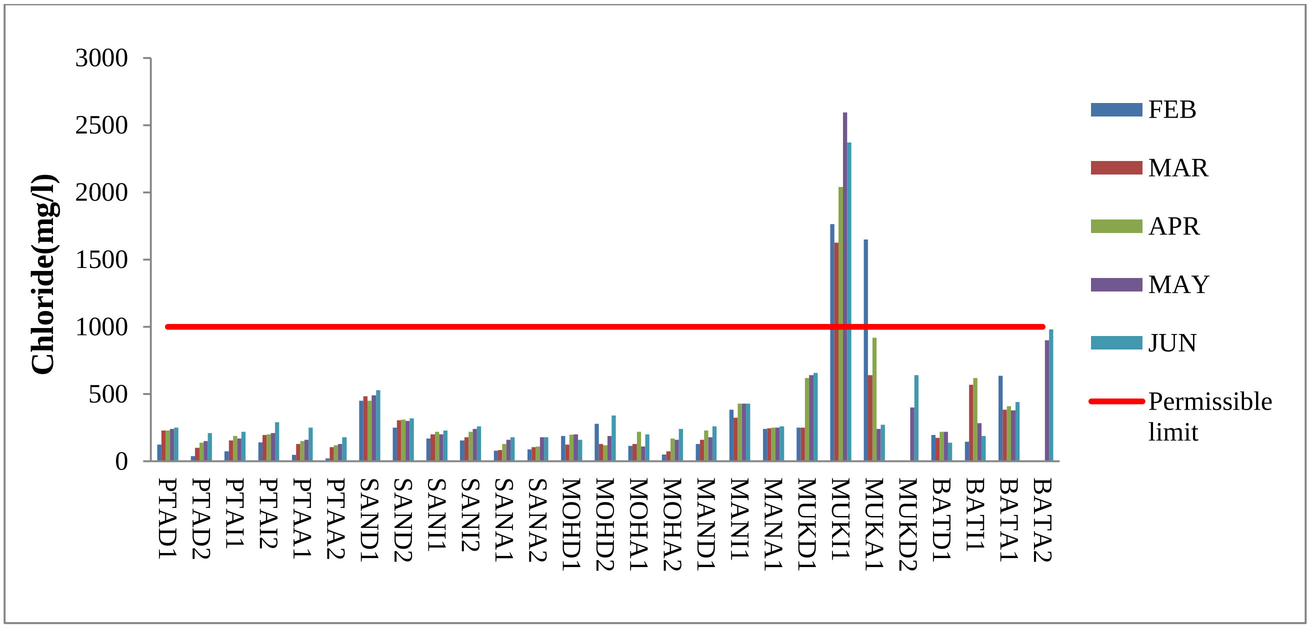


Figure 5.9 Variation of Chloride in different sampling sites

The maximum (2594 mg/l) chloride content is found at Muktsar district in May and the minimum chloride content (22 mg/l) is found in Patiala district in February. In the other districts the chloride content was more than its desirable limit but less than maximum permissible limit. The higher concentration of the chloride was appearing because the excess use of inorganic fertilizers. The desirable concentration of chloride is essential for disinfection process of water.

The sulphate (SO_4^{2-}) concentration in study area vary from 0 to 4601 mg/l. The mean concentration of sulphate concentration in study area was recorded 672.182 mg/l. The maximum sulphate was recorded in the Mukatsar district and the minimum is recorded in the Patiala agriculture area in February. The permissible limit of sulphate content is 400mg/l as per IS10500-2012. In the present study, 40% of the samples found above the permissible limit of the sulphate as shown in Figure 5.10.

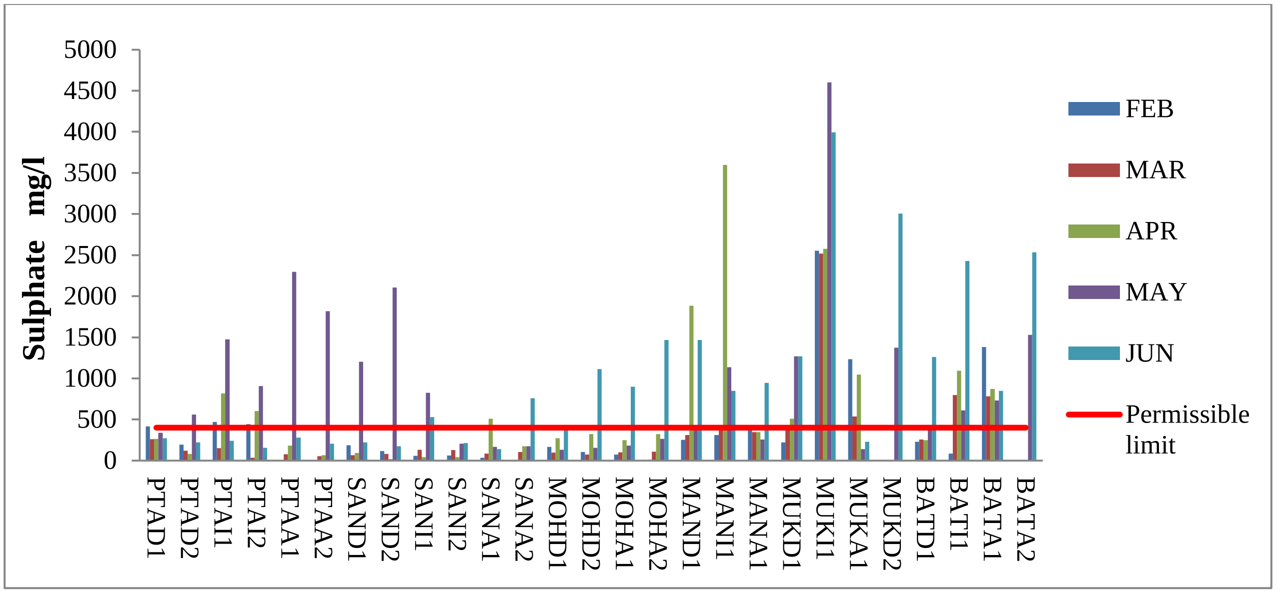


Figure 5.10 Variation of Sulphate in different sampling sites

The sources of generation of sulphate content in groundwater are leaching of sulphates, inorganic weathering of soil and other human activities (Miler et al. 1979). It creates health problems if it exceeds its maximum allowable limits i.e. 400mg/l. It effects on human health with laxative effect (Subramani et al.2015).

5.4.7 FLUORIDE AND NITRATE

The fluoride concentration if groundwater observed in range of 0.17 to 0.98 mg/l. The mean fluoride content recorded as 0.49 mg/l in study area the variations of fluoride content in study area shown in Figure 5.11, which shows the monthly variation of the fluoride with respect to all the sampling sites. The maximum concentration of fluoride (0.98mg/l) was recorded in the Patiala Agriculture sector and the minimum (0.17mg/l) recorded in Patiala domestic sector. The maximum (0.98mg/l) and minimum (0.17 mg/l) recorded in the months of March and June. The 60% samples of the study area below the required minimum fluoride content i.e. 0.50mg/l.

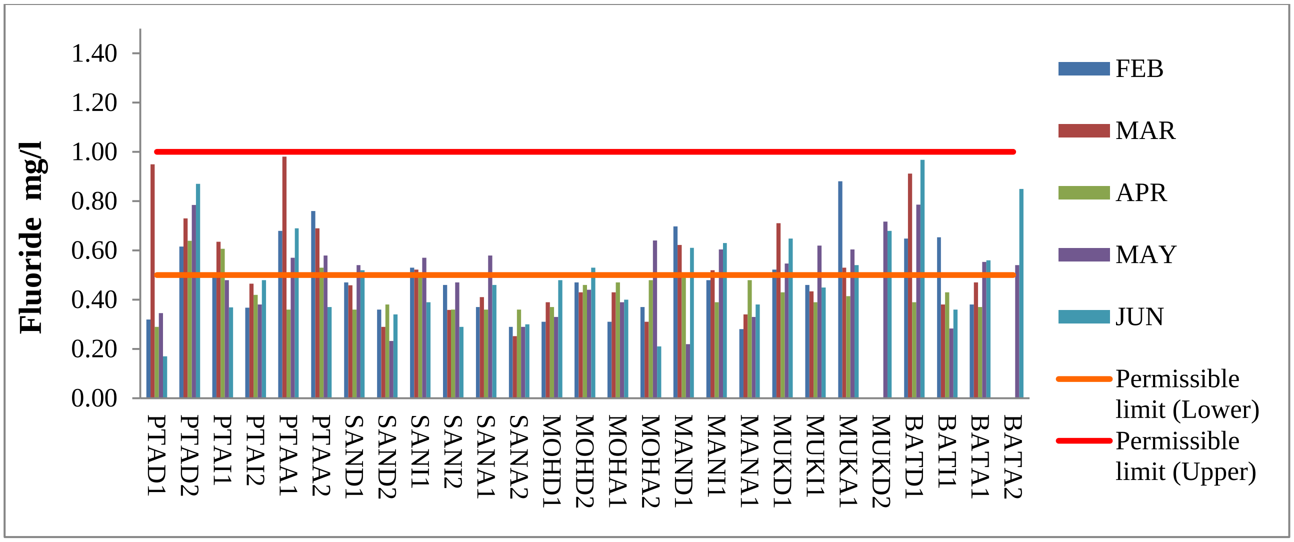


Figure 5.11 Variation of fluoride in different sampling sites

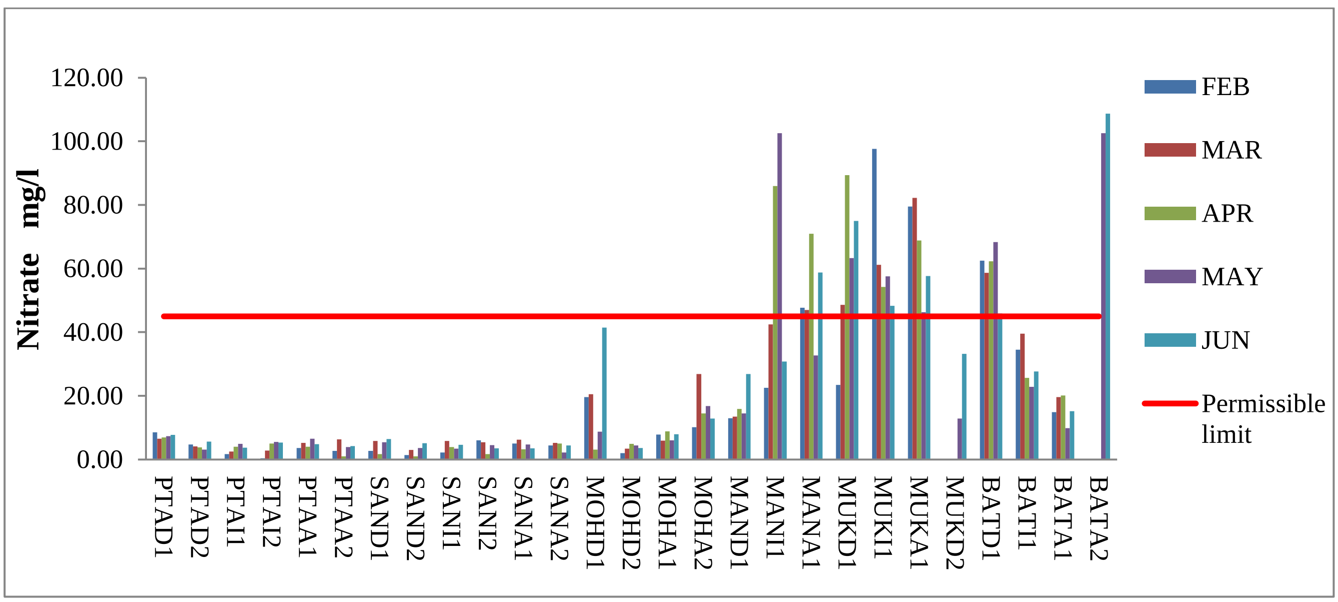


Figure 5.12 Variations of nitrate in different sampling sites

This minimum content of fluoride in groundwater is required to prevent the dental problems and the bone development in human body.

The nitrate content in the study area was varied from 0.35 mg/l to 108.69 mg/l. The minimum (0.35 mg/l) nitrate content found in the Patiala agriculture area and the maximum (108mg/l) nitrate content found in the Bathinda agriculture area as shown in Figure 5.12 given below. The mean nitrate content in the study area recorded was 22.75 mg/l. The permissible limits of nitrate concentrations is 45mg/l as per IS 10500-2012 and WHO Guidelines. It is found that, the groundwater of SAS Nagar (Mohali), Mansa, Mukatsar and Bathinda district contains nitrate beyond permissible limit.

The groundwater samples of the districts SAS Nagar Mohali, Mansa and Bathinda were collected from shallow depth. From that we found that the nitrate concentration in groundwater at shallow depth was higher than the deep depths. The groundwater at shallow depth was more in contact with the anthropogenic activities, sanitation activities and the fertilizers used in agriculture purpose have nitrate rich minerals which becomes in contact with groundwater when they dissolved in agriculture water.

5.4.8 HEAVY METALS

The ground water collected in the month of March from Industrial area of all six districts is tested for presence of heavy metal. The present study only considers the analysis of lead, Cadmium, Chromium, Sodium and Potassium. The samples collected were tested in Sophisticated Analytical Instrument (SAI) Lab of Thapar Institute. Table 5.6 shows the concentration of heavy metal present in ground water of the study area. It is found that the lead content in all the samples of six districts was beyond the permissible limit. The chromium and cadmium content of all the sample were within the permissible limits. But the Sodium and potassium content in the samples of district Bathinda, Mansa and Sangrur are above its permissible limits. The results of the samples were tested in the laboratory is shown in Table 5.6. The entire tests were performed with the APHA specifications.

Table5. 6 *The data of heavy metals collected from selected samples*

Sr.No	**Heavy Metal**	**Sample ID**	**Permissible limit**	**Observed Value**	**Standard Method**
1	Lead (Pb)	BATI1	0.01 mg/l	0.22	APHA 23rd Edition 3120 B
		MANI1	0.01 mg/l	0.16	APHA 23rd Edition 3120 B
		MUKI1	0.01 mg/l	0.07	APHA 23rd Edition 3120 B
		MOHD1	0.01 mg/l	0.03	APHA 23rd Edition 3120 B
		SANI1	0.01 mg/l	0.37	APHA 23rd Edition 3120 B

Sr.No	Heavy Metal	Sample ID	Permissible limit	Observed Value	Standard Method
		PTAI1	0.01 mg/l	0.05	APHA 23rd Edition 3120 B
2	Chromium(Cr)	BATI1	0.05 mg/l	<0.05	APHA 23rd Edition 3120 B
		MANI1	0.05 mg/l	<0.05	APHA 23rd Edition 3120 B
		MUKI1	0.05 mg/l	<0.05	APHA 23rd Edition 3120 B
		MOHD1	0.05 mg/l	<0.05	APHA 23rd Edition 3120 B
		SANI1	0.05 mg/l	<0.05	APHA 23rd Edition 3120 B
		PTAI1	0.05 mg/l	<0.05	APHA 23rd Edition 3120 B
3	Cadmium (Cd)	BATI1	0.001 mg/l	<0.001	APHA 23rd Edition 3120 B
		MANI1	0.001 mg/l	<0.001	APHA 23rd Edition 3120 B
		MUKI1	0.001 mg/l	<0.001	APHA 23rd Edition 3120 B
		MOHD1	0.001 mg/l	<0.001	APHA 23rd Edition 3120 B
		SANI1	0.001 mg/l	<0.001	APHA 23rd Edition 3120 B
		PTAI1	0.001 mg/l	<0.001	APHA 23rd Edition 3120 B
4	Sodium (Na)	BATI1	200mg/l	347	APHA 23rd Edition 3120 B
		MANI1	200mg/l	205	APHA 23rd Edition 3120 B
		MUKI1	200mg/l	98	APHA 23rd Edition 3120 B
		MOHD1	200mg/l	40.7	APHA 23rd Edition 3120 B
		SANI1	200mg/l	1225	APHA 23rd Edition 3120 B
		PTAI1	200mg/l	81.5	APHA 23rd Edition 3120 B
5	Pottasium (K)	BATI1	12mg/l	23.8	APHA 23rd Edition 3120 B
		MANI1	12mg/l	16.2	APHA 23rd Edition 3120 B
		MUKI1	12mg/l	9.90	APHA 23rd Edition 3120 B
		MOHD1	12mg/l	4.83	APHA 23rd Edition 3120 B
		SANI1	12mg/l	49.4	APHA 23rd Edition 3120 B
		PTAI1	12mg/l	8.66	APHA 23rd Edition 3120 B

5.5 CORRELATION ANALYSIS

The correlation analysis was performed in SPSS 20 statistical software. The Pearson's correlations coefficients were calculated as shown in Table 5.7. The correlation analysis was performed at the 0.01 and 0.05 significance level. With the correlation analysis the trend analysis with different parameters were also determined. Fig 5.13 and 5.14 shows the variation of fluoride and nitrate with pH respectively.

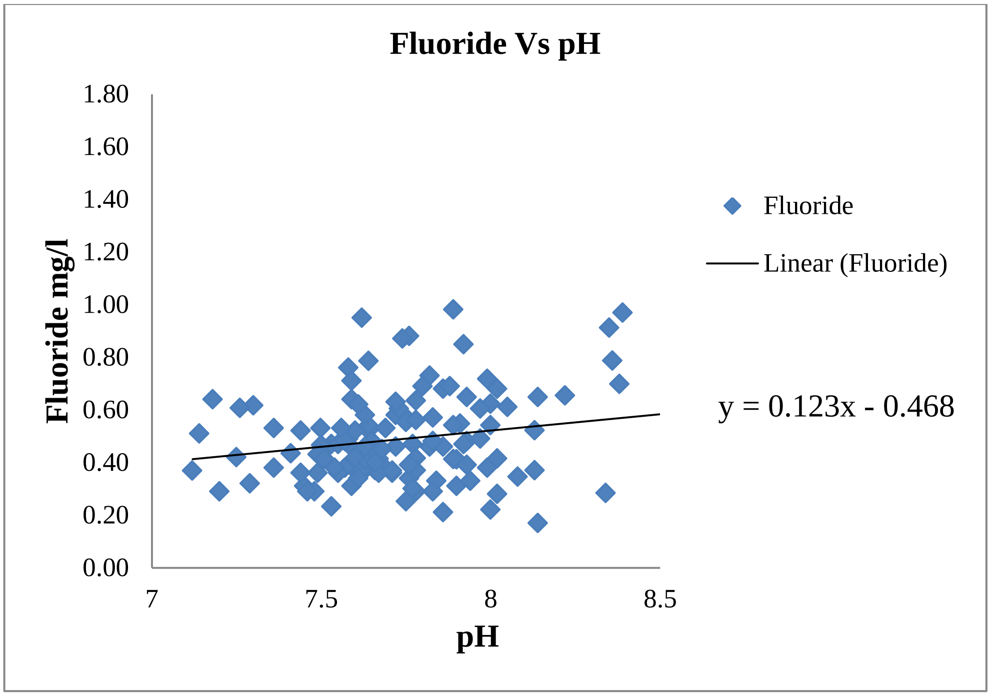


Figure 5.13 Fluoride Relationship with pH

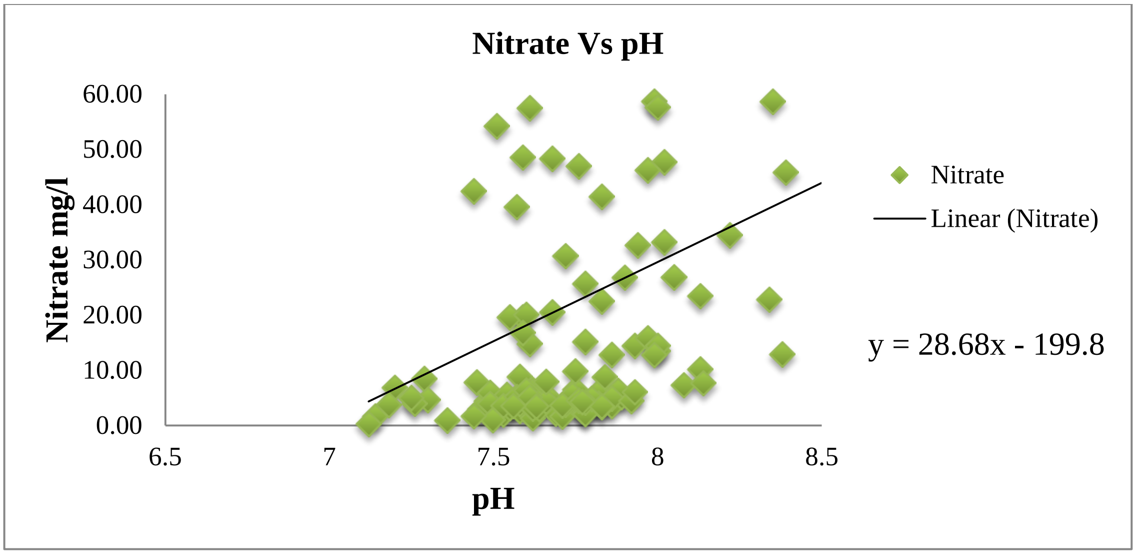


Figure 5.14 Nitrate relationship with pH

From Figure 5.13 and 5.14, it is seen that there is a significant correlation exist between the F^- and pH, NO_3^- and pH. It is also seen from Figure 5.13 and 5.14 that, the concentration of fluoride and nitrate increases as the pH value of sample increases. There is positive significant correlation is existing between pH and F^- and NO_3^- and pH having pearson correlation coefficient r=0.208 and 0.293 respectively at significance level 0.01.

The positive correlation between pH and fluoride occurs due to the dissolution of fluoride bearing minerals in ground water (Sharma et al. 2014).

$$CaF_2 + CO_3^{2-} \rightarrow CaCO_3 + 2F^- \qquad (5.1)$$

$$CaF_2 + 2HCO_3^{2-} \rightarrow CaCO_3 + 2F^- + H_2O + CO_2 \qquad (5.2)$$

Similar trends of fluoride with the pH were also seen in the previous studies. It is also found that the enrichment of CaCO3 in groundwater also leads to increase the fluoride in groundwater (Saxsena et al.2001). The chemical reactions takes place with CaCO3 as below:-

$$CaCO_3 + H^+ + 2F^- \rightarrow CaF_2 + HCO_3^- \qquad (5.3)$$

Handa et al., 1975 also found that there is a relationship between fluoride and alkalinity of groundwater. The fluoride concentration also increases with the increase in the alkalinity of the groundwater. In present study it is also realized that the positive significant correlation between fluoride and alkalinity at significance level 0.05. Figure 5.15 shows a variation of the fluoride content with the Alkalinity.

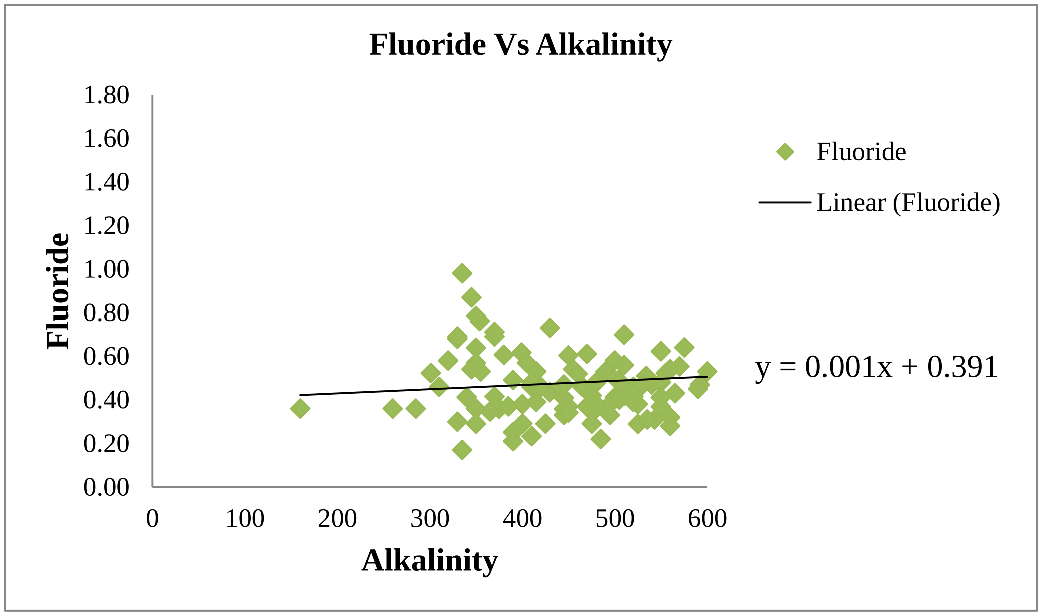


Figure 5.15 Fluoride relationship with Alkalinity

The strong significant correlation is found in the present study between the parameters EC-TDS (r=0.972.p<0.05), EC-Alkalinity(r=0.342, p<0.05). Similarly, it is also found that there is significant correlation exists between F^- - pH-EC-TDS (r=0.18 to 0.21, p<0.05).

The strong positive significant correlation is found between the parameters EC and TDS (r=0.972), Alkalinity(r=0.342), TH(r=0.781), Ca^{2+} (r= 0.634), Mg^{2+}(r=0.771), Cl^- (r= 0.954), SO_4^{2-} (0.694), and NO_3^-(r=0.600) at significant levels of p<0.01 as shown in the Table 5.7.

From the correlation analysis results it is observed that the TDS, Alkalinity, TH, Ca^{2+},Mg^{2+}, Cl^-, SO_4^{2-}, and NO_3^- are affected the EC of groundwater.

Besides that the F^- shows the weak significant correlation with the TDS (r=0.189), Alkalinity (r=0.204) and pH (r=0.208) as shown in Table 5.7 at the significant level 0.05.

Table 5.7 *Correlation matrix of all parameters*

	pH	Turbidity	Conductivity	TDS	Alkalinity	Total Hardness	Calcium	Magnesium	Chloride	Sulphate	Fluoride	Nitrate	Depth
pH	1												
Turbidity	0.08	1											
Conductivity	-0.012	0.118	1										
TDS	-0.014	0.111	**.972****	1									
Alkalinity	0.09	0.089	**.342****	**.347****	1								
Total Hardness	**-.221***	**.200***	**.781****	**.776****	0.096	1							
Calcium	**-.362****	0.088	**.634****	**.640****	-0.018	**.866****	1						
Magnesium	-0.111	**.241****	**.771****	**.760****	0.151	**.956****	**.679****	1					
Chloride	-0.065	0.101	**.954****	**.931****	**.203***	**.797****	**.678****	**.768****	1				
Sulphate	0.091	0.115	**.694****	**.716****	0.166	**.566****	**.418****	**.584****	**.732****	1			
Fluoride	**.208***	0.123	0.169	**.189***	**.204***	-0.033	-0.039	-0.025	0.101	0.123	1		
Nitrate	**.293****	0.014	**.600****	**.598****	**.363****	**.366****	**.224***	**.404****	**.547****	**.496****	**.259****	1	
Depth	**-.230****	**-.251****	**-.412****	**-.394****	**-.313****	**-.365****	**-.249****	**-.388****	**-.373****	**-.355****	**-.235****	**-.300****	1

*. Correlation is significant at the 0.05 level (2-tailed).

**. Correlation is significant at the 0.01 level (2-tailed).

The F^- did not show any correlations with the parameter instead of pH, TDS & Alkalinity. Both F^- (r=-0.235) and NO_3^- (r=-0.300) shows a significant negative correlations with the depth of groundwater table at significant level of $p<0.01$.

The graphical variation of the F^- and NO_3^- with depth of the groundwater table shown in the Figure 5.16 and 5.17 respectively.

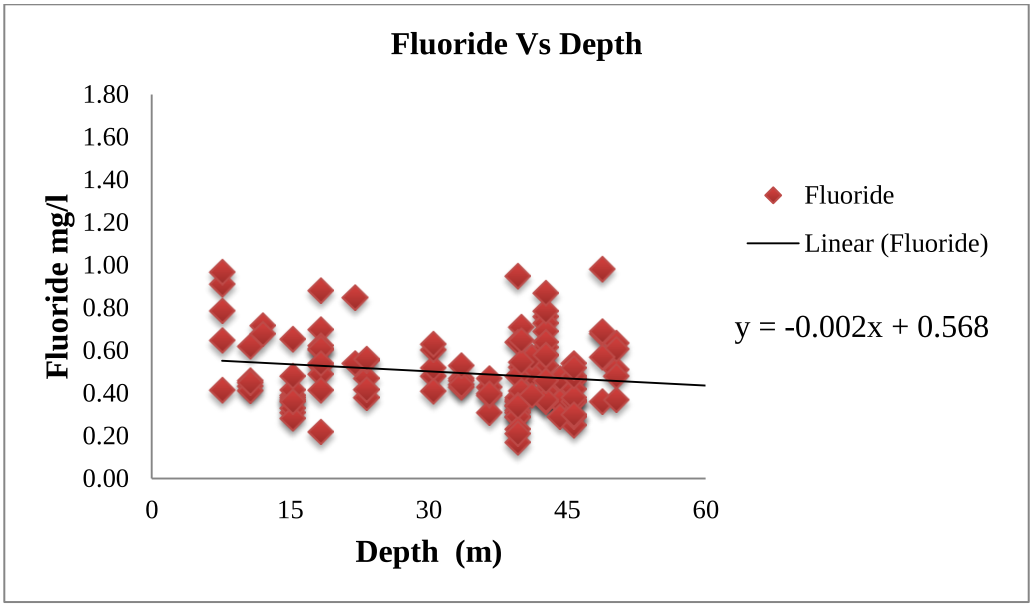


Figure 5.16 Relation of Fluoride with Depth of groundwater

From Figure 5.16, it is found that the F^- content in groundwater of the study area at its more concentration within the shallow depths of ground water. From this we can say that the soil strata at the shallow depth have fluoride bearing minerals. These minerals dissolved in groundwater and then the concentration of fluoride in groundwater influenced. Sharma et al. 2014 also found the similar trend of the fluoride at same study area.

If we see the relationship between the NO_3^- with the depth of the groundwater table it also shows the negative trend with negative significant correlations. From the correlation analysis and graphical variation of nitrate with the depth of the groundwater table in Figure 5.17, it is found that the soil layer at the shallow depth is more in contact with the anthropogenic sources which influence the Nitrate concentration level in the groundwater of the study area.

The Mukatsar, Bathinda and Mansa districts are highly affected by the excess nitrate content which leads to the serious health problems.

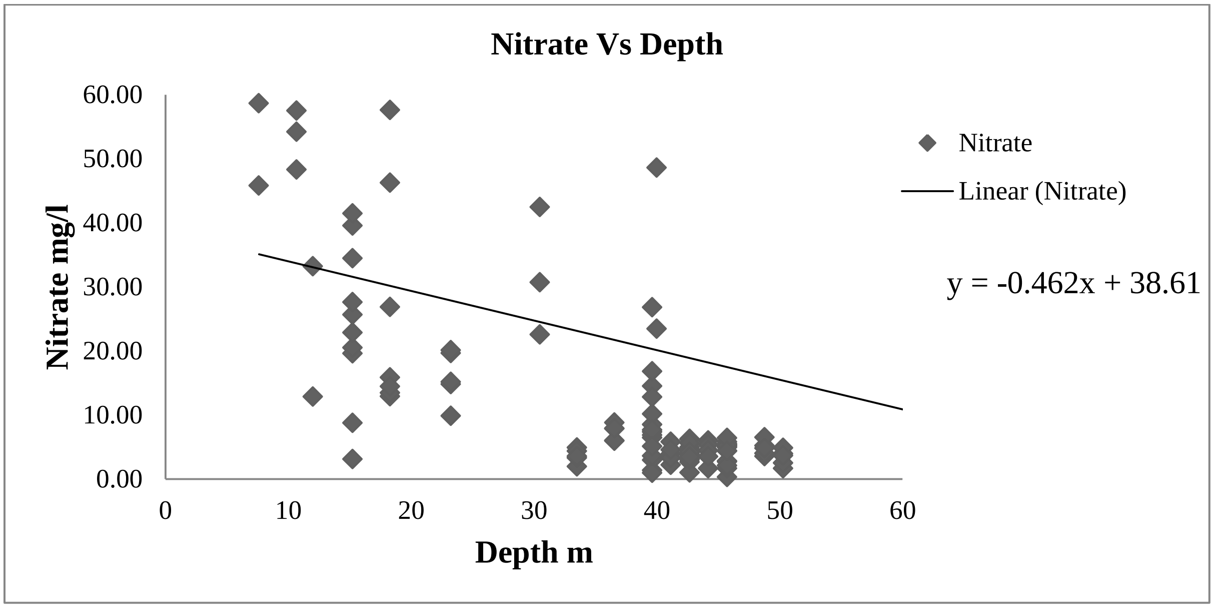


Figure 5.17 Nitrate relationship with Depth of groundwater

From Figure 5.17 it is found that the NO_3^- shows negative significant correlation with groundwater table depth. It is found that the nitrate content at the shallow water table have highly affected with the concentration of the NO_3^- .

From the above analysis it is found that there is major salt dominance as shown from the correlation analysis in the correlation matrix. The EC has a strong significant correlations with the TDS (r=0.972), Alkalinity(r=0.342), TH(r=0.781), Ca^{2+} (0.634), Mg^{2+}(r=0.771), Cl^- (r= 0.954), SO_4^{2-} (0.694), and NO_3^-(r=0.600) which shows the groundwater in the study area has salt dominance due to which the fluoride, nitrate and other physic-chemical parameters are above its permissible limits.

The physic-chemical parameters show the presence of the salts concentrations in the groundwater of study area has major dominance role in groundwater quality status. The districts of study area Bathinda, Mansa, Mukatsar and Mohali area highly affected from this problem of groundwater quality.

5.6 CONCLUDING REMARKS

In this chapter the analysis of the physic-chemical parameters of various sample collected from six districts in different periods are made. It is found that the salts concentrations and the nitrate content in the study area are above its permissible limits as per IS10500 and WHO guidelines. The results are classified under different criteria based on the previous study. The correlation analysis shows that the study area groundwater has under major dominance of salts concentrations and higher salinity (EC) content which also affected the fluoride and nitrate content on the groundwater. It is also found that the lead (Pb) content in all the six districts above its permissible limit 0.01mg/l as per IS 10500-2012. It indicates the Excess in the lead content in groundwater is the serious problem for health point of view. Therefore there is need a great monitoring for groundwater quality as well as for heavy metals under the study area.

CHAPTER 6

WATER QUALITY INDEX

6.1 INTRODUCTORY COMMENTS

In previous chapter the analysis of the physico-chemical properties based on the results calculated from the laboratory tests is performed. From that analysis, it is found that the quality of water is poor in the study area due to the presence of higher salt concentrations and also lead concentration in sample water of all the study area is found above its permissible limits as per BIS standards. The present chapter describes regarding various method to determine the Water Quality Index (WQI) which represents the all the water quality parameters in overall quality of the drinking water. It is the mathematical tool which signifies the quality of the water on the basis of physico-chemical parameters.

6.2 WATER QUALITY INDEX

What is Water Quality Index?

The WQI is the basic tool for monitoring the water quality and policy implementations. There are many researchers studied on measurement of water quality index. The WQI helps to modify policies made by the different environment agencies. It collects data from number of sources and combined them.

The WQI introduced by the (Brown et al. 1970) and corrections applied by the Designer for the Scottish development department in 1975. Horton in 1965 recommended that the different water quality database combined into an overall water index (Horton et al. 1965). Subsequently various researchers introduced different methodology to determine the water quality index. Some of these methods are NSFWQI, Florida Stream Water Quality Index (FSWQI), British Columbia Water Quality Index (BCWQI), Canadian Council of Ministers of Environment (CCME) and Oregon Water Quality Index (OWQI). CCME WQI is certified from Canadian Council of Ministers of Environment and is again modified by the in form of original by BCWQI (Said et al.2004). The WQI in India developed in pioneer work of Bhargava, which gives the water quality index in range of 0 to 100. Here ‘0’ indicate the most polluted water and ‘100’ indicate the pure water which gives integrated affect of the parameters which amplifying the pollution load (Bhargava,1983).

On the basis of these physico-chemical properties, the technical term like drinking water quality index(WQI) are to be made which represents the all the water quality parameters in overall quality of the drinking water. The water quality indexes are calculated from two steps. The first step is to assign the weight to each physico-chemical parameter of tested water sample of the study area and the second step is the aggregation of assigned weight of each parameter for calculating the water quality index.

6.3 METHEDOLOGY FOR GROUND WATER QUALITY INDEX (GQI)

The first Groundwater Quality Index (GQI) introduced by the Ribeiro et al. 2002 which was based on the evaluation of the physico-chemical parameters of the groundwater. On the basis of those parameters the quality of groundwater is to be judged. The guidelines values of the WHO and BIS 10500-2012 is used to check the permissible values for the each physico-chemical parameters.

The groundwater quality index in present study is calculated with the tested results of all physico-chemical parameters of 130 number of collected sample in laboratory which were collected from February to June 2019. On the basis of these parameters the groundwater quality index can be calculated from equation 6.1 (Ehya et al.2018) as given below:-

$$GQI = 100 - \left(\frac{\sum_{i=1}^{n} r_i \ w_i}{n} \right) \qquad (6.1)$$

Here r_i= quality parameter ranking

w_i= weight of quality parameter

C_i =Concentration factor

The factor r_i depends on the value of C_i and the value of C_i (Concentration factor) which is varies between -1 and 1.

The value of the concentration factor is further depends on the measured concentration of the physico-chemical parameter (C_{im}) and standard limit of the relating physico-chemical parameter (C_{is}). The concentration factor is calculated by the equation 6.2.

$$C_i = \frac{(C_{im} - C_{is})}{(C_{im} + C_{is})} \quad (6.2)$$

On the basis of that value of C_i the quality parameter ranking (r_i) is to be determined from the equation 6.3 given below:-

$$r_i = 0.5C_i^2 + 4.5C_i + 5 \quad (6.3)$$

Subsequently, the weightage (w_i) is assigned to each parameter which is determined by the equation 6.4 from the value of $\bar{r_i}$ which is mean value of quality parameter ranking.

$$w_i = \bar{r_i} + 2 \quad (6.4)$$

From equation 6.1 it is clear that the higher the number of the parameters better will be the groundwater quality index.

6.4 GROUNDWATER QUALITY INDEX OF STUDY AREA

The GQI is calculated with this methodology gives us the quality significance of the groundwater.The descriptive statistics of the groundwater quality index is shown in the Table 6.1 given below which shows that the groundwater quality variations in the study area.

Table 6.1 *Descriptive analysis of GQI of study area*

District	Max GQI	Min GQI	Mean GQI	Std.Deviation
Patiala	82.69	74.95	78.70	2.19
Sangrur	82.69	72.13	78.46	2.64
Mohali	82.45	71.53	77.33	3.08
Mansa	77.17	70.17	74.15	2.23
Mukatsar	77.99	58.93	68.22	5.73
Bathinda	78.86	64.11	71.60	4.35

From Table 6.1, the mean value of the groundwater quality index varies from the 68.22 to 78.70. The classification of the groundwater quality on basis of different studies of water quality indices are to be classified for the gradation of the quality of groundwater in the study area.

The monthly variation in the groundwater quality as shown in the Fig 6.1 which indicates the quality of ground water varied from the minimum value 58.93 in Mukatsar Industrial area and the maximum value recorded at the 83.12 in Patiala agriculture area. It is concluded with respect to GWQI that, the water quality of the Mukatsar District is poor as compared to the other districts in the study area.

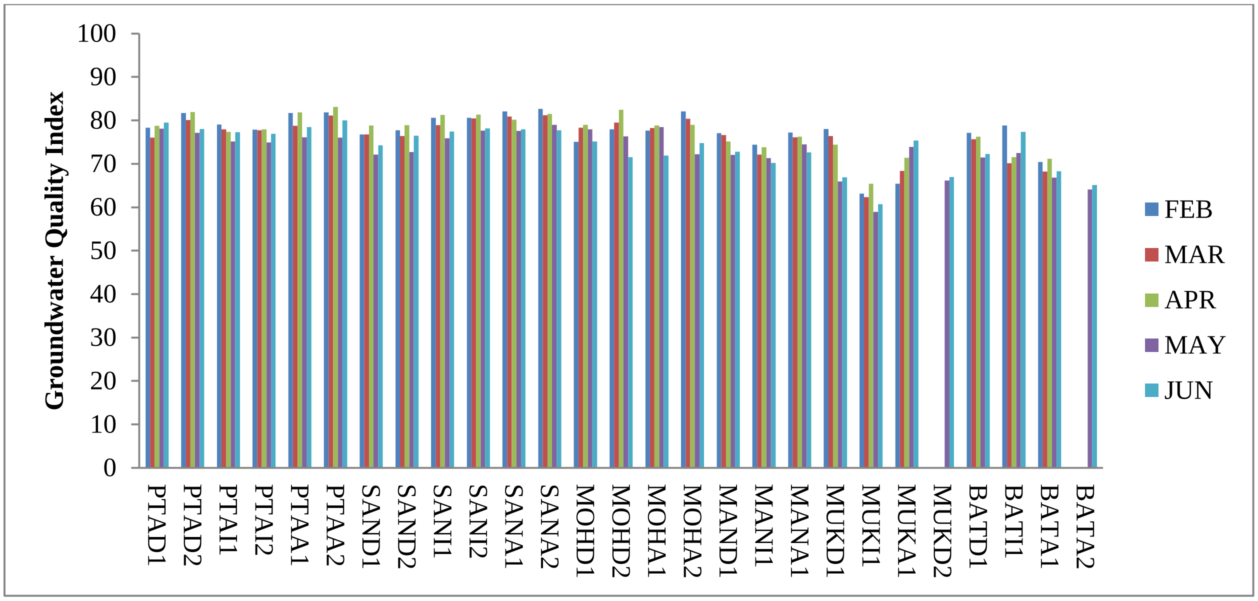


Figure 6.1 Variations of GQI in the study area

The groundwater quality index of all the districts lies near about 70 to 80 except the Mukatsar district. The groundwater quality of the Mukatsar district has higher concentration of physico-chemical parameters also shown in the chapter 5 of the report. The mean GQI variations are shown in Figure 6.2 which also indicates that the groundwater quality with standard deviations.

From Figure 6.2 it is found that the standard deviation of the Mukatsar (5.73) district and the Bathinda (4.35) district is on higher side and fall under the poor water quality. So from future point of view, there is need of continuous monitoring of the groundwater quality of these two districts.

The other districts such as Patiala, Sangrur and Mohali districts have good water quality as compare to the other three districts. The classification of GQI with different WQI shown in Table6.2.

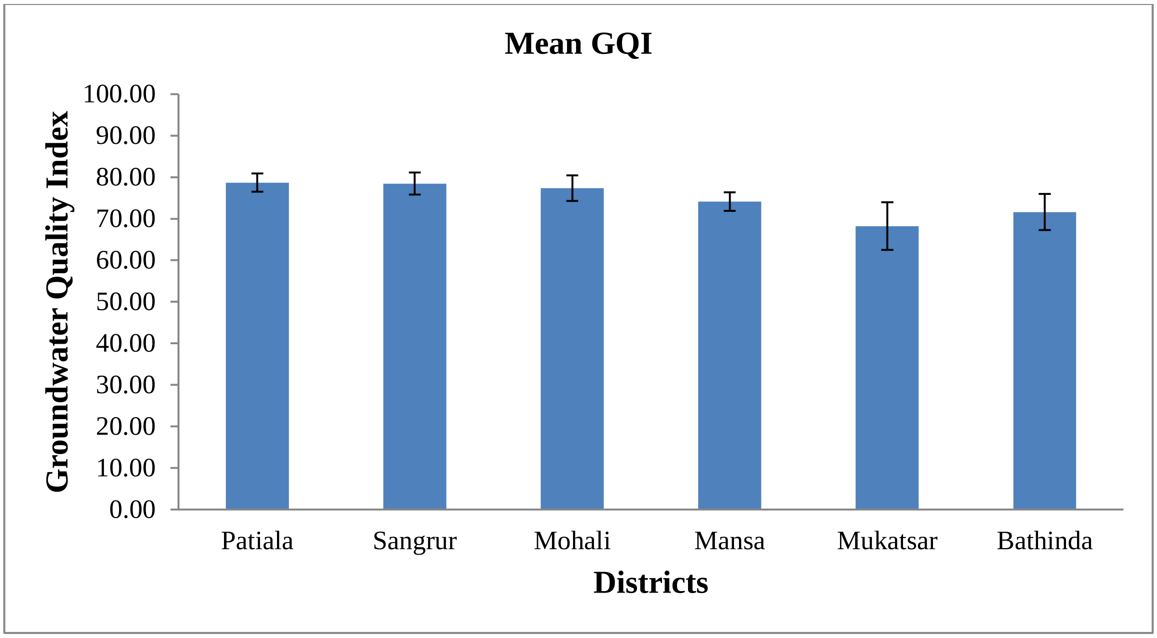


Figure 6.2 Mean Groundwater quality index.

Table 6.2 *Classifications of groundwater quality Index*

National Sanitation Foundation Water Quality Index (NSFWQI)		
WQI Value	**Rating of Water Quality**	**Districts Under the WQI value**
91-100	Excellent water quality	No district under this criteria
71-90	Good water quality	Mansa, Mohali, Sangrur & Patiala
51-70	Medium water quality	Mukatsar & Bathinda
26-50	Bad water quality	No district under this criteria
0-25	Very bad water quality	No district under this criteria
Canadian Council of Ministers of the Environment Water Quality Index (CCME WQI)		
95-100	Excellent water quality	No district under this criteria
80-94	Good water quality	Sangrur
60-79	Fair water quality	Bathinda, Mohali, Patiala, Mansa
45-59	Marginal water quality	Mukatsar
0-44	Poor water quality	No district under this criteria
Oregon Water Quality Index (OWQI)		
WQI Value	**Rating of Water Quality**	**Districts Under the WQI value**
90-100	Excellent water Quality	No district under this criteria
85-89	Good water Quality	No district under this criteria

WQI Value	Rating of Water Quality	Districts Under the WQI value
80-84	Fair water quality	Sangrur
60-79	Poor water quality	Patiala, Mohali, Bathinda, Mansa.
0-59	Very poor water quality	Mukatsar.

6.5 GROUNDWATER QUALITY INDEX FOR IRRIGATION PURPOSE

6.5.1 MAGNESIUM ABSORPTION RATIO (MAR)

The rate of crop yield depends on quality of water used for irrigation. For the irrigation purpose, generally two parameters such as Electrical Conductivity and Magnesium Absorption Ratio signify the groundwater quality for the irrigation use. The groundwater having high MAR affects the quality of soil and irrigation water. The groundwater having higher MAR makes the soils alkaline which led to reduce the agriculture yield (Kumar et al. 2007).

Eq. 6.5 represents the determination of MAR (Paliwal, 1972) in which the Ca^{2+} and Mg^{2+} are in units of meq/l.

$$MAR = \frac{Mg \times 100}{Ca + Mg} \qquad 6.5$$

The concentration of Mg and Ca are determined for each collected sample and MAR is calculated using Eq. 6.5. Fig 6.3 shows the value of MAR in the form of bar chart for the various sample collected in all the six districts.

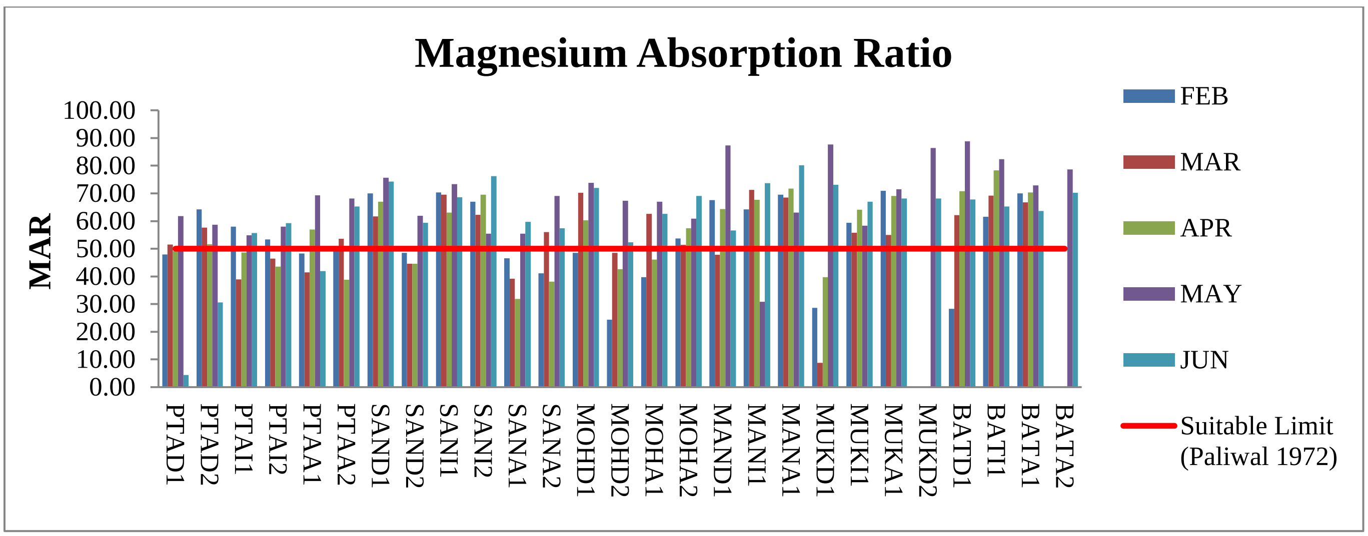


Figure 6.3 MAR variations in study area

It is seen from Figure 6.3 that, MAR value varies from the minimum value of 4.38 in Patiala Domestic to the maximum value of 88.42 in Bathinda Domestic area. It is also found that the mean value of the MAR in the study area is above the permissible limits i.e. above 50 as shown in Table 6.3

Table 6.3 *Descriptive statistics of MAR in study area*

District	Max	Min	Mean	Std deviation
Patiala	69.32	4.39	50.94	12.65
Sangrur	76.23	31.86	59.25	12.38
Mohali	73.84	24.38	56.53	12.60
Mansa	87.38	30.83	65.63	13.29
Mukatsar	87.64	8.80	60.69	19.72
Bathinda	88.84	28.26	68.66	12.71

Table 6.3 shows the statistical analysis of MAR reported in all the six districts. The mean MAR in Bathinda and Mukatsar are at the extreme value. Figure 6.4 shows the graphical representation of the mean MAR in all districts.

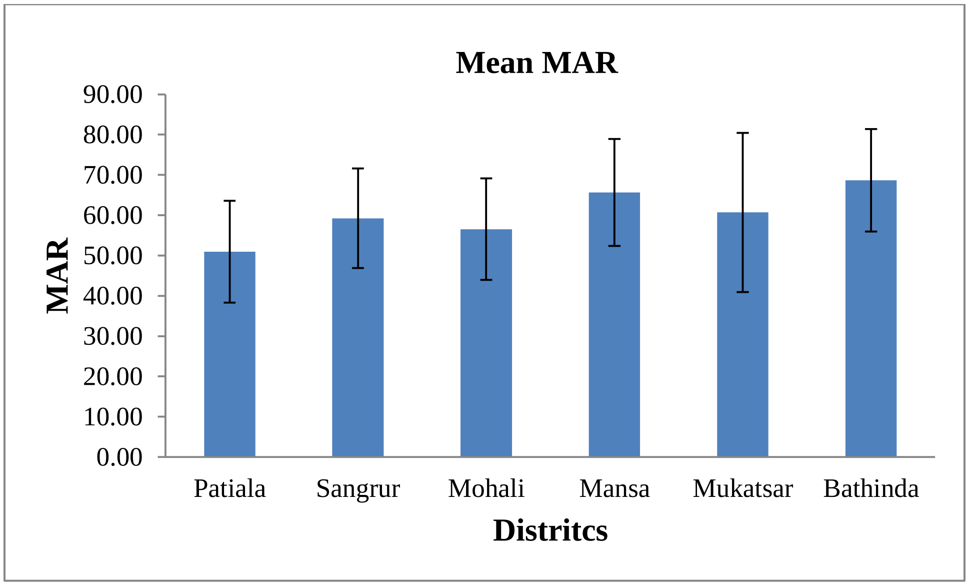


Figure 6.4 MAR variation in all districts

6.5.2 ELECTRICAL CONDUCTIVITY (EC):-

EC is the main parameter of identifying the total salt concentrations in soil. It also affects the crop yield. The large variations of EC were noticed which varies from 294 µS/cm to 11640 µS/cm at Bathinda Industrial sector in June (BATI1) and Mukatsar Industrial sector in June respectively. The variations of EC in all five months are shown in Figure 6.5. It is observed that the maximum EC was recorded in Mukatsar district in both agriculture and industrial area of the district. In the period of the five months from February to June, it is observed that the EC in Agriculture area of Patiala District is lying within the permissible limits (483.3 to 569.7µS/cm).

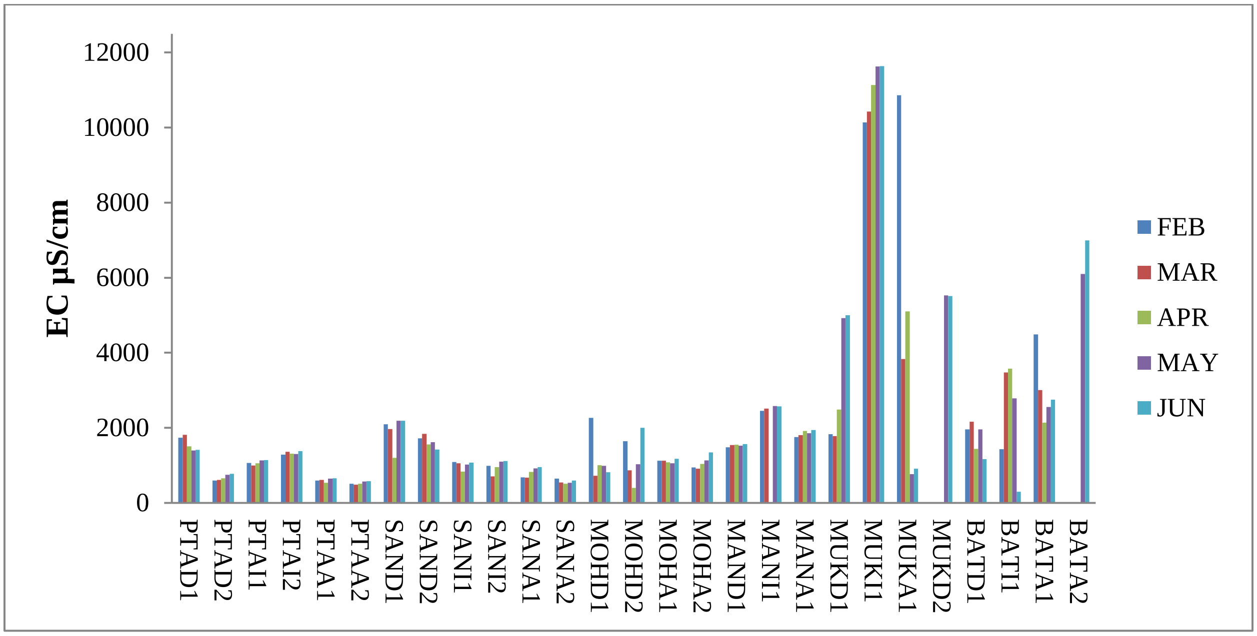


Figure 6.5 Variation of EC in different sampling sites

Table 6.4 and Fig 6.5 shows the statistical analysis of EC in district wise. From Table 6.4 it is found that the mean concentration of EC in Mukatsar and Bathinda district are beyond the permissible limits.

Table 6.4 *Mean concentrations of EC in all the districts of study area*

District	Mean EC	Max	Min	Std .deviation
Patiala	965.03	1811.00	483.30	405.64
Sangrur	1154.06	2192.00	509.50	516.34
Mohali	1132.68	2268.00	394.80	422.22
Mansa	1803.38	2579.00	2.64	641.98
Mukatsar	6087.67	11640.00	761.30	4024.18
Bathinda	2839.12	6993.00	294.00	1720.82

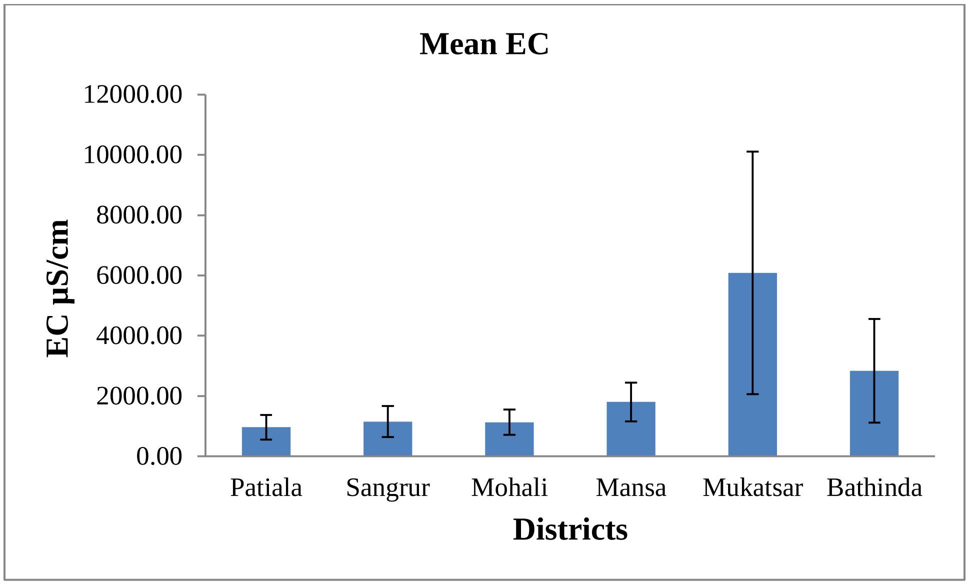


Figure 6.6 Means of EC in all districts

From Figure 6.6 it is found that, the mean value of EC of the district Mukatsar and Mansa has higher concentration of the Salts.

The agriculture parameters such as EC and MAR in the present study is compared with the classification of groundwater made by the Wilcox, 1955 for EC and Paliwal,1972 for MAR as shown in Table 6.5.

Table 6.5 *Irrigation Water Quality Classification*

Parameter	**Reference**	**Range**	**Classification**	**Districts under the classification**
EC	Wilcox (1955)	Less than 250	Excellent	No District fall under this criteria
		250-750	Good	Patiala & Sangrur
		750-2250	Permissible	Sangur & Mohali
		2250-5000	Doubtful	Mansa & Bathinda
		>5000	Unsuitable	Mukatsar, Mansa & Bathinda
EC	IS 11264-1986	Less than 1500	Low	Patiala, Sangrur & Mohali
		1500-3000	Medium	Mansa , Bathinda & Mohali

Parameter	Reference	Range	Classification	Districts under the classification
		3000-6000	High	Mansa & Bathinda
		>6000	Very High	Mukatsar
MAR	Paliwal 1972	Less than 50	Suitable	Some part of Patiala,Sangrur & Mohali
		Greater than 50	Unsuitable	Bathinda, Mukatsar & Mansa

The classification of EC is also compared with the IS 11264-1986 for irrigation water quality parameters.

From the Table 6.5 it is found that groundwater of the study area has a major salts concentration and EC is generally increased with increase in the ionic concentrations in the groundwater (Shah et al. 2015). It is found that the water sample from Bathinda, Muktsar and Mansa district was unsuitable for irrigation as per the classification of groundwater made by the Wilcox, 1955 for EC where as water sample from Muktsar district was highly unsuitable for irrigation as per the classification of groundwater made by the IS 11264-1986 for EC.

Similarly the water sample from Bathinda, Mukatsar & Mansa MAR district was unsuitable for irrigation as per the classification of groundwater made by the (Paliwal 1972) for MAR.

6.6 CONCLUDING REMARKS

The present chapter classifies the groundwater of the study area form the drinking as well as irrigation point of view. The overall quality of the groundwater has been quantified in the form of water quality index which is calculated by considering the presence of various physico-chemical parameters in groundwater with various concentrations. It is found that the overall groundwater quality of the study area varies from the marginal to medium level according to drinking point of view. From irrigation pint of view, it is found that Bathinda, Mukatsar & Mansa district is unsuitable for irrigation with respect to both MAR and EC criteria. So there is need for the continuous monitoring of the groundwater for analyzing the groundwater quality and to make the preventive measures for its improvement.

CHAPTER 7

CONCLUSIONS

The present study is conducted to analyze the groundwater quality scenario of Malwa region, Punjab. Groundwater sample is collected from six districts of study area. The water sample is collected from domestic, agricultural and industrial sector of each district. The physic-chemical testing of water sample is made in the laboratory and analysed its suitability with respect to domestic as well as agricultural use. From the above study, it is found that the groundwater quality of the study area varies from marginal to medium levels according to GQI analysis with respect to domestic purpose. The physico-chemical analysis indicates the salt dominance of the cations such as calcium and magnesium and anions such as sulphates, chlorides and nitrate. The order of the salt dominance in the area is $SO_4^{2-} > Mg^{2+} > NO_3^{-} > Ca^{2+}$. The Strong correlations are existed between the EC and other parameters such as TDS (r=0.972), Alkalinity(r=0.342), TH (r=0.781), Ca^{2+} (r= 0.634), Mg^{2+} (r=0.771), Cl^- (r= 0.954), SO_4^{2-} (0.694), and NO_3^- (r=0.600) at significant levels of $p<0.01$. The pH value shows the basic nature of groundwater but lies in permissible limit as per IS 10500-2012. The EC content of groundwater in study area is at its peak value in the Mukatsar and Bathinda districts. From the correlation analysis it is shown that the EC of the groundwater of the study area affected by the salts concentration in the groundwater of study area. It is also found that the NO_3^- content is beyond its permissible limits as per IS 10500-2012 and WHO guidelines value and showing the negative trend with the depth of the groundwater table. It is found that the groundwater at the shallow depth have higher nitrate content as compared to the groundwater table at deep depth. This behavior of the nitrate ions shows that, the use of fertilizers in agricultural activities impact on increase in nitrate concentration in groundwater. Since there is a high possibility of mixing of nitrate in shallow groundwater table, the concentration of nitrate found more in comparison to when the groundwater table is at higher depth.

Also the quality of the groundwater is examined with respect to its use for agriculture purpose and for this EC and MAR of the samples is determined. It is found that that Bathinda, Mukatsar & Mansa district is unsuitable for irrigation.

FUTURE SCOPE

1. The present study analyzed the various physico-chemical parameter present beyond its permissible limit in the groundwater of the study area but the source of the certain chemical parameter is not identified in the present study which may be the future scope of this analysis.
2. The solution of the groundwater contamination problem is also not studied in the present analysis which may also be the future scope of the study.

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