MONITORING AND ASSESSMENT OF GROUND WATER QUALITY IN PALWAL DISTRICT

A THESIS SUBMITTED
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by

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Under the Guidance of

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CANDIDATE DECLARATION

I hereby certify that the work is being presented in thesis entitled "**Monitoring and Assessment of Groundwater Quality in Palwal District"** in fulfillment of the requirements for the award of the Degree of Doctor of Philosophy in Chemistry, submitted in School of Basic and Applied Sciences, Galgotias University, Greater Noida is an authentic record of my own work carried out by me during a period April 2019 to September 2022 under the supervision of **Prof. Meenakshi Pundir**,

The matter embodied in this thesis has not been submitted by me for any other degree of this or any other University/Institute

(Ritu Bir)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge

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[1] Bir, R., Singh, M (2020). Study of Biosorption of Heavy Metals Using Agricultural and Microbial Biomass: A Review. Pollution Research, Vol 39, Nov Suppl. Issue, 2020; Page No.(153-160).

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[1] Bir, R., Singh, M (2021). Pattern and Consequences: Australian Bushfires. Paper presented atIIT, Delhi.

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Abbreviations Used

APHA	American Public Health Association
BIS	Bureau of Indian Standards
BG	Brilliant Green
CAI	Chloro Alkaline Index
Km^3	Kilometer cube
KI	Kelly Index
mg/l	Milligram/liter
M	Meter
Mm	Millimeter
MO	Methyl Orange
m^3	Cubic meter
mEq/L	Milliequivalent per liter
MH	Magnesium Hazard
NTU	Nephelometric Turbidity Unit
NP	Nanoparticles
PANI	Polyaniline
PI	Permeability Index
%	Percentage
ppm	Parts per million
RSC	Residual Sodium Carbonate
SAR	Sodium Absorption Ratio
SSP	Soluble Sodium Percentage
Sq Km	Square kilometer
UNO	United Nation Organization
UN	United Nations
µS/cm	micro siemens/cm
UNWWD	United nation world water development (UNWWD)
WHO	World Health Organization

Chapter-1

Introduction

1.1Introduction

Water is elixir for living. It is required by all living organisms for their well-being and survival. Importance of water has been even mentioned in Rigveda, our oldest manuscript. Our sages since time immortal have stressed on the importance of pure water. Over more than 71% of earthis covered with water and when seen from space our world looks like a blue dot hence the name 'Blue Planet'. In historical times all major towns and cities were situated near the water bodies. Seventy percent of the body is made up of water and all life processes are directly or indirectly dependent on water. It is not only essential for humans but plants and animals also need water for their survival. Water is essential for maintaining body temperature,energy generation during respiration and removal of wastes from the body. Availability of clean drinking water is an important issue in developing countries(Treacy, 2019). Water distribution on earth's surface is highly uneven. 97% of water is found as salty water in the form of oceans and only 3% is found as fresh water. Of the freshwater, 69% is locked in polar ice caps, 30% as groundwater and only 1% is accessible asrivers,streamsand swamps in form of surface water thus earth's surface contains only one percent of water which can be used by humans and ninety nine percent of usable quantity is stored below the ground as groundwater.

Surface water and groundwater are the most common sources which satisfy the drinking and irrigation needs.80% of Indian population is dependent on groundwater for satisfying its thirst. Traditionally groundwater is considered clean source of potable water as various strata of soil, sand and gravel filter out many microorganisms and chemicals as water percolates below but many anthropogenic activities which include eloquent use of chemical fertilizers and pesticides in farm-lands, leachate from mismanaged landfills untreated wastes from septic tank and toxic chemicals from underground storage tanks have contaminated the groundwater sources. Drinking contaminated water can have serious health effects(Kumar, 2006) therefore it is necessary to curb the activities which involve the degradation of groundwater quality.

1.2 Major Sources of Groundwater Pollution

Main sources of groundwater pollution can be categorized into:

1.2.1 Agricultural Sources

•Fertilizers

Modern agriculture involves the use of fertilizers to increase the crop yield by providing them with additional nutrients like nitrogen, potassium and phosphorus but all fertilizers used are not absorbed by plants, extra fertilizers are lost as runoff or accumulates in the soil. High use of nitrogen fertilizers along with high solubility of nitrates in water causes groundwater pollution (Farhadinejad et al., 2014) and is a major health threat.

•Pesticides

Pesticides are used to control pests which can disrupt crop yield. Pesticides used can mix with water leading to pesticide leaching, move through the layers of soil and contaminate groundwater. Water soluble pesticide and sandy soil further increases the pesticide leaching(Perez Lucas et al., 2018).

1.2.2 Industrial Sources

•Mining

Minerals are necessary for the economic health of any country but extracting minerals, processing ores, discharged mining effluents and seepage from tailings can threaten the groundwater resource(Gupta et al., 2016). Water pollution caused by waste and derelicted mining sights needs to be managed for decades. Mechanizing the mining operations has increased the risk of groundwater pollution multifold.

•Industrial effluents

Increasing industrialization has resulted in an increase in discharge of toxic chemicals in the layers of soil and then their subsequent washing down of the pollutants in the groundwater(Li et al., 2017). The pollutants released by industrial activities contain many toxic chemicals, acids, bases, dyes and heavy metals which are non-biodegradable sources of water pollution.

•Storage Tanks

Various kinds of tanks situated above or below the ground are used in industries for storing oil, chemicals, gasoline and various toxic chemicals. Any leakage from such tanks can result in leaking of contaminants which can have lethal effects on groundwater quality.

•Hazardous Wastes

Waste sites of industries contain many barrels of hazardous material, any leakage of barrels or accident at such waste sites can lead to infiltration of contaminants below the soil leading to contamination of groundwater(Rotaru et al., 2008).

1.2.3 Municipal Sources

•Landfills

Municipal solid wastes are collected from houses, hotels, schools and offices and dumped in sanitary landfills where aerobic decomposition results in degradation of organic wastes into smaller particles along with the release of a chemical cocktail called leachate. Landfills have a protective layer at the bottom to prevent leakage of leachate into groundwater but badly designed landfills can result in leakage of contaminants below in the groundwater. Many researches have shown leachate as a major source of groundwater pollution(Mor et al., 2006; Al-Sabahi et al., 2009)

•Leaking sewage pipes

Leaking effluents from sewer lines contain raw sewage which mostly consists of faecal matter, soaps, detergents, oil residues and may contain industrial chemicals. These leaking sewer pipes can contaminate the groundwater supply by addition of salts, microorganisms, trace metals and heavy metals(Reynolds et al., 2003; Held et al., 2006). Leaking pipes can increase the BOD and COD of groundwater.

•Septic System

These are the waste water disposal systems for those buildings which are not connected to the main sewer system. These septic systems drain the wastes released at a slow rate but a badly designed and maintained septic system can leak the effluents in the groundwater thus contributing to groundwater pollution(Rock et al., 2017).

1.3Reducing the groundwater pollution

Both surface water and groundwater are interconnected, presence of contaminants can contaminate both the sources of water therefore proper management approach is necessary. Once effluents seep inside the soil pores and enter inside the aquifer it becomes very hard to reinstate the quality of groundwater. Groundwater is used by a large sector of population for quenching its thirst and meeting other domestic needs. Agricultural activities are also dependent on groundwater for irrigation

The Green revolution has brought a quantum jump in the food production in India especially the state of Haryana which has been possible due to regular use of groundwater for irrigation. High agricultural yields brought economic prosperity which along with rapid pace of urbanization, population growth and industrialization have degraded the water quality of surface and groundwater. Various human activities,chemicalfertilizers and pesticides used to promote crop productivity,untreated waste disposal both from domestic and commercial units have led to decline of quality of groundwater in theHaryana state.

Managing water quality takes into account both the existing quality of water and its scope in future use. Ensuring proper water quality is not only important for polluted areas but also as a precautionary measure for safe areas. Analysingwaterqualityis necessary for all resources of water. Surface and groundwater quality is necessary to be maintained at a level designated for its intended purpose. Once polluted, cleaning groundwater reserves is an extremely tedious and a costly affair hence mitigation of groundwater contamination is essential and proper management approach should be followed to curb the entry of pollutants in the aquifers and proper study should be done to determine the effect of wastewater entering the groundwater aquifers.

1.4 Objectives of designated research work

The proposed research work focuses on analysis of groundwater quality and detailed information regarding the quality deterioration in the Palwal District, Haryana. The main objectives of this exhaustive research are:

1. To find quality of groundwater in villages of Palwal District.

2. Tofindconcentrationcations, anions&heavymetalsfoundgroundwater.

3. To compare the concentration of cations, anions and heavy-metal obtained inresearch work to the BIS and WHO standards.

4. To study the geochemistry of the area by groundwater quality data.

5. To find out the geochemical facies of the area.

6. To study groundwater chemistry by correlating groundwater quality data and geochemistry of the area.

7. To findappropriatenessofwaterof the studied area for potability purpose.

8. To assess possibilities of water related diseasesinvillages of study area.

9. Toinvestigate appropriateness of groundwater usage for watering crops.

10. Interpretation of ground water quality data to be fit for drinking and irrigation use.

11. Investigate and calculate the water Quality Index so as to transform the complex dataset into a simplified index which is easily understoodbygeneral public.

12. To synthesize a novel ternary bio-nanocomposite for the removal of brilliant green and methyl orange dyes which are used in textile industry.

Chapter-2

REVIEW LITERATURE

2.1

Groundwater is an important natural resource required by millions of people both for potable uses and irrigation. It is very essential to maintain the quality as well as quantity of groundwater(Juneja et al., 2013) so that it can be designated for its intended purpose but anthropogenic activities like industrialization, agriculture with excessive use of fertilizers and pesticides, faulty sewage drainage have deteriorated the quality of groundwater to such an extent that regular consumption of such contaminated water can lead to serious health implications in living beings.

Presence of contaminants in groundwater, greater thanpermissible limit can hinder the potable use of groundwater and since water is a vital compound essential for survival, studying about the groundwater quality has been the subject of many research scholars. Anthropogenic activities like industrialization(Krishna et al., 2019; Li et al., 2021)), modern agriculture methods(Hallberg., 1987; Jeyaruba et al., 2009) and mismanaged municipal wastes(Deshmukh et al., 2016; Rajkumar et al., 2010) have a negative influence on thegroundwaterquality which can hinderpotable use of groundwater. Presence of heavy metals(Rahman et al., 2020; Vetrimuruganetal., 2017), nitrates(Prakash et al., 2006; Wick., 2012), organic matter(Lapworth., 2012)groundwater an issue of serious concern. All the effluents released along with runoff or rain seep through the soil pores and contaminate the ground aquifers. Groundwater contamination in India has reached alarming levels and needs urgent monitoring.

Northern plains of India are densely populated areas due to presence of fertile alluvial landswell connected transport means and perennial rivers. Due to easy availability of raw materials and cheap labour northern plains of India can boast of a well-established industrial sector. Industries, increasing population along with the labour migration from surrounding areas contribute to large amounts of waste generation. Northern plains especially Punjab and Haryana are the food bowls of India and use of extensive fertilizers in cultivated lands contributes to higher amounts of nitrates and phosphates in the groundwater(Dixit et al., 2021). Number of Haryana villages had a fluoride concentration in groundwater(Meenakshi et al., 2004; Kumar et al., 2004) that causes dental fluorosis in children. Mewat district, Haryana because of both industrial and domestic wastewater dumping the groundwater parameters have crossed much beyond the permissible Indian limits (Prakash et al., 2012). Growing urban clusters have deteriorated the groundwater quality in Rohtak and Sonipat district of Haryana(sheikh et al., 2017).

2.2 Review work done on Haryana for surveying the groundwater quality.

Rout et al., (2011) analyzed the Physico-chemical parameters of groundwater in Ambala cantonment, Haryana to check the suitability of groundwater for potability. 26 samples of water were randomly picked from various parts of study area and were investigated for different physicochemical parameters present in groundwater. Obtained results were collated with permissible limits set (WH)and (BIS). All the parameters were within the prescribed limit. Correlation matrix was also found out. pH values obtained showed water has pH value greater than seven and the TH was 116.6 mg/l indicating the water needs to be softened before use.

Singh et al., (2010)analyzed the groundwater quality by testing the various Physico-chemical parameters from 15 different locations of Ambala, Haryana. The results obtained were collated with the standard limits set byBIS, WHO& (ICMR) Indian council of medical research. Correlation matrix was also calculated. EDXRF technique was also used to find the elemental analysis of three samples. The study concluded by sayinggroundwater quality of the studied location is of mediumthus needing suitable treatment before use.

Pradhan et al., (2011)analyzed the groundwater quality in Gohana district of Haryana to check its usability for irrigation purpose. 60 samples of groundwater were picked from selected locations of the studied location inpremonsoon&aftermonsoon season and were investigated for selected Physico-chemical parameters which included pH, cations like (sodium, calcium, potassium and magnesium) EC, anions (chloride, nitrates, fluoride, carbonates, bicarbonates), water quality indices like sodium absorption, Mg/ Ca ratio. pH was 8.67 in the premonsoon and 8.48 in postmonsoon season respectively. Most abundant cation was Na followed by Mg, Ca, K in both the seasons. SAR value fluctuated from 3.23 to 36.1 for pre-monsoon period. Correlation matrix confirmed that EC is correlated with Mg, Ca, Na and Cl. The study came to a conclusion that the groundwater can be used suitably for agricultural purpose.

Warish et al., (2017) assessed the effect of industrial contaminants on cultivated farmland and quality of groundwater in Mewat region of Gurugram, Haryana. Water samples were collected and sampled for EC, TDS, alkalinity, pH, DO, phosphates, sulphates, BOD, COD, total hardness and nitrates. The results obtained were compared with BIS and the tested parameters were beyond the permissible limit. The water quality was having a negative impact on soil chemistry, health of humans and livestock and agricultural farms. It was concluded that water should be treated before consumption.

Sultan et al., (2012) investigated the groundwater samples from Safidon and Julana region of Jind district, Haryana. Collected water samples were tested for selected Physico-chemical parameters.Parameters obtained were collated with WHO, BIS and ICMR values for potable water quality. Correlation coefficient was calculated and t-test was done for comparing the results. The study concluded that high variability was observed inwater quality ofstudied location.

Sanjay et al., (2013)analyzed the groundwater quality which was used for irrigating the crops in Kalanpur region of Rohtak district, Haryana. Groundwater was picked from tube wells and various Physico-chemical parameters were examined to determine the groundwater spatial variability. EC of the samples varied from 2-3 ds/cm, pH was 7.08-8.81 and SAR range varied from 9-12 (m mol/l). 22% of the water samples examined were found to be of good quality, 51.1% saline and 26.9% water samples were saline.

Ahmad et al., (2020)analyzed the groundwater quality in Trans Yamuna alluvial area in Palwal district of Haryana and upon testing the various Physico-chemical parameters it was concluded that water is safe for irrigation but high TDS in some of the samples can lead to salinity problem when used for a longer time.

Gupta et al., (2009) collected and analyzed the groundwater samples for the selected Physicochemical parameters in Kaithal city, Haryana from twenty different sampling points and concluded that few of the water samples were non potable as the parameters were above the permissible limits of Indian Council of Medical Research and an attempt was made to findquality of consumable water in the city.

Kumari et al., (2014)surveyedthe(WQI) and correlation analysis for quality ofwater in Smalkhan region of Panipat, Haryana to categorize the water quality for potable use, entertainment and other uses. Various Physico-chemical parameters of water were measured which were evaluated to find (WQI) water quality index and correlation metric which wasrange 89.09 – 146.67. It came into light that three of the fourteen samples had good water quality, eleven fell in the range of poor category which reflected that majority of groundwater is not fit for drinking purpose due to contamination of groundwater by anthropogenic activities.

Krishan et al., (2016)analyzed the groundwater quality of Mewat district, Haryana to study its use for drinking and agricultural purpose. Along with the declining water table level, salinity was seen as the major problem in the study area. It was observed that both before monsoon as well as after monsoon season TDS levels in collected waterduringtimeframe (2011-15) was highly inconsistent. It was suggested that constant monitoring of groundwater samples is required to have a clear picture of the study area so that solutions can be found out accordingly.

2.3 Review work done nationally for surveying the quality of groundwater

Shivaraju., (2012)analyzed and carried the complete analysis for potablewaterqualityin Mysore city. Water samples were taken from overhead tanks of studied location. Obtained valuescompared with the permissible limitset up by BIS and it was observed some of the obtained samples were beyond the desired values set and the microbial analysis which was done through MPN method revealed a high number of harmful bacteria in the drinking water. The study suggested use of alternative methods for control of contamination in drinking water.

Kaur et al., (2017)analyzed the groundwater quality in Malwa region, southwest part of Punjab and revealed that majority of water samples collected had anions, cations and other Physico-chemical parameters above the Indian standard permissible limits, the area also had hard water and the fluoride content was greater than allowed limits in seventy five percent of the samples. Concentration of arsenic, a heavy metal showed variation with changing season and showed an increase in winter season. Sodium adsorption ratio and sodium percentage revealed water can be used for irrigation and suggested continuous monitoring of groundwater quality should be done for effective use of water.

Shivaprasad et al., (2014) assessed the water quality index of Mandya city, Karnataka. 40 GW samples were taken and subjected to selected Physico-chemical parameters including calcium, magnesium, chlorides, nitrates, sulphates, fluoride, iron, alkalinity, TDS, total hardness, alkalinity which are necessary for finding WQI,asis an intelligent instrument to predictquality of water.

Nirbhavane., (2016)worked on the groundwater qualityaroundAmbarnath industrial belt in Maharashtra. Groundwater samples from six different sampling points were collected for a period of 6 months (June 2013-January 2014) and studied for various Physico-chemical parameters which included pH, conductivity, temperature, TDS, alkalinity, chloride, total hardness. Obtained results were compared with the permissible limit set by WHO and BIS. It was concluded that water in open wells was contaminated more as compared to bore wells and hand pumps and the water in Kanasi Gaon and Bhimnagar showed a higher value of EC as compared to other places in the studied area.

Adimalla (2019) evaluated the quality of groundwater in Telangana state for various Physico-chemical parameters and tests showed that fortyeight % of the groundwatershowednitrate concentration more than the maximum permissible limit allowed by World Health Organization. High fluoride amount occurred in fifty seven percent of the samples and results indicated that children were more prone to health conditions on drinking contaminated water with respect to nitrates and fluoride in the investigated location.

Garg., (2004)assessedgroundwater in four villages of Jind district, Haryana and concluded variations occurred between analyzed samples in relation to their chemical composition, major portion of collected groundwater samples had parameters above the prescribed limit and concentration of fluoride varied from .3 to 6.9which resulteddental fluorosis, especially among small children of the selected area.

Yadav et al., (2012)analyzedthegroundwater status in the Agra city from twelve different sampling points and assessed upon complete monitoring of groundwater that many parameters of water were higher than the permissible limit and concluded that groundwater was not of good quality for drinking.

Ranjana., (2012) collected and analyzed groundwater samples from thirteen different locations of Kotputli town, Rajasthan. Study ofselectedPhysico-chemical parameters was undertaken and also a comparative study of samples in different seasons was conducted and was concluded that there was no significant change in parameters in different seasons but EC anTDS decreased rainy weather whereas Total Hardness and alkalinity increased after the rains.

Kaushik et al., (2004)analyzed the groundwater quality of Faridabad and Rohtak, two cities of Haryana and groundwater pollution status was compared by using deviation index. High amount of TDS, hardness, alkalinity and electrical conductivity was found in groundwater of both the cities and seventy four percent of water samples from Rohtak had high levels of fluoride. Disposal of wastes had an important part in groundwater pollution.

Kumar et al., (2020)analyzed the groundwater quality in Ranebennurtaluk district of Karnataka. Five villages which were affected by rapid industrialization were selected to find the quality of drinking water. ComparingPhysicochemical results analysis showed that majority of samples were fit for consumption and irrigation purpose. The average pH value of groundwater is 7.5-8.5 which is within the prescribed limit but the pH value is increasing which makes the water unfit for consumption. Fifty percent of water samples collected, had chloride amount exceeding 250 mg/l which could lead to cardio vascular problems, also twenty five percent of water samples showed total hardness greater than 300 mg/l which is undesirable.

Saleem et al., (2016)analyzed the groundwater quality using the nine Physico-chemical parameters including Nitrates, Fluoride, Sulphate, Magnesium, Calcium, Total Hardness, Total Hardness, TDS and Alkalinity from ten different locations of Greater Noida, Uttar Pradesh. It was observed that ninety percent of samples collected were of good quality and only ten percent of water samples had moderate or poor quality. They proposed for water treatment before its usage and protection of study area from further contamination.

Annapoorna et al., (2015)analyzed quality of groundwater in twenty-two wells situated in the rural areas of Ingaldhal copper mines of Chitradurga district, Karnataka for drinking purpose based on various Physico-chemical parameters studied ingroundwater. Most of the samples studied were above the guidelines set by national (BIS) and International (WHO) for drinking purpose.

Nirmala., (2013)analyzedqualityofwater for consuming use and irrigating crops under the influence of changing seasons. Mysore city, Karnataka was divided into four zones and water samples were tested both before monsoon and after monsoon. Various Physico-chemical parameters were done and results were compared with both the national and international guidelines, it was seen some of the water samples met the standards and some samples exceeded the permissible limits.

Priyadarshi et al., (2019) assessed the groundwater quality for various Physicochemical parameters in towns of Iglas and Beswan in Aligarh district of Uttar Pradesh. pH of the towns was 7.1 and 7.7 respectively. Overallmajor parameters were within the desired limit except high concentration of chloride in Iglas but the study concluded that wider spatial and temporal scales are advised for detailed analysis of groundwater.

Jadhav et al., (2012)analyzed the groundwater quality in borewells of Ajara district, Maharashtra for selected Physico-chemical parameters present in groundwater. The results obtained were collated with both BIS and WHO quality values and it was observed forty eightout of fifty-one water samples were within the desired limit and were safe for consumption.

Anilkumar et al., (2015) studied themunicipal solid wastes leachate effect on quality of groundwater in Thiruvananthapuram district, Kerala. Samples of groundwater were collected from wells dug one km away from solid waste dumping site and control samples were taken ten km away from the dumping site both in pre monsoon and post monsoon. It was concluded after testing on various parameters that quality of groundwater near the dumping site of wastes was more polluted than the control samples in both the seasons.

Karthik et al., (2019) analyzed that the global climate change has led to water crisis in Velliangadu area of Coimbatore district. To overcome the water shortage, number of bore wells have been dug and the water obtained from these bore wells was assessed for selected Physico-chemical parameters including pH, Alkalinity, TDS, Chloride, EC, Total Hardness and it was concluded that water from these bore wells instudied area was withinguidelines set by BIS and WHO standards.

Prasad et al., (2019)analyzed the groundwater quality in Obulavaripalli Mandal YSR district in Andhra Pradesh based on water quality index. Groundwater from twenty different locations was taken and Physico-chemical parameters including pH, Alkalinity, TDS, Chloride, EC, total hardness, Sulphate, fluoride, magnesium were evaluated & it was concluded 30% of collected waterwas below the set limits provided by BS and ICMR, 40% were within the borderline limits and 30% of the groundwater samples parameters were beyond the guidelines set by national and international standards.

Alagumuthu et al., (2010)surveyed the complete analysis of groundwaterofSankarankovil (Tenksai district of Tamil Nadu) which is the only source of quenching thirst in this district. Selected Physico-chemical parameters including pH, Alkalinity, TDS, Chloride, EC, total hardness, magnesium, carbonate, calcium, fluoride and chloride were measured. Correlation coefficient calculation among the various Physico-chemical parameters was performed and it was observed that majority of water samples did not comply with BIS and WHO drinking water standards. Dental fluorosis was common among people, especially among children due to fluoride level varying from 0.66 to 3.84 mg/l. Majority of groundwater samples were unsatisfactory and required a treatment before using for potable purpose.

Rani et al., (2016)analyzed the groundwater quality in HSIIDC industrial area of Sonipat (kundli), Haryana. Selected Physicochemical parameters including pH, Alkalinity, TDS, Total suspended solids, water quality index and correlation coefficient were measured. Twenty water samples from randomly selected locations of investigated area were picked and out ofthese 10 samples were within set limit provided by BS& ICMR and the remaining samples required some treatment before using for drinking purpose.

Ramakrishnaiah et al., (2009)analyzedthe(WQI) for groundwater of Tumkur taluk, Bangalore. Picked water samples were subjected to complete physical and chemical analysis of ground water. WQI of water samples varied from 89.21-660.56. High amounts of Physico-chemical parameters were responsible for increasing the WQI value. It was concluded that water of surveyed area needed treatingbefore being consumed and requires to be protected from further contamination.

Kalra(2012)surveyedgroundwater in five blocks Bhojpur district of Bihar and from each block, ten samples of groundwater were taken and assessed for selected Physico-chemical parameters present in water. The results obtained werecollated withnational and international limits and it was observed there was a wide variation between the various parameters and only few water samples met the required guidelines and majority of water samples neededchemical treatment before drinking and it was also proposed chemical analysis of water samples should be done on regular basis to ensure that water quality is not further contaminated.

Verma et al., (2017) examined the quality of groundwater in Sabour block of Bihar. Fifty-nine water samples from selected places of studiedareawere selected to examine the groundwater for potabilityand watering crops.SelectedPhysico-chemicals parameters including pH, EC, calcium, magnesium, bicarbonate, sodium, magnesium, chloride, carbonate and fluoride were measured. Using the radial basis function, surface maps of groundwater quality were prepared. Larger number of the water samples had thePhysico-chemical parameters within the values set thus it was concluded ground water ofstudied location could be used for drinking and watering purpose.

Dass (2016)surveyedgroundwater and municipal groundwater in Kaithal district of Haryana to check its utilization for drinking purpose. Physico-chemical parameters which includedwereanalyzedout and results obtained were collated with national and international set values. It was observed that total hardness, TDS, fluoride and magnesium level exceeded the permissible limit set for consumption purpose.

Logeshkumaran et al., (2015)evaluatedthe Physicochemical parameters and geochemical parameters of groundwater. Twentyfourgroundwater selected places of studied location were selected and tested for complete analysis of water. Obtained results were examined with BIS and WHO drinking water limits. It was seen that groundwater varies from being fresh to moderately brackish. Sodium and chloride are the most important cations and anion present in groundwater. Chloride, magnesium and calcium are within the permissible limits barring few water samples. It was concluded majority of watercan be used for consuming purpose.

Mohan et al., (2013) surveyed the contamination of groundwater in Hapur district, Uttar Pradesh. Groundwater samples were randomly picked from hand pumps located at different locations of study area and WQI was analyzed using the selected Physico-chemical and biological parameters including pH, EC, TDS, chloride, fluoride, nitrate, sulphate, total hardness, BOD, DO and COD. Results obtained were compared by the guidelines set by BIS and WHO. Average values obtained for pH- 7.86, sulphate-160.39 mg/l EC- 1206.67 mho/cm, TDS- 734.17 mg/l, fluoride- 0.77 mg/l, nitrate- 45.99 mg/l,COD- 12.79 DO- 4.08chloride- 85.50 . It was concluded that WQI of Hapur district is of poor quality and needs treatment before it can be used for drinking purpose.

Dandwate., (2012)analyzed the Physico-chemical analysis of groundwaterfrom various investigated places in Kopargaon, Maharashtra with the aim to ascertain the quality of drinking water from the study area. Values obtained from Physico- chemical parameters were collated with both BIS and WHO standards and correlation coefficient was also calculated. It came into light that most of the water samples were within the acceptable limits and safe for consumption.

Chavan et al., (2014) assessed the Physicochemical parameters of groundwater in Solapur city in Maharashtra. In the months from September 2011 to February 2012 groundwater was picked randomly from seven varied places in Solapur city. pH, magnesium, calcium, chloride, sulphate, total dissolved solids were some of the parameters which were studied to get information about the water status. It was concluded exceptTDS level which was 956 this groundwater was suitable for domestic consumption.

Patil et al., (2010) assessed the Physicochemical parameters of groundwater in Amalner town in Maharahtra. Groundwater sample was collected from five different locations and results were compared with WHO and ISI 10500-91 standards. At few sampling sites namely Cotton Market, Shivaji Nagar and Shirud Naka groundwater samples were found contaminated and at rest of places water samples were within the set standards. Correlation coefficient was also calculated for examining thewater status.

Kannan et al., (2018)surveyedthe groundwaterin different parts of Nagapattinam, Tamil Nadufor complete Physical &chemical parameters of water. The results were contrasted withBIS standard values and it was concluded all parameters studied were beyond the permissible limit and groundwater was not fit forconsuming.

Parween et al., (2015)analyzed the various parameters of groundwater from various studied locations in Aligarh, Uttar Pradesh. Samples of groundwater were taken from 16 different locations of the studied area and on comparing with standards set by national level the observed parameterswere within the prescribed limit. The study showed that drinking water quality in the study area isgoodneeding some minor treatment before using for drinking purpose.

Abinanandan., surveyedvariousPhysical and chemical parameters of groundwater ofVellore, Tamil Nadu during April-May 2011. Parameters including pH, acidity, alkalinity, chlorides, sulphates, DO, turbidity and hardness were evaluated using American public health Association standard method. The results obtained were collated with BIS and WHO prescribed drinking water quality limits. Correlation analysis and ANOVA was also done and it was observedmeasured parameters were within the permissible limits and showed a positive correlation.

Bharati et al., (2011) surveyed the quality groundwatercoming out of borewells in Vidharbh region located in southern area of Nagpur city. Detailed and complete analysis of water samples picked from diverse areas located in the same city was done and various parameters pH, total hardness, conductivity, total alkalinity, chlorides, sulphates, fluoride, sodium and potassium were analyzed. The study concluded that there is a regular need to monitor the water supply in the studied area.

Tambekar et al., (2012) surveyed the groundwater quality of Chandrapur city which is considered one of the most polluted cities of India due to rapid industrialization in the area. Physico-chemical parameters including pH, COD, turbidity, total hardness, alkalinity, DO, BOD, chlorides, fluorides and TDS were analyzed from the water samples taken from different places in the Chandrapur city. Physico-chemical analysis of collected water samples was done using APHA standards and results were compared with limits set by WHO and BIS standards. It came into light that water of investigated place can be used suitably for drinkingt.

2.3 Review work done internationally for surveying the quality of ground water

M. Shakerkhatibi et al., (2019)analyzed the quality of groundwater for potability in rural areas of northwest Iran. Water samples were picked up from 39 wells for measuring various anions, cations and heavy metals during the summer and spring season. GIS maps and Gibbs diagram was drawn to see thedistribution of studied parameters. EC values were of 461 and 2600 μs/cm. CaCO3 was 220 and 720 mg/l. Mg^{2+}> Na^{+}> Ca^{2+} were the major cations while HCO_3- > $SO4^{2-}$> Cl^{-}> NO_3^{-} > F^{-} were the anions. According to Gibbs maps, low water quality was seen in several parts of the study area. Aluminium, iron, boron and manganese concentration was found higher than the prescribed limit in certain areas and excluding certain portions of the studied area water was suitable for drinking purpose without requiring any specific treatment.

Rezaei et al., (2019) focused their research work ongroundwater of investigatedplaceby evaluatingpresence of heavy metals, various physicochemical parameters. Pollution evaluation indices and statistical tools were also used to identify the pollution sources and to observe the ground water quality. Various physicochemical parameters pH, EC, DO, temperature, oxidation-reduction, TDS, cations(K+, Na+, Ca2+ and Mg2+) anions (Cl^-, HCO_3^-, $SO4^{2-}$ and NO3−) were carried out. Four pollution indices and hydrogeochemical facies of water samples was done to knowlevel of heavy metal pollution. Studies proved moderate contamination in the observed area which was not dangerous for consumption.

Jafari surveyed the groundwaterinAbhar city of Iran. Analytical studies proved high levels of EC (100%), TDS (40%), Mg (23%), So42- (13.3%), Hardness (66.7%) indicating the results of water samples obtained were significantly different from WHO Iran standards for potable water.

Khodapanah et al., (2009)analyzed the groundwater quality in Eshtehard area of Iran which has less quantity of surface water and is dependent on groundwater to meet the domestic as well as agricultural needs. Groundwater was collected through tubwells and dug wells and weas checked for TDS, pH, EC, Na^+, Ca^{2+}, K^+, Mg^{2+}, HCO_3, and SO_4^{2-}. Sodium absorption ratio (SAR) and salinity diagrams were made on the basis of results obtained. Groundwater quality obtained was not fit for consumption and domestic use in major samples. 37% of the water samples had moderate salinity level whereas 15% and 48% of the water levels showed high and very high salinity hazard respectively and needed remediation measures.

Hadian et al., (2015)analyzed the ground water quality in RancaekekJatinangor district of West Java, Indonesia. Collected groundwater samples from 31dug wells were investigated for parameters which included EC, pH, TDS, Ca, Na, Mg, SO_4, Cl, K, HCO_3 were determined, the results obtained were compared with WHO standards. The results proved the water in studied location can be used suitably for drinking and wateringuse.

Behailu et al., (2017)analyzed the groundwater quality in Konso region of southwestern Ethiopia. Groundwater was picked from 23hand pumps and motorized supply system. Physico-chemical parameters which included cations(Li^+, K^+, Na^+, Ca^{2+} and Mg^{2+}), anions(F-, Cl-, $PO4^{2-}$, $SO4^{2-}$) heavy metals(Mn, Pb, Ni, Co, Zn Cu), temperature, turbidity, alkalinity, EC, total hardness, total suspended solids were analyzed and the results obtained were collated with WHO and national set standard. Most of the results were within the normal range but some parameters were in high level thereby requiring specific water treatment before use.

Shawai et al., (2019) through their research tried to locate the major sources of water pollution in Kano state, northwest Nigeria.Completeparametric analysis of groundwater samples was performed and it was observed that the examined parameters were within the WHO recommended standards set for potable water. It was also concluded industrial effluents discharged were the major contributors of water pollution and a recommendation regarding the closure of industries which failed to adhere to government policies in regard to environmental regulations. Phytoremediation should be used for pollutants removal from water.

Idris et al., (2014)analyzed fourteen groundwater samples for their Physico-chemical characteristics in the northwestern region of PulauTioman region of Pahang, Malaysia.The study concluded that the parameters tested were within the prescribed limit and can be satisfactorily used for drinking and agricultural purpose. It also showed Ca-Mg-HCO3 as the major ions present in water samples and there was a strong correlation between Ca and EC.

Wang., (2020)analyzed the ground water of Yancheng city Province Jiangsu in China. Various Physico-chemical parameters pH, fluoride, sulphates, chloride, total alkalinity, sodium, potassium, TDS were measured. Statistical analysis which included R mode, correlation analysis and factor analysis were done each month from 2010-2015. Fluoride concentration in 22% collected water was lower ,which enhanced rate of teeth cavities especially in children. Studies also showed that solubility of fluoride in drinking water is dependent on total alkalinity which was also confirmed by R mode cluster analysis. This study gave useful data to the health department of Yancheng city regarding fluoride concentration and total alkalinity in groundwater.

Chiamsathit et al., (2020) analyzed the heavy metal pollution index in groundwater supply of Kaeng village of Kalasin province in Thailand. Heavy metal concentration of heavy metals in ground water was performed by using atomic absorption spectrometer. Samples of groundwater were collected from eight different locations both during the rainy as well as post monsoon season. Results obtained were collated with drinking water standardset up by WHO&Thailand department of Health standards. Major portion of collected water were below prescribed value except Fe and Mn concentration during the monsoon period. Heavy metal pollution index mean values in monsoon and post monsoon were 70 and 46 respectively which stands below the threshold of 100.

Xin et al., (2020) investigated the groundwater quality of Pulau-Bidong province of Malaysia. Samples of groundwater were collected from five different sampling stations in the time period of June 2016 to October 2016. In-situ physical parameters like TDS, DO, pH, salinity and specific conductivity were performed. (NH_4^+), ($NO3^-$), (NO_2^-), (PO_4^{3-}) were also done. DO, salinity, nitrates, ammonium and nitrites showed starling differences in June which had the lowest amounts of rains as compared to following months. Temperature correlated with specific conductivity and $NH4^+$ correlated with dissolved oxygen, nitrite and nitrates also a negative correlation was seen with rainfall and Physico-chemical parameters. Major of the parameters except pH were within the normal range set up by WHO and National drinking water quality standards.

Malana et al., (2011) investigated the groundwater quality from Dera Ghazi Khan a city in Pakistan. 32 samples from different locations were selected and surveyed for Physico-chemical parameters of groundwater with special focus on arsenic which was found within the satisfactory range in most of the samples excluding few. EC, TDS, sulphate, calcium, magnesium and total hardness values were much greater than the recommended values given by WHO guidelines.

Sehar et al., (2011) investigated the Physical, chemicaland microbial parameters (bacterial count MPN/100 ml coliform) in groundwater of KallarSyedan, Pakistan by taking water samples from five different locations in study area and results obtained were compared with both national and international standard and it was concluded Taryala and Luni sampling sites contained contaminated water whereas Bhakral another sampling site contained groundwater within the prescribed limit and is safe for drinking purpose.

Saana., (2016)tested the quality of groundwater innorthern states of Ghana. Various parameters within waterwereanalyzed and majorwater samples were within prescribed limit but a regular monitoring of the study area was recommended to ensure the safe supply of drinking water.

Rahmanian et al., (2015)studieddrinking waterin Perak, Malaysia. Complete Physical, chemical and microbial analysis of drinking water was performed for both summer and winter months and results were compared with international (WHO) and national (NDWQS) standards. Values of various parameters was within the prescribed limit and water was found to be safe for drinking but it was recommended monitoring should be done on a regular basis to check the contamination of drinking water.

Aliewi et al., (2015)analyzed the groundwater in Salfit district which is situated in northern part of Palestine and through his work evaluated the groundwater pollution and risks of drinking contaminated water on the inhabitants' health.

Pei-Yue et al., (2010)analyzed the groundwater quality in Pengyang County using seventy-four water sample sand these samples were subjected to twenty-six different Physicochemical analysis tests. Water quality index of the samples varied from 12.4 – 205.24 but ninety percent of the samples had WQI below 100. It was concluded groundwater needs long term planning and conservation policies to protect the groundwater from industries and agricultural misuse.

Popoola et al., (2019)analyzed the quality of groundwater which was collected from two residential and industrial areas of Lagos Metropolis. Various Physicochemical parameters of groundwater which included and heavy metals Cu, Zn, Co, Cr, Fe, Pb, Mn were done. All parameters excluding pH, TDS, EC, Fe and Mn were within the permissible limits in industrial areas while pH,Pb, Mn &Fe were higher than the permissible limits in residential locations. Effluents discharged from industries were responsible for high TDS and EC.

Aderemi et al., (2011)analyzed the Physicochemical and microbial parameters in leachate and groundwater samples taken from several locations near the solid waste landfill to understand the effect of percolation of leachate in groundwater quality. TDS, EC and sodium levels were higher in 62.5%, 100%, 37.5% water samples. pH was higher in 75% of the water samples and a large number of enterobacteria was seen in the groundwater samples. It was concluded that leachate discharged from landfill had low impact on the quality of groundwater becausesoil stratigraphy which consisted of clay which did not allow leachate to deteriorate the ground water quality.

2.4 Strengths of Review Literature

This literature will be informative for assessing and comparing the various Physio-chemical parameters of water in different sampling sites used by research scholars.Many researches which are based on Physio-chemical analysis of groundwater have been carried out throughout the world and also a large volume of literature is also available on the same, which will guide at each path of research.

In order to meet the objective of present research, this critical review of literature will provide insight into various physio-chemical parameters of groundwater, heavy metals present in water and their ill-effect on consumption. Correlation among physio-chemical parameters of groundwater will give a fair idea of groundwater quality.

2.5 Drawbacks of Review literature

Samples of groundwater collected from various sampling sites byresearchers are insufficient in number thus a true picture of Physico-chemical analysis is difficult to obtain.

Another weakness in this literature review is much data regarding physicochemical analysis of groundwater in study area could not be obtained.

2.6 Gaps in Literature review

Research on Physico-chemical analysis of groundwater for various parameters has been done by many research scholars throughout the world. Palwal became the 21st district of Haryana in 15th August, 2008 and due to industrialization, faulty agricultural practices involving excessive use of fertilizers and pesticides and rapid urbanization there has been an increased stress on groundwater quality and not much significant work on the water quality in this region has been done, hence it strengthens the need of a detailed and exhaustive.

Chapter-3

3.1 History of Palwal

Palwal city got its name in the reign of Pandavas by the killing of demon ‘Palawasur’ by Balram, elder brother of Lord Krishna. Every year “Baldevchhat Ka mela” is celebrated to mark this occasion.A temple dedicated to Balram is also built near the railway station. During British era, Mahatma Gandhi was arrested for the first time near the railway station of Palwal. Gandhi ashram was built in the memory of the father of the nation. In British era Palwal was a part ofGurgaon district and Punjab province. Under the influence of Mahatma Gandhi many people took part in revolt against the British empire.Post-independence in August, 1979 Gurgaon district was bifurcated to the district of Faridabad with Palwal a part of Faridabad district and eventually on 15th August, 2008 Palwal became the 21st district of Haryana.

3.2 Location

Palwal, 21st district of Haryana lies between 27° 50’ N latitudes and 77° 05’ E longitudes with a total geographical area of 1364.55 Sq kms. Palwal which is the district headquarter has four administrative blocks namely Palwal, Hodal, Hathin and Hassanpur. Western side of the district is bounded by Mewat, Uttar Pradesh lies on east .Studied place contains two main canals- Agra canal which passes through western part of the district and Gurgaon canal which passes through the central part of the district from north to south direction. Budia nala which flows in the north side of the district discharges its water in theriverYamuna. Gaunchi drain which flows between Agra canal and Gurgaon canal flows in the north-south direction of the district.

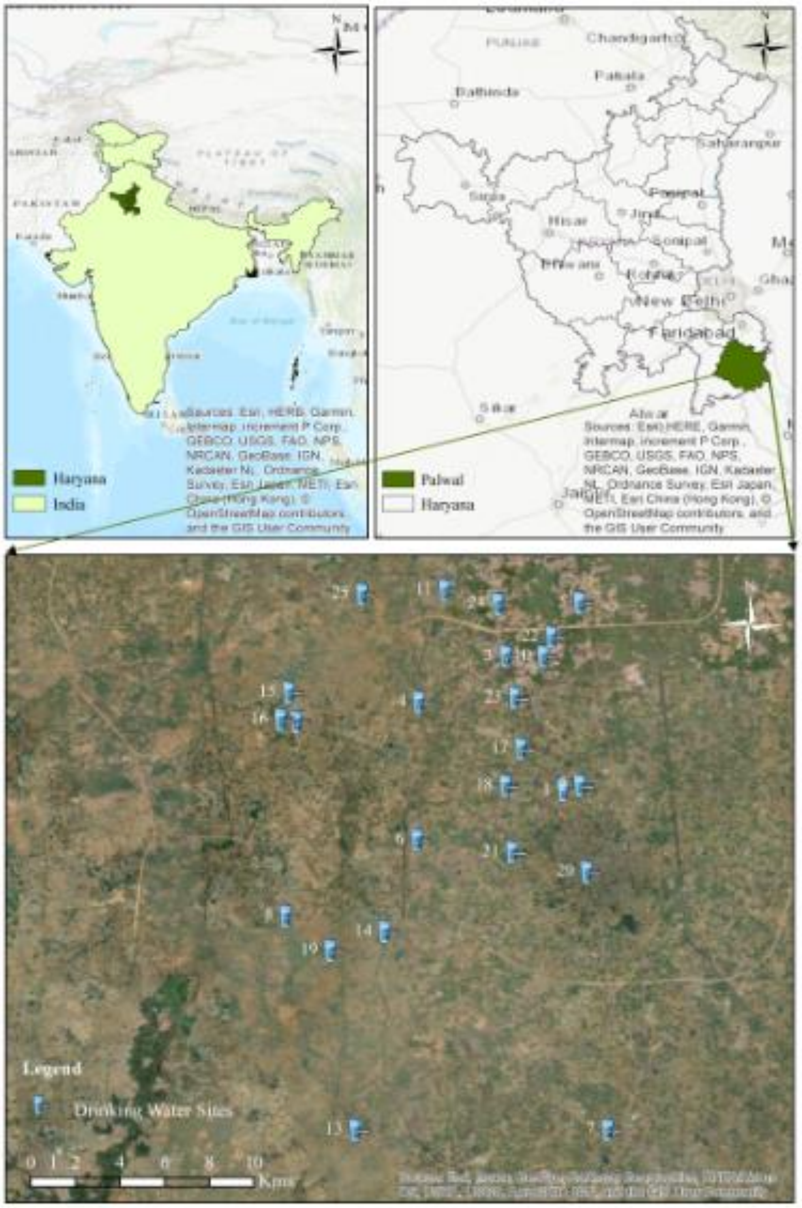


Fig 3.1 Location of Palwal district in Haryana

3.3 Demography

According tocensus, population of Palwal is 1,042,708 of which number of males and females are 554,497 and 488,211 respectively. population density of 767 persons/ square km and in 2001, population of Palwal was 829,121 and number of males and females were 445,390 and 383,731 respectively with a population density of 607 people per Sqkms. 25.76 percent was the population change in 2021 as compared to the census of 2001. In the 2001 census, of the total Palwal population 22.69 percent of people lived in urban areas of the district and the remaining 77.31 percent of people lived in rural areas. Sex ratio has increased to 880 from 862 in the census of 2021 as compared to census 2001. Male literacy rate has increased to 82.66 in 2021 from 55.10 in 2001. Hinduism is the religion followed by majority of people followed by Islam, Sikhism, Christianity, Buddhism and Jainism. Female literacy rate has gone higher from 40.80 (2001 census) to 54.23 (2021 census) and the average literacy has increased to 69.32 (2021 census) from 59.20 (2001 Census).

3.4 Physiography

Palwal district is a plain through which river Yamunaflows in the eastern side and its low- lying floodplain is a narrow belt, called as Khadar which is formed of new alluvium and shows marked variation from the remaining upland area, called as Bhangar which is formed of older alluvium. Khadar width is 3-5 kms, is prone to floods from theYamuna River during the monsoon season. After thereceding of water fine silt remains, containing adequate moisture which is easy to plough.

Palwal district can be divided into Palwal plain&Yamuna Khadar region.Palwal plain which includes central, western and south-western partof district forms the majority of the Palwal. Yamuna Khadar is on the eastern side of the districtwiththedirection of slope facing the southern direction.

3.5 Drainage

Yamuna, which is the perennial river, flows through the eastern border of the district. The drainage in Palwal is similar to semi-arid areas. Inland streams flowing is seasonal, dry up during summer season and do not have well defined channels. It forms a boundary between Palwal district in Haryana and Bulandshahr and Aligarh districts in Uttar Pradesh. Due to diversion of Yamuna water into western Yamuna canal and Agra canal there is very little flow of water in river.

During monsoon season, an island known as Jairnala is formed by flooding of stream which causes heavy damage during floods or heavy rains.

The southern stream passes through villages like Sirohi, AlampurBenkhera and eventually falls into the marsh at village Sarmathla in Palwal district. A small stream from south of Dhauj village reaches TikriKhera and is siphoned to Sikrona drain near Firozpur Kalan. Many bunds are built for irrigation and reducing the effects of floods. There are two artificial lakes in the district namely Dhauj lake and Peacock Lake which was created at Suraj Kund and drains into ephemeral lake.

3.6 Groundwater quality and Depth

Groundwater in Palwal is found withinrange of 0-20 meters below the ground level(m.bgl). In southwestern parts of Palwalgroundwater is found in 10-20m.bgl whereas in Khadar belt it is observed in 0-1.5m.bgl. Nature of top soil decides the quality of groundwater, top soil being saline groundwater is of alkaline nature. Groundwater in villages of Kakrali, Karna, Bamnika, KairakaRajolaka, Aharwan, Badha and Nangli is highly alkaline.

3.7 Climate and rainfall pattern

Palwal district has a subtropical continentaltype of climate where there is complete seasonal distinctness between hot summer, cold winter, erratic rainfall pattern with great variation in temperature. Air is dry for most part of the year except in monsoon months which extend from July to mid-September. During these months, moist air from oceans penetrates into the district and causes high humidity and rainfall. South-west monsoon winds which originate from Indian ocean set in the end of June to first week of Julyare responsible for 85% of the rainfall. During rainy months, especially in July rainfall peaks to 184mm. Cold season starts from mid Novemberendingin mid-February with gradual increase in temperature. Fog is also a common feature of the winter season. Cold air blows in the region and sometimes the minimum temperature falls below the freezing point.Summer season starts from month of March and continues till June end. During the April (end half), May and June the average temperature is 37°C. Hot winds locally called as ‘looh’ blow in the May and June months which are the hottest months with mean maximum temperature reaching up to 40.2°C. Temperature in these months sometimes reaches 45°C. Palwal district does not have any meteorological observation centre therefore Gurgaon is taken as the representative of the district.

3.8 Forests

Palwal district does not have a rich forest belt and tropical dry deciduous forests are found in the area. Forest land in Palwal district is classified by its ownership rights, viz-forest land which is owned by individuals and corporate bodies is included as private forest and the other category is referred to as state forests which include protected and reserve forests. Jand tree (Prosopis cineraria) is a very common tree found everywhere in the district and is used as fodder for cattle in the winter season. Apart from Jand, trees of Kikar, Gular, Dhak, Hins, jal, Ratunj, Lasura and Kadam are fairly common in the district. Shisham, Arjan, Bakain and Siris trees can be seen bordering the roadsides. Kikar tree is found growing all over the Palwal district and is successfully grown in the notified areas by the forest department. Neem trees are especially found growing on Nuh-Palwal and Palwal - Rewari roads. Some scattered Semul trees are found in the southern part of the district. Jharberi plant (Ziziphus nummularia) is very commonly seen all over the district and used by local people for a varietyofuses.Munj (Saccharum munja), Khip (Leptadeniapyrotechnica) are some other common shrubs found in the district. Black buck, hyena, wolf, jackal, monkey, fox, nilgai, hare, porcupine, chinkara are the common wild animals found in the district. Leopards are occasional visitors in the district. Blue bulls are seen on the western part of Palwal and near the Yamuna khadar. Variety of birds like sand grouse, blue rock pigeons, partridge, peafowl and bush quails are common in the district.

3.9 Soil and cropping pattern in Palwal

Palwal district has mountainous physiography containing alluvial deposits. These alluvial plains are traversed into Bangar and Khadar by a ridge running in north-south to NNE-SSW direction. Banger which is upland, less fertile, formed of older alluvial and is spread towards the west side of the district whereas the Khadar which is low lying, fertile and formed of newer alluvium. Yamuna Khadar area has loamy and silt loamy soil having less water retaining capacity and these kinds of soils are difficult to work on drying. The soil texture of Palwal Plain area is loamy (Bhangar) to sandy loam. Loamy soil is more fertile. Brown soils are found in the major part of the district. Soil in Palwal is mostly deficient in organic content which is generally 0.2-0.4% except in Hathin where the organic content found in soil varies from 0.42-0.75 %. Average pH of the soil varies from 6.5 to 8.7. Kharif locally known as sawani and rabi locally called sadhi are the two main categories of crops grown in the district.Kharifis the harvest of summer season while rabi is called harvest of winter season. Main Kharif crops grown in this are bajra,groundnut, cotton, jowar, pulses, kharif vegetables. Major winter crops of the district are barley, mustard, gram, oil-seeds, wheat and winter vegetables. Period between May and July is used for raising Zaid crops especially in those areas with sufficient irrigation facilities.

Pattern of land use

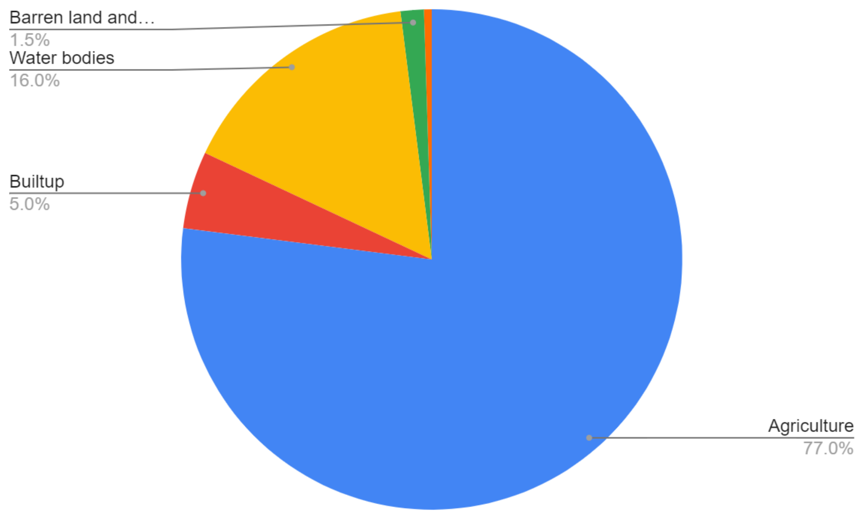


Fig 3.2: Pattern of land use in Palwal

Palwal occupies an area of 35625 hectares and land utilization of Palwal is divided into six major categories- agriculture which is done in 77% of the area, water bodies occupying 16%, built up area 5%, barren and cultivable wastelands 2% and forests with a small share which is even less than 1%.

Economy

Primary sector is the dominant sector in Palwal. Agriculture as well as small scale industries are the major source of livelihood of people. Higher agricultural productivity is seen in Khadar (Newer alluvium) as contrast to Bhangar (older alluvium) but agricultural output of many villages of Palwal is low due to high soil salinity. Cotton and cotton-based industries which include weaving, dyeing and handlooms are the main industries located in the study area. Due to start of new infrastructural projects- Kundli Manesar Palwal, Kundli Ghaziabad Palwal, Zevar airport economic activity has taken a spurt in Palwal.

Chapter-4

4.1 Introduction

Green revolution has brought economic prosperity to the state of Haryana and made India self-sufficient in food production. This green revolution was possible due to intensive irrigation using groundwater and extensive use of fertilizers. This spurt of crop increase resulted in flux of people from rural to urban places and rapid industrialization which started degradation of natural resources.

Research begins with identifying a problem and then finding a solution to that particular problem. This chapter describes the materials and methodsfollowedto find thegroundwaterquality status instudied region, statistical techniques used for the assessment and interpretation of collected samples along with the methodused for evaluating the quality index of water and appropriateness ofwater for irrigating purpose. This chapter also emphasizes for finding a locally available, low-cost biosorbent which can be used to remove the chemical dyes contaminating the aqueous system.

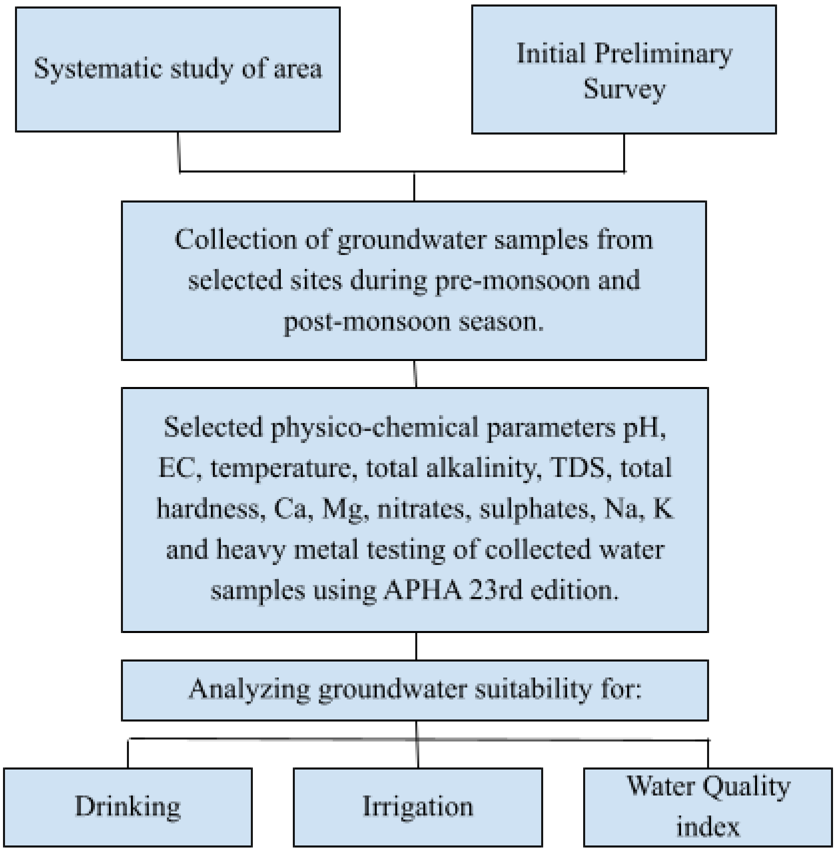
4.2 Methodology

Methods used in the following research can be divided into:

- Field Study
- Collection of water samples from selected sites both during premonsoon and postmonsoon season
- Selected Physico-chemical parameters pH, EC, temperature, TA, TDS, TH, cations nitrates, sulphates, anions and heavy metal testing of collected water samples using APHA method 23rd edition.
- Checking thequality of groundwater for potability and irrigational purpose
- Checking impact of groundwater quality on health of people
- Finding wqi

- GISmap for findinggroundwater status.
- To synthesize a novel ternary bio-nanocomposite for the removal of brilliant green and methyl orange dyes (used in textile industry) from aqueous solution.

Flowchart for the methodology was drawn as shown below:



4.2.1 Field Study

Palwal district is a part of National Capital Region (NCR) and located in Haryana. Palwal district can be divided into six blocks- Badoli, Hasanpur, Palwal, Hathin, Hodal and Prithla. Palwal being the newest district of Haryana is witnessing a dramatic increase in groundwater pollution due to expansion in agriculture, mushrooming industries and improper solid waste management therefore Palwal district was chosen as the study area to help policy makers and leaders to get hygienic and clean potable water to local population. Area under study was surveyed exhaustively by questioning the local people to know their grievances regarding the quality of drinking water, based on this questionnaire survey given to people, 25 sites were considered for collection of groundwater samples in which groundwater was collectedbothduring the premonsoon and postmonsoon season and was assessed for selected Physico-chemical parameters and trace metals.

Table 4.1Sample codes of collected groundwater

Sample code	Name of village	Source of Water	Latitude	Longitude
S1	Alahapur	Handpump	28.175695	77.309854
S2	Firozpur	Hand Pump	28.172312	77.3354
S3	Prithla	Hand Pump	28.230161	77.294307
S4	Sikanderpur	Hand Pump	28.211716	77.259216
S5	Asawati	Hand Pump	28.2518	77.3241
S6	Allika	Hand Pump	28.162343	77.254587
S7	Rehrana	Hand Pump	28.095508	77.320136
S8	Joharkhera	Hand Pump	28.125426	77.205431
S9	Kishorpur	Hand Pump	28.170996	77.213568
S10	Tatarpur	Hand Pump	28.230154	77.309511
S11	Harfali	Hand Pump	28.256874	77.269692
S12	Teharki	Hand Pump	28.203498	77.229227
S13	Badha	Hand Pump	28.123455	77.233476
S14	NagliPanchagi	Hand Pump	28.119134	77.245462
S15	Chandpur	Hand Pump	28.215605	77.206773
S16	Jaindapur	Hand Pump	28.20467	77.203465
S17	Patli Kalan	Hand Pump	28.192924	77.30044
S18	Patli Khurd	Hand Pump	28.178035	77.294171
S19	Rakhota	Hand Pump	28.111512	77.223542
S20	Naya Gaon	Hand Pump	28.14327	77.32698
S21	Megpur	Hand Pump	28.151343	77.296848
S22	Jatola	Hand Pump	28.238029	77.3128
S23	Meerapur	Hand Pump	28.2135	77.2979
S24	Gadpuri	Hand Pump	28.250783	77.278788

S25	Sehrala	Hand Pump	28.255302	77.236288

Collection of groundwater samples

Groundwater samples were taken in prewashed 1 litrepolypropylene sample containers. Before using these bottles for sample collection, these were immersed in 10% nitric acid for a daythereafter were rinsed with DWandwere dried at 50^{0}C for seven hrs.Samplesgroundwatercollected from hand pumps located near industrial, agricultural and residential were taken in theJunemonthand in Octobermonthinyears 2019, 2020, 2021 consecutively.

4.2.3 Physico-chemical testing of selected groundwater

Collectedsamplesof groundwater were tested for selected Physico-chemical parameters using theAPHA (American Public Health Association) standard method, 23rd edition. Procedures adopted for testing the various chemical parameters are described:

Table 4.2Procedure to testvariousPhysico-chemical parameters

S.No	Physico-chemical parameter	Methods involved in testing
1.	pH	pH of the selected groundwater sample was measured by pH- meter(Patsio pH-700) which was calibrated with buffers of pH 4, 7 and 10 prior to use which were brought from LobachemiePvt. Ltd.
2	Electrical Conductivity	EC is measured by the conductivity meter (Orion-013005MD). Before using the meter, it was calibrated with buffers of 1413, 84 and 12.88 mhos/cm.
3	Total Dissolved Solids	Evaporating dish (borosil) was pre-weighed and filtered 100ml groundwater sample was put in the same evaporating dish and was kept in preheated oven 180C for 1 hour/ full evaporation after which evaporating dish was reweighed.

4	Total Hardness	Total hardness is found using EDTA (Ethylenediaminetetraacetic acid) which is used as a titrant and indicator used as EBT(Eriochrome blackT) with the change of colour from red to steel blue as the end point.
5	Calcium	Calcium in groundwater samples is measured by EDTA titration method. This titration is carried out at 12-14 pH to avoid the interference of magnesium by converting it to magnesium hydroxide. Ammonium purpurate murexide was used as an indicator with purple colour as the endpoint.
6	Magnesium	Magnesium is calculated by subtracting hardness as calcium carbonate - calcium as calcium carbonate.
7	Turbidity	Turbidity is measured by a nephelometer with its unit NTU. Before use it is calibrated with 400 NTU standard solution which is prepared by mixing 5ml hydrazine sulphate and 5ml of hexamethylenetetramine for 24 hours in a volumetric flask and making it to 100 ml by addition of water after the required time.
8	Sodium	Sodium is measured with a flame photometer (Elico CL-360) Calibration is done with distilled water containing no sodium, standard solution containing 10, 20, 30….100mg/l sodium. Direct value of sodium is shown by the instrument in mg/l.
9	Potassium	Potassium is measured with a flame photometer (Elico CL-360) Calibration is done with distilled water containing no potassium, standard solution containing 10, 20, 30….100mg/l potassium. Direct value of potassium is shown by the instrument in mg/l.
10	Total Alkalinity	Groundwater sample was titratedwith phenolphthalein (which works on low pH) and methyl orange (which works on pH<7). Endpoint is the change of yellow into orange colour. Total alkalinity is calculated as calcium carbonate in mg/l.
11	Fluoride	Fluoride level was calculated by spectrophotometer (HACH DR-2800) by using SPADNS method (dye). Fluorine is reacted with red zirconium dye solution to form a colourless complex and a dye. It works on the principle that absorbance decreases with concentration and preparing standard curves.
12	Chloride	Chloride is measured by argentometric method. The collected sample is titrated against $AgNO_3$ solution with K_2CrO_4 (indicator), endpoint is brick red colour due to silver chromate

		formation.
13	Sulphates	Sulphates are measured by the turbidimetric method by using a spectrophotometer(HACH DR-2800). Sulphate ions are measured by absorbance of light by barium sulphate(ppt of barium sulphate) by addition of barium chloride and then compared with standard curves.
14	Nitrates	Nitrates are measured by spectrophotometer (HACH DR-2800) with use of reagent H193723-0.

4.2.4Groundwater quality suitable for drinking

Groundwater isrequired by living beings for potability and agriculture. All countries have specified the range of various Physico-chemical parameters which can be permitted in drinking water. In India this job is carried out by BISwhich specifies consumable water quality standards &regularly checks water supply so as to give people safe drinking groundwater. Internationally WHOprovides standard limitfor various Physical and chemical parameters present groundwater.

Table4.3Drinking water specifications for important parameters set by BIS

Parameter	Acceptable (required)limit	Permissible (In absence of alternative) limit
Turbidity	1	5
T H	200	600
pH	6.5-8.5	6.5-8.5
Cl	250	1000
F	1	1.5
E C	-	-

Ca	75	200
Mg	30	100
Na	-	-
K	-	-
Total Hardness as $CaCO_3$	200	600
Sulphates	200	400
Nitrates	45	-
Iron	0.3	-

4.2.5Appropriateness of groundwater for agricultural purpose

Groundwaterused for watering plants differs in various regions due to different amounts of rainfall, groundwater extraction through tube wells and recharging rate of aquifers through precipitation. Tropical regions with low rainfall show increased groundwater salinity which is detrimental for cultivation of crops. Quality of groundwater used for irrigating crops is dependent on concentration and composition of dissolved salts present in water. Water salinity(EC), sodium hazard(SAR-sodium adsorption rate), ion toxicity(especially Na, Ca, Mg, K and Cl accumulate in crops to damage them) and residual sodium carbonates(RSC) are the parameters crucial for deciding thewater status used for agricultural as mentioned in US Salinity Laboratory staff published in 1954 (USSL staff 1954; Bresler et al.1982). To meet the above-mentioned criteria, attention is also required for knowing electrical conductivity(EC), cations and anions.

Table4.4Effect of irrigation water based on dissolved salt content and electrical conductivity (Follett et al., 2002)

Detrimental effect on crops	Dissolved salt content in ppm	Electrical conductivity (µs/cm)
No damage to crops	500	750
Detrimental effect on sensitive crops	500-1000	750-1000
Adverse effect on major crops	1000-2000	1500-3000
Can be used for salt tolerant crops	2000-5000	3000-7500

4.2.6Effect of drinking groundwater on health of people

Nearly 50 people were selected randomly from the study area and were given a questionnaire regarding the quality of groundwater to fill. These people shared their problems and grievances which they were suffering due to water quality.

Table 4.5 Questionnaire regarding groundwater quality

- **Name of person**
- **Name of Village**
- **Age**
- **Sex**
- **Education**
- **Occupation**
- **Source of drinking water**

  (A) Tubewell (C) Packed water

  (B) Handpump (D) Public water supply

- **Is water quality in your area satisfying (A) yes (B) No**
- **What are the major water problems in your area?**

  (A) Changed taste (C) Changed colour

  (B) Smell (D) Quality issues

- **Treatment method for water used at your home:**

  (A) Boiling (C) RO

  (B) chlorine tablets (D) No Treatment

- **Major source of water pollution in your area**

(A) Industries(C) Agriculture

  (B) Faulty sewerage (D) All of these

- **Toilet Facility available at your home**

  (A) Sewer System (C) Open Defecation

  (B) Septic Tank (D) None of these

- **Are there health issues in your area due to drinking water (A) yes (B) No**
- **If yes, tell about diseases in your area caused due to consumption of polluted water**
- **Has the government taken any action about controlling water pollution?**

4.2.7 WQI

WQIis an important tool for deciding drinking water standards in residential& industrial areas. Horton in 1965 first used this WQI to measure water quality(Akter et al., 2016). It is a numerical value which can be used for the description of water quality based on certain water parameters. It simplifies complex data of parameters into easily understandable information which can be understood by the general public.

WQI calculation involves three steps

- Various Physico-chemical parameters are selected
- Quality function of each parameter is determined
- Calculation using weighted arithmetic index formula.

This WQI represents a number which illustrates water classification of a particular sample, check its feasibility for designated purposes.

4.2.8 Hydro-geochemical facies of the study area

Ever-increasing population, increasing industrialization and rapid shift of people from rural to urban areas has put a huge pressure for the demand of fresh water so judicious management and regular quality analysis of this resource has become essential for the sustainable use of this precious resource. Various soft-wares were designed to study thegeochemical facies of Palwal district.

- Piper Plots- To study about the hydrogeochemical regime of the Palwal district, the collected and analysed data was plotted on Piper plots which consists of trilinear diagram (Peeters et al., 2014). This consists of two triangles, one for representing anions and other plot for cations. Both the anion and cation triangles combineto join from which inference is drawn to representchemical relationship of various cations and anions present in the groundwater.
- Durov Diagrams- is another option similar to piper plots used to study the hydro-chemical facies. These represent major ions in two triangles where anions and cations are set to 100% and are expressed in mEq/l. The two base triangles data is projected into a square which lies perpendicular to each triangle third axis. Clustering of groundwater quality is also shown which represents geochemical process affecting water genesis.
- Wilcox Diagrams- Sodium % is an important parameter in analysis of groundwater samples as it can reduce the permeability of water in soil and replace it with other

cations present in groundwater.Wilcox diagrams were drawn to evaluate thecharactersticsof water to be used for watering plants. In this diagram, electrical conductivity/ salinity was plotted against sodium percentage (Alavi et al., 2014).

- Gibbs Diagram- is an important representation which is used for the identification of several geochemical processes affecting water quality (Egbueri et al., 2019). These were drawn by plotting TDS against Na^+/ (Na^+ + Ca^{2+}) and Cl^- / (Cl^- + HCO_3^-).
- Ternary Diagram- also called as triangular diagram is a graph consisting of an equilateral triangle and in which relative proportions of three ends are expressed as percentages and are represented by the equation (a + b + C = 100%). These graphs are commonly used in physical chemistry and other physical sciences to showcase the composition of species, rocks and minerals forming a particular system.

4.3 Dye removal from aqueous solution

Great attention during recent times is being paid to develop competent biosorbents for carrying away of organic dyes from aqueous medium. current work deals withremoval of anionicMOandcationicBGfrom an aqueous medium was done through adsorption technique which involved the chemical interaction of dyes with a novel nanocomposite made up of neem leaf powder (NLP), ZnO and L-cysteine grafted PANI. Prepared nanocomposite was prepared by in-situ polymerization and showed promising adsorption capacity for dyes as compared to pure PANI due to presence porosities on it and was investigated as a function of pH, adsorbent dose, contact time and initial adsorbate concentration. Synthesized nanocomposite was characterized usingSEM,FTIR and(XRD. Adsorption equilibrium and adsorption kinetics were investigated. Adsorption equilibrium was explained with the help of Langmuirisotherm for both dyes. Kinetics of adsorption was explained with the help ofPSO) kinetic model for both MO and BG. Thermodynamic studies to reveal the nature of adsorption were also performed.

Chapter-5

5.1 Introduction

25 groundwatersamples taken from the study place and were assessed for selected Physicochemical parameters both duringpremonsoon and postmonsoon season during three successive years- 2019, 2020 and 2021. The various physical and chemical parameters which were analyzed are as follows:

5.1 Physical Parameters

5.1.1 pH

It is the logarithmic scale which inversely tells H^+ ions concentration insolution. It specifiesacidicor basic nature ofaqueous solutions. Solutions with a pH value smaller than 7 are considered acid, solutions with pHgreater than 7 are basic while solutions at 7 pH are neutral. pH of drinking water is an important indicator which reflects the quality of water and has a great importance to living forms as entire cell structure and proper functioning of microbial population is hindered by even a minute change in pH.

BIS range for drinking water quality has set pH desirable range from 6.5-8.5 and consumable water both below and above the range can show harmful effects on living beings. Water having a pH below 7 can show corrosive quality and can corrode metals like lead, zinc, copper, iron from plumbing pipes and may cause illness (Tam et.al., 2009) and impart metallic and bitter taste to drinking water. Water having high pH is not linked with health issues but is an aesthetic concern. Scale, precipitate formation on pipes, dishes and bathroom fixtures is not a very good sight and also imparts baking soda like taste to drinking water.

pH of water should be controlled to prevent the corrosion of water supplying pipes and networks. This corrosion can adversely change the appearance and taste of water. Metal contamination is also increased by change in pH of water.

Summary ofpH in collected groundwaterboth in premonsoon and postmonsoon season during study period (2019-2021) is shown in Table 5.1 and 5.2.

Groundwater samples analysis showcollected samplespHwas mild acidictobasic in nature but during postmonsoon season pH of collected samples showed a slight decline in alkalinity. pH of water is affected by catchment area geology and water's buffering capacity.

The study revealed that pH of collected watervaried from 6.48 to 7.53 withmean of 6.93 in the premonsoon and 6.21 to 7.24 withmean of 6.62 inpostmonsoon of year 2019, pH differed from 6.5-7.65 with a mean of 6.93 in the premonsoon and ranged from 6.23 to 7.25 with a mean of 6.60 of the year 2020 while in the year 2021 pH of groundwatervaried from 6.55-7.72 withmean of 7.04 in the premonsoon and ranged from 6.31 to 7.2 with a mean of 6.60. Frequency distribution graphs for pH in groundwater have been shown in Fig 5.1, 5.2, 5.3 and 5.4 and spatial maps for pH in groundwater samples have been in Fig 5.5.

Kumar & Hooda (2013) studied the groundwater samples of Haryana and analyzed that pH of collected groundwater varied6.5-8.9. Similar studies were done by researchers in many parts of India. Singh & Hussain (2016) in Uttar Pradesh; Shinde &Choudhari (2021) in Maharashtra;Nagetal (2017) confirmed the same. Rainfall is important for remediation of groundwater samples by recharging of aquifers (Zereg et al., 2018).

Table 5.1 Groundwater samples showing pH variation during years (2019-2021)

Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021

Alahapur	6.8	6.25	6.75	6.3	6.9	6.32
Firozpur	6.82	6.3	6.88	6.23	6.95	6.45
Prithla	6.9	6.65	7	6.45	7.05	6.75
Sikanderpur	7.06	6.85	7.01	6.87	7.05	6.8
Asawati	7	6.78	7.06	6.89	7.08	6.56
Allika	6.78	6.23	6.87	6.43	6.79	6.34
Rehrana	7.09	6.79	7.15	6.86	7.15	6.67
Joharkhera	6.84	6.45	6.9	6.5	6.95	6.54
Kishorpur	7.21	7	7.13	6.97	7.2	6.85
Tatarpur	6.48	6.56	6.5	6.55	6.55	6.45
Harfali	7.05	6.87	7.02	6.89	7.06	6.57
Teharki	7.21	6.98	7.56	7.04	7.45	7.02
Badha	7.08	6.87	7.01	6.75	7.15	6.89
NagliPanchagi	6.56	6.23	6.7	6.45	6.9	6.51
Chandpur	7.04	6.69	6.96	6.45	7.1	6.7
Jaindapur	6.94	6.45	6.9	6.4	7.02	6.6
Patli Kalan	6.88	6.45	6.67	6.35	7.03	6.55

Patli Khurd	6.62	6.21	6.68	6.34	6.85	6.31
Rakhota	6.72	6.56	6.7	6.38	6.9	6.51
Naya Gaon	7.53	7.24	7.65	7.25	7.72	7.2
Megpur	7	6.68	6.85	6.38	7.05	6.45
Jatola	6.58	6.3	6.67	6.36	6.98	6.45
Meerapur	6.78	6.45	6.56	6.34	6.9	6.35
Gadpuri	7.12	6.78	7.05	6.9	7.15	6.54
Sehrala	7.22	6.97	7.1	6.78	7.25	6.67

Table 5.2 Summary of observed pH in groundwater samples during the study period

Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Min	6.48	6.21	6.5	6.23	6.55	6.31
Max	7.53	7.24	7.65	7.25	7.72	7.2
Mean	6.9324	6.6236	6.9332	6.6044	7.0472	6.602
Std. Deviation	0.243	0.287	0.270	0.283	0.221	0.221

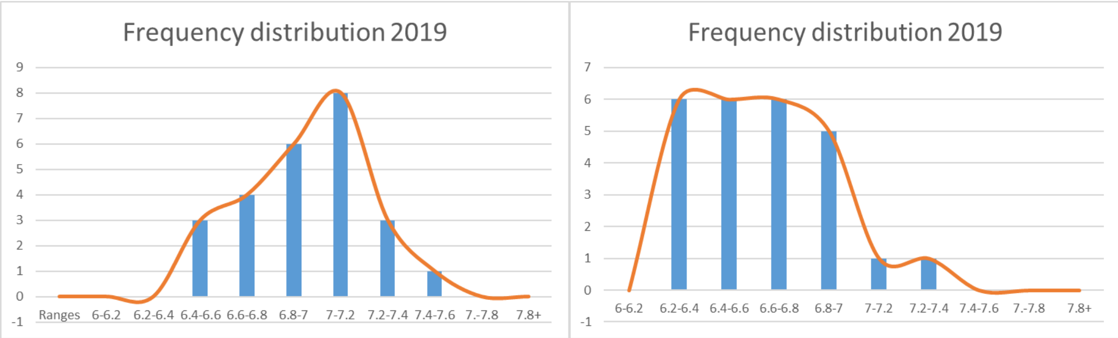


Fig: 5.1 frequency distribution of pH 2019 (Premonsoon and Postmonsoon)

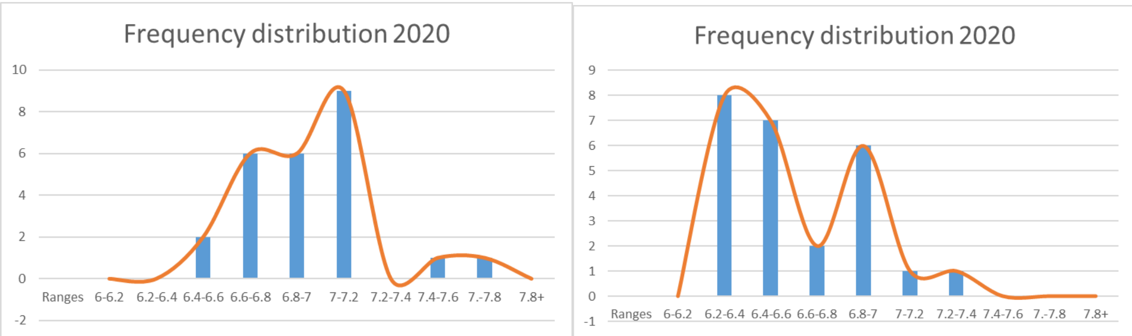
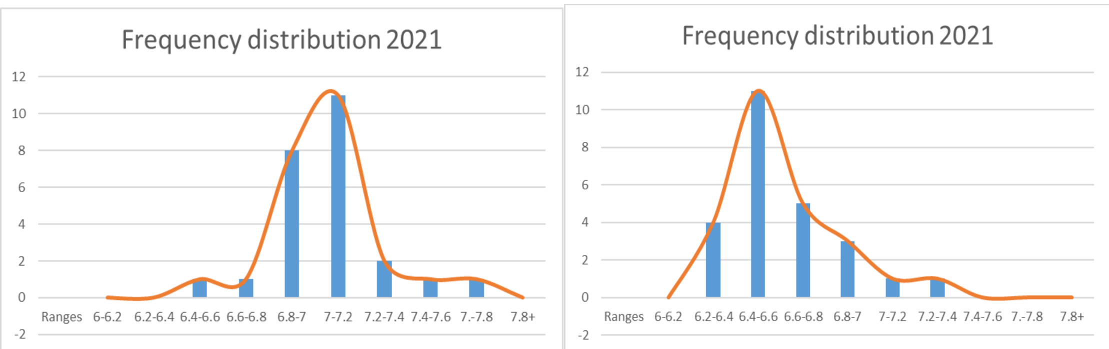
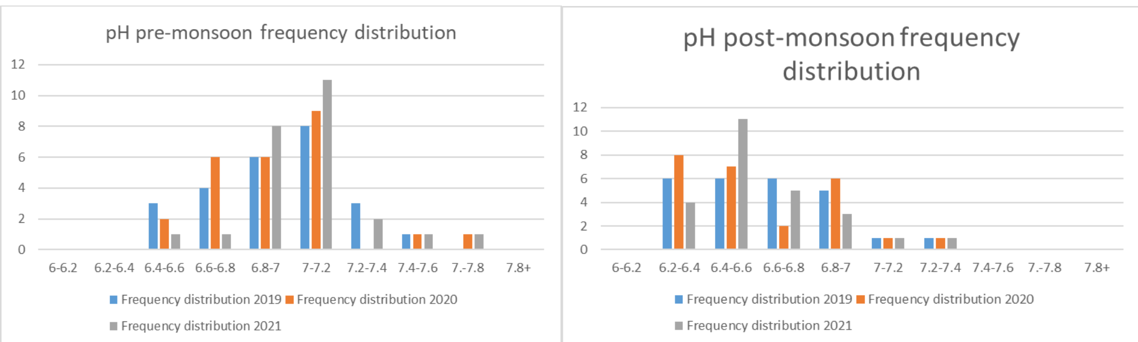


Fig:5.2: frequency distribution of pH 2020 (Premonsoon and Postmonsoon)



Frequency- pH 2021 (Premonsoon and Postmonsoon)



Cumulative Frequency2019-2021 (Premonsoon and Postmonsoon)

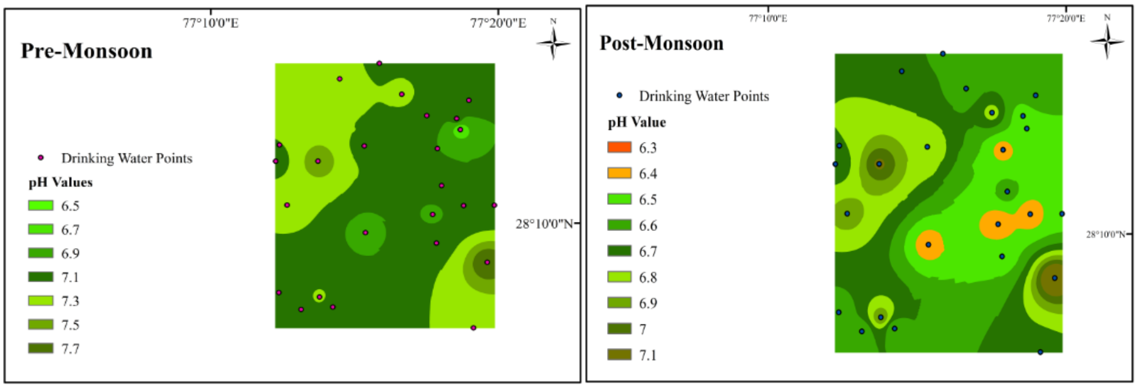


Fig 5.5: GIS maps showing pH variation in groundwater samples during pre & post monsoon of 2021

5.1.2 Electrical Conductivity

Electric conductivity of water ismeasure of water to conduct electric current through it. EC in water is directly proportional to ions concentration present in water. Various dissolved solids and inorganic materials like alkali, carbonates, chlorides, sulphates contribute to ions responsible for conduction in water. Higher the ions present in water, greater will be the conductivity. Evaporation, rain, temperature and ionic mobility both influence conductivity values in groundwater.

EC is usefulformeasuringquality of water. An increase in conductivity can explain the discharge of contamination in a water source which may show ill-effects on the health of living beings. Higher the conductivity value, greater is the dissolved solid concentration in water (Rusydi et al., 2018) which can also alter the taste of water.

Electric conductivity is dependent upon temperature. Rise in temperature is responsible for increase in conductivity of water. Inorganic solutes show a better conductivity as compared to organic solutes due to the latter's inability to dissociate into ions. High EC therefore shows the presence of inorganic pollutants in water.

Table 5.3 and Table 5.4 show the EC variation in groundwaterduringstudiedphase. ECingroundwaterof studied place show a wide variation. During the premonsoon of 2019, EC ofstudied location varied702 µS/cm-9810 µS/cm withmean 3262 µS/cm while in postmonsoon EC of groundwater differed from 677 µS/cm to 9487 µS/cm showingmeanvalue 3021 µS/cm.

Premonsoon 2020, EC values varied from 815 µS/cm to 10432 µS/cm withmean 3251 µS/cm while in postmonsoon EC values changed from 756 µS/cm -10122 µS/cm with mean ranging2986 µS/cm.

Premonsoon season of 2021, EC values varied from 780µS/cm to 10327 µS/cm with mean ranging3378 µS/cm while in postmonsoon, EC values ranged 738µS/cm-10275 µS/cm with mean value3129 µS/cm. Frequency distribution graphs for EC in groundwater have been shown in Fig 5.6, 5.7, 5.8 and 5.9 and spatial maps for EC in groundwater samples have been in Fig 5.10.

From analytical results it came into light, that in most of the samples, EC of groundwater decreased after monsoon season which reflected that groundwater ionic strength decreased after rains. Precipitation led to recharging of aquifers which reduced the groundwater ionic concentration. Most of the groundwater samples showed a decrease in conductivity but in Alahapur and Jatola study locations EC of the groundwater showed an increase of EC. The rise of EC can be due to agricultural discharge from adjoining farmlands. High EC shows a higher concentration of cations and anions in water thus making it overall unfit for consumption.

WHO has not given any threshold limit for EC in drinking water, ICMR (Indian Council of Medical Research) has given 300 as the desirable limit of EC in consumablewater. Rebello et al., (2020) have shown there is a direct correlation of EC with TDS in water. High EC values in groundwater samples was found in OwaOyem et al., (2014). Similarly high EC variation in groundwater samples was seen by Deepu et al., (2018) in Chittur block, Kerala and Mahato et al., (2018) analyzed the same in eastern Terai region of Nepal.

Table5.3Groundwater samples showing EC variation (µS/cm) during years (2019-2021)

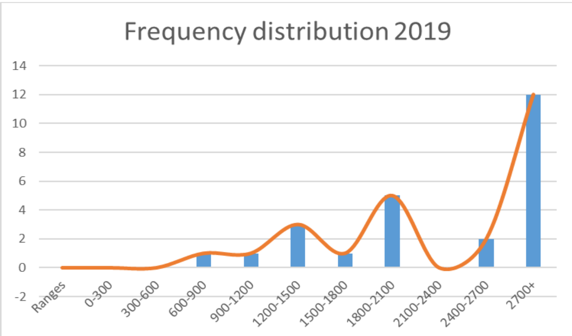
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Alahapur	2010	2180	2008	2187	2018	2200
Firozpur	1900	1877	1927	1807	1956	1882
Prithla	3500	1877	3594	1885	3504	1908
Sikanderpur	3400	3321	3308	3217	3385	3566
Asawati	2444	2403	2805	2311	2605	2357
Allika	8004	7689	7824	7400	8022	8102
Rehrana	3102	2733	3251	2988	3201	2901
Joharkhera	5121	4880	5312	4981	5228	4961
Kishorpur	702	677	815	756	780	738
Tatarpur	9810	9487	10432	10122	10327	10275
Harfali	1988	2014	2174	2287	2301	2211
Teharki	1211	1089	1421	1205	1302	1257

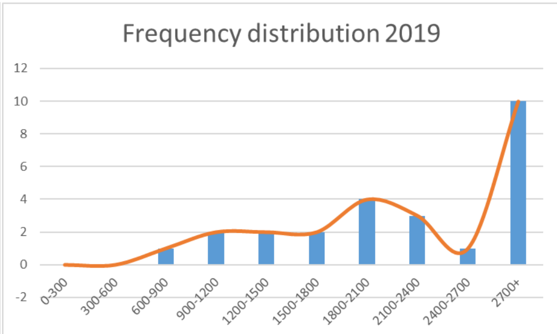
Badha	2048	2003	2084	2057	2192	2134
NagliPanchagi	3289	3177	3376	3294	3544	3408
Chandpur	1314	1273	1267	1234	1406	1346
Jaindapur	1688	1636	1701	1675	1794	1743
Patli Kalan	6102	5497	5876	5501	5945	5733
Patli Khurd	6855	6384	6221	5800	6721	6603
Rakhota	2512	2245	2367	1905	2244	2001
Naya Gaon	976	939	1024	973	1134	1097
Megpur	3409	2907	3217	2800	3607	2866
Jatola	3899	3906	3708	3210	4844	3578
Meerapur	3100	2356	2605	2208	3169	2341
Gadpuri	1832	1708	1706	1645	1942	1700
Sehrala	1344	1278	1256	1205	1289	1321

Table5.4Summary of observed EC variation in groundwater of investigatedlocation

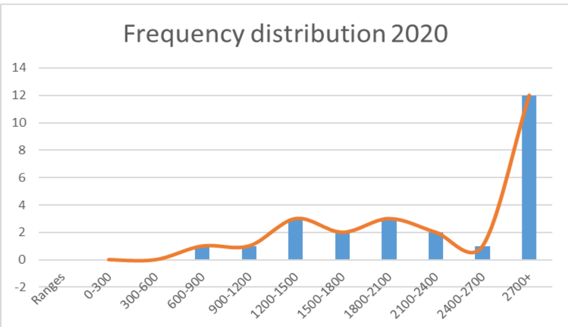
Name of village	**Premonsoon 2019**	**Postmonsoon 2019**	**Premonsoon 2020**	**Postmonsoon 2020**	**Premonsoon 2021**	**Postmonsoon 2021**
Min	702	677	815	756	780	738
Max	9810	9487	10432	10122	10327	10275

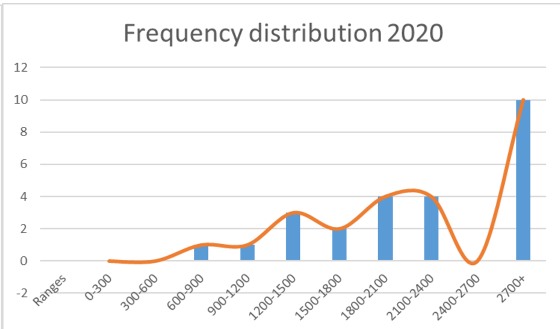
Mean	3262.4	3021.44	3251.16	2986.12	3378.4	3129.16
Std. Deviation	2292.037	2194.576	2299.915	2213.970	2332.769	2332.609



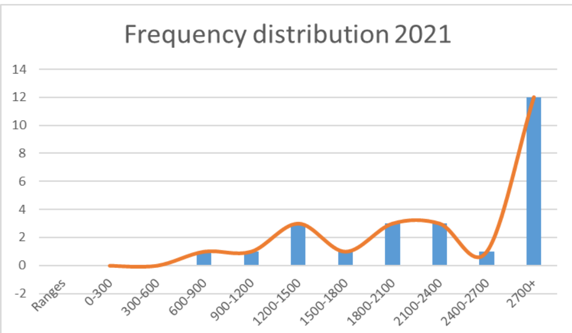


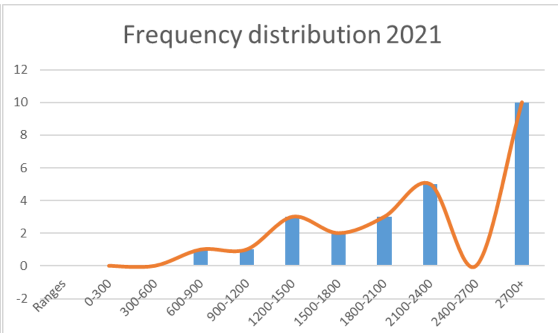
frequency EC 2019 (Premonsoon and Postmonsoon)



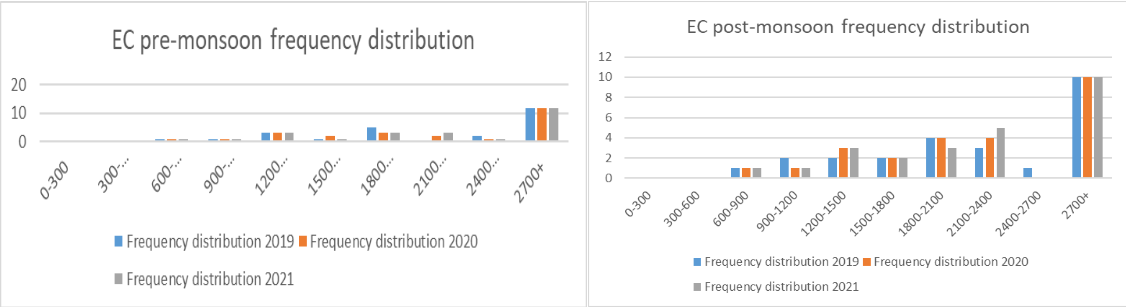


frequency EC 2020 (Premonsoon and Postmonsoon)

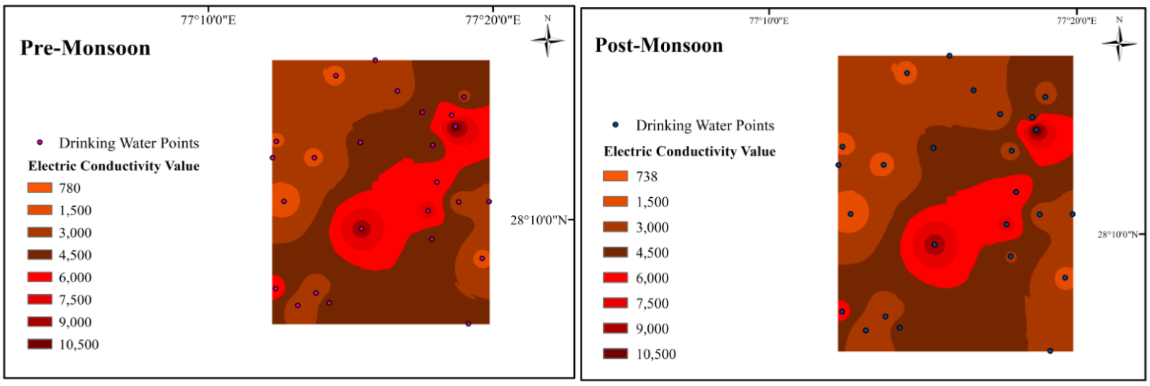




frequency EC 2021 (Premonsoon and Postmonsoon)



Cumulative frequency EC 2019-2021 (Premonsoon and Postmonsoon)



GIS maps showing EC value range during premonsoon and postmonsoon season of 2021

5.1.3TDS

TDS tells us about the concentration of substances dissolved in drinking water. Both organic matter and inorganic salts which constitute both the cations (calcium, sodium, potassium, and magnesium) and anions (chloride, carbonates, nitrates, bicarbonates) constitute the TDS.

Anthropogenic sources like sewage, agricultural run-off, wastewater from industries, domestic waste all enter as impurities in water and contribute to TDS. High TDS in water is not a major health hazard but people with comorbidities, especially kidney and heart problems can face the negative consequences of high TDS in drinking water (Chakraborty et al., 2019). High TDS in drinking water may also show laxative effects. High TDS imparts bitter taste to water and results in water hardness, contributes to scale and precipitate formation on pipes, fixtures and utensils.

According to Sarath Prasanth et al., (2012) vegetative decomposition, effluent discharge from industries, and chemical weathering of rocks are the major reasons for high TDS in groundwater.

TDSbothduring the premonsoon and postmonsoon season of Palwal district in three years (2019-2021) has been shown in Table 5.5 and Table 5.6.

BIS fixed acceptable range of TDS in potablewater as 500 which can be elevated to 2000 devoidof any othersource of water. WHO has not specified any guidelines for TDS in drinking water based on human health but TDS limit in drinking water should not exceed 500 mg/l and TDS above 1000 mg/l in drinking water alter its taste (Devesa et al.,2018). TDS of the study area in premonsoon of 2019 varied 673-7987 with mean of 2695 while in postmonsoon TDS in groundwater ranged from 600 to 7568 with mean of 2526 .

TDS in groundwater in Palwal studied place changed from 557 -8480 with mean of 2554in premonsoon of 2020 while during postmonsoon , TDS in groundwater ranged from 498 -8267 with mean of 2407 .

TDS of studiedregion in premonsoon of 2021 varied 705-8000 with mean of 2765 while in postmonsoon,TDS in groundwater ranged from 598 -7789 with mean of 2460.

Frequency distribution graphs for TDS in groundwater have been shown in Fig 5.11, 5.12, 5.13 and 5.14 and spatial maps for TDS in groundwater samples have been in Fig 5.15.

Study area samples also revealed that in postmonsoon season groundwater samples had lesser dissolved solids as in comparison withpremonsoon season. All groundwater samples except (Kishorpur in post-monsoon 2020) were seen above the acceptable zone set by BIS. 48% of the studied locations had TDS above the allowed range set bythe BIS. Similarly high TDS above BIS allowed limit in groundwater was found in western region of India by Singh., (2020); Wagh., (2021) in Maharashtra. Sharma ., (2014) in Banasthali (Rajasthan) by analysis showed TDS above the BIS permissible limit in groundwater samples.

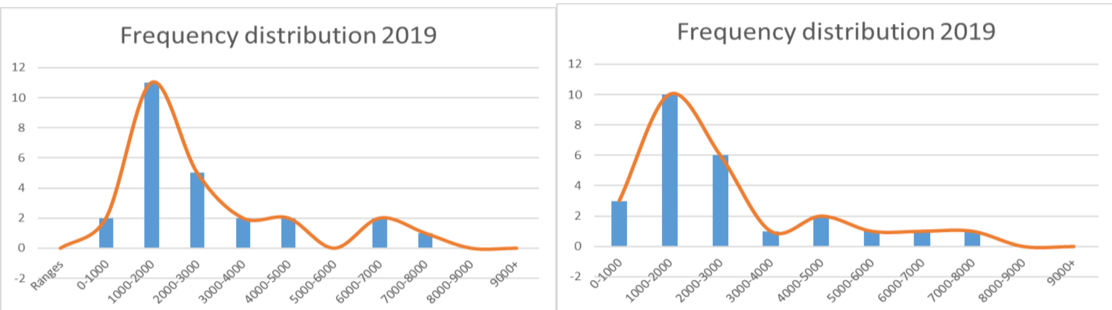
Table5.5Groundwater samples showing TDS variation (mg/l) during study years (2019-2021)

Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Alahapur	1819	1801	1813	1796	1825	1789
Firozpur	1775	1725	1770	1719	1790	1708
Prithla	1808	1788	1800	1780	1848	1798
Sikanderpur	2650	2566	2587	2501	2777	2590
Asawati	1528	1506	1550	1500	1575	1487
Allika	6420	6385	6425	5985	6785	6400
Rehrana	2357	2198	2120	1985	2567	2190
Joharkhera	4566	4395	4500	4275	4675	4218
Kishorpur	673	600	557	498	705	598

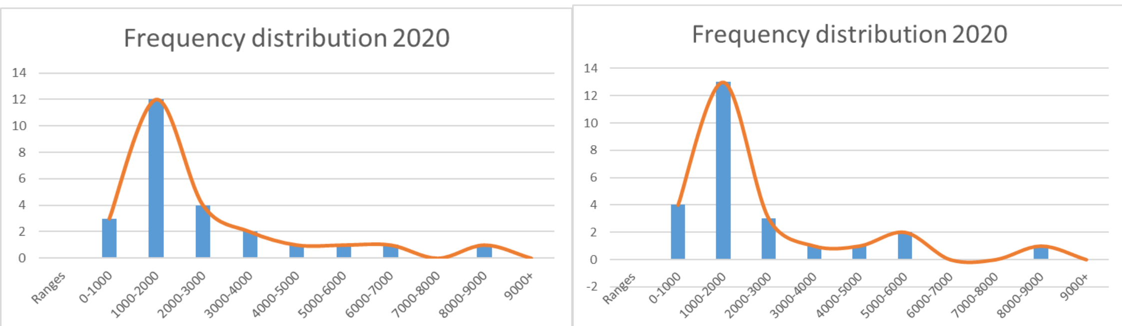
Tatarpur	7987	7568	8480	8267	8000	7789
Harfali	1544	1495	1400	1350	1589	1346
Teharki	1002	974	976	856	1149	890
Badha	1811	1789	1789	1698	1823	1767
NagliPanchagi	3110	2983	2798	2576	3242	2765
Chandpur	1183	1085	1089	990	1200	1067
Jaindapur	1389	1287	1278	1198	1400	1200
Patli Kalan	4820	4065	3986	3768	4600	3998
Patli Khurd	6400	5876	5987	5764	6600	5786
Rakhota	2171	2088	1989	1800	2089	1897
Naya Gaon	834	789	765	698	876	750
Megpur	2230	2000	1987	1900	2498	1956
Jatola	3790	3505	3500	2987	4000	3205
Meerapur	2820	2097	2169	1987	2765	1985
Gadpuri	1464	1398	1355	1267	1500	1276
Sehrala	1239	1188	1189	1043	1250	1045

Table5.6Summary of TDS variation in groundwater samples during the studyperiod

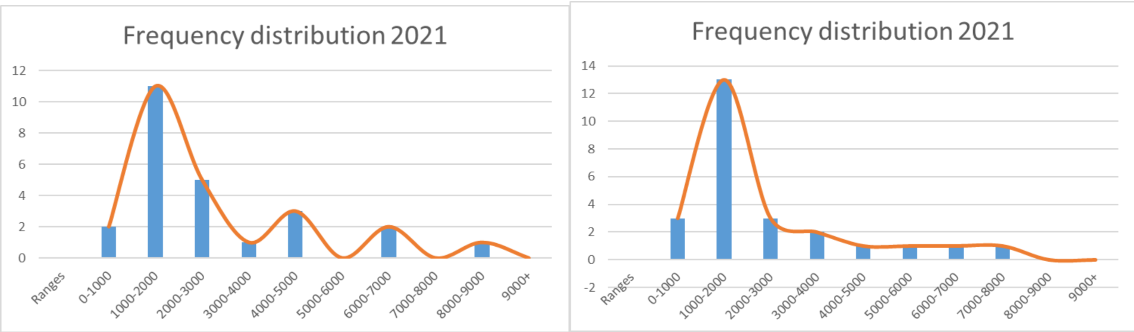
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Min	673	600	557	498	705	598
Max	7987	7568	8480	8267	8000	7789
Mean	2695.6	2526.04	2554.36	2407.52	2765.12	2460
Std. Deviation	1931.449	1819.968	1947.958	1875.158	1964.278	1847.123



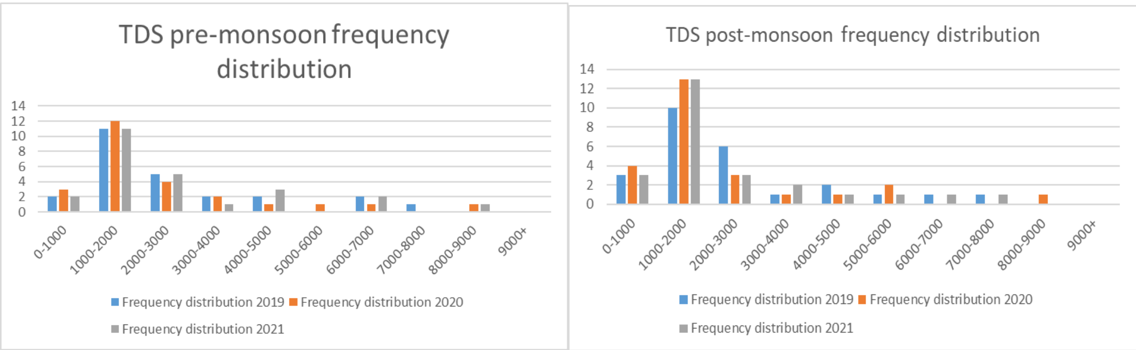
Frequency distribution of TDS 2019 (Premonsoon and Postmonsoon)



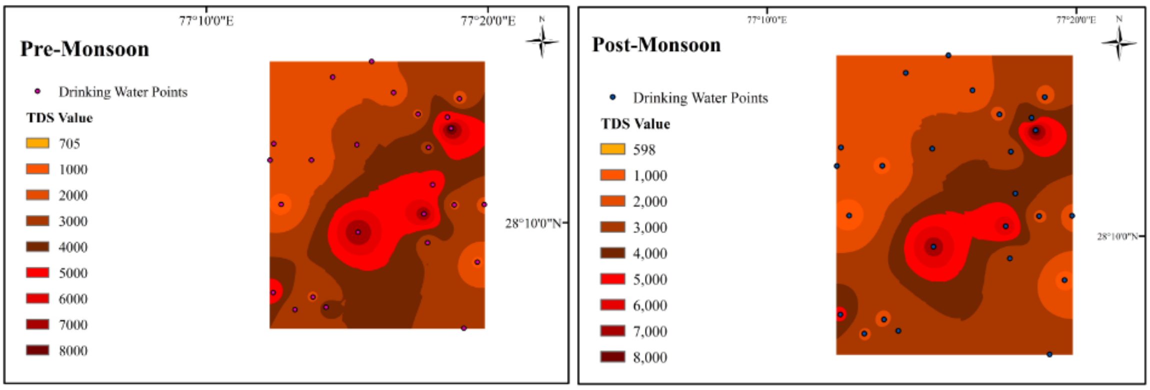
Frequency distribution of TDS 2020 (Premonsoon and Postmonsoon)



Frequency distribution of TDS 2021 (Premonsoon and Postmonsoon)



Cumulative frequency distribution of 2019-2021 (Premonsoon and Postmonsoon)



GIS maps showingvariation of TDS during premonsoon and postmonsoon of year 2021

5.1.4 Chloride

Fair amounts of chlorides are present naturally in water resources.Chloride occurs as a naturally found element in water and is generally found as a component of sodium chloride (salt). Rock weathering, salt spray deposition, intrusion of salty water in groundwater reserves in coastal areas, effluent discharged from industries, leachate infiltration in the ground, oil wells operation are some of the methods responsible for addition of chloride in drinking groundwater. Uplands and hilly domains have low chloride concentration as compared to groundwater and rivers (Kelly et al., 2012). Halite deposits from sedimentary rocks increase the chloride concentration in groundwater. Abnormally high concentration of chloride can increase through pollution especially through sewage (Mullaney et al., 2009). Chloride high concentration in water indicates organic as well as inorganic pollution. Anthropogenic sources are the primary reason for the increase of chloride concentration in water. Human and animal excreta are the major source for releasing chlorides and nitrates in water.

Chloride is an element found in living beings essential for maintaining good health. Generally,chlorideis not a major health hinderance but most concern is related to high levels of chloride linked with increased sodium level.

Chloride concentration in (mg/l) in the three consecutive years of (2019-2021) has been given in Table 5.7 & 5.8. In the study period chloride concentration in groundwater samples range199- 4842 with mean of 1502 inpremonsoon season of 2019 while in postmonsoon 2019, chloride concentration varied from 165-4657with mean of 1433.

Inyear 2020 chloride concentration in premonsoon varied from 167 - 4734 with mean of 1455 while in postmonsoon chloride concentration ranged 123 -4567 with mean of 1378 .

Inyear 2021 chloride concentration in premonsoon varied 210 -4987 with mean of 1549 while in postmonsoon chloride concentration ranged 150 -4703with a mean of 1380 .

Frequency distribution graphs for chloride in groundwater have been shown in Fig 5.16, 5.17, 5.18 and 5.19 and spatial maps for chloride in groundwater samples have been in Fig 5.20.

Industrial effluents, sewage discharge contribute for high chlorides values in water (Shivaraju., 2011).Chloride concentration decreased from premonsoon to after monsoon season becauseof aquifer recharge.Potash (potassium chloride) fertilizer is used extensively in the study area which also adds to chloride content in groundwater.

Though increased chloride concentration in water is not a big health issue, chloride concentration above 250 in drinking water can impair water taste and may show a laxative effect. BIS has set an acceptable range of chloride as 250 and 1000 in absence of any other source. 52 % of studied samples had chloride concentration abovepermissible limit set bynational standard limit. Similarly high concentration of chloride in groundwater was analyzed by Khan et al., (2015) in Shahjahanpur. Seasonal variation of chloride was also studied by Afshan et al., (2021) in Mysuru district (karnataka).

Table5.7Groundwater samples showing chloride concentration (mg/l) during study years (2019-2021)

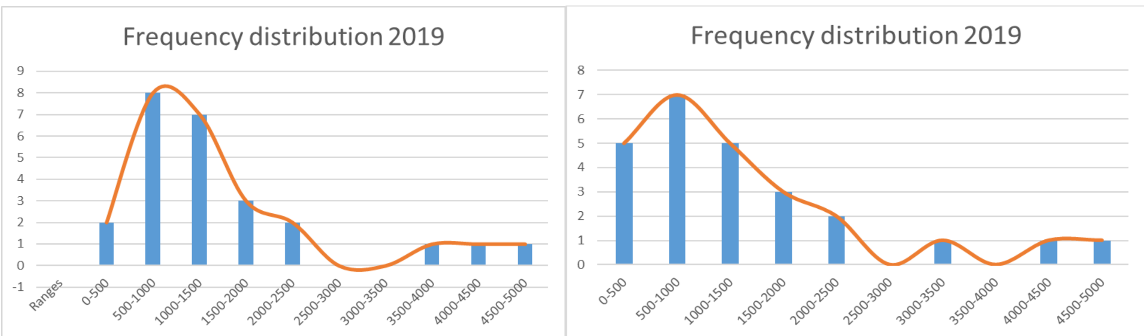
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Alahapur	966	949	947	936	980	937
Firozpur	1314	1297	1296	1286	1320	1276
Prithla	937	921	925	916	949	928
Sikanderpur	1377	1346	1345	1325	1378	1316
Asawati	1030	976	987	902	1057	956
Allika	4842	4657	4734	4567	4987	4703

Rehrana	1264	1200	1234	1189	1309	1202
Joharkhera	2371	2254	2267	2167	2456	2234
Kishorpur	355	314	321	298	379	278
Tatarpur	4331	4109	4091	3987	4567	3967
Harfali	703	654	658	620	756	611
Teharki	533	519	512	534	556	498
Badha	987	964	965	929	1001	935
NagliPanchagi	1724	1698	1689	1654	1747	1602
Chandpur	511	498	487	464	524	435
Jaindapur	1389	1278	1354	1234	1434	1205
Patli Kalan	2414	2345	2378	2009	2512	2232
Patli Khurd	3550	3245	3489	3123	3678	3200
Rakhota	1314	1234	1298	1202	1365	1195
Naya Gaon	199	165	167	123	210	150
Megpur	1044	989	987	952	1098	860
Jatola	1740	1679	1678	1598	1764	1478
Meerapur	1626	1587	1601	1548	1658	1495

Gadpuri	525	489	487	447	546	400
Sehrala	504	467	488	456	512	425

Table5.8Summary of observed chloride concentration in groundwater samples during studiedphase

Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Min	199	165	167	123	210	150
Max	4842	4657	4734	4567	4987	4703
Mean	1502	1433.36	1455.4	1378.64	1549.72	1380.72
Std. Deviation	1191.021	1132.213	1156.345	1097.222	1238.829	1129.100



frequency distribution of chloride 2019 (Pre-Monsoon and Post-monsoon)

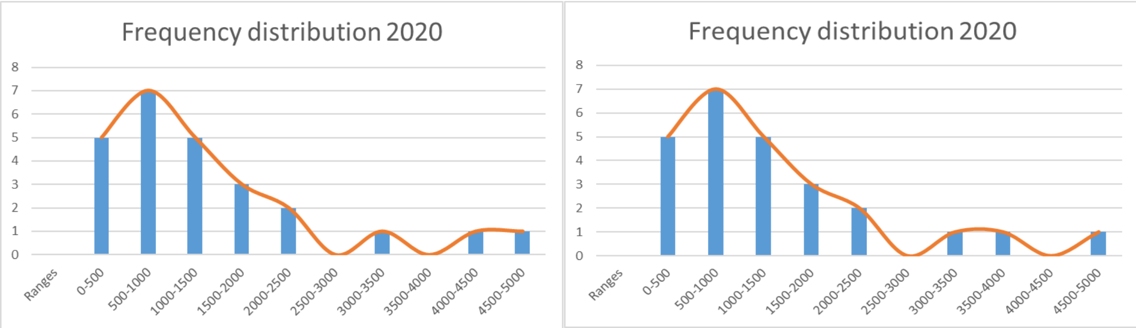


Fig 5.17: frequency chloride 2020 (Premonsoon and Postmonsoon)

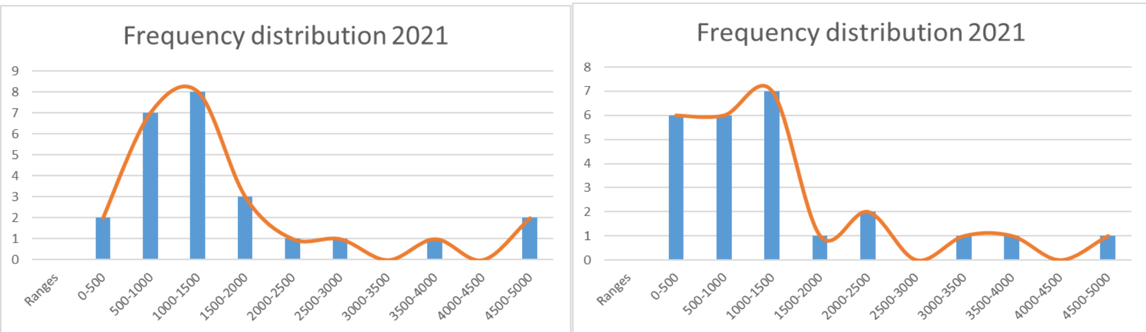


Fig 5.18: frequency chloride 2021 (Premonsoon and Postmonsoon)

Fig 5.19: Cumulative frequency 2019-2021 (Premonsoon and Postmonsoon)

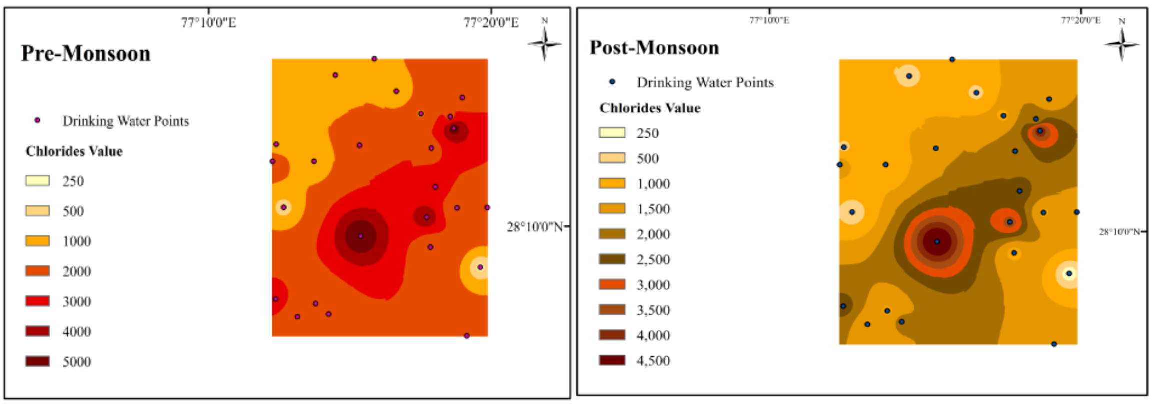


Fig 5.20: GIS maps showing variation of chloride in groundwater samples during premonsoon and postmonsoon season of year 2021

5.1.5 Fluoride

Fluorine is the 24th most abundant element which makes 0.065% of the earth' crust. It is freely distributed in nature and found as a component of soil, plants, rocks, animals and air.

Fluorine being highly reactive is not found in elemental form in nature but exists as fluorides in various minerals of which cryolite, fluorspar and fluorapatite being most common. Fluorspar being the most important mineral of fluoride on illumination shows bluish tinge, a property known as fluorescence.

High fluoride concentration in groundwater during teeth development phase of children generally (1- 4) years of age causes dental fluorosis in which enamel shows increased porosity and low mineral content. Skeletal fluorosis is seen in adults which disturbs the metabolism of calcium in body resulting in weakening and softening of body which can further cripple and paralyze the person, may also lead to rickets in children, osteomalacia in adults, may also lower spermatozoa motility thus also lowering the fertility rate (Peckham et al., 2014).

Greaterlevelof fluoride in drinking water have been witnessed in Rajasthan, Madhya Pradesh, Tamil Naidu, Karnataka, areas of Punjab, Andhra Pradesh, Gujarat and areas of Haryana (Khairnar et al., 2015).

According to BIS, fluoridelevelin water meant for consuming should not exceed 1.5 but India is an endemic belt of fluorosis which is proving to be a major health hindrance. Many areas of Haryana like Mahendergarh, Rohtak, Jind, Rewari, pockets of Palwal, Gurugram and Kaithal have elevated levels of fluoride in water(Marya ., 2014). Similarly, areas of Punjab show high levels of fluoride (Sharma et al., 2016). Similarly high levels of fluoride in groundwater have been seen in Gujarat (Kotecha ., 2012).

Fluoride (mg/l) during studiedtime (2019-21) have been shown in Table 5.9 and 5.10. During the premonsoon season of year 2019 fluoride concentration in groundwater samples varied from 0.18-3.22 with mean 1.4 while in postmonsoon fluoride concentration varied from 0.15 - 3.14 with mean of 1.3 .

In the year 2020 fluoride concentration in premonsoon varied from 0.12 - 3.12 with meanvalue1.33while in postmonsoon fluoride concentration ranged 0.1- 3.07 mg/l with mean of 1.21 .

In the year 2021 fluoride concentration in premonsoon varied 0.25- 3.35 with mean of 1.51 while in postmonsoonfluoride ranged from 0.16- 3.01 with mean of 1.22 .

Frequency distribution graphs for fluoride in groundwater have been shown in Fig 5.21, 5.22, 5.23 and 5.24 and spatial maps for fluoride in groundwater samples have been in Fig 5.25.

52 % of the study locations had fluoride in groundwater above safe limit given by BIS. Postmonsoon fluoride concentration in groundwater showed a decline due to dilution of aquifers due to precipitation.

WHO has set 1.5 as the permissible limit of fluoride in drinking water and BIS has limit1.0 as fluoride as desirable limit and 1.5 mg/l as the safety limit for fluoride in drinking water with the remark ‘Less is better’. Many people affected by fluoride contamination are generally residents of tropical countries with higher per capita consumption of water due to existing climatic conditions (Reddy., 2009). Not only high levels of fluoride but also absence or low levels of fluoride in drinking water for a long time can cause dental weakening. Dental fluorosis has been observed in individuals consuming 1.0 fluoride through water forlong period. Skeletal fluorosis has been observed in people who have consumed (3-6) mg/l of fluoride and crippling paralysis has been observed in people with consumption of 10 of fluoride in water for a big time (Everett., 2011). Fluorosis is a burden on the health of people hence preventing its consumption in drinking water is the only solution.

High fluoride levels in groundwater samples have been observed by Sankhla et al., (2018); Amalraj et al., (2013) in Tamil Nadu; Verma et al., (2017) in southern parts of India.

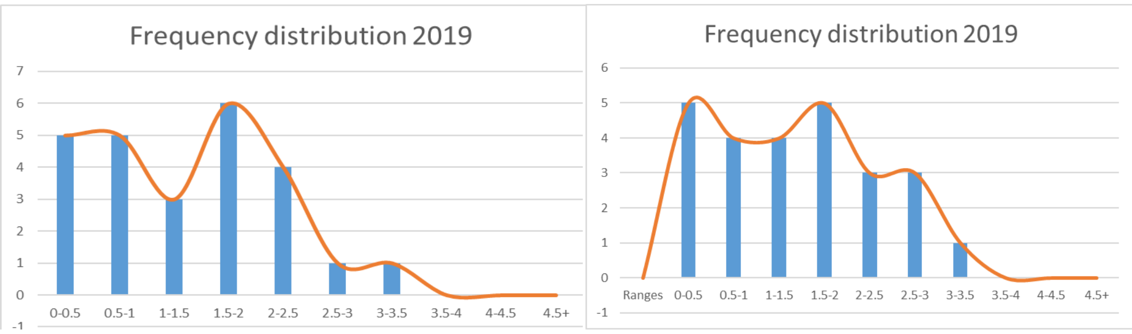
Groundwater samples showing fluoride seasonal variation (mg/l) during study years (2019-2021)

Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Alahapur	2.54	2.34	2.36	1.98	2.56	1.86
Firozpur	1.27	1.08	1.18	1.02	1.27	1.1
Prithla	1.74	1.58	1.45	1.41	1.68	1.26
Sikanderpur	0.32	0.26	0.26	0.19	0.36	0.21
Asawati	2.54	2.32	2.21	2.14	2.53	2.15
Allika	2.75	2.56	2.56	2.48	2.78	2.21
Rehrana	1.63	1.58	1.57	1.46	1.72	1.32
Joharkhera	0.88	0.74	0.69	0.57	0.89	0.56
Kishorpur	3.22	3.14	3.12	3.07	3.35	3.01

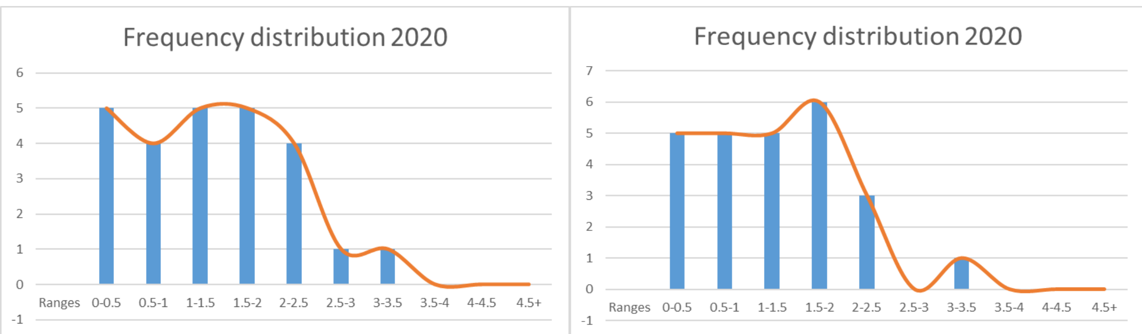
Tatarpur	1.93	1.86	1.76	1.57	1.95	1.76
Harfali	1.02	0.98	1	0.5	1.05	0.91
Teharki	0.21	0.17	0.18	0.14	0.25	0.16
Badha	1.45	1.32	1.34	1.25	1.56	1.36
NagliPanchagi	0.49	0.37	0.37	0.31	0.53	0.29
Chandpur	0.67	0.57	0.53	0.51	0.69	0.49
Jaindapur	1.94	1.75	1.67	1.59	1.98	1.61
Patli Kalan	2.21	2.16	2.15	2.09	2.2	2.09
Patli Khurd	1.74	1.61	1.65	1.58	1.78	1.59
Rakhota	0.18	0.15	0.12	0.1	1	0.19
Naya Gaon	2.05	1.97	1.97	1.76	2.06	1.89
Megpur	1.36	1.28	1.25	1.11	1.42	1.12
Jatola	0.72	0.67	0.68	0.63	0.74	0.58
Meerapur	0.73	0.68	0.7	0.64	0.76	0.65
Gadpuri	2.21	2.02	2.14	1.99	2.29	2.01
Sehrala	0.47	0.43	0.34	0.26	0.56	0.31

Summary of observed fluoride concentration in groundwater samples during three years

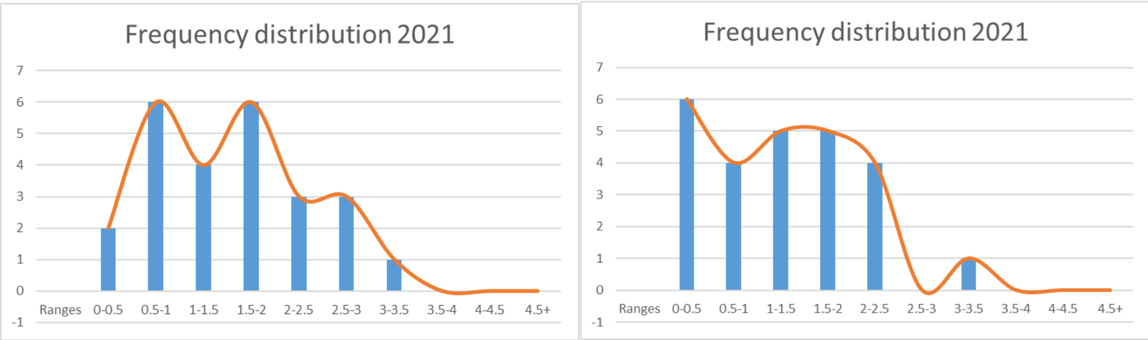
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Min	0.18	0.15	0.12	0.1	0.25	0.16
Max	3.22	3.14	3.12	3.07	3.35	3.01
Mean	1.4508	1.3436	1.33	1.214	1.5184	1.2276
StdDeviation	0.863	0.831	0.831	0.815	0.831	0.780



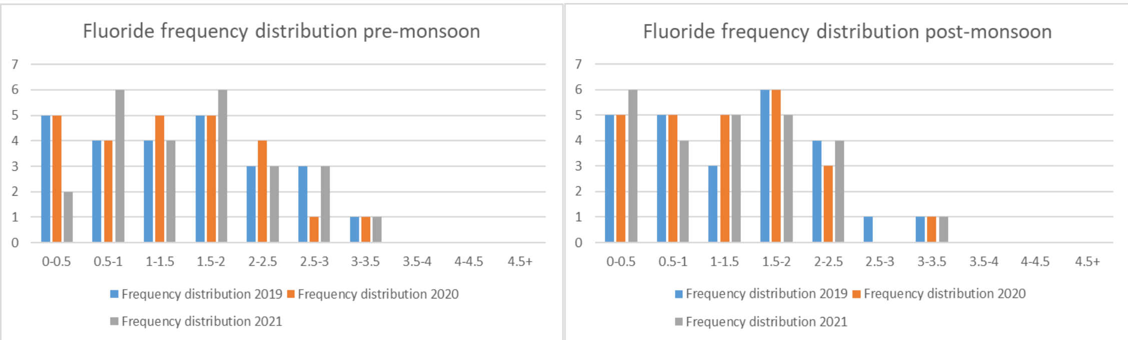
frequency distribution of fluoride 2019 (Premonsoon and Postmonsoon)



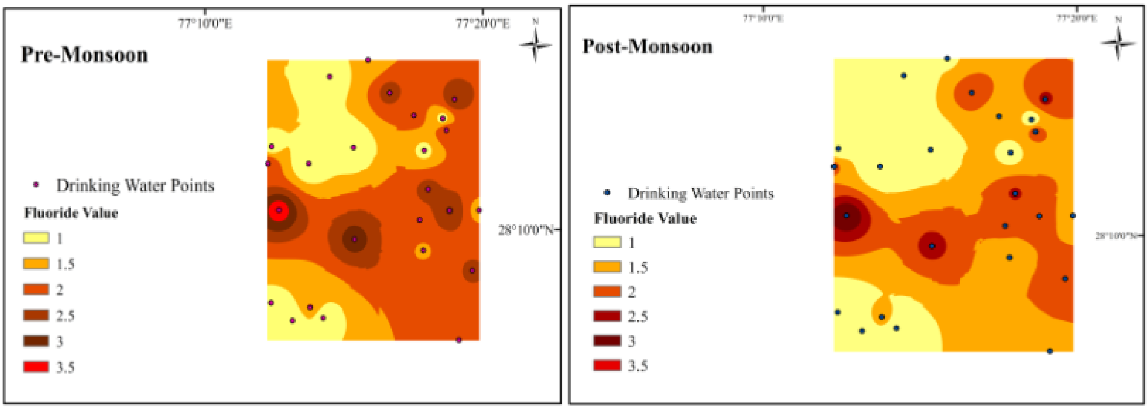
frequency distribution of fluoride 2020 (Premonsoon and Postmonsoon)



frequency distribution of fluoride 2021 (Premonsoon and Postmonsoon)



Cumulative frequency distribution of fluoride 2019-2021 (Premonsoon and Postmonsoon)



GIS maps showing spatial variation of fluoride in groundwater samples during premonsoon and postmonsoon season of year 2021

5.1.6 TA

Alkalinity inwater is its ability to neutralize various acids present in water. It measures carbonates, bicarbonates, hydroxyl ions present in water. Alkalinity tells about the capacity of water to resist any change in pH that could make the water acidic. TAis natural property of water formed due to dissolution ofCO_2 in water. Alkalinity in water also comes from calcium carbonate which leaches from rocks and soil, it also enhances due to construction and mining as limestone and soil rich in carbonate are more alkaline. Effluents discharged from waste water treatment plants are also responsible for increasing the alkalinity in water. Sewage generated from homes also contains carbonates and bicarbonate thus contributing to increase of alkalinity in water. High alkalinity gives a bitter taste to water. Alkalinity present in water does not have a negative impact on human health but total alkalinity > 200 mg/l when present in water gives it an unpleasant taste.

Table 5.11 and 5.12 represent TA in samples during the studied period (2019-2021). In the year 2019, total alkalinity varies 121 -880 mean of 558 in premonsoon while in postmonsoon total alkalinity varied 103 -825with mean of 529 .

In the year 2020 total alkalinity in premonsoon varied 108 -845 mean of 543 while in postmonsoon total alkalinity ranged 98- 812mean of 521.

In the year 2021 total alkalinity in premonsoonvaried 136- 888 with mean of 575while in postmonsoon total alkalinity ranged 95 - 768 mean of 584 .

Frequency distribution graphs for total alkalinity in groundwater have been shown in Fig 5.26, 5.27, 5.28 and 5.29 and spatial maps for total alkalinity in groundwater samples have been in Fig 5.30.

BIS has set an acceptable value of 200 mg/l (CaCo3) for alkalinity and 600 in absence of any other alternative source. Postmonsoon season showed a decline in alkalinity due to aquifer recharge. In Allika study location during the postmonsoon season (2020) value of alkalinity had shown an increase.

Except Alahapur, Firozpur, Sikanderpur, Asawati, Allika, Rehrana, Joharkhera and Gadpuri which constitute 32 % of the study locations total alkalinity in groundwater within allowedrange set by BIS. Total alkalinity in Jind (Haryanaa) was found in values of 292-814 byMor et al., (2003). Similar trends in total alkalinity in groundwater samples were observed by Chavan et al., (2014) in Solapur (Maharashtra); Kumar et al., (2015) in Lucknow (Uttar Pradesh).

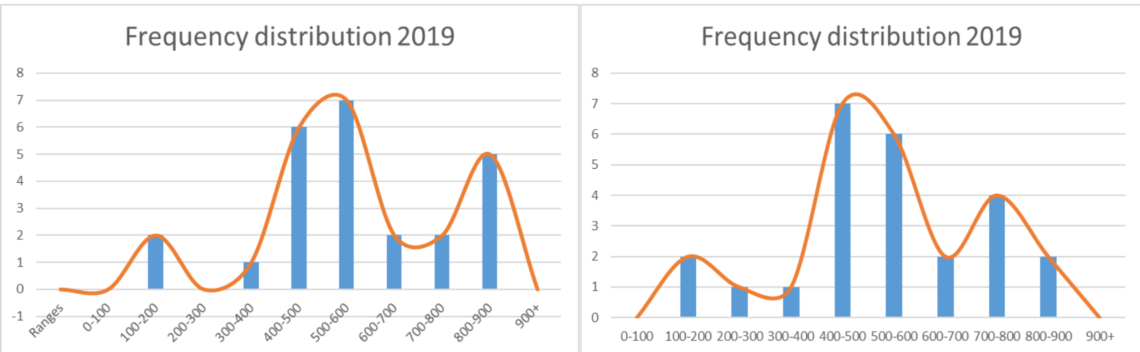
Table 5.11 Groundwater samples showing alkalinity seasonal variation (mg/l) during study years (2019-2021)

Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Alahapur	740	702	725	687	765	650
Firozpur	840	798	832	786	865	755
Prithla	550	496	580	543	604	545
Sikanderpur	690	643	645	600	706	587
Asawati	880	825	832	812	856	768
Allika	810	765	768	789	867	730
Rehrana	830	802	789	723	843	721
Joharkhera	820	795	845	803	888	768

Kishorpur	130	104	108	98	145	95
Tatarpur	460	403	432	398	476	385
Harfali	570	576	578	582	589	515
Teharki	450	424	432	445	465	404
Badha	440	420	423	436	465	415
NagliPanchagi	440	412	426	418	456	421
Chandpur	400	386	376	367	410	350
Jaindapur	560	534	543	521	576	510
Palli Kalan	300	287	276	265	305	259
Patli Khurd	450	432	465	440	476	426
Rakhota	540	512	513	478	532	490
Naya Gaon	121	103	135	110	136	102
Megpur	520	498	504	478	532	458
Jatola	620	578	602	589	598	598
Meerapur	560	534	543	523	576	513
Gadpuri	720	689	702	656	723	654
Sehrala	530	520	524	501	542	502

Summary of observed total alkalinity in groundwater samples.

Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Min	121	103	108	98	136	95
Max	880	825	845	812	888	768
Mean	558.84	529.52	543.92	521.92	575.84	504.84
Std. Deviation	204.041	197.858	200.074	193.044	207.698	185.067



frequency distribution of 2019 (TA Pre-Monsoon and Post-monsoon)

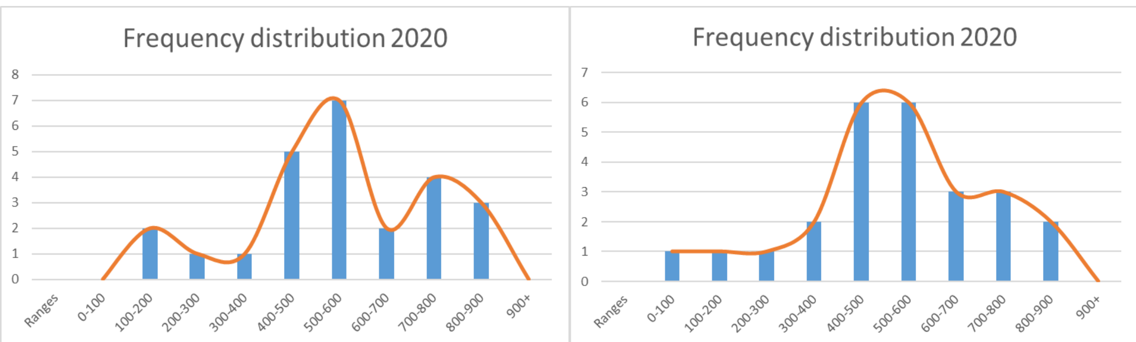
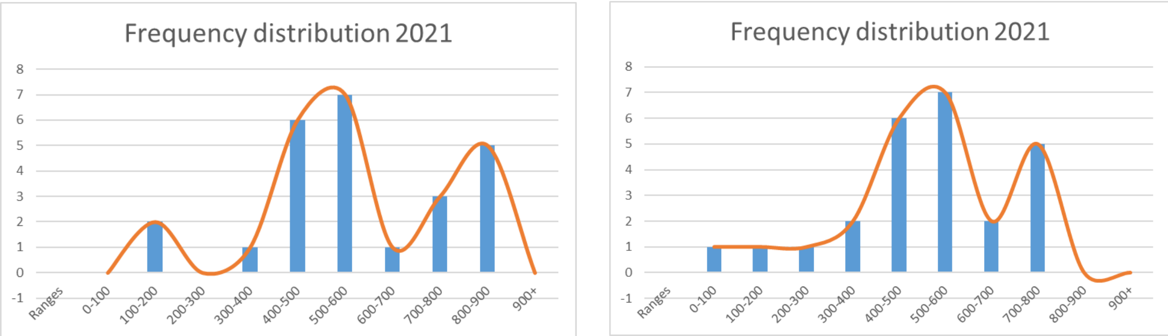
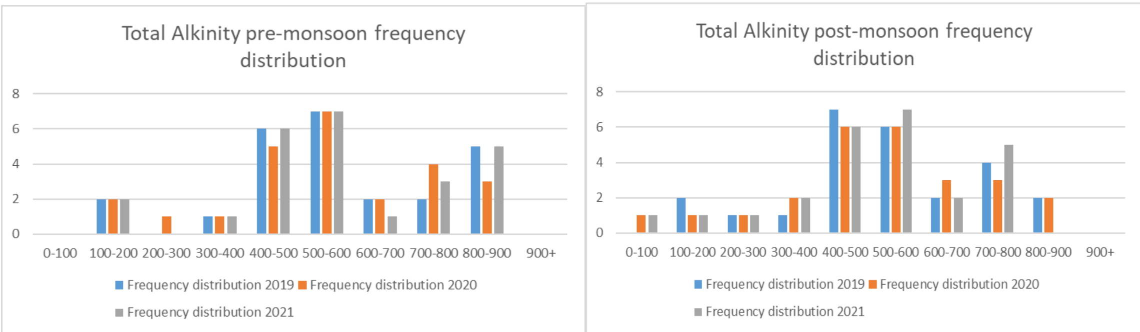


Fig 5.27: frequency distribution of 2020 (TA Premonsoon and Postmonsoon)



frequency distribution of 2021 (TA Premonsoon and Postmonsoon)



Cumulative frequency distribution of 2019-2021 (Premonsoon and Postmonsoon)

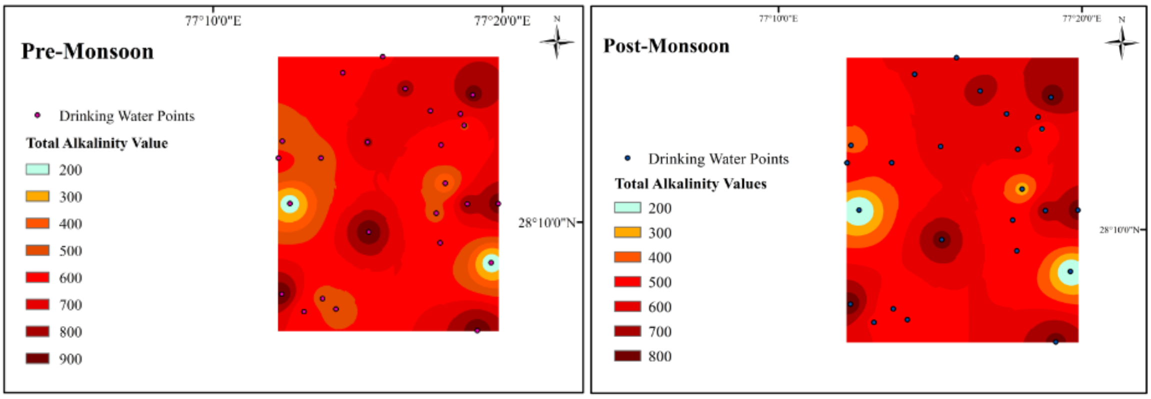


Fig 5.30: GIS maps with variation of TA in groundwater samples during premonsoon and postmonsoon of year 2021

5.1.7 Sulphates

Sulphates are found naturally in water ranging from minute concentration to present in very high concentration. Salts of calcium and magnesium are responsible for imparting permanent hardness to water.

Sulphates are found in many minerals like Barite (barium sulphate), Gypsum (calcium sulphate, Glauber sulphate (sodium sulphate) and Epsom (magnesium sulphate). These minerals dissolve in water and when this water flows through rocks and soil some of the sulphates dissolve in groundwater to increase the sulphate content.

Paper mills, tanneries, textile industries, mining and smelting all contribute to discharge the sulphate content in water. Acidic rains, sulphur dioxide released by combustion of fossil fuels and various metallurgical operations also add to sulphate in water. Bacterial reduction is the main factor converting sulphates into hydrogen sulphides which emanate out during coal production.Sulphates along with calcium and magnesium impart hardness to water.

Sulphates concentration in groundwater samples have been shown in Table 5.13 and 5.14. In year 2019 sulphate in premonsoon season varied from 52-193 with mean of 130 while in postmonsoon sulphate concentration ranged from 45-187 with a mean of 124.

In year 2020 sulphate concentration in groundwater in premonsoon season varied from 48-186 with mean of 124 while in postmonsoon sulphate in groundwater ranged from 44 - 181 with mean of 119 .

In year 2021 sulphate concentration in premonsoon varied 56 - 190 with mean of 134while in postmonsoon sulphate concentration in groundwater ranged from 46- 183 with mean of 123 mg/l.

Frequency distribution graphs for sulphates in groundwater have been shown in Fig 5.31, 5.32, 5.33 and 5.34 and spatial maps for sulphate concentration in groundwater samples have been in Fig 5.35.

Sulphate concentration in groundwater was at a higher level in premonsoon season because of evaporation and lowering of ground water-table. Low value of sulphate concentration in groundwater was seen in the postmonsoon season due to recharge of aquifers. BIS has set 200 as desirable range for sulphates in water and 400 as permissible limit for sulphate concentration in drinking water in absence of any alternative source. All studied samples were in the desirable limit setfor sulphate range in collected water. Sulphates present in groundwater are absorbed poorly in the intestine and eliminated quickly through the kidneys of mammals. Excess of sulphates present in drinking water also leads to corrosion of water distributing pipes. Excess Drinking water containing sulphates above 500 mg/l makes the water bitter and sulphates above 1000 mg/l can show gastro-intestinal problems.

Sulphate in groundwater Rohtak district (Haryana) was within the acceptable limit set by BIS (Bishnoi et al., 2007) and similar trend was observed by Sharma et al., (2013) in Yamunanagar (Haryana).

Groundwater samples showing sulphates seasonal variation (mg/l) during study years (2019-2021)

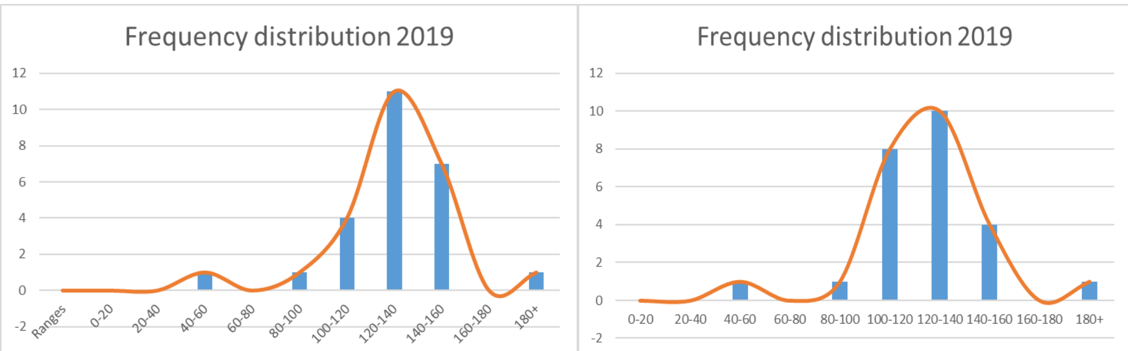
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon2021
Alahapur	135	129	127	122	141	125
Firozpur	151	145	147	141	156	136
Prithla	121	117	118	112	128	115
Sikanderpur	158	150	147	142	162	145
Asawati	132	126	127	121	137	129
Allika	132	127	125	120	134	121
Rehrana	193	187	186	181	190	183

Joharkhera	140	136	133	136	143	132
Kishorpur	52	45	48	44	56	46
Tatarpur	137	131	132	127	138	130
Harfali	121	115	116	111	122	118
Teharki	89	83	82	78	91	76
Badha	140	135	136	131	144	155
NagliPanchagi	140	134	132	126	147	125
Chandpur	135	130	128	121	141	126
Jaindapur	139	133	131	126	145	121
Patli Kalan	117	112	123	119	126	120
Patli Khurd	121	115	116	110	127	116
Rakhota	128	124	120	117	131	121
Naya Gaon	112	107	117	112	123	119
Megpur	151	145	146	142	154	137
Jatola	154	141	145	137	156	140
Meerapur	120	114	115	109	123	116
Gadpuri	117	113	112	106	123	116

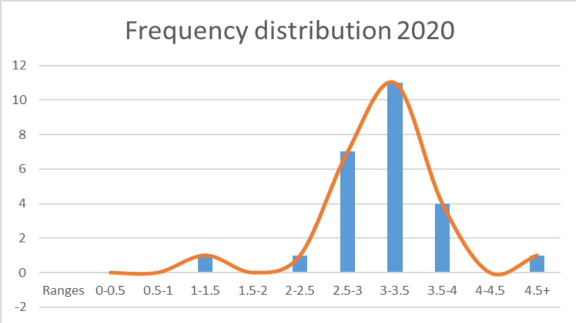
Sehrala	118	110	113	105	123	116

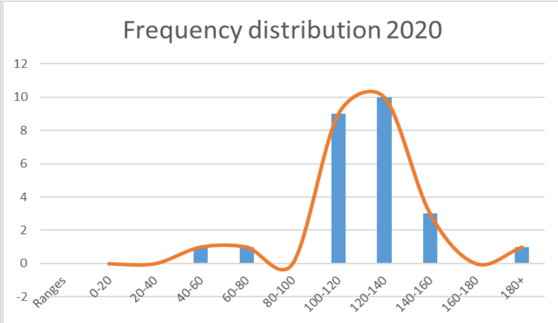
Summary of observed sulphates in water samples during the period.

Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Min	52	45	48	44	56	46
Max	193	187	186	181	190	183
Mean	130.12	124.16	124.88	119.84	134.44	123.36
Std. Deviation	25.508	25.304	24.461	24.429	24.661	24.496

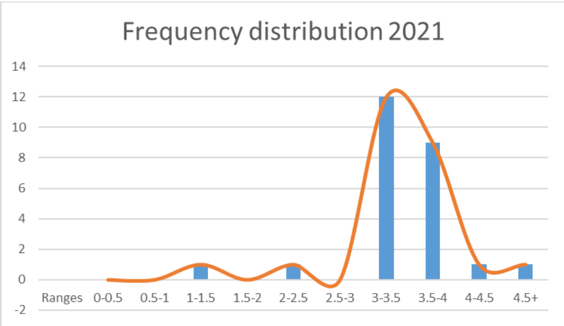


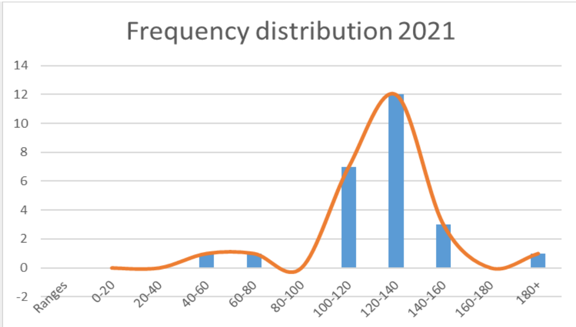
frequency distribution of sulphates 2019 (Premonsoon and Postmonsoon)



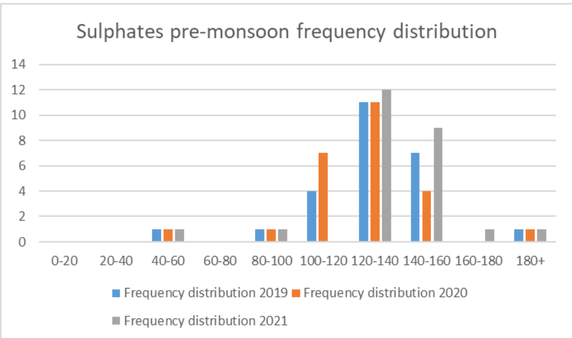


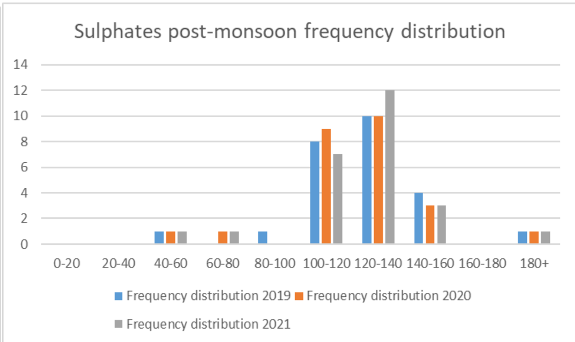
frequency distribution of sulphates 2020 (Premonsoon and Postmonsoon)



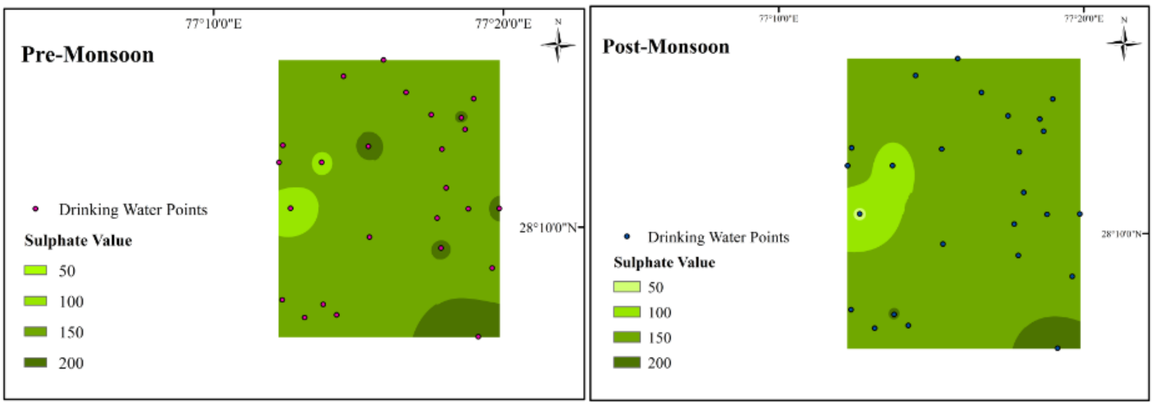


frequency distribution of sulphates 2021 (Premonsoon and Postmonsoon)





Cumulative frequency distribution of Sulphates 2019-2021 (Premonsoon and Postmonsoon)



GIS maps showing range of sulphates in groundwater during premonsoon and postmonsoon of year 2021

5.1.8 Turbidity

Turbidity in groundwater tells about the presence of suspended materials like inorganic, organic, silt and sand present in it. Cloudiness in water exhibits the turbid nature of water. Decaying flora and fauna, disturbance in settled sediments and contaminated water influx are the various reasons contributing to increase in turbidity which in turn reduces the transmittance of light through water. This decreased light transmittance can decrease the rate of photosynthesis thus disturbing aquatic ecosystems. High turbidity can make the water unpalatable. Though turbidity is not a major health threat but is an issue of aesthetic concern and visible turbidity present in drinking water may indicate presence of hazardous materials present in water. Excess turbidity present in groundwater can result in staining of clothes, utensils and machines.

Turbidity in groundwater study area is shown in Table 5.15 and Table 5.16. In the current study period, turbidity ranged from 1 -7 with mean 2.5 in the premonsoon of 2019 while in postmonsoon turbidity occured 0 to 5 NTU with mean of 0.88.

In year 2020 turbidity in premonsoonshowed from 0 - 6with mean of 2 while in postmonsoon turbidity showed from 0 to 4 with mean 0.48.

In year 2021 turbidity in premonsoonvaried from 0 -10 with a mean of 2.6 while in postmonsoon turbidity ranged 0 -4 with mean of 1.32. Frequency distribution graphs for turbidity in groundwater have been shown in Fig 5.36, 5.37, 5.38 and 5.39 while GIS maps for turbidity in groundwater samples have been in Fig 5.40. Similar trend was observed by Rout et al., (2016) in Ambala (Haryana).

BIS has given 1 as the desirablelimitsfor turbidity in drinking water and 5 as the permissiblelimit for turbidity in water meant for drinking. All collectedsamples except Tatarpur were within the permissible limit set by BIS for turbidity in water used for drinking.

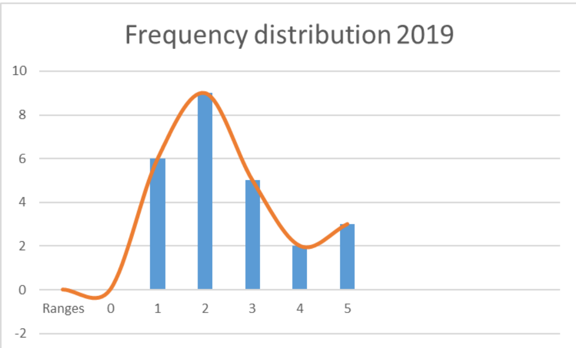
Groundwater samples showing turbidity seasonal variation (NTU) during study years (2019-2021)

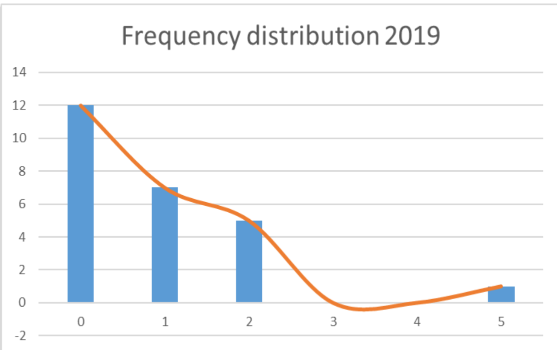
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Alahapur	2	0	1	0	2	1
Firozpur	3	1	2	0	3	2
Prithla	2	1	2	0	1	0
Sikanderpur	3	1	3	1	3	1
Asawati	2	1	2	0	2	1
Allika	4	2	3	1	5	3
Rehrana	5	2	4	1	5	3
Joharkhera	3	2	3	1	4	2

Kishorpur	1	0	0	0	1	0
Tatarpur	7	5	6	4	10	4
Harfali	2	0	1	0	1	1
Teharki	1	0	1	0	1	1
Badha	2	0	2	1	3	2
NagliPanchagi	3	1	4	1	3	2
Chandpur	1	0	1	0	1	0
Jaindapur	2	0	1	0	2	1
Patli Kalan	4	2	3	1	3	2
Patli Khurd	5	2	4	1	4	2
Rakhota	2	1	1	0	3	1
Naya Gaon	1	0	0	0	0	1
Megpur	2	0	2	0	2	1
Jatola	3	1	2	0	2	1
Meerapur	2	0	1	0	2	1
Gadpuri	1	0	1	0	1	0
Sehrala	1	0	0	0	1	0

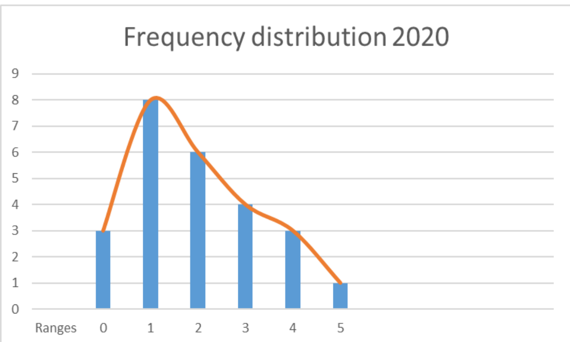
Summary of observed turbidity (NTU) in groundwater samples during the study period.

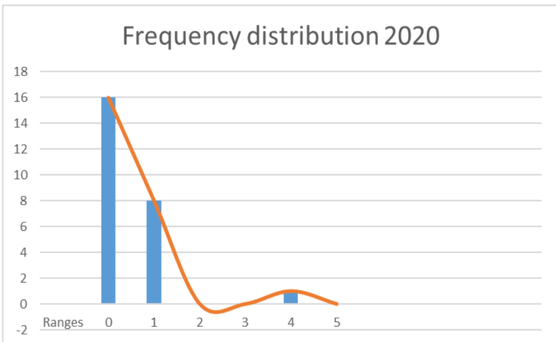
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Min	1	0	0	0	0	0
Max	7	5	6	4	10	4
Mean	2.56	0.88	2	0.48	2.6	1.32
Std. Deviation	1.502	1.166	1.471	0.871	2.020	1.029



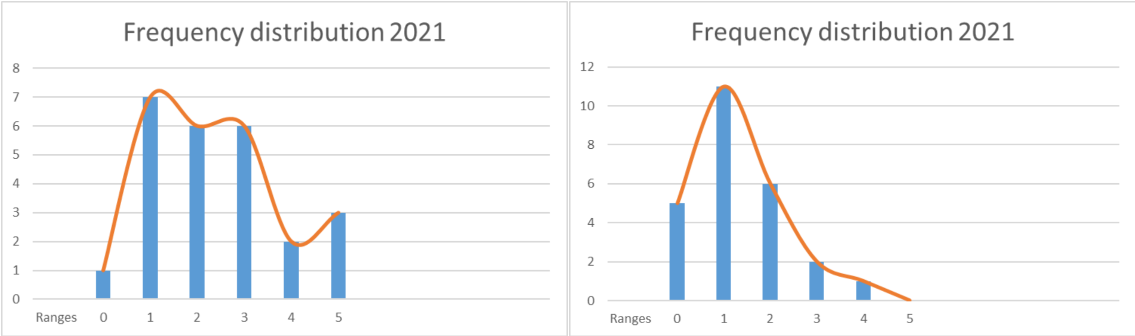


frequency distribution of turbidity 2019 (Pre-Monsoon and Post-monsoon)

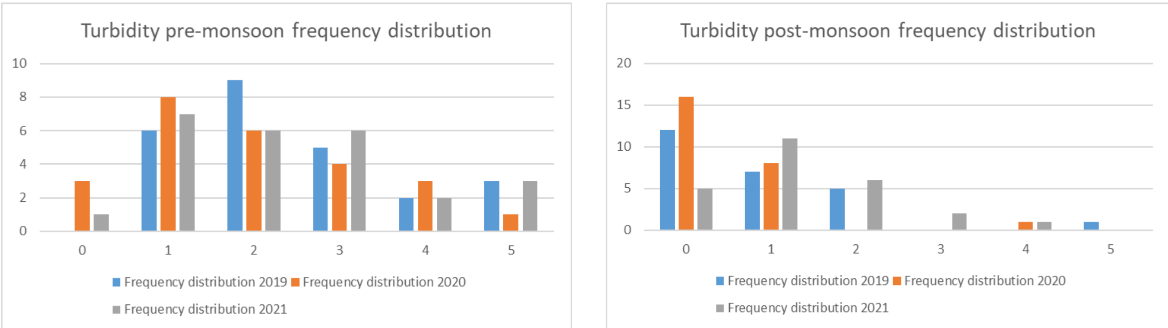




frequency distribution of turbidity 2020 (Premonsoon and Postmonsoon)



frequency distribution of turbidity 2021 (Premonsoon and Postmonsoon)



Cumulative frequency distribution of turbidity 2019-2021 (Premonsoon and Postmonsoon)

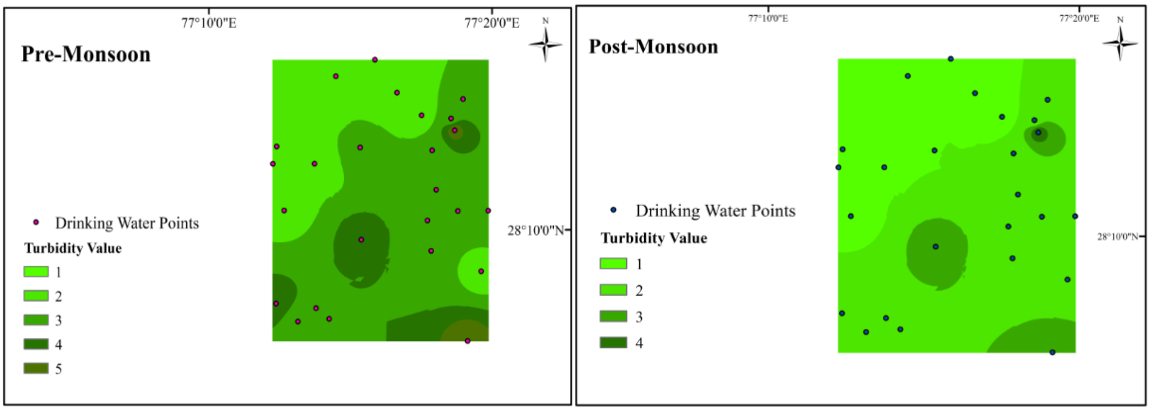


Fig 5.40: GIS maps showing variation of turbidity during the premonsoon and postmonsoon of year 2021

5.1.9 Total Hardness

Originally hardness was measured by water's capacity to react with soap as hard water needed extra amount of soap to form lather. Total hardness in water is described as water containing high amounts of Ca &Mg expressed as $CaCO_3$.

Presence of Mg & Ca carbonates in the water depicts temporary hardnessin water which can be removed by boiling whereas dissolved SO4 and Cl of Ca and Mgmakewater permanently hard which cannot be removed by boiling. Natural hardness in water is due to drainage basin geological nature. Boiling point of water shows an increase with increasing hardness. Excess hardness in water is responsible for stains and scales production in pipes, taps, geysers and pipes.

Water containing chalk, gypsum and limestone when it percolates below the ground it results in hard water. Thick layers of topsoil rich in limestone contribute to hard water in the ground whereas areas with thin topsoil and less reserves of limestone result in soft water below the ground. Generally, groundwater is comparatively harder as compared to surface water as weathering of rocks add calcite, gypsum and dolomite minerals to groundwater. Effluents released from industries, paper industry and mining add to hardness in water. Construction sites and various salts of calcium also contribute to total hardness in water. Industrial units which include paper manufacturing, fertilizer production and wastewater treatment plants use calcium salts mainly lime (CaO) and slaked lime ($Ca(OH)_2$) thus increasing waterhardness. Based on their classification, all the water samples came in a very hard category.

Classification of water based(Durfor& Becker) hardness

S.No	Conc (mg/l)	Classification	% Of observed samples
1	< 60	Soft	-

2	61-120	Moderate	-
3	121- 180	Slight Hard	-
4	> 181	Very Hard	100

In year 2019 total hardness in premonsoon season varied 200- 5550 with mean of 1581while in postmonsoonTH ranged 195-5234 with mean of 1490 .

In year 2020 total hardness in premonsoon varied 245 - 5425 with mean of 1526 while in postmonsoon season hardness ranged from 202-5214 with mean of 1461.

In year 2021 total hardness in premonsoon varied 232 -5560 with mean of 1633 while in postmonsoonTH ranged 198- 5189 with mean of 1432 .

BIS has made acceptable valueof200 ofTH (in form of CaCo3) in drinking water and permissible limit as 600 devoidof any other drinking water . Only 20% investigatedsamples were in permissible rangeset by BIS and rest samples exceeded the values.

Frequency distribution graphs for total hardness in groundwater have been shown in Fig 5.41, 5.42, 5.43 and 5.44 and spatial maps for total hardness in groundwater samples have been in Fig 5.45.

Total hardness values showed a decline in the postmonsoon season due to recharging of aquifers. Run-off from agricultural lands is one of the biggest contributors to total hardness in groundwater (Rout et al., 2011).

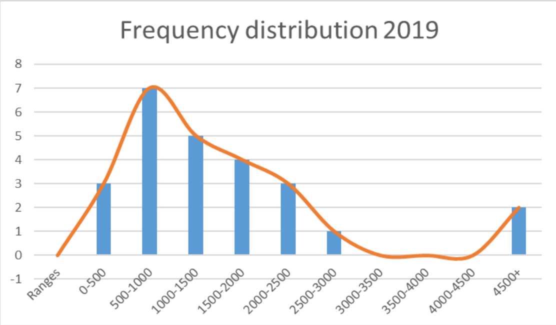
Table 5.18 Groundwater samples showing total hardness seasonal variation (mg/l) during study years (2019-2021)

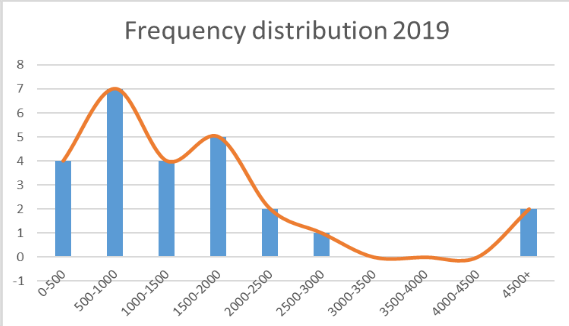
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Alahapur	660	598	705	634	810	690
Firozpur	1210	1165	1120	1043	1325	1056
Prithla	1320	1245	1265	1190	1400	1235
Sikanderpur	1330	1256	1400	1323	1459	1278
Asawati	800	745	756	700	805	750
Allika	2380	2167	2145	2078	2265	2045
Rehrana	1000	956	985	921	1065	932
Joharkhera	1570	1502	1465	1395	1500	1403
Kishorpur	410	394	435	400	460	398
Tatarpur	5450	5200	5398	5167	5560	4489
Harfali	980	935	945	900	1000	876
Teharki	760	724	725	697	794	689
Badha	1570	1502	1532	1494	1600	1513
NagliPanchagi	2200	2102	2004	1945	2105	1925
Chandpur	700	623	645	600	750	621
Jaindapur	740	704	678	634	722	613

Patli Kalan	2810	2567	2467	2376	2987	2216
Patli Khurd	5550	5234	5425	5214	5430	5189
Rakhota	1910	1876	1865	1803	1967	1798
Naya Gaon	200	195	245	202	232	198
Megpur	1160	1098	1456	1456	1654	1487
Jatola	2220	1996	2006	1985	2325	1987
Meerapur	1690	1623	1620	1587	1700	1621
Gadpuri	410	391	387	345	422	354
Sehrala	500	476	478	437	512	445

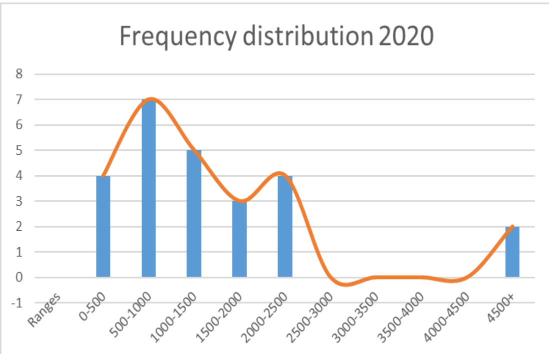
Summary of observed total hardness in samples during studied period.

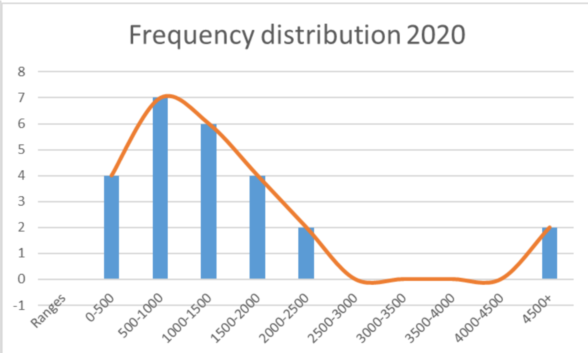
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Min	200	195	245	202	232	198
Max	5550	5234	5425	5214	5560	5189
Mean	1581.2	1490.96	1526.08	1461.04	1633.96	1432.32
Std. Deviation	1359.556	1284.293	1315.995	1272.053	1347.053	1182.675



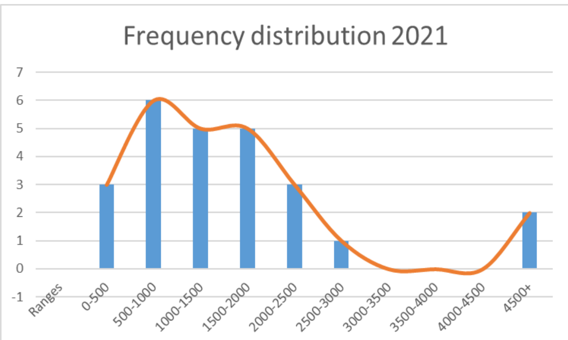


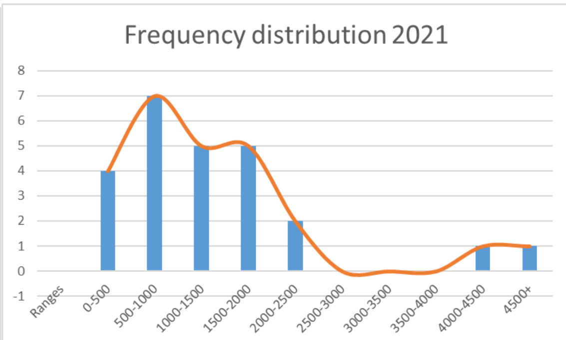
frequency distribution of total hardness 2019 (Premonsoon and Postmonsoon)



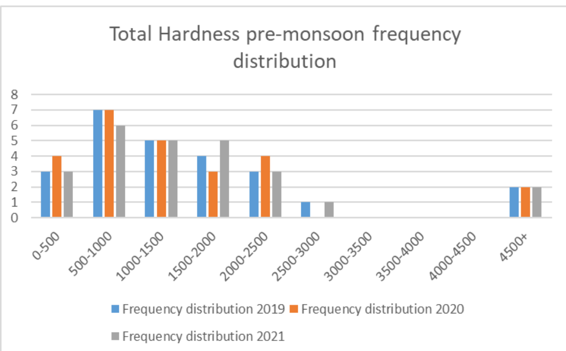


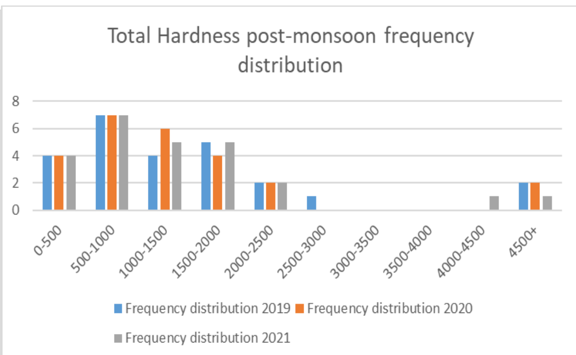
frequency distribution of total hardness 2020 (Premonsoon and Postmonsoon)



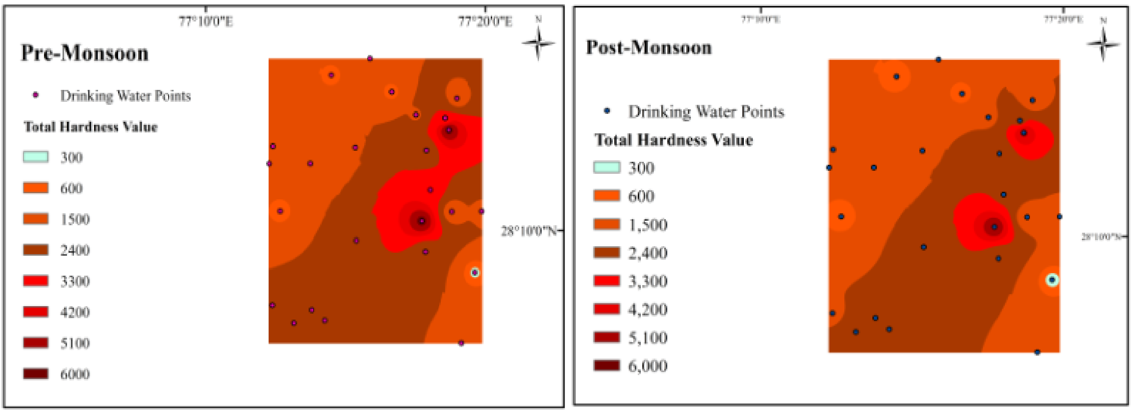


frequency distribution of total hardness 2021 (Premonsoon and Postmonsoon)





Cumulative frequency distribution of total hardness 2019-2021 (Premonsoon and Postmonsoon)



GIS maps showing TH variation during premonsoon&postmonsoonof year 2021.

5.1.10 Calcium

Calcium occupies 5th position among elements of abundance found naturally. Calcium is an important component of rocks. Pyroxene, amphibole and plagioclase are the important metamorphic and igneous rocks which release calcium in groundwater while gypsum, dolomite and limestone are important sources of sedimentary rocks releasing calcium in groundwater. CaCO3solubility is an important factor for determining calcium reserves in groundwater.

Calcium- an essential nutrient for living organisms playsessential role for dentine and bone structure. Calcium is responsible for imparting hardness to water and enhances the toxicity of other elements like zinc, lead, copper. When hard water is used for irrigating crops for a long time, calcium present in hard water immobilizes iron thus creating a shortage of iron in soil (Morrissey et al., 2009). Calcium hardens the pipes especially in higher temperatures thus decreasing the life span of pipes and fixtures. Calcium interacts with detergents and soaps, decreasing the efficiency of detergents and increasing the application of detergents and soaps (Abeliotis et al., 2015).

Calcium concentration for three consecutive years (2019-2021) in (mg/l) has been shown in Table 5.20 and 5.21. In year 2019 calcium concentration in premonsoon season varied from 32 - 437 with mean of 106 while in postmonsoon calcium concentration ranged from 30 - 434 with a mean of 103 .

In year 2020 calcium range in premonsoonvaried 30 - 440 with mean 104 while in postmonsoonCa concentration ranged from 28-438 with mean of 101.

In year 2021 Ca concentration in premonsoonseasonranged 33-439 with mean of 106 while in postmonsoon calcium ranged from 27- 430 with mean of 98 .

Frequency distribution graphs for calcium concentration in groundwater have been shown in Fig 5.46, 5.47, 5.48 and 5.49 and GIS maps for calcium concentration in groundwater samples have been in Fig 5.50.

Low concentration of calcium Vs sodium in study samples of groundwater indicates calcium present in groundwater has been replaced by sodium due to base -exchange reactions (Shalu et al., 2015). High calcium levels in drinking water even up to 2000 does not have adverse health impact on living forms but Ca concentrationabove 75 can cause encrustation of water supplying pipes so BIS has set an acceptable range of 75for Cain consuming water and permissible limit devoid of any alternative source of potable water. Tatarpur and Patli Khurd which compose 8% of the study locations had calcium concentration in groundwater above safe limits set by BIS. Most samples showed a decline in calcium concentration during the post-monsoon season due to aquifer recharging. Higher concentration of calcium is linked with cardiovascular defects in the older population. People with kidney stones and bladder stones should take precaution and avoid consuming hard water. On the other hand, consuming a lesser amount of calcium is linked with hypertension, osteoporosis, rectum cancer and insulin resistance (Ndii et al., 2020). Sharma et al., (2014) analyzed groundwater samples in Muktsar (Punjab) and reported calcium concentration in groundwatervarying 48- to 250. Similar trends in calcium concentration in groundwater from 47 -336 was reported by Nag et al., (2016) in Rajnagar (West Bengal).

Table 5.20 Groundwater samples showing seasonal variation in calcium (mg/l) during study years (2019-2021)

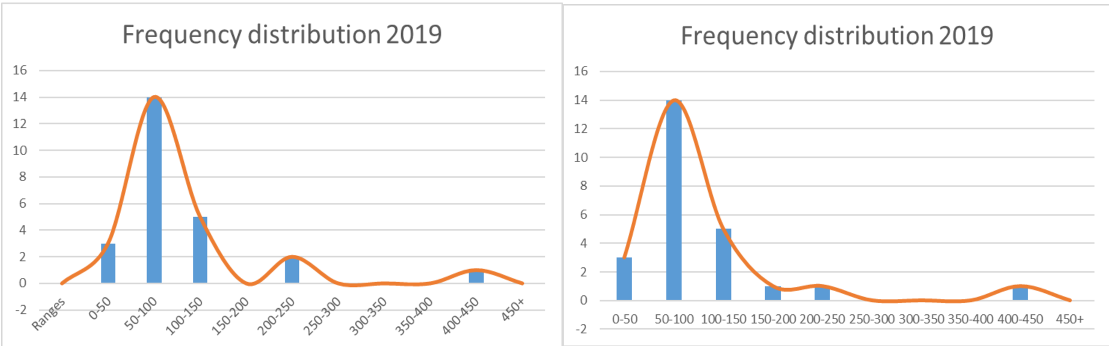
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premmonsoon 2021	Postmonsoon 2021
Alahapur	136	132	132	129	139	123
Firozpur	64	61	67	63	70	59
Prithla	92	90	90	87	93	85
Sikanderpur	68	65	70	67	71	62
Asawati	68	64	65	61	69	58
Allika	112	110	110	107	113	102
Rehrana	200	196	197	194	202	189
Joharkhera	132	128	127	124	130	122
Kishorpur	68	63	64	61	66	58
Tatarpur	437	434	440	438	439	430
Harfali	84	82	85	83	87	78
Teharki	48	46	45	42	46	38

Badha	72	69	70	72	70	65
NagliPanchagi	88	85	86	84	87	80
Chandpur	64	62	62	59	65	56
Jaindapur	132	129	130	127	134	125
Patli Kalan	80	77	77	74	79	72
Patli Khurd	224	221	220	218	222	215
Rakhota	92	89	87	84	89	82
Naya Gaon	60	62	58	56	60	54
Megpur	56	54	54	51	57	49
Jatola	112	110	111	108	112	104
Meerapur	84	81	81	79	83	75
Gadpuri	32	30	30	28	33	27
Sehrala	48	45	47	45	49	43

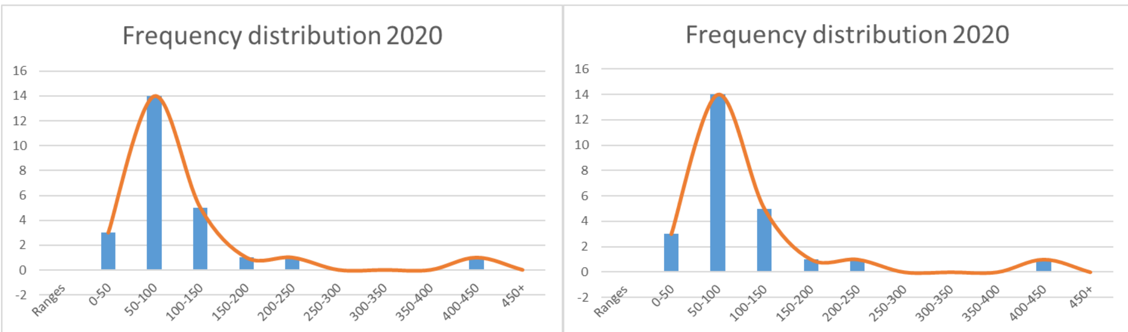
Summary of observed calcium in samples during the studiedframe.

Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Min	32	30	30	28	33	27

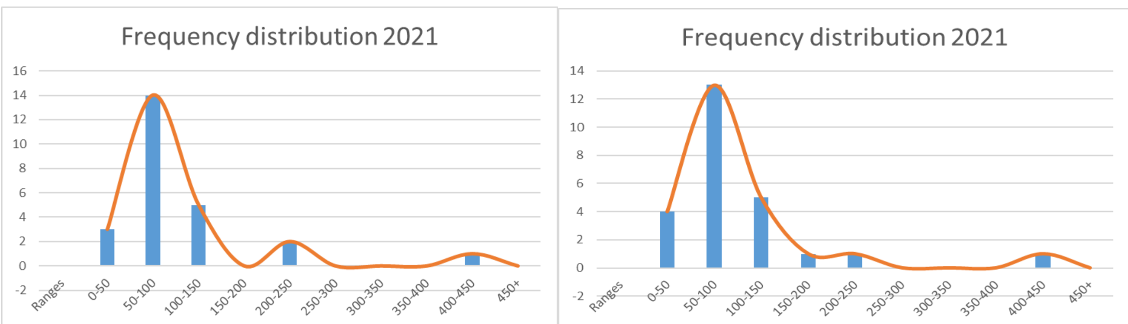
Max	437	434	440	438	439	430
Mean	106.12	103.4	104.2	101.64	106.6	98.04
Std. Deviation	82.371	82.120	82.887	82.955	82.584	82.006



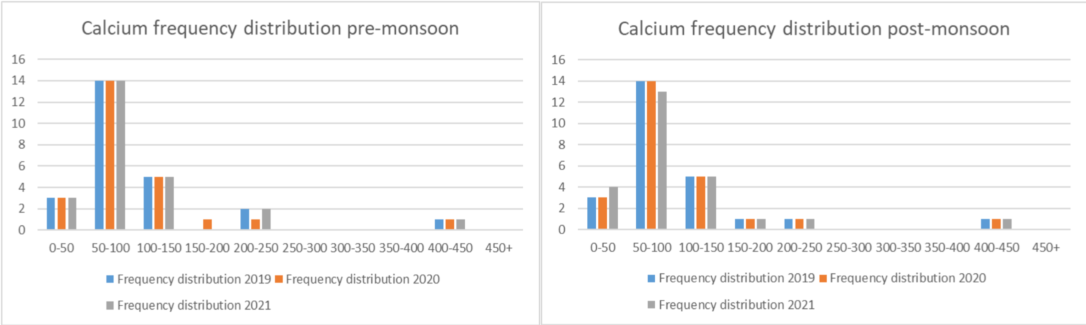
frequency distribution of calcium 2019 (Pre-Monsoon and Post-monsoon)



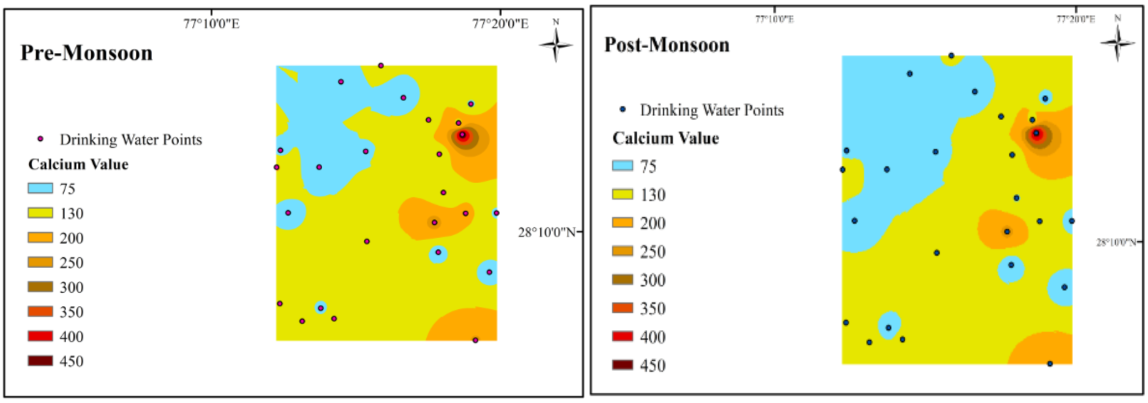
frequency distribution of calcium 2020 (Premonsoon and Postmonsoon)



frequency distribution of calcium 2021 (Premonsoon and Postmonsoon)



Cumulative frequency distribution of calcium 2019-2021 (Premonsoon and Postmonsoon)



GIS maps showing variation of Ca inpremonsoon and postmonsoon of 2021

5.1.11 Magnesium

Similar to calcium, magnesium is found in sedimentary rocks such as serpentine, hornblende and dolomite. Dark coloured igneous rocks having abundant magnesium deposits such as pyroxene, olivine, biotite. Tremolite-schists and talc are the metamorphic rocks bearing magnesium reserves. Generally, in groundwater concentration of calcium exceeds the concentration of magnesium which is in sync with their respective abundance in rocks. Magnesium carbonate similar to that of calcium carbonate is more soluble in water as compared to sodium salts. Municipal wastes and industrial effluents due to their discharge also increase the magnesium concentration in groundwater. Magnesium at concentration at which is generally found in unadulterated water sources is not toxic but high magnesium concentration along with sulphate in potable water can show laxative effects on humans.

In year 2019 magnesium concentration in premonsoon varied 12 - 1190 with mean of 315 while in postmonsoon magnesium ranged from 11 -1187 with mean of 311 .

In year 2020 Mg concentration in premonsoon varied from - to 1186 with mean of 311 while in postmonsoon magnesium ranged from 9- 1184with mean of 308.

In year 2021 magnesium concentration in premonsoon varied from 12 - 1192 with mean of 317 while in postmonsoon Mg concentration ranged from 7 - 1173 with mean of 305.

BIS has set desired limit for magnesium as 30 in drinking water and allowed limit 100 in absence for any other source. All study locations exceeded the desirable limit set by BIS. Alahapur, Kishorpur, Jaindpur, Nayagaon, Gadpuri, Sehrala which constitute 24% of studiedsample were in permissible limits set by national standards. Magnesium concentration above 500 mg/l can impart an unpleasant taste to drinking water.

Frequency distribution graphs for magnesium concentration in groundwater have been shown in Fig 5.51, 5.52, 5.53 and 5.54 and spatial maps for magnesium in groundwater samples have been in Fig 5.55.

Magnesium concentration in groundwater showed decrease in postmonsoon season because of recharging aquifers. Similar trends of decline in magnesium concentration season were studied by Palmajumder et al., (2021) in Bankura district of West-Bengal. Dissolution of gypsum and dolomite has led to increase of magnesium concentration in groundwater of studied place. Both calcium and Mg do not behave in similar pattern. High levels of magnesium have been found in Palwal due to presence of exchangeable sodium (Shalu et al., 2015).

Magnesium is an essential nutrient required by living organisms. Magnesium is an important constituent of chlorophyll required for photosynthesis. Magnesium along with sulphates in drinking water can show laxative effects, hypertension, myocardial infections and osteoporosis (Rapant et al., 2017). Potable water with magnesium concentration above 500 mg/ l has a bitter taste.

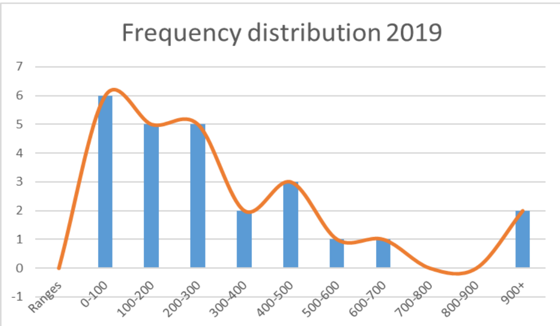
Groundwater samples showing seasonal variation in magnesium (mg/l) during study years (2019-2021)

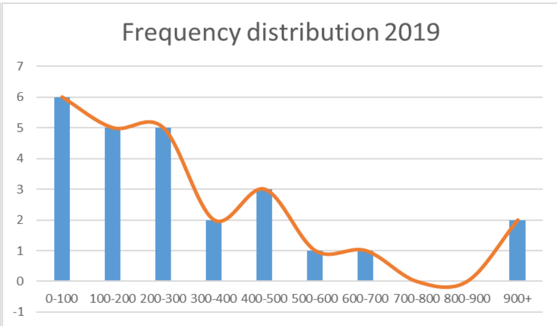
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Alahapur	77	74	74	70	81	72
Firozpur	252	249	248	244	256	233
Prithla	262	257	258	253	266	255
Sikanderpur	278	280	273	268	280	265
Asawati	151	147	147	144	151	139
Allika	504	500	500	497	506	495
Rehrana	120	117	116	118	121	115
Joharkhera	298	294	290	285	296	285
Kishorpur	58	55	52	47	58	49
Tatarpur	1044	1037	1038	1031	1048	1030

Harfali	185	182	181	175	187	169
Teharki	154	150	151	147	156	145
Badha	334	330	331	327	335	329
NagliPanchagi	475	470	471	467	478	461
Chandpur	130	126	132	127	134	124
Jaindapur	98	95	95	93	97	92
Patli Kalan	622	619	618	614	625	615
Patli Khurd	1190	1187	1186	1184	1192	1173
Rakhota	403	400	401	397	406	391
Naya Gaon	12	11	10	9	12	7
Megpur	245	241	241	237	247	231
Jatola	466	462	462	457	467	453
Meerapur	355	352	353	350	356	345
Gadpuri	79	75	80	77	82	74
Sehrala	91	86	87	84	91	85

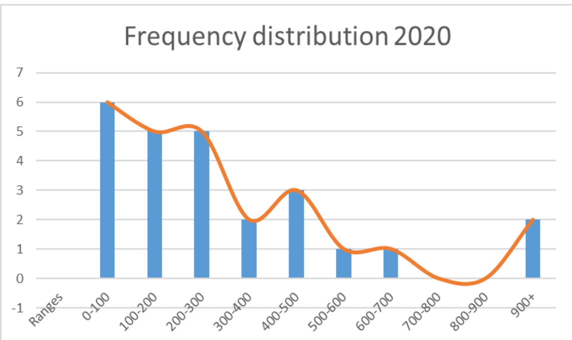
Summary of observed magnesium concentration in groundwater samples during studied years.

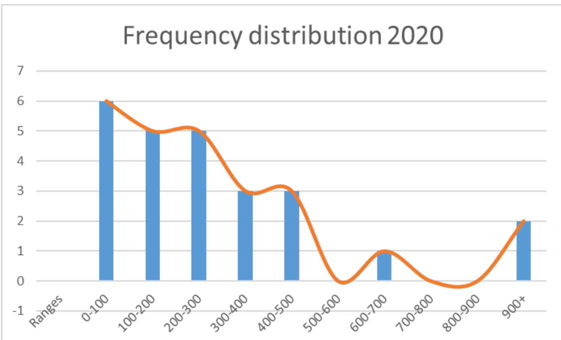
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Min	12	11	10	9	12	7
Max	1190	1187	1186	1184	1192	1173
Mean	315.32	311.84	311.8	308.08	317.12	305.28
Std. Deviation	289.245	288.817	288.663	288.283	289.725	287.118



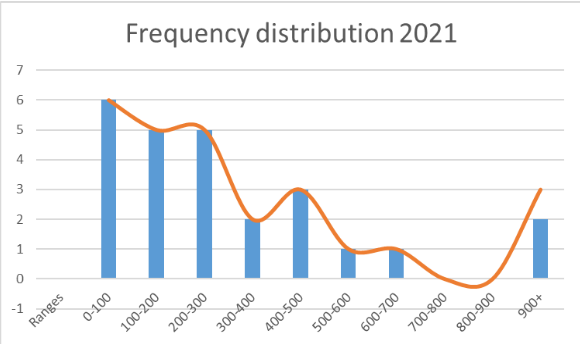


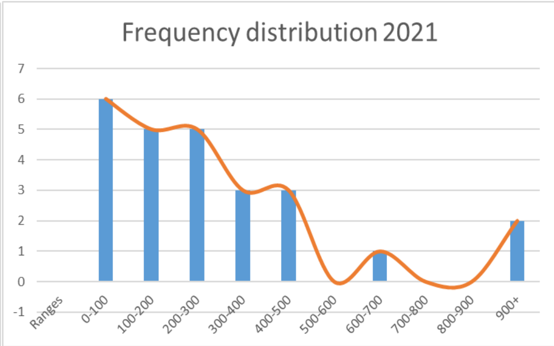
frequency distribution of magnesium 2019 (Premonsoon and Postmonsoon)



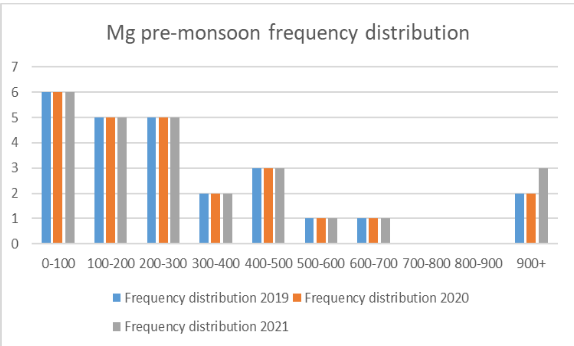


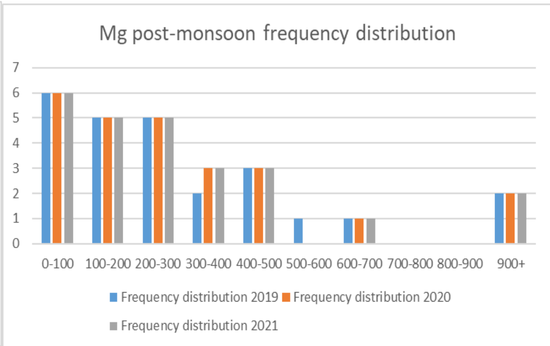
frequency distribution of magnesium 2020 (Premonsoon and Postmonsoon)



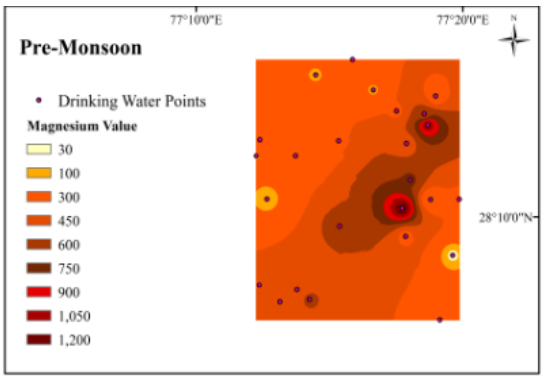


frequency distribution of magnesium 2021 (Premonsoon and Postmonsoon)





Cumulative frequency distribution of magnesium 2019-2021 (Premonsoon and Postmonsoon)



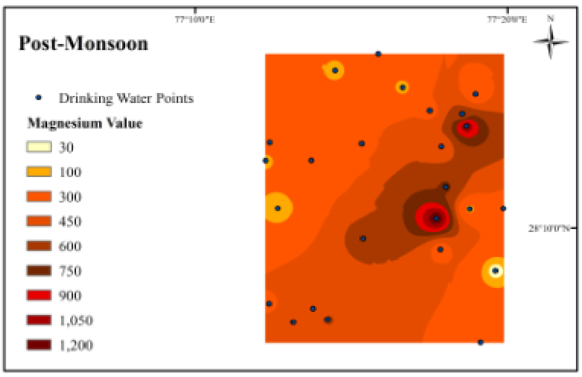


Fig 5.55: GIS maps showing variation of Mg in premonsoon and postmonsoon for year 2021

Sodium

Sodium issixth common element found on earth. Na is not found in free state in nature and in combined state forms 2.6% of earth's crust. Feldspar, glaucophane, sodalite and plagioclase are some of the sodium bearing minerals. Zeolites and clay minerals are also responsible for increasing sodium concentration in groundwater by base-exchange process.

Sodium is an important mineral required by living organisms for maintaining electrolyte balance of the body. It is also required for proper functioning of nerves and muscles. Sodium is also needed by plants for enzyme activation, protein synthesis, osmotic pressure regulation and electric potential maintenance. Sodium is important in maintaining well-being of all living organisms especially aquatic life. Sodium being highly soluble in water is found in abundance in all water sources. Sodium when present in high concentration can alter the electrolyte balance so salt water is unfit for most human uses including drinking, irrigation and various other domestic uses.

Groundwater analysis with respect to sodium concentration in groundwater has been shown in Table 5.24 and Table 5.25. In year 2019 sodium concentration in premonsoon season varied from 40 -1039with mean of 249 while in postmonsoonNa concentration ranged 37 - 1019 with mean of 242.

In year 2020Na concentration in premonsoon varied from 46-1021 with mean of 243 while in postmonsoon sodium concentration ranged 37 -1017 with mean of 237 .

In year 2021 sodium concentration in premonsoon season varied from 49-to 1034 with mean of 252 while in postmonsoon sodium values ranged 5 - 1020 with a mean of 238.

Frequency distribution graphs for sodium concentration in groundwater have been shown in Fig 5.56, 5.57, 5.58 and 5.59 and spatial maps for sodium distribution in groundwater samples have been in Fig 5.60.

BIS has not set any standards for sodium in drinking water and WHO has given a taste threshold of 200 for sodium in water used for drinking. all studied locations it was analyzed 44% of the study locations exceeded the sodium taste threshold value. Pre-monsoon season showed higher values of sodium concentration in groundwater which decreased in post-monsoon due to recharging of aquifers present below the ground. Similar trend was observed by Kamble et al., (2016) in Jaipur district of Rajasthan. Anubha et al., (2000) in Ambala (Haryana) showed that sodium conc in water exceeded the safety limit in more than half of collected wwater.

Seasonal variation forNaconcentration in water is significant concern. Sodium concentration in groundwater increases due to agricultural run-off, effluents coming from sewage, interaction between rocks and water and dissolution of minerals.

High sodium concentration in the form of sodium chloride results in hypertension. High salinity in soil can wilt the plant or even result in its death. High salinity can harm the permeability of soil.Sodium salts being soluble in water are reactive in nature. Varying amounts of salt concentration are observed in all sources of water.

Groundwater samples showing seasonal variation in Na during studied years (2019-2021)

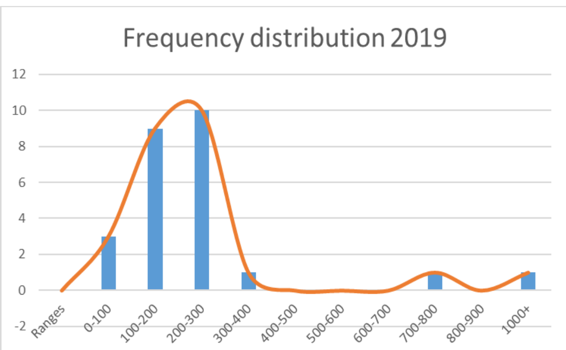
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Alahapur	298	276	276	248	295	271
Firozpur	390	378	374	367	392	379
Prithla	40	37	46	37	49	35

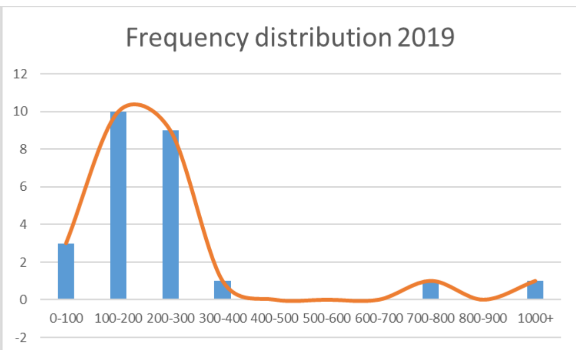
Sikanderpur	241	236	237	231	246	230
Asawati	185	181	176	178	185	171
Allika	167	161	162	157	170	151
Rehrana	153	147	149	145	156	143
Joharkhera	260	253	253	247	265	255
Kishorpur	58	54	59	56	60	51
Tatarpur	209	204	205	198	213	207
Harfali	205	201	201	198	208	195
Teharki	196	187	200	195	198	185
Badha	202	195	205	199	207	185
NagliPanchagi	195	186	191	182	197	181
Chandpur	1039	1019	1021	1017	1034	1020
Jaindapur	799	781	789	778	805	775
Patli Kalan	233	226	221	215	239	221
Patli Khurd	271	275	264	264	289	276
Rakhota	135	128	131	126	136	119
Naya Gaon	56	51	53	49	58	45

Megpur	243	235	237	231	246	239
Jatola	134	127	130	126	135	121
Meerapur	111	108	107	105	113	101
Gadpuri	180	173	171	167	185	169
Sehrala	235	231	231	229	237	227

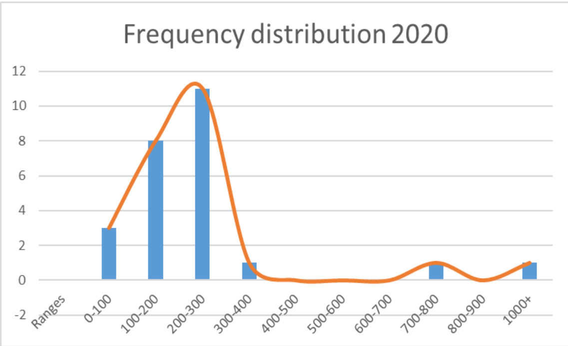
Summary of observed sodium concentration (mg/l) in groundwater samples during the study period.

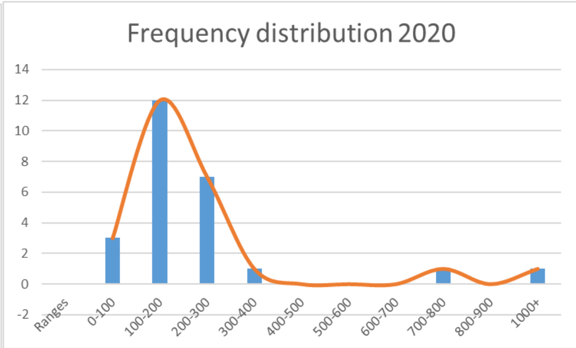
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Min	40	37	46	37	49	35
Max	1039	1019	1021	1017	1034	1020
Mean	249.4	242	243.56	237.8	252.72	238.08
Std. Deviation	218.801	214.977	215.032	214.303	217.876	216.086



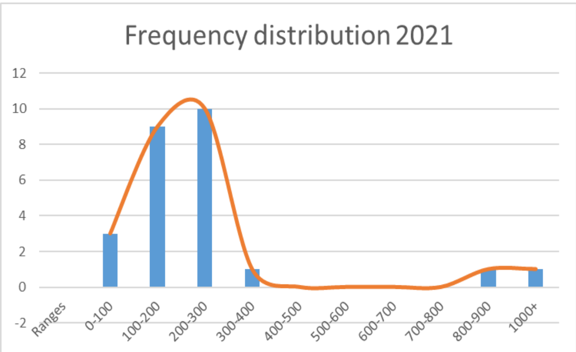


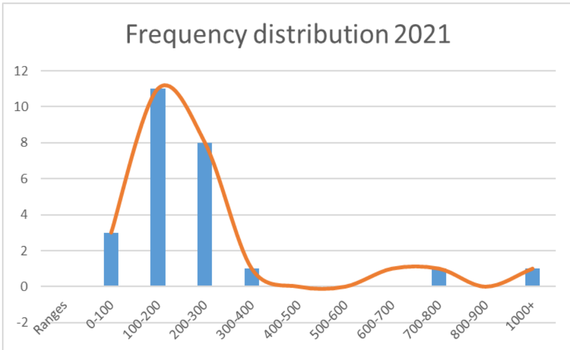
frequency distribution of sodium 2019 (Premonsoon and Postmonsoon)



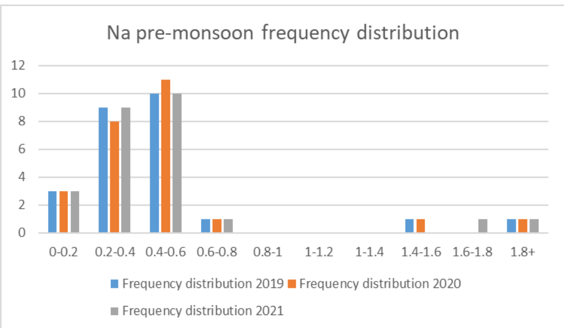


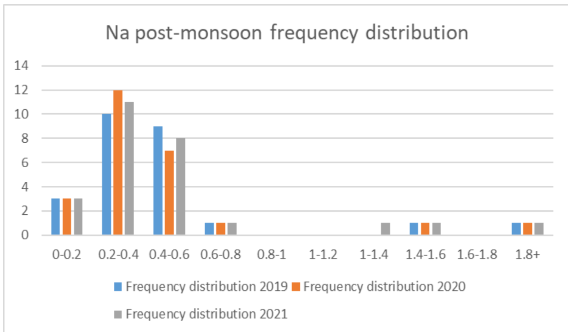
frequency distribution of sodium 2020 (Premonsoon and Postmonsoon)



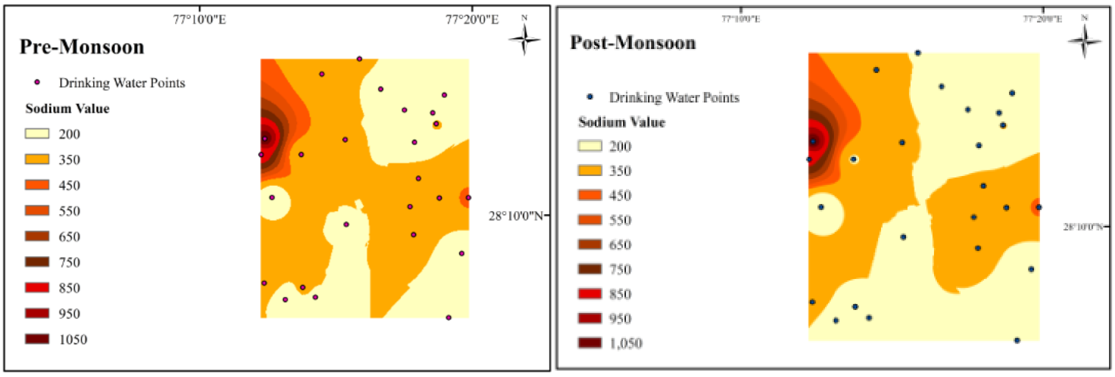


frequency distribution of sodium 2021 (Premonsoon and Postmonsoon)





Cumulative frequency distribution of sodium 2019-2021 (PremonsoonandPostmonsoon)



GIS maps showing Naconcentration during the premonsoon and postmonsoon for year 2021

5.1.13 Potassium

Potassium similar to that of sodium is commonly found along with igneous&metamorphic rocks but its occurence in groundwater reserves is very minute. Minerals like Feldspar (orthoclase and microcline) are the principal sources of potassium which on weathering release potassium. Some clay minerals also contain potassium deposits which end up in seawater through natural routes. Fertilizers especially potassium nitrate when used to boost crop production and the surplus run-off not only pollutes the surface water but leaches below the ground polluting the groundwater. Waste water disposal also increases the concentration of potassium in water. Potassium concentration in phosphate form varies due to various conditions like rain, agricultural run-off and other surface run-off.

Potassium plays essential use as a dietary requirement for living organisms. Potassium is also necessary in healthy growth &plants development. Excess potassium concentration can hamper root development, cause nitrogen deficiency leading to stunted growth (Xu et al., 2020) and necrosis. Potassium in drinking water is not a health hindrance but high levels of potassium in drinking water may act as a laxative.

Groundwater analysis with respect to potassium concentration in groundwater has been shown in Table 5.26 and Table 5.27.

In year 2019 potassium concentration in premonsoon varied from 12 -1192with mean of 317 while in postmonsoonK concentration ranged 7- 1173 with mean of 305 mg/l.

In year 2020 K concentration in premonsoon varied 12 -1192 with mean of 317 while in postmonsoon potassium valuesranged 7-1173 with mean of 305 mg/l.

In year 2021 potassium concentration in premonsoon varied 12 - 1192 with mean of 317 while in postmonsoon potassium concentration ranged 7 -1173 with mean of 305 .

Frequency distribution graphs for potassium concentration in groundwater have been shown in Fig 5.61, 5.62, 5.63 and 5.64 and spatial maps for potassium distribution in groundwater samples have been in Fig 5.65.

Both BIS and WHO have not provided any acceptable and safe limits for K concentration in water as potassium isessential nutrient required by humans for various metabolic processes. A healthy individual 19–50-year male and female requires 3400 mg and 2600 mg of potassium respectively to meet their daily requirement so even high concentration of potassium in water cannot show any significant effect on healthy individuals.

Groundwater samples showing seasonal variation in potassium (mg/l) during study years (2019-2021)

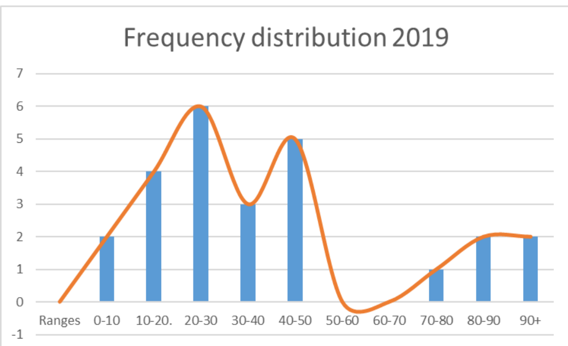
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Alahapur	44	40	38	35	47	41
Firozpur	76	71	71	67	78	69

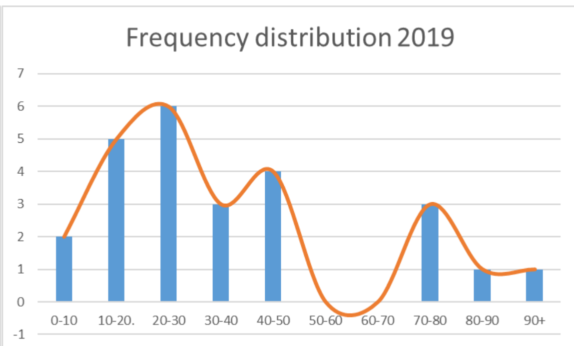
Prithla	47	42	52	47	55	49
Sikanderpur	80	74	76	71	82	79
Asawati	27	22	23	19	27	20
Allika	16	12	14	11	18	13
Rehrana	270	256	265	244	272	258
Joharkhera	37	32	32	28	39	29
Kishorpur	6	4	5	3	8	5
Tatarpur	49	46	52	49	56	51
Harfali	9	7	7	6	10	7
Teharki	15	12	13	11	18	15
Badha	18	14	16	12	20	15
NagliPanchagi	30	24	26	21	32	25
Chandpur	92	86	87	83	95	87
Jaindapur	27	24	22	19	29	24
Patli Kalan	25	21	22	19	28	23
Patli Khurd	23	20	20	16	27	22
Rakhota	49	44	53	50	57	43

Naya Gaon	22	18	18	15	26	21
Megpur	35	30	31	27	38	29
Jatola	18	15	16	12	20	14
Meerapur	40	33	34	29	46	35
Gadpuri	27	23	21	18	32	25
Sehrala	80	73	73	68	86	75

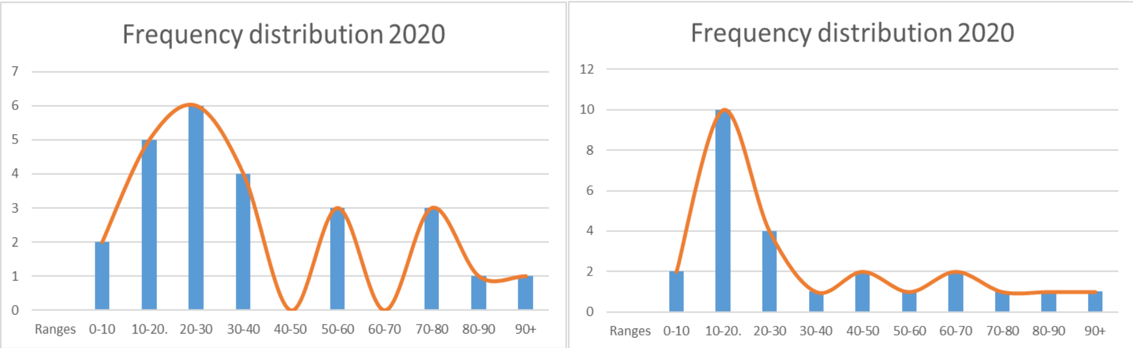
Summary of observed potassium concentration in groundwaterduringstudiedregion.

Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Min	6	4	5	3	8	5
Max	270	256	265	244	272	258
Mean	46.48	41.72	43.48	39.2	49.84	42.96
Std. Deviation	52.058	49.915	51.546	48.199	52.134	50.261

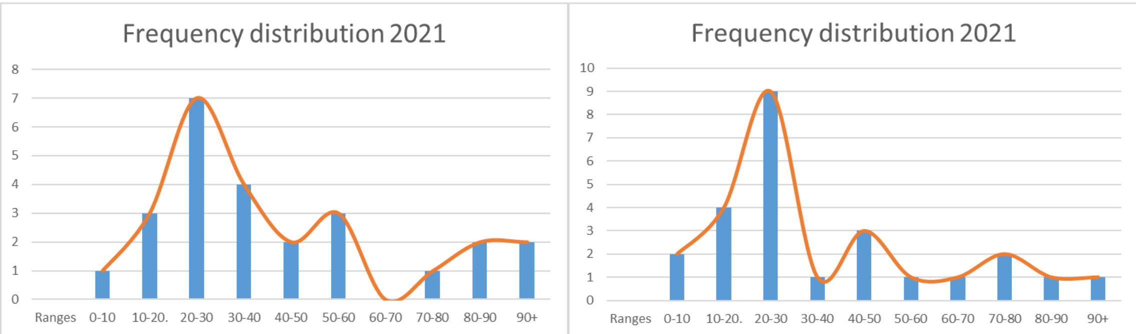




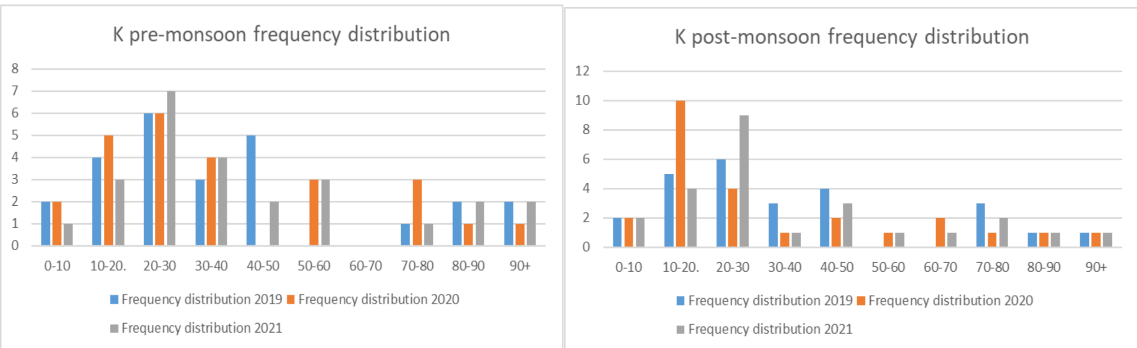
frequency distribution of K 2019 (Premonsoon and Postmonsoon)



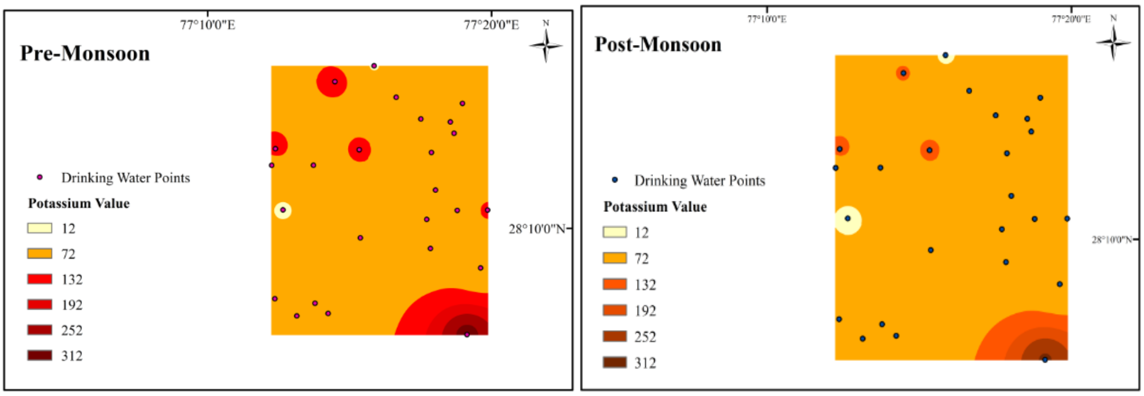
frequency distribution of K 2020 (Premonsoon and Postmonsoon)



frequency distribution of K 2021 (Premonsoon and Postmonsoon)



Cumulative frequency distribution of K 2019-2021 (Premonsoon and Postmonsoon)



GIS maps showing variation of K concentration during the premonsoon and postmonsoon of year 2021

5.1.14 Nitrates

Naturally occurring nitrates are generally found in very low concentrations but anthropogenic activities like agriculture, accumulation of animal manure as a heap, emission from combustion engines, effluents from industrial and domestic sector contribute to high nitrate concentration in water. Nitrate is the second most pollutant in groundwater threatening the health of people consuming contaminated water. (Wick et al., 2012).

Nitrates occurs in many forms as elemental nitrogen, nitrate and ammonia. Nitrates present in the atmosphere react with rain water to form nitrates and ammonium ions.

Enhanced fertilizers used to increase the crop production has substantially increased the nitrate concentration in groundwater (Craswell et al., 2021). Nitrate consumption in small concentrations is not a health hindrance as nitrates are converted into nitrites by oral bacteria present under the tongue or inside the mouth (Ma et al., 2018). Nitrites produced react with haemoglobin present in blood and oxidizes Fe^{2+}into Fe^{3+} and gets changed into methemoglobin which decreases the blood capacity to transport oxygen. Adults have a higher tolerance to nitrates than young children (Karwowska et al., 2020). Excess nitrate consumption interferes with the ability of blood to transport oxygen which causes oxygen deficiency in the body, causingmethemoglobinemianicknamed as ‘bluebaby syndrome’ due to bluish appearance of skin near nail-beds, earlobes and lips. This condition is especially fatal for young infants as small as six-month-old babies (Manassaram et al., 2006).

Seasonal variation of nitrates in groundwater samples have been given in Table 5.28 & 5.29.

In year 2019 nitrates concentration in premonsoon varied0.41- 97 with mean of 10.9 while in postmonsoonnitrates concentration ranged from 0.36- 96 with a mean of 10.6 .

In year 2020 nitrates concentration in premonsoon varied 0.37 - 96.7 with mean of 10.7 while in postmonsoon nitrates concentration varied 0.32- 96.2 with a mean of 10.41 .

In year 2021 nitrates concentration in premonsoon varied 0.51 -97.3 with mean of 11.2 while in postmonsoon nitrates concentration range d0.32- 95.5 with mean of 10.4 .

Frequency distribution graphs for nitrates concentration in groundwater have been shown in Fig 5.66, 5.67, 5.68 and 5.69and spatial maps for nitrate distribution in groundwater samples have been in Fig 5.70.

BIS has set permissible limits of 45 for nitrates in potablewater with no relaxation. Sikanderpur and Asawati, which constitute 8 % of the samples in the study location, were above the limit set by BIS.

A wide range of variation in nitrates level in drinking water was analyzed in water samples collected from Haryana with no recognizable pattern of nitrate distribution (Majumdar et al., 2000).Nitrate concentration in groundwater was observed from 1.8 - 79 in the Rohtak district of Haryana (Deswal et al., 2014).

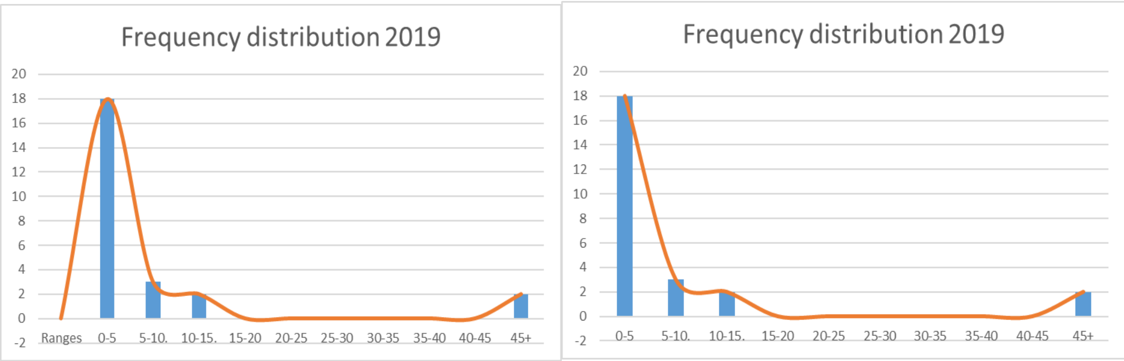
Table27Groundwater samples showing seasonal variation in nitrates during investigated years (2019-2021)

Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Alahapur	3.7	3.5	3.3	3.1	3.8	3.1
Firozpur	4.1	3.7	3.8	3.6	4.4	3.2
Prithla	3.7	3.4	3.5	3.1	3.9	3.2
Sikanderpur	83.2	82.8	82.8	82	83.1	81.3
Asawati	97	96.6	96.7	96.2	97.3	95.5
Allika	2.7	2.4	2.5	2.1	2.9	2.1
Rehrana	11.5	11	11.1	10.7	11.9	10.9
Joharkhera	12.7	12.2	12.4	12.1	13	12.2
Kishorpur	2.1	1.7	1.8	1.4	2.3	1.8
Tatarpur	4.1	3.7	3.8	3.3	4.5	3.8
Harfali	7.4	7.1	7.6	7.2	7.8	7.01
Teharki	2.9	2.5	2.6	2.7	3	2.68
Badha	4.3	3.9	4	3.7	4.5	3.9
NagliPanchagi	6.6	6.2	6.3	5.8	7	6.2
Chandpur	3.3	2.7	2.8	2.4	3.3	2.7
Jaindapur	3.3	2.9	3	2.7	3.5	2.9

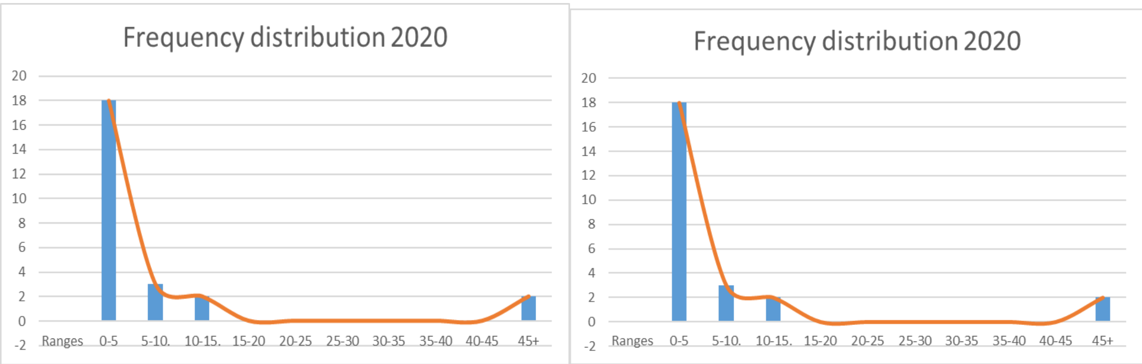
Patli Kalan	0.41	0.36	0.37	0.32	0.51	0.32
Patli Khurd	3.9	3.6	3.5	3.2	4.1	3.4
Rakhota	2.8	2.4	2.4	2.6	3	2.3
Naya Gaon	5.8	5.4	5.4	5.1	6	5.1
Megpur	2.1	1.8	1.8	1.6	2.3	1.9
Jatola	2	1.7	1.8	1.5	2.4	1.9
Meerapur	1.2	1	0.9	0.8	1.4	1.1
Gadpuri	1.6	1.3	1.4	1.1	1.9	1.4
Sehrala	2.5	2.1	2.3	2	2.8	2.3

Table5.28Summary of observed nitrates concentration in groundwater samples of studied place.

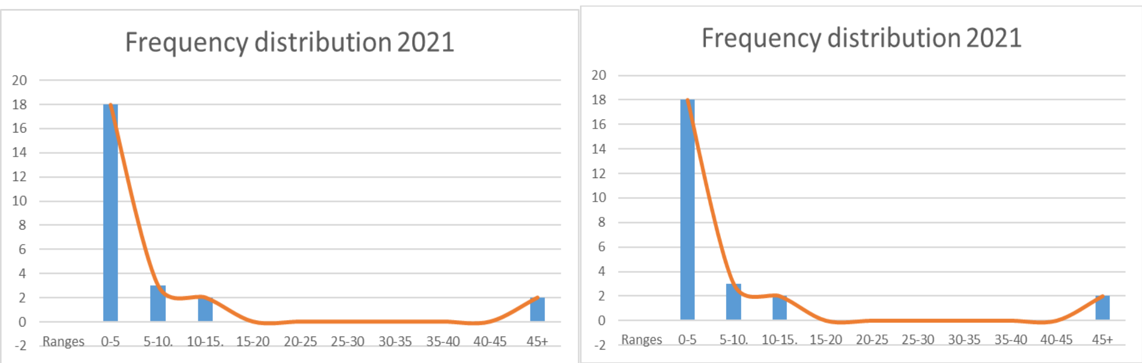
Name of village	Premonsoon 2019	Postmonsoon 2019	Premonsoon 2020	Postmonsoon 2020	Premonsoon 2021	Postmonsoon 2021
Min	0.41	0.36	0.37	0.32	0.51	0.32
Max	97	96.6	96.7	96.2	97.3	95.5
Mean	10.9964	10.6384	10.7148	10.4128	11.2244	10.4884
Std. Deviation	24.063	24.044	24.043	23.936	24.036	23.702



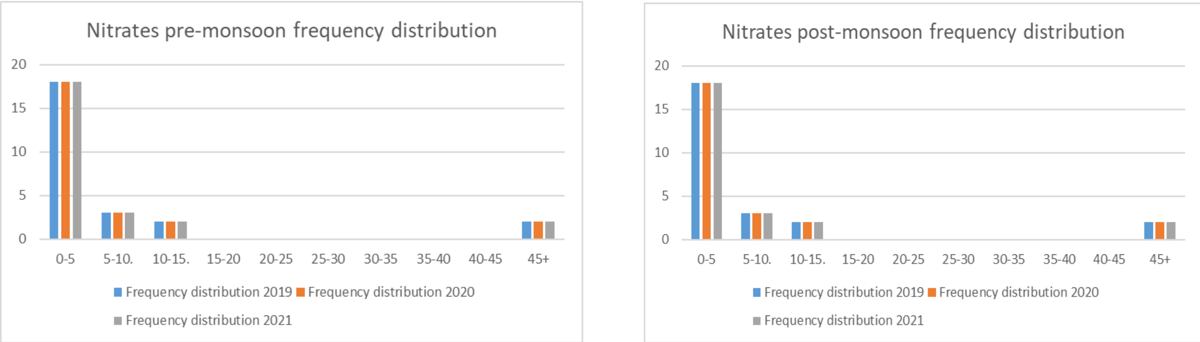
frequency distribution of nitrates 2019 (Premonsoon and Postmonsoon)



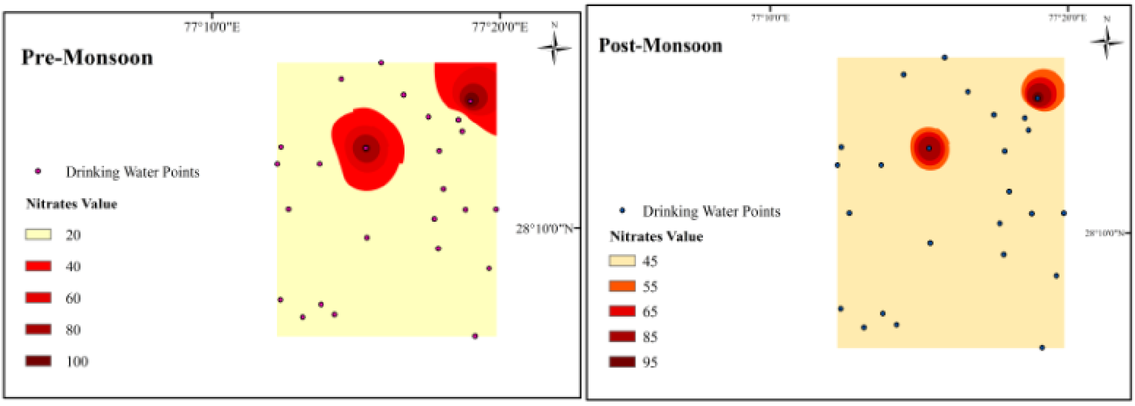
frequency distribution of nitrates 2020 (Premonsoon and Postmonsoon)



frequency distribution of nitrates 2021 (Premonsoon and Postmonsoon)



Cumulative frequency distribution of nitrates 2019-2021 (Premonsoon and Postmonsoon)



GIS maps showingnitratesrangeinpremonsoon and postmonsoon of year 2021

5.2

ASSESSMENT OF GROUNDWATER SAMPLES FOR HEAVY METALS AND ADVERSE EFFECTS ON HUMAN HEALTH

5.2 Introduction

Heavy metals are elements which occur naturally and show a high atomic weight and density (Jamshaid et al., 2018). Heavy metalsexistence in consumable water has been receiving paramount focus from environmentalists all over the world due to the highly toxic nature of heavy metals. These are generally present naturally in trace amounts in water but most of them are toxic even when present in minute concentration (Mohod., 2013). Heavy metals Zn, Cr, Pb, Cd, As& Hg are toxic even present in low concentration. Many industries which include cement factories, textiles and dyes, battery industries, tanneries, metal plating, fertilizer and pesticide manufacturing units discharge their effluents containing metals either directly or after inadequate treatment into fresh water which is responsible for increasing the concentration of heavy metals (Chowdhury et al., 2016).

Some of the heavy metals, especially those present in the fourth period of the modern periodic table are important for proper functioning of human bodies assisting in smooth functioning of enzymes and hormones (Masindi et al., 2018). But these are required in trace amounts; other heavy metals like lead, mercury and plutonium are toxic even in small concentrations and these bioaccumulate in bodies over the time and can lead to serious health issues (Singh et al., 2011). In the current study, analysis of certain important trace metals was done and their discussion is done below.

5.2.1 Zinc

Zinc constitutes approximately 0.004% of the earth’s crust and occupies 4th rank in order of element abundance found in earth’s crust. After iron zinc is the second most commonly found trace metal. Zinc mostly occurs in silicate and oxide form. Due to its limited mobility from the place where weathering takes place, zinc is found in less concentration in surface water. Type of rock and nature of soil decide the amount of zinc found in soil and water (Sharma et al., 2013). Zinc blend is the most commonly found ore of zinc. Among the anthropogenic sources- mining, iron and steel industries are the main sources of release of zinc in the environment. Zinc content in domestic water supply can also increase due to zinc dissolution from water supplying pipes. Galvanized food containers also enhance zinc concentration in human bodies.

Zinc plays crucial part in cell division,synthesis of proteins, cells growth, healing of wounds. Many enzymes and hormones which are important for DNA replication need zinc for their smooth functioning. Zinc is necessary as a cofactor for carbonic anhydrase enzymes where it facilitates water for creating proton and hydroxide ions. Zinc is an important trace element necessary for various metabolic processes. A healthy 18-year-old male requires 11 mg of zinc per day while a female needs 8 mg but in conditions of pregnancy and lactation more amounts of zinc are required (Roohani et al., 2013) but at higher concentrations above 15 mg/l zinc becomes toxic for living organisms. Excess zinc concentration in human bodies can cause nausea, dizziness, vomiting, anemia, renal failure, liver problems and impair proper growth (Plum et al., 2010).

BIS has set an acceptable limit of 5 for zinc in water meant for consuming and 15 as permissible range for zinc in absenteeism of any alternative sources. WHO has provided a taste threshold of 4 mg/l and not any health based directives for zinc concentration in the groundwater. Drinking water containing zinc above 3 mg/l gives it an undesirable bitter taste and when boiled it shows a greasy film.

Zinc range in groundwater samples of the investigated location has been shownTable 5.2.1 and 5.2.2.

In the study period, zinc concentration in premonsoonvaried 0.095-6.982 with mean 3.001 while in postmonsoonzinc concentration in the groundwaterranged from 0.074- 6.757 with mean of 2.747 . Allstudiedsamples excluding which were collected inBadha, Chandpur, Jaindpur and Patli Kalan were in desirable limit . Badha, Chandpur, Jaindpur and Patli Kalan, which constitute 16 % of collected samples, werewithin permissible range given by BIS.

Zinc concentration in groundwater samples showed reductioninpostmonsoon because of recharge of ground aquifers in monsoons.

Zinc concentration in groundwater within permissible limits set by BIS was observed by Mittal et al., (2014) in Bathinda, Punjab. Krishan et al., (2021) studied the groundwater samples of Punjab and revealed the same.

Table5.2.1Variation of Zinc concentration (mg/l) in collected groundwater samples during the premonsoon&postmonsoon season of 2021

Name of village	Premonsoon 2021 (mg/l)	Postmonsoon 2021(mg/l)	Name of village	Premonsoon 2021 (mg/l)	Postmonsoon 2021(mg/l)
Alahapur	2.05	1.749	NagliPanchagi	4.203	3.763
Firozpur	0.837	0.741	Chandpur	5.864	5.487
Prithla	0.701	0.629	Jaindapur	5.956	5.766
Sikanderpur	2.254	2.156	Patli Kalan	5.115	4.983

Asawati	4.768	4.12	Patli Khurd	2.9	2.807
Allika	1.309	1.173	Rakhota	3.908	3.702
Rehrana	0.095	0.074	Naya Gaon	1.902	1.738
Joharkhera	2.877	2.315	Megpur	5.155	4.901
Kishorpur	0.801	0.766	Jatola	3.982	3.769
Tatarpur	1.932	1.645	Meerapur	2.78	2.655
Harfali	1.025	0.883	Gadpuri	0.887	0.686
Teharki	1.757	1.537	Sehrala	4.05	3.889
Badha	6.982	6.757			

Table5.2.2Statistical Summary of zinc conc (mg/l) in GW

Summary of Zn conc	Premonsoon2021(mg/l)	Postmonsoon 2021 (mg/l)
Min	0.095	0.074
Max	6.982	6.757
Mean	3.001	2.747
Std. Deviation	1.960	1.865

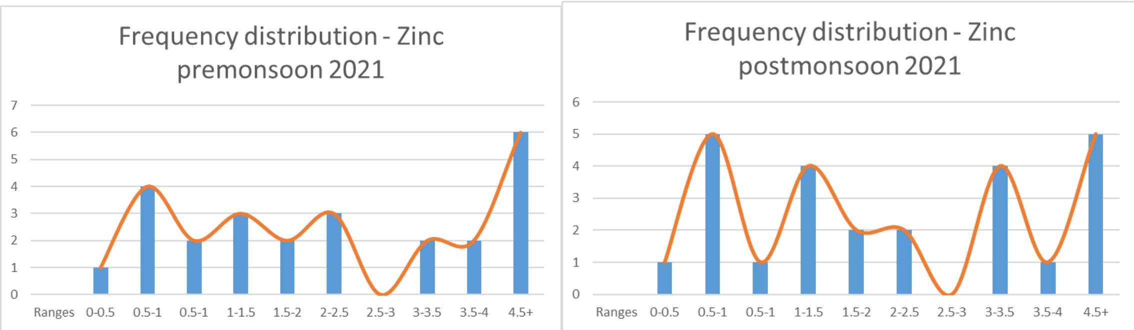


Fig5.2.1Frequency distribution of Zinc concentration in pre & post monsoon season of 2021

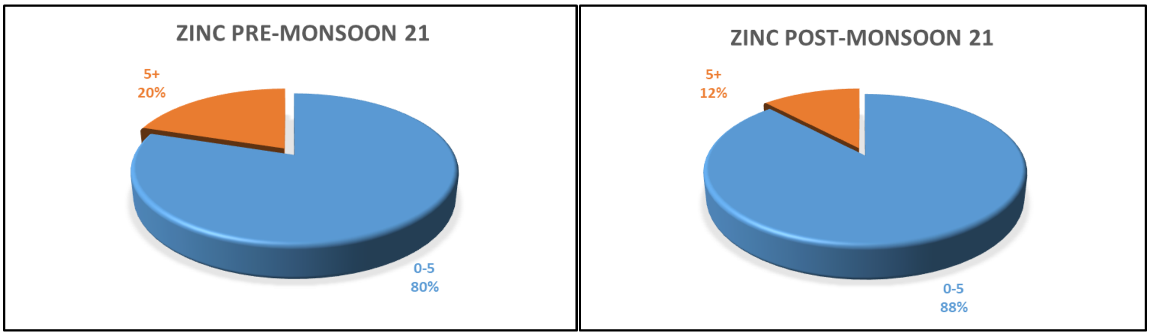


Fig5.2.2Study Locations beyond the acceptable limit set by BIS and WHO for zinc concentration in drinking water.

5.2.2Lead

Lead is a silvery metal with a slight bluish tinge in a dry atmosphere. On contact with moist air, it tarnishes, forming a complex compound. Industrial processes including batteries, toys, paints, lead bullets, gasoline production and processing, plumbing pipes, ceramics, and alloys are the main source of lead emission (Jaishankar et al., 2014).

Lead ishardlyfoundnaturally in drinking water but reaches the water system due to corrosion and tear &wearof lead from pipes. Insecticides and pesticides used in agriculture are also responsible for emission of lead in groundwater.

Lead is an undesirable trace metal which is responsible for showing toxic effects in animals, plants and humans. Lead can cause toxicity in cells of living beings by ionic mechanism and then by imbalance between free radical production and antioxidant generation to detoxify the occurred damage.

BIS has set an acceptable range of .01 for lead in drinkingwaterandno further relaxation. WHO has provided guidelines on the basis of which 10 µg/l is threshold for lead in drinkingwater. Lead accumulation inbody can cause lead poisoning leading to kidney damage. Chronic lead accumulation in body can result in weight loss, teeth loss, anaemia and retard proper functioning of enzymes responsible for smooth functioning of body. Consuming water having lead above the prescribed concentration for a long time can show various effects on the body like cognitive defects, learning ability impairment and increased distraction in young children, birth defects, reduced sperm count, increased mutagenic effects and carcinogenicity (Jyothi., 2020).

Lead variation in groundwaterofinvestigated location has been shown Table 5.2.3 and 5.2.4.

In the current investigation, lead range in groundwater samples inpremonsoonvaried .005 - 0.01 mean 0.008 . In postmonsoonleadrange in groundwater samples varied 0.003-0.01with mean of 0.007. Groundwater samples of studied regionareinsafe range given by BIS and WHO.

Concentration of heavy metals in premonsoon season is more as compared to postmonsoon season. Similar trend was seen in case of lead in groundwater which indicates heavy metals accumulate in the soil when industrial and domestic wastes are dumped in soil. Recharging of ground aquifers in the rainy season also played a role in dilution of lead concentration in groundwater.

Rout et al., (2016) analyzed the groundwater samples of Barara block of Ambala, Haryana and observed lead concentration in groundwater samples rangefrom 0.033 -0.057 which lies withinpermissible limit set by BIS. Similar trend was observed by Nadu., (2016) in Chennai, Tamil Naidu.

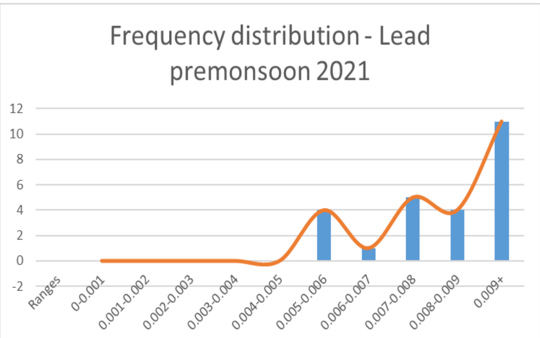
Table5.3Variation of Lead concentration (mg/l) in collected groundwater samples during the premonsoon&postmonsoon season of 2021

Name of village	Premonsoon 2021 (mg/l)	Postmonsoon 2021 (mg/l)	Name of village	Premonsoon 2021(mg/l)	Postmonsoon 2021(mg/l)
Alahapur	0.005	0.003	NagliPanchagi	0.007	0.006
Firozpur	0.007	0.007	Chandpur	0.01	0.008
Prithla	0.006	0.005	Jaindapur	0.005	0.003
Sikanderpur	0.005	0.004	Patli Kalan	0.008	0.007
Asawati	0.008	0.007	Patli Khurd	0.01	0.009
Allika	0.01	0.01	Rakhota	0.01	0.01
Rehrana	0.009	0.009	Naya Gaon	0.007	0.005
Joharkhera	0.01	0.008	Megpur	0.007	0.003
Kishorpur	0.008	0.007	Jatola	0.008	0.008
Tatarpur	0.01	0.01	Meerapur	0.009	0.007
Harfali	0.005	0.004	Gadpuri	0.01	0.01

Teharki	0.01	0.009	Sehrala	0.01	0.009
Badha	0.007	0.01			

Table5.4Statistical Summary of Lead conc (mg/l) in GW

Summary of Pb conc	Premonsoon 2021(mg/l)	Postmonsoon 2021
Minimum	0.005	0.003
Maximum	.01	.01
Mean	.00804	.00712
Std. Deviation	0.0018	0.0024



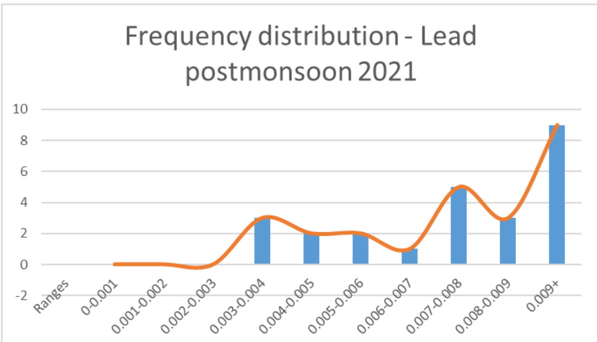
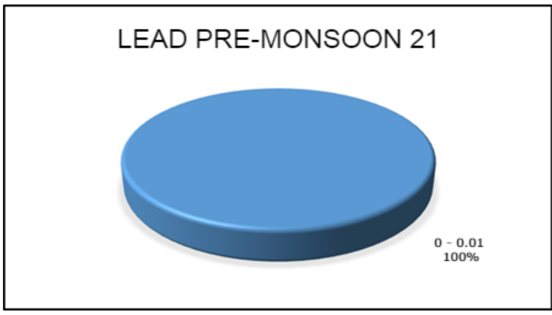


Fig5.2.3Frequency distribution of Lead in pre & post monsoon season of 2021



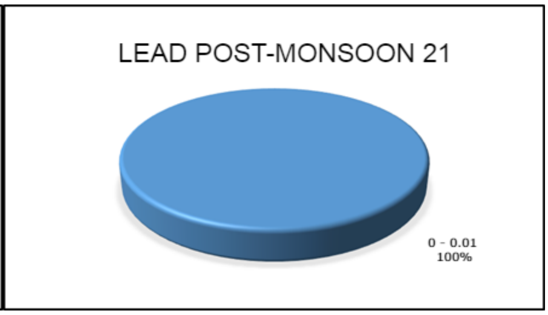


Figure5.2.4All study locations are in the acceptable limit set by BIS & WHO for lead concentration in drinking water.

5.2.3Cr

Chromium is a heavy metal found inside crust of earth and sea water. Chromium shows many oxidation states starting from -2 to 6 of which Cr (III) and Cr (V1) forms are stable forms of chromium (Balali- Mood et al., 2021). Cr (III) in small concentration is essential for smooth conduction of metabolic functions especially lipid and glucose metabolism but Cr (VI) is responsible for causing carcinogenicity in humans (Wang et al., 2017). Depending upon the pH of the aqueous medium, Cr (VI) is seen in chromate (Cr_2O_4) and dichromate (Cr_2O7-) form.

Many industrial operations like tanneries, leather manufacturing units, paints, dyes, textiles, electroplating, mining, ceramics, photography generate effluents containing chromium. Except for the regions which contain chromium deposits, concentration of naturally occurring Cr in groundwater is very low. BIS has set an acceptable limit of 0.05forCr indrinkablewater with no further relaxation. WHO has set 50 µg/lpermissiblelimit for chromium in drinkwater.

Cr rangein groundwater samples ofstudiedlocationhas been shown in Table 5.2.5 and 5.2.6.

In the current investigation, Cr range in groundwaterinpremonsoon season differed0.002 0.005 with mean of 0.003. In postmonsoonchromiumin groundwater samples varied from 0.001-0.003 with mean of 0.001. Allgroundwater of studied area were in the safe permissible range given by BIS and WHO.There was a decline in chromium concentration in groundwater in the postmonsoon due to dilution of aquifers.

Chromium concentration in groundwater within the standard value set by WHO was observed by Eslami et al., (2022) in South-eastern Iran.

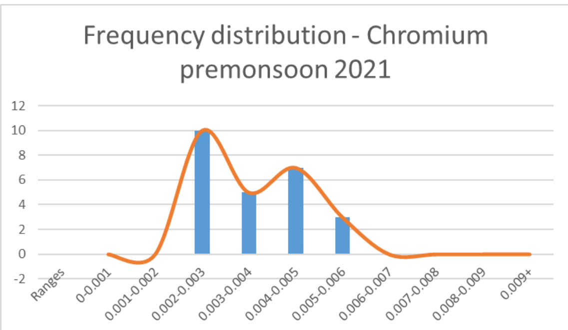
Table5.5Variation of chromium concentrationincollected groundwater during premonsoon&postmonsoon season of 2021

Name of village	Premonsoon 2021	Postmonsoon 2021	Name of village	Premonsoon 2021	Postmonsoon 2021
Alahapur	0.005	0.003	NagliPanchagi	0.002	0.001
Firozpur	0.002	0.002	Chandpur	0.002	0.001
Prithla	0.004	0.003	Jaindapur	0.002	0.001
Sikanderpur	0.003	0.002	Patli Kalan	0.002	0.001
Asawati	0.002	0.002	Patli Khurd	0.004	0.002
Allika	0.002	0.001	Rakhota	0.004	0.003
Rehrana	0.002	0.001	Naya Gaon	0.003	0.002
Joharkhera	0.005	0.003	Megpur	0.002	0.001
Kishorpur	0.004	0.002	Jatola	0.003	0.002
Tatarpur	0.005	0.003	Meerapur	0.004	0.003
Harfali	0.004	0.002	Gadpuri	0.004	0.002

Teharki	0.003	0.002	Sehrala	0.002	0.001
Badha	0.003	0.002			

Table5.6Statistical Summary of chromium conc (mg/l) in GW.

Summary of Cr conc	Premonsoon 2021 (mg/l)	Postmonsoon 2021
Minimum	0.002	0.001
Maximum	0.005	0.003
Mean	0.003	0.001
Std. Deviation	0.001	0.0007



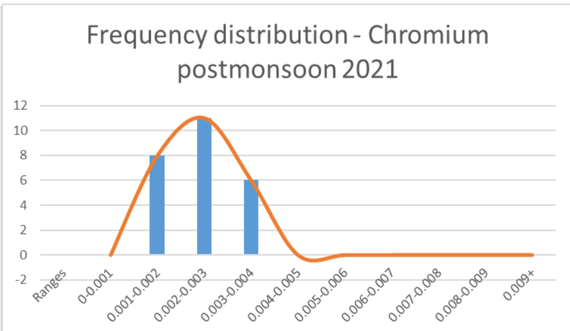


Figure5.2.5Frequency distribution of chromium concentration in pre & post monsoon season of 2021

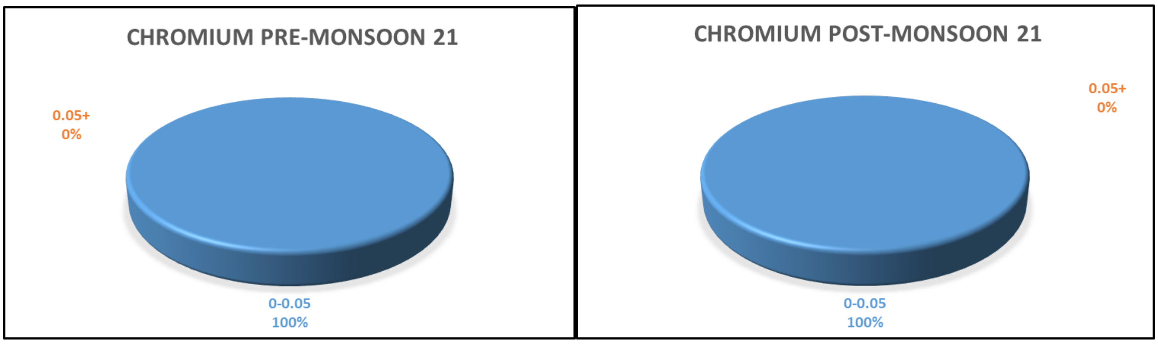


Figure5.2.6All study locations arein the acceptable limit set by BIS & WHO for Cr in drinking water.

5.2.4 Cadmium

Cadmium is a naturally occurring element which shows similar chemical characteristics as that of zinc. It exhibits itself as a divalent cation. Cadmium occupies 0.1 ppm in the earth crust. Cadmium is generally found along with zinc or lead deposits as an impurity. Cadmium also exists in combined forms in water such as chlorides, hydroxides and sulphates.

Cadmium naturally, is found in very low amounts in groundwater andmainly enters groundwater supply through anthropogenic activities. Industrial effluents emitting out of electroplating, stabilizers, batteries, plastic, textiles, dyes, paint generate cadmium and contaminate natural water sources. Cadmium is highly toxic and induces carcinogenicity (Huff et al., 2007). Cigarette smoke is one of the major causes of cadmium in humans. Smokers' blood and kidneys show a high level of cadmium in their bodies (Bernhoft., 2013). Even in minute quantities cadmium can show adverse effects on the kidneys. Cadmium accumulated in the body can interfere with smooth functioning of enzymes and can cause a painful disease- Itai-itai (Nishijo et al., 2017).

Cd range in groundwater samples of studiedplacehas been shown in Table 5.2.7 and 5.2.8. BIS has specified 0.003as permissible range for Cd in drinking with no further relaxation. On the basis of toxicity WHO, (2017) has set 3 µg/l as the threshold for cadmium concentration in drinking water.

In the current investigation, cadmium conc in groundwater samples in premonsoon ranged 0.002-0.009 with mean of 0.005 . In premonsoon only Joharkhera, Harfali,Patli Kalan, which constitute 12% of the studied zone, were within the permissible limit specified by BIS. In postmonsooncadmiumin groundwater samples showed from 0.002 0.007 with mean of 0.004 and 40 % of tested samples met permissible limit specified by BIS for cadmium rangein drinkable water.

High Cd range n groundwater was analyzed by Kumar et al., (2019) in Sirsa district of Haryana. Idrees et al., (2018) analyzed high concentration of cadmium in western region of Uttar Pradesh.

Table5.7Variation of cadmium concentration (mg/l) in collected groundwater samples during the premonsoon&postmonsoon season of 2021

Name of village	Premonsoon 2021	Postmonsoon 2021	Name of village	Premonsoon 2021	Postmonsoon 2021
Alahapur	.004	.002	NagliPanchagi	0.008	0.007
Firozpur	0.005	0.003	Chandpur	0.004	0.003
Prithla	0.009	0.007	Jaindapur	0.006	0.004
Sikanderpur	0.004	0.003	Patli Kalan	0.003	0.002
Asawati	0.007	0.005	Patli Khurd	0.004	0.003

Allika	0.005	0.005	Rakhota	0.008	0.007
Rehrana	0.008	0.007	Naya Gaon	0.004	0.002
Joharkhera	0.002	0.002	Megpur	0.005	0.003
Kishorpur	0.006	0.006	Jatola	0.006	0.004
Tatarpur	0.006	0.005	Meerapur	0.007	0.006
Harfali	0.003	0.002	Gadpuri	0.009	0.007
Teharki	0.007	0.007	Sehrala	0.008	0.006
Badha	0.008	0.007			

Table5.8Statistical Summary of cadmium conc (mg/l) in GW.

Summary of Cd concentration	**Premonsoon 2021**	**Postmonsoon 2021**
Minimum	.002	.002
Maximum	.009	.007
Mean	.005	.004
Std. Deviation	0.0020	0.0019

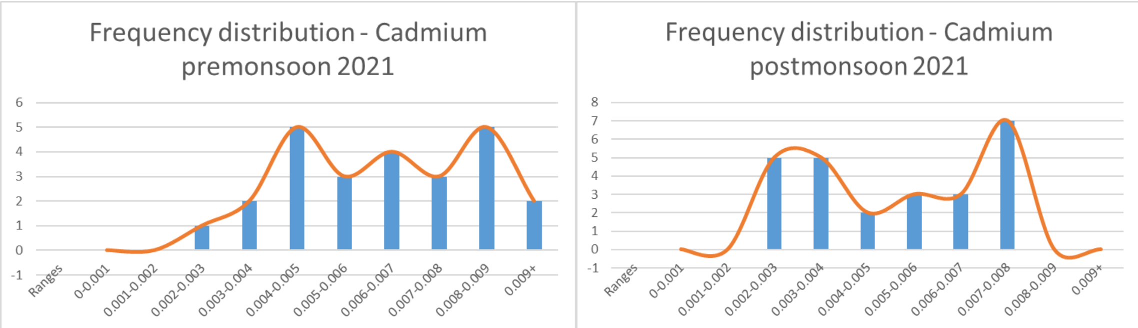


Fig5.7Frequency distribution of cadmium concentration in pre & post monsoon season of 2021

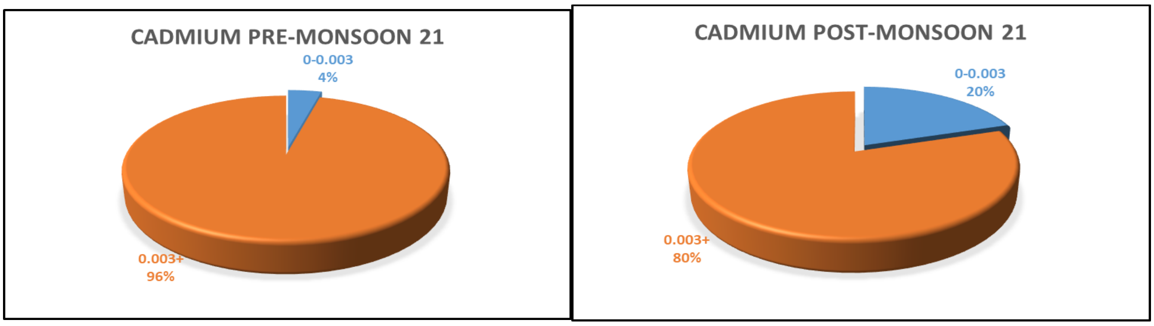


Fig5.8Study locations beyond the permissible limit set by BIS and WHO for Cd in groundwater.

5.5Arsenic

Arsenic is a highly toxic element present in ecosystem in varying concentrations. Weathering of rocks, volcanic eruptions and geological processes including sedimentary rocks, arsenic minerals are the natural causes which contribute arsenic in the ecosystem. Arsenic is found as As (III) and As (V) in inorganic forms and dimethyl arsenate (DMA) and monomethyl arsenate (MMA) as organic forms.

Mining, especially smelting, ore processing, certain fertilizer and pesticide manufacturing units, paint, dyes, soaps, semiconductor and certain drug preparation industries are the anthropogenic sources releasing arsenic in the environment (Shaji et al., 2021). Arsenic contaminated drinking water is a major threat for arsenic toxicity in 70 countries of the world

(Bagchi., 2007). Keratosis and pigmentation on skin are the specific characteristic of arsenic toxicity (Smith et al., 2002). Nausea, vomiting, erythrocyte and leukocyte reduced rate of production, abnormal heart rate beat and damage of blood vessels can be seen by exposure to lower levels of arsenic (Shankar et al., 2014; Kumar et al., 2020) while long term exposure of arsenic can result in lesions on skin, neurological problems, hypertension, cancer affecting body parts, cardiovascular diseases and diabetes mellitus (Rahman et al., 2009). Chronic toxicity of arsenic (arsenicosis) can damage the vital organs and lead to mortality (Adeloju et al., 2021). Over the years due to harmful effects of arsenic on human health arsenic use in various products has declined but its adverse effects on human health will show its impact for a long time.

As concentration in groundwater samples of the investigated location has been shown in Table 5.2.9 and 5.2.10.

As per BIS standards, maximum permissible allowance for Asin drinking water is 0.01 with no further relaxation. On the basis of toxicity WHO, (2017) has set 10 µg/l as the threshold for arsenic concentration in drink water.

Current investigation arsenic concentration in groundwater samples in the premonsoon ranged 0.004- 0.007 with mean of 0.005. After monsoon season arsenic in groundwater varied from nil- 0.005 with mean of 0.004 . All samples of studied areas were in safe permissible values set by BIS and WHO. After monsoons the region showed a decline in arsenic concentration in groundwater due to aquifer recharging in the monsoon season.

Arsenic concentration in range 0.05 4.53 which is in the permissible limit was analyzed by Yadav et al., (2020) in Fatehabad district of Haryana.

Table5.9Variation of Arsenic concentration (mg/l) in collected groundwater samples during the premonsoon&postmonsoon season of 2021

Name of village	Premonsoon 2021	Postmonsoon 2021	Name of village	Premonsoon 2021	Postmonsoon 2021
Alahapur	.003	0.0	NagliPanchagi	.004	.004
Firozpur	0.005	0.004	Chandpur	0.004	0.003
Prithla	0.007	0.005	Jaindapur	0.005	0.004
Sikanderpur	0.007	0.004	Patli Kalan	0.006	0.005
Asawati	0.004	0.003	Patli Khurd	0.006	0.004
Allika	0.006	0.005	Rakhota	0.007	0.005
Rehrana	0.006	0.005	Naya Gaon	0.005	0.003
Joharkhera	0.005	0.004	Megpur	0.007	0.005
Kishorpur	0.006	0.005	Jatola	0.005	0.004
Tatarpur	0.005	0.005	Meerapur	0.004	0.003
Harfali	0.004	0.004	Gadpuri	0.006	0.004
Teharki	0.006	0.005	Sehrala	0.005	0.003
Badha	0.004	0.004			

Table5.10Statistical Summary of arsenic conc (mg/l) in GW.

Summary of Arsenic conc	Premonsoon 2021	Postmonsoon 2021
Minimum	.004	0.0
Maximum	.007	.005
Mean	.005	.004
Std. Deviation	.0010	.0011

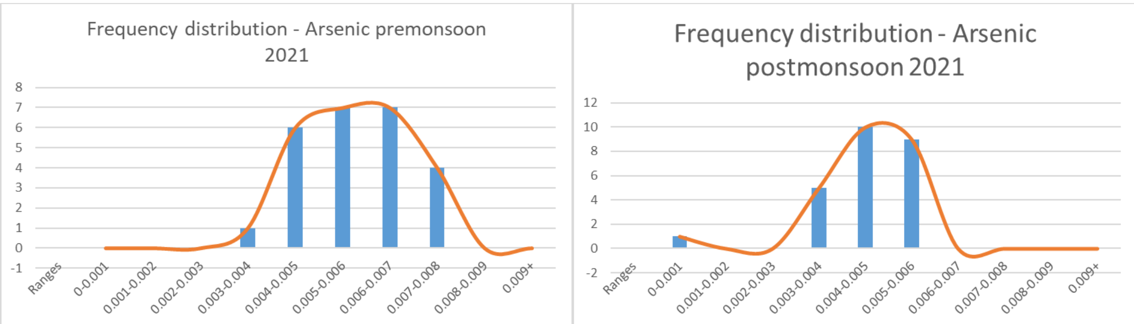


Fig5.2.9Frequency of As variation in pre & post monsoon of 2021

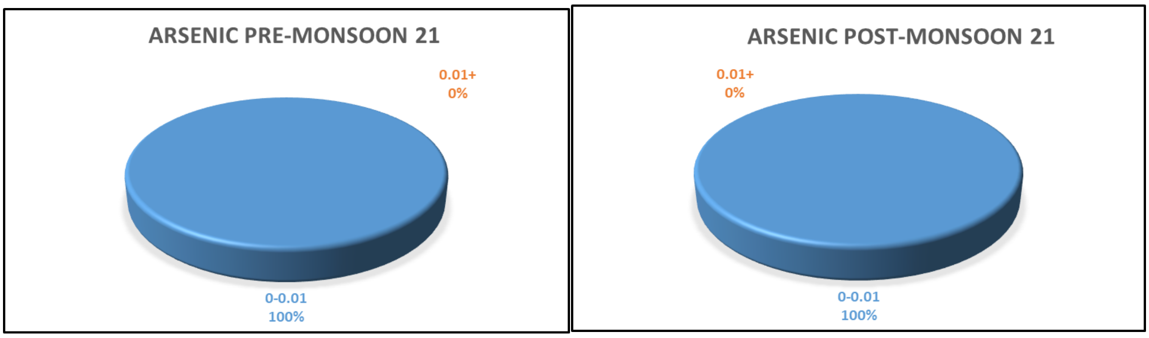


Fig5.2.10All study locations arein the permissible limit set by BIS & WHO for As.

5.3

ASSESSMENT OF GROUNDWATER QUALITY FOR HEALTH OF LOCAL POPULATION

5.3Introduction

Groundwater is a precious resource which is essential for quenching thirst, crops growth and survival of life. Drinking contaminated and untreated groundwater lead to harmful effects on humans leading to many life-threatening diseases.

As seen in previous subchapter when the WQI for the study area was calculated, it was observed thatnone of the sample was in the excellent category during premonsoon season, 4% of groundwater samples had good category, 28% came in poor category, 40% groundwater samples came in very poor category while 28 % groundwater samples were unfit for consumption. WQI for the post monsoon % compliance again showed none ofwater came under excellent, 4% collected samples wereof good range, 32% in poor category, 36% in very poor range and 28% of the groundwater samples were unfit for consumption.

Groundwater contamination has become a serious issue which needs adequate public attention and with expanding urbanization, increasing population growth and rapid industrial spurt the issue of water contamination has become even more threatening and is showing its dire consequences on human health.

Fluoride, nitrates, sodium, calcium are some examples of contaminants which are observed in groundwater. These contaminants when consumed with untreated groundwater can cause a number of ailments and also have a harmful effect on human health. Consuming water which has nitrates exceeding 45 mg/l is especially harmful for infants, can cause methemoglobinemia and even result in stomach cancer. Similarly drinking water in which fluoride amount exceeds safety limits can result in number of skeletal&dental deformities.

Groundwater contamination can also hamper the sustainable development (Chen et al., 2021) of the environment therefore the quality of potable groundwater has captured the attention of many research scholars world-wide.

This chapter describes how reduced groundwater quality can hamper human health leading to many diseases. BIS (IS-10500, 2012) has laid water quality standards and drinking water having water quality parameters above the permissible limits can have detrimental effects on human health.

Table5.3.1Water quality range for consumable water & their adverse effects onhealth of humans

S. No.	Parameter	Prescribed Limit (IS 10500, 2012)		Adverse Effect
		Desired Limit	Permissible Limit	
1	Colour Hazen unit	5	15	Water appears aesthetically undesirable
2	Odour		Agreeable	Waterappears non consumable
3	Taste		Agreeable	Water appears aesthetically undesirable
4	pH	6.5	8.5	Indicates acidic or alkaline

				nature of water, changes taste of water and water with low pH can corrode plumbing pipes and can also leach metals.
5	Hardness as CaCo3 (mg/l)	200	600	Results in scale build-up in plumbing pipes, stained sinks, excess soap consumption, dry skin and hair, can also lead to kidney stones and stomach disorders.
6	Chloride (mg/l)	250	1000	Dehydration, fluid loss, diarrhea or high levels of sodium in blood, poor blood sugar levels in diabetic persons.
7	Total Dissolved Solids (TDS) (mg/l)	500	2000	High TDS levels can cause nausea,vomiting, dizziness, rashes and long-term exposure to high TDS can result in liver and

				kidney ailments.
8	Calcium (mg/l)	75	200	Frequent urination leads to dehydration and increased thirst, upset tummy, gastro-intestinal problems, nausea, vomiting and constipation.
9	Magnesium (mg/l)	30	100	Long term exposure, irregular heart-beat, low blood pressure, dizziness and low breathing rate.
10	Sulphate (mg/l)	200	400	Can corrode plumbing pipes, water can taste bitter, can cause gastro-intestinal problems and high concentrations can also have a laxative effect similar to magnesium.
11	Nitrates (mg/l)		45	Methemoglobinemia (blue baby syndrome) in infants, can show harmful effects on the

				cns&heart,stomachcancer..
12	Fluoride (mg/l)	1.0	1.5	Can lead to fluorosis affecting teeth and bones. Long term intake can cause skeletal fluorosis.
13	Alkalinity (mg/l)	200	600	Can change body pH, results in nausea, vomiting and hand tremors which leads to alkalosis.

Table5.3.2Water quality parameters in irrigation water and their adverse effects on plant growth

S. No.	Parameter	Prescribed Limit (IS 10500, 2012)		Adverse Effect
		Desired Limit	Permissible Limit	
1	EC (µs/cm at 25°C)		No detrimental effect seen < 750 Sensitive plants 750-1500	Retarded plant growth with stunted growth of stems, leaves, flowers and fruits.

			Semi Tolerant plants 1500-3000 Tolerant crops 3000-7500	
2	Salinity ppm		No detrimental effect seen < 500 Sensitive plants 500- 1000 Semi Tolerant plants 1000-2000 Tolerant crops 2000-5000	Retarded plant growth with stunted growth of stems, leaves, flowers and fruits.
3	SAR	SAR < 10 10- 18 18-26 SAR > 26	Excellent Good Doubtful Unsuitable	Effects soil permeability, reduces the infiltration rate of water to plants, plant wilting.

4	RSC (m Eq/l)	RSC < 1.25 1.25-2.5 RSC > 2.5	Excellent Good Unsuitable	Increase the sodium content thus showing a negative effect on plant growth.
5	Sodium %		No Guidelines	Reduces the plant's ability to uptake water, stunted growth of plants and reduces cell development.
6	Chloride (mg/l)		No Guidelines	Show similar adverse effects as sodium, scorching of leaf margins, reduced plant growth.
7	Nitrates (mg/l)		No Guidelines	An essential nutrient for plants but excess may delay fruit development and maturity.

5:3:1 Adverse Effects of elemental contamination on Health

Elements are called the building block of life. A human body requires both the macro and micro nutrients in adequate amounts for its smooth functioning. All living beings contain chemical elements which play a vital role in their well-being. Calcium not only plays an important role in teeth and bone formation but is important for protein synthesis, maintaining suitable potential difference between cell membranes. Sodium and potassium are vital for nerve transmission. Chlorine along with sodium and potassium contributes to smooth liver functioning. Magnesium is essential for enzymes to work efficiently. This section will focus on adverse effects on the health of living beings due to excess and deficiency of non-metallic parameters found in drinking water.

5:3:1:1 TDS

Source:

Agricultural and residential run-off, weathering and rock degradation, industrial discharge, landfills, leaching of soil pollution and wastes of livestock.

Adverse Effects:

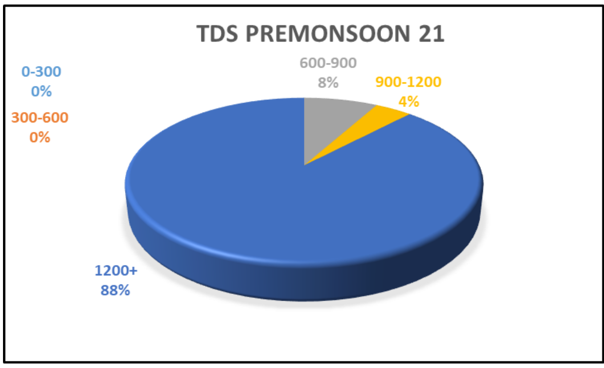
High levels of TDS in drinking water makes it unfit for potable use and may lead to problems like nausea, rashes, vomiting, dizziness and long-term drinking water with high TDS can cause cancer, nervous system disorder, weakened immunity and liver problems.

Treatment for high TDS:

Reverse Osmosis, Ion-exchange method and Distillation

Study area mostly contains salty water. Freshwater zone overlying the brackish water is of limited thickness. Excess salinity present in groundwater has reduced the crop variety which can be grown, decreased the crop yield and long-term irrigating soil with brackish water can make the land unfit for agriculture. Hard water results in more consumption of soaps and detergents and installation of softeners lead to economic expenditure. Run-off groundwater with high TDS into adjacent water bodies can change the biodiversity and result in salt-tolerant species over time.

Fig5.3.1TDS concentration in groundwater samples among study locations both during premonsoon and postmonsoon seasons.



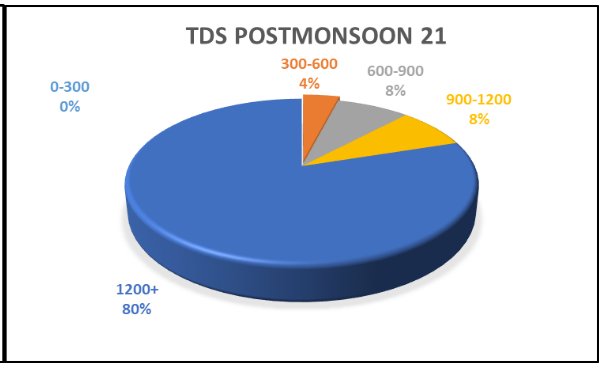


Fig5.3.3Percentage compliance ofcollectedwater samples based on TDS values.

TDS	Category	% Compliance Premonsoon	% Compliance Postmonsoon
< 300	Excellent	0	0
300-600	Good	0	4
600-900	Moderate	8	8
900-1200	Poor	4	8
> 1200	Unsuitable	88	80

5.3.1.2Total Hardness as $CaCO_3$

Source:

Run- off and seepage from soil, sedimentary rocks (especially limestone and dolomite)

containing calcium and magnesium.

Adverse effects:

As per BIS (2012) 200is the desirable limit for TH. It mayleadto skin irritation, dry skin, increased risk of cardiovascular diseases, high blood pressure, kidney diseases and lead to growth retardation in children. Long-term drinking hard water can cause colon cancer, gastric and esophageal cancer.

Treatment for high hardness:

Reverse Osmosis, water softener, Ion-exchange.

Hard water especially when total hardness exceeds 600 mg/l affects the pipes by causing scaling and excess calcium weakens bones, causes kidney stones and leads to calcification of arteries.

Fig5.3.3Total Hardness in groundwater samples among study locations both during premonsoon and postmonsoon season.

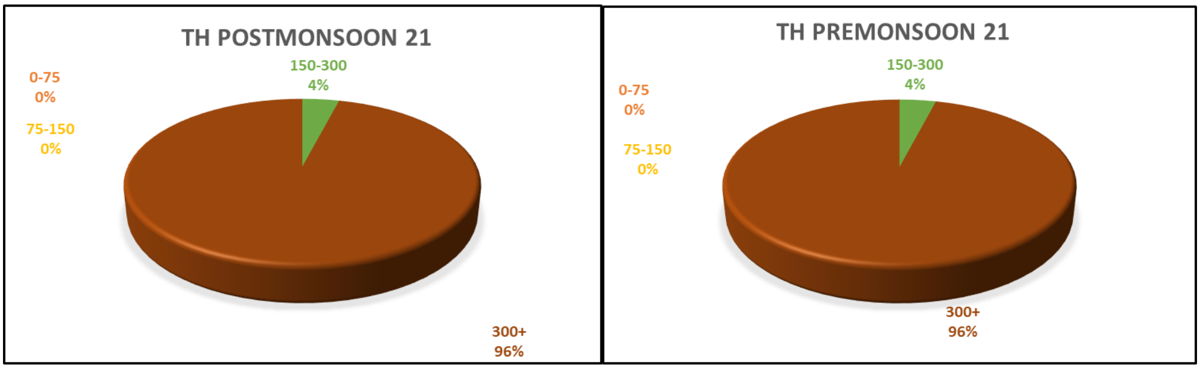


Table5.3.4Percentage compliance of groundwater samples based on TH.

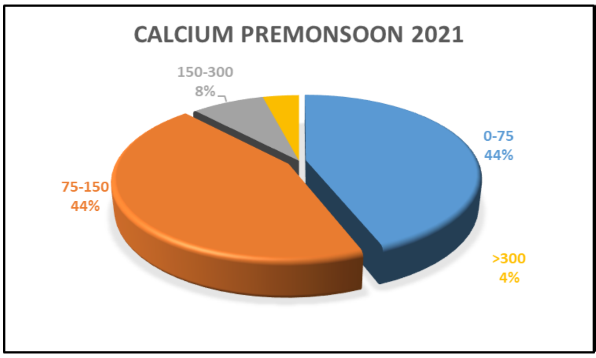
TH as $CaCO_3$	Water Category	% Compliance Premonsoon	% Compliance Postmonsoon
> 75	Soft	0	0
75- 150	Moderately Hard	0	0
150-300	Hard	4	4
> 300	Very Hard	96	96

5.1.3 Calcium

According to WHO drinking hard water has no major adverse effects on the health of living beings. Hard water in fact acts as a supplement to the total dietary intake of calcium allowed. Intestinal absorption processes limit the excess intake of calcium through dihydroxy vitamin D. Calcium can combine with iron, phosphorus, zinc and magnesium present in the intestine to limit their further absorption (Sengupta., 2013).

BIS (2012) has prescribed limit for Cain potable water at 75-200 mg/l&all locations of studied area except Rehrana, Tatarpur and Patli Khurd show calcium levels within the prescribed limit set by WHO.

Fif5.3.4Calcium concentration in groundwater samples among study locations both during premonsoon and postmonsoon seasons.



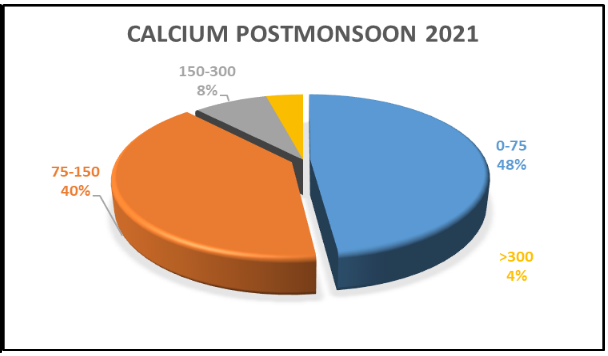


Table5.3.5Percentage compliance of groundwater samples based on Calcium concentration.

Ca (mg/L)	Water Category	% Compliance Premonsoon	% Compliance Postmonsoon
> 75	Soft	44	48
75- 150	Moderately Hard	44	40
150-300	Hard	8	8
> 300	Very Hard	4	4

5.3.1.4Magnesium

According to WHO, no adverse effects are seen in drinking water having excess magnesium. Many studies have pointed out the inverse relationship between drinking water hardness and cardiovascular diseases (Yang et al., 1999). Excess intake of magnesium along with sulphates can have a laxative effect. BIS (2012) has allowed the magnesium intake to be 30-100 mg/l.

Alahapur, Kishorpur, Jaindpur, Nayagaon, Gadpuri and Sehrala which constitute 24% of the study locations had magnesium levels within the prescribed limit.

Fig5.3.5 Magnesium concentration in groundwater samples among study locations both during premonsoon and postmonsoon seasons.

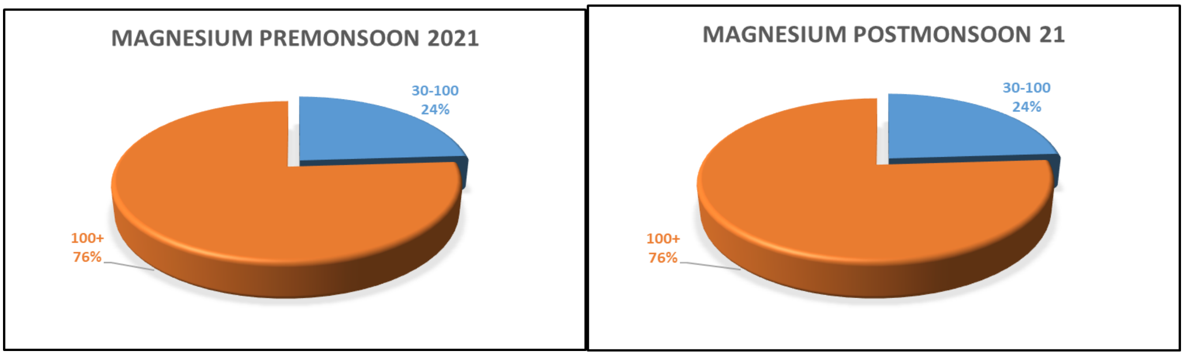


Table5.3.6 Percentage compliance of groundwater samples based on magnesium concentration.

Mg (mg/l)	% Compliance Premonsoon	% Compliance Postmonsoon
30-100	24	24
>100	76	76

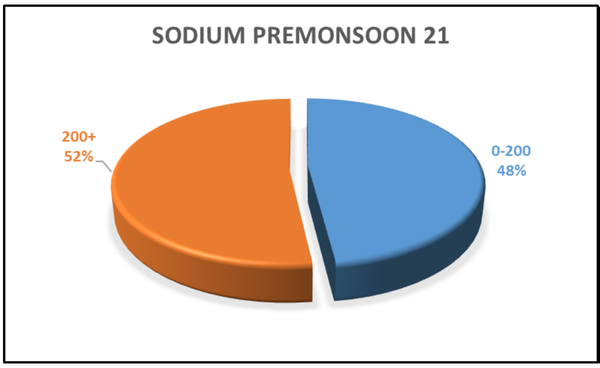
5.3.1.5Sodium

Excess intake of sodium for a short term is not toxic because of kidneys efficiency to excrete sodium but acute effects can result in nausea, vomiting, organ dehydration, pulmonary edema and long-term use can aggravate heart problems but in infants due to immature kidneys small children can suffer from gastrointestinal problems, fluid loss and increased sodium level in the plasma. Elevated sodium levels also increase the risk of hypertension which could trigger heart disease, stroke and coma.

According to guidelines for Canadian drinking water supply, drinking water taste becomes offensive at concentration greater than 200 mg/l therefore 200 is aesthetic objective of Na in potablewater.

48 % of studiedplacesin all the three premonsoon seasons (2019-2021) and 52 %, 60% and 56% of the study locations in the postmonsoon seasons of 2019,2020 and 2021 respectively had sodium levels below 200 mg/l.

Fig5.3.6Sodium concentration in groundwater samples among study locations both during premonsoon and postmonsoon seasons.



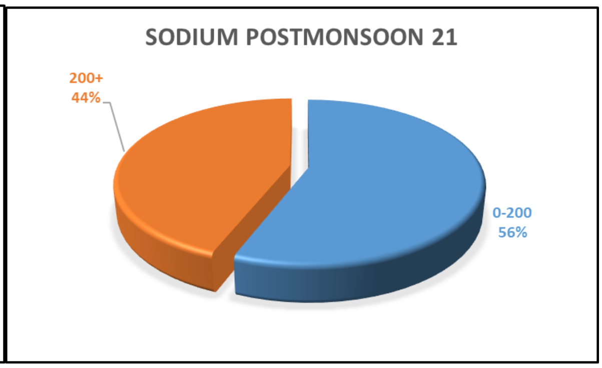


Table5.3.7Percentage compliance of groundwater samples based on sodium concentration.

Na (mg/l)	% Compliance Premonsoon	% Compliance Postmonsoon
0-200	48	56
>200	52	44

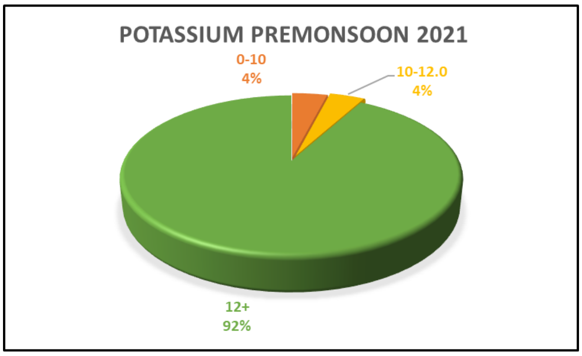
5.3.1.6Potassium

Potassium is an essential nutrient present in human bodies which plays a vital role in many cell functions like growth and repair of cell, nerve stimuli, regulation of muscles contraction, regulation of blood pressure and maintenance of electrolyte and fluids present in the body. At higher concentration potassium chloride can inhibit proper nerve stimuli, thus affecting proper functioning of heart muscles. WHO and BIS have not laid any guidelines regarding the accepted limit for potassium but according to a council directive (1980) related to water quality intended for human use the safety range for K is 12 mg/l.

Intake of potassium is generally not harmful for healthy people as it excretes out rapidly from kidneys but in case of people suffering from kidney ailments, older population, people with existing comorbidities (hypertension, diabetes and heart ailments) and infants because of immature kidneys can cause hyperkalemia and toxicity can cause nausea, diarrhea, breath shortness, fatigue and cardiovascular issues.

8 % study locations in the pre-monsoon season had potassium levels in prescribed limits of 12 mg/l,16 % studied locations in postmonsoon season followed compliance of prescribed limit in year 2019. 8% in premonsoon and 24% in postmonsoon of 2020& 8% studiedlocations in both before & after monsoon of 2021 were within permissible limit.

Fig5.3.7 Potassium concentration in groundwater samples among study locations both during premonsoon and postmonsoon seasons.



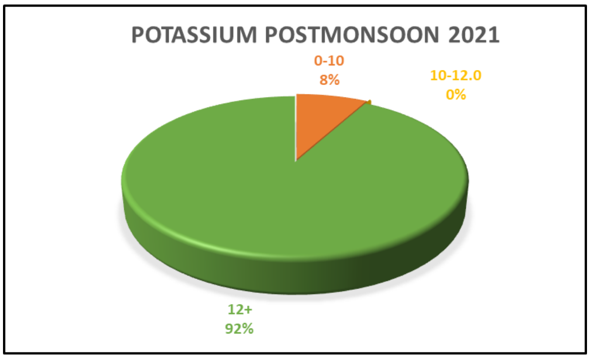


Table5.3.8Percentage compliance of groundwater samples based on potassium concentration.

K (mg/l)	% Compliance Premonsoon	% Compliance Postmonsoon
0-10	4	8
10-12	4	0
>12	92	92

5.3.1.7Chloride

Source: Inorganic fertilizers, landfill leachate, effluents discharged from industries, animal feed, intrusion of seawater in coastal belts.

Adverse effects:

Cough, sore throat, wheezing, eye and skin irritation, difficulty in breathing, tightness in chest and long-term exposure can lead to pulmonary edema.

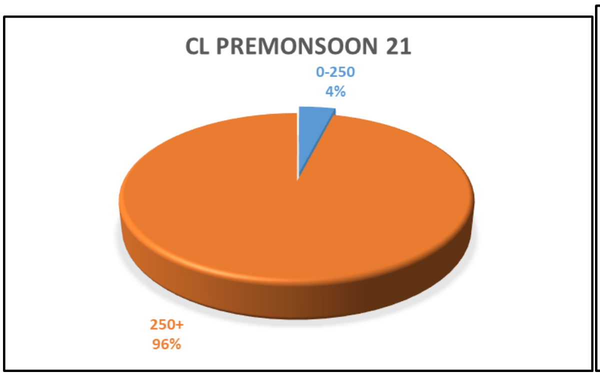
Treatment:

Reverse osmosis, anion exchange method, distillation, deionization.

Chloride is an essential nutrient necessary for maintaining human health and many foods especially tomatoes, celery and lettuce are the rich source of chloride in the body. Chloride in drinking water is not harmful and the major threat lies in increased concentration of chloride along with increased sodium concentration. No guidelines have been provided by BIS/ WHO for the chloride levels in drinking water but Canadian drinking water guidelines has recommended aesthetic objective of 250 mg/l for chloride levels in drinking water based on the increased threat of pipes and sewage line corrosion and taste change above desirable limit of 250 mg/l in drinkable water.

Chloride level in premonsoon varied from 210 mg/l to 4987 before monsoon while after monsoon season it was from 150-4703 mg/l.

5.3.8Chloride concentration in groundwater samples among study locations both during premonsoon and postmonsoon seasons.



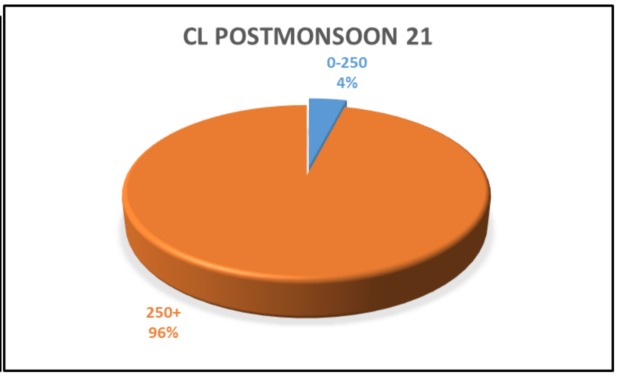


Table5.3.9Percentage compliance of groundwater samples based on chloride concentration.

Cl (mg/l)	% Compliance Premonsoon	% Compliance Postmonsoon

0-250	4	4
>250	96	96

5.3.1.8Nitrates

Source:

Fertilizers, septic tanks, domestic sewage, wastewater treatment plants, animal feed and excreta, diaries and natural reasons.

Adverse Effects:

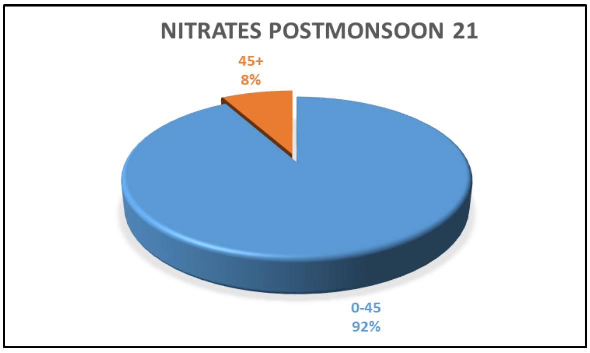
Nitrate in drinking water consumed abovesafe limit of 45 especially affects infants which are under one year of age by increasing the risk factor of getting methemoglobinemia which can cause the skin to turn a bluish tinge and can even result in their death by altering the combination of haemoglobin with oxygen. People suffering from cardiovascular diseases, lung diseases, sepsis are more vulnerable to getting methemoglobinemia. Most of the healthy people are not affected by high concentrations of nitrates as it is excreted out through urine but long-term consumption of nitrates above the prescribed limit can lead to low blood pressure, increased heart rate and palpitation, headache, vomiting, cramps and increased incidence of gastric and colon cancer due to nitrosamines formation in body (which is known to cause cancer).

Treatment:

Ion-exchange, reverse osmosis, distillation. Treatment.

Sikanderpur and Asawati, which constitute 8 % of the studied locations, had nitrate concentration beyond 45 mg/l in both the seasons.

Fig5.3.9Nitrates concentration in groundwater samples among study locations both during premonsoon and postmonsoon seasons.



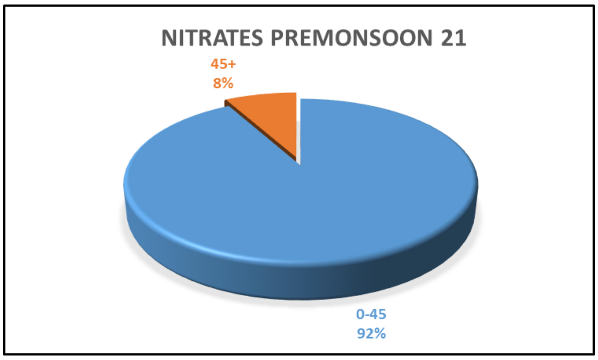


Table5.3.10Percentage compliance of groundwater samples based on nitrate concentration.

NO3(mg/l)	% Compliance Premonsoon	% Compliance Postmonsoon
0-45	92	92
>45	8	8

5.3.1.9Fluoride

Source: Occurs naturally as a run-off from rocks containing fluoride like fluorspar (CaF_2) which is a sedimentary rock, cryolite (Na_3AlF_6) an igneous rock and leaching from soil in groundwater reserves and anthropogenic sources include coal based power plants and industrial effluents which come as a run-ff directly or indirectly into water sources, insecticide usage, phosphate fertilizers containing 1-3 % of fluoride as an impurity, aluminum manufacturing, steel manufacturing units and domestic sewage which contains fluoridated water supply.

Adverse effects:

5.3.1.10Effect of increased fluoride concentration in drinking water on human health.

Fluoride concentration (mg/l) in groundwater	Effect on Human Health
0.2	1 % children show mottled teeth
0.8	No adverse effect seen
1.0- 1.5	Dental caries rate reduced in milk teeth
Above 2	Regular high consumption of fluoride for a long duration especially during teeth development can disturb enamel and dentin formation, thus leading to dental fluorosis and can lead to lower IQ development in children.
Above 4	Skeletal fluorosis associated with joint pain, stiffness in joints, problems of mobility, muscle weakness and irritable bowel syndrome
Above 5	Abdominal pain, diarrhoea, weakness, hands and feet tetany, hypotension.
Above 6	Bone outgrowth, limitation in joint movement, joint and spine deformities contribute to neurological problems.

Above 8	Prolonged exposure can cause renal disease, swelling in kidneys, fibrosis, glomeruli atrophy and tubular necrosis.

(Ullah ; 2017)

fluoride elevated range in groundwater above level of 1 mg/l as seen in several study locations has led to onset of many symptoms of fluoride varying from dental fluorosis, itching in body and scalp to many joint problems due to skeletal fluorosis.

Fig5.3.10Fluoride concentration in groundwater samples among study locations both during premonsoon and postmonsoon seasons.

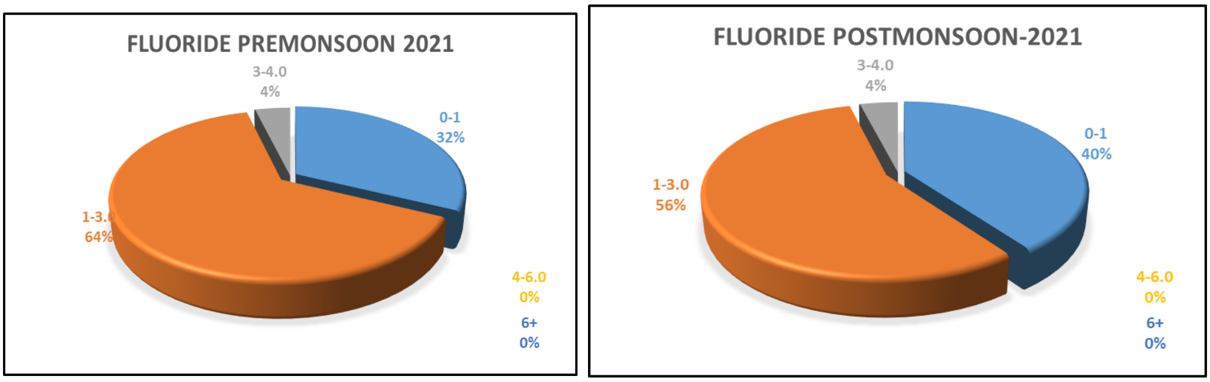


Table5.3.11Percentage compliance of groundwater samples based on fluoride concentration.

Fluoride (mg/L)	Adverse effects on health	% Compliance Premonsoon	% Compliance Postmonsoon
< 1	Safe for consumption	32	40
1-3	Dental fluorosis, mottling and discoloration of teeth	64	56

3-4	Pain and stiffness in joints, onset of skeletal fluorosis.	4	0

5.3.1.10Health Survey of Local Population

A health questionnaire based on groundwater quality was given to local residents to fill. Based on the questionnaire, it came to light that nearly all residents complained about the poor quality of groundwater and people also told their woes about recurrent occurrences of jaundice, tummy upset, joint problems, dental fluorosis especially in children, itching and skin rash in skin and scalp.

Many residents due to the lack of resources and their financial condition were forced to drink water from hand pumps without any treatment and complained about the bad/saline taste of groundwater.

Some photographs and medical prescriptions have been shared to show the ailments suffered by the local population.

Pictures of the local population being affected by contaminated water.

5.4

ASSESSMENT OF WQI OF GROUNDWATER OF STUDY AREA

5.4.1

Groundwater is an important resource and is one of the biggest sources of freshwater (Jha et al., 2020). Half of drinking water supplies are met by groundwater in the low-income regions of the world (Carrard et al., 2019). One of the biggest advantages of groundwater for its use as a drinking water source is it is protected from many naturally occurring contaminants (Gronwall et al., 2020) but agriculture involving excessive use of fertilizers and pesticides, urbanization, exponential population growth and industrialization (Burri et al., 2019) are some of the threats which have deteriorated the groundwater quality. Quality of groundwater is a relevant concern especially in Indian villages where a large number of people are mostly dependent on groundwater for quenching its thirst (Sekhri et al., 2014). Consuming polluted water leads to many water-related diseases and thus puts an unnecessary burden on pockets of people therefore it is important for regular checking of groundwater for seeing usefulness for consumption&accordingly follow methods for its conservation. Many techniques and methods are used to studyqualityof groundwater based on various parameters (Adnan et al., 2019; Jing et al., 2013; Bhunia et al., 2018). WQI) is an efficient methodfor getting knowledge about quality of groundwater. WQI is a mathematical formula which converts large data of various parameters into a simple numerical value which can be easily understood by the general public (Kawo et al., 2018).

5.4.2Need for wqi

(WQI) is a vital tool which is used for evaluating qualityof water by converting chosen Physico-chemical parameters of water intonumerical dimensionless value which provides information aboutqualityof water in a specific location and can be easily understood by the general public. By the easy nature of WQI and their scientific basis WQI has become an important tool in the evaluation of water quality. World-wide many methods of WQI assessment have been developed but up-till now there has been a dearth for calculating the steps used in finding WQI in a uniform pattern thus there is a growing interest to find the accurate WQI.In 1965, WQI was developed by Horton based on eight water parameters.(CCME) again worked on WQI in the mid-nineties (Dede et al., 2013). Following steps were used for finding WQI based on weighted arithmetic index method:

5.4.3Weighted arithmetic index method for WQI

In 1st step, each of the selected eleven chemical values were allocated weight(wi) 1-5 based on its relevance in water quality (Batabayal et al., 2015) as shown in table 2. Nitrates was assigned the maximum weight of 5, fluorine, pH, sulphates and TDS were allotted weight of 4, chlorine, total alkalinity (TA) was given 3 and calcium, magnesium and total hardness were given a scale of 2 depending on the overall influence in the water quality.

In 2ndstep, RW(Wi) of everychemical parameter was found by weighted arithmetic index method(Kachroud et al., 2019).

Table5.4.1Weight(wi) and relative (Wi) to each parameter

PhysicoChemical Parameter	Standard	(wi)	RW (Wi)
pH	6.5-8.5	4	.1212
TH	300-600	2	.0606
TA	200-500	3	.0909
Ca	75-200	2	.0606
Mg	30-100	2	0.0606

Cl	250-1000	3	0.0909
TDS	500-2000	4	0.1212
SO4	200-400	4	0.1212
NO3	45-100	5	0.1515
F	1-1.5	4	0.1212
		∑wi=33	∑Wi= 1

$$W_i = \frac{w_i}{\sum_{i=1}^{n} w_i}$$

- All chemical parameters except pH are in mg/l.
- Lower value gives the desirable weight and higher value denotes the permissible range

3rdstep is calculated by using the below equation

qi =(Ci/Si) x100

- Where q = quality rating
- Ci = Conc of everyparameterused in given sample of water.
- Si = Indian standardsforwater meant for drinking for all chemical parameters of water.

In 4th step, for calculation of WQI the subindex (SI) for each chemical parameter is determined by adding all the sub index values of samples of groundwaterobtained.

SIi = Wi x qi

5.4.4Quality of water based on WQI

pH pH is one of relevant and common testparameters used for evaluation of water quality. pHis a measure of hydrogen ion concentration was determined usingpotentiometric method which involves using a standard hydrogen electrode and a reference electrode. Standard limit for pH in potablewater varies from 6.5-8.5 as per IS of drinking water. Health-wise there is no threat from altered pH in drinking water but pH less than 6.5 or greater than 8.5 can result in staining and scaling.

The pH of the study area varied from 6.5- 7.65 in the premonsoon season with an average mean of 6.93 which is within the acceptable range whereas in postmonsoon pH concentration varied from 6.23 to 7.25 with an average mean of 6.60.From the table it is clear that pH range of groundwater in the Palwaldistrict is in permissible limit as referred by BIS (10500:2012) standard.

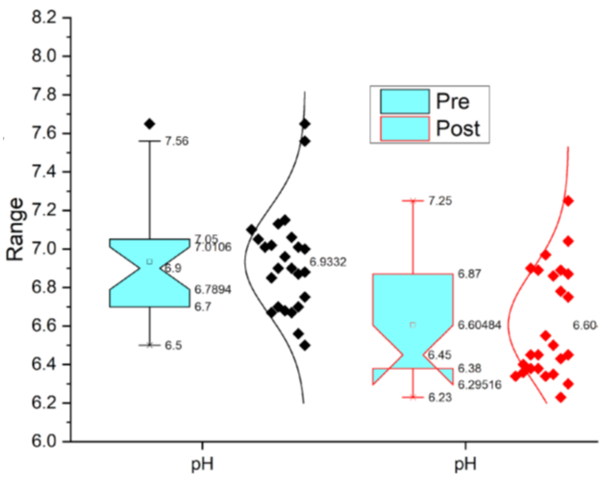


Fig5.4.1Box-Whisker graph of pH in the study location.

Calcium: is the most abundant cation in an uncontaminated source of drinking water, responsible for hardness in water and was determined by EDTA titration. Acceptable limit set by BIS for Ca in drinking water is 75 and 200has been set up as a permissible range. Ca conc in groundwater in premonsoon varied from 30-440 showing an average mean value of 104.2 mg/l. Ca concentration in postmonsoon ranged 28 - 438 with average mean of 101.64.

Tatarpurshowedhighest calcium range (440 mg/l) while Gadpuri showed minimum concentration of calcium as 28 mg/l.

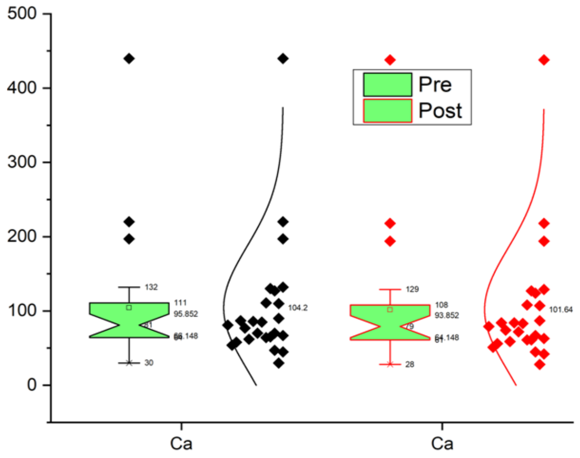


Fig5.4.2Box-Whisker graph of Ca in the study location.

Magnesium: is one of the most abundant cations in freshwater and is necessary for both plants and animalsnutrition. Mg is responsible for causing hardness in water. Standard values of 30 (accepted limit) and 100 (permissible limit) have been set up by BIS for magnesium. ConcofMg in groundwatervaried from 9- 1184 with an average mean of 308 in premonsoon and in postmonsoon Mg conc varied 10 -1186. Concentration of magnesium was minimum in Nayagaon village and maximum concentration was found in Patli Khurd.

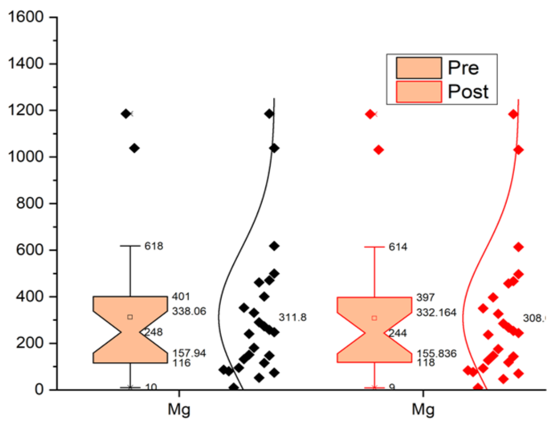


Fig5.4.3Box-Whisker graph of Mg in studied location.

Chloride: Groundwater naturally contains chloride along with alkali and alkaline earth metals. BIS has recommended 250 as desirable limit for chloride in groundwater. Large amounts of chloride in drinking groundwater can alter the taste of water. Most of villages in studied area showed high range of chlorides in drinking water. Before monsoons, chloride range varied from 167 (seen in Nayagaon) - 4734 (Allika) with average mean of 1455.4 whereas the postmonsoon chloride levels varied 123 - 4567 .

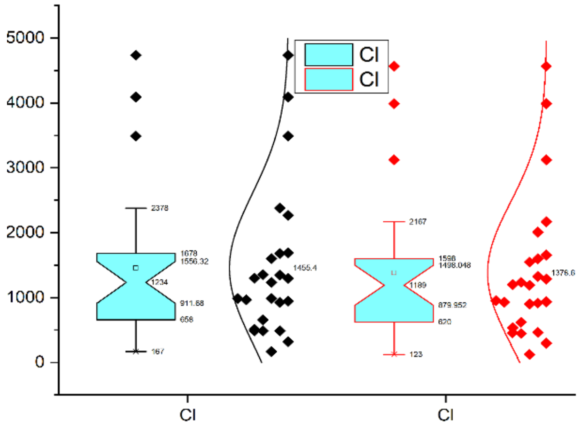


Fig5.4.4Box-Whisker graph of Cl in the study location.

Fluoride: is an element found naturally in groundwater because of weathering of rocks &minerals and sediments leaching containing fluoride. BIS has prescribed 1as the acceptable range and 1.5 as permissible range for fluoride in drinking water. Long term exposure to water containing excess fluoride can result in dental and bone disorders. HighFrangein groundwater was seen in villages of Alahapur, Firozpur, Prithla, Sikanderpur, Asawati, Allika and Patlikalan. Kishorpur recorded the highest concentration of fluoride with a value of 3.12 . In premonsoonfluoride value varied from 0.12 (Rakhota) to 3.12 an average mean of 1.33 mg/l whereas in postmonsoon the concentration of fluoride varied 0.1- 3.07.

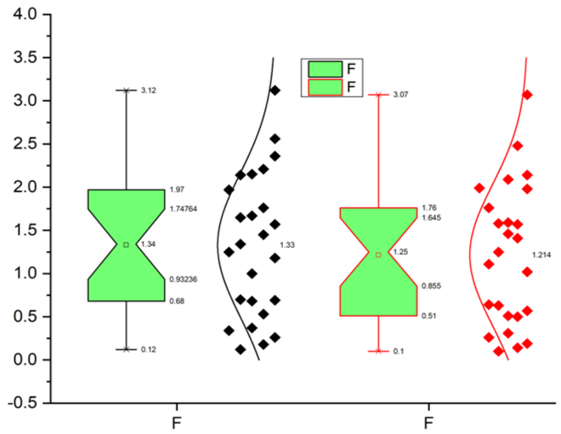


Fig5.4.5Whisker graph of F in the study location.

Nitrates: is an important parameter of groundwater capable of inflicting diseases especially among infants. Fertilizers, industrial and domestic sewage are the major contributors of nitrogenous wastes. BIS has prescribed as acceptable range for nitrates in drinking water. In premonsoon NO3 concentration varied 0.37 - 96.7with an average mean of 10.71 while in postmonsoonNO3 ranged 0.37 - 96.2 with average mean of 10.41l. Asawati recorded highest nitrate concentration while the lowest was observed in Paltli Kalan.

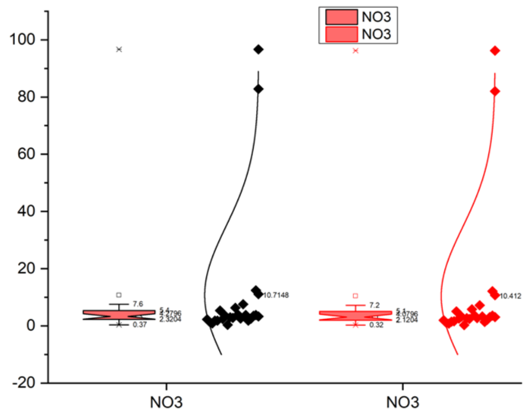


Fig5.4.6Box-Whisker graph of NO_3 in the studied location.

Sulphates: come from disintegration of sulphuric acid salts and are seen naturally in all sources of water. BIs has prescribed 200 as the acceptable limit and 400 (permissible range) for sulphates and these are not a major source of health threat. Sulphate range in premonsoonranged from 48- 186 with an average of 124.88 whereas postmonsoon concentration varied from 44- 181 with average of 119.84.

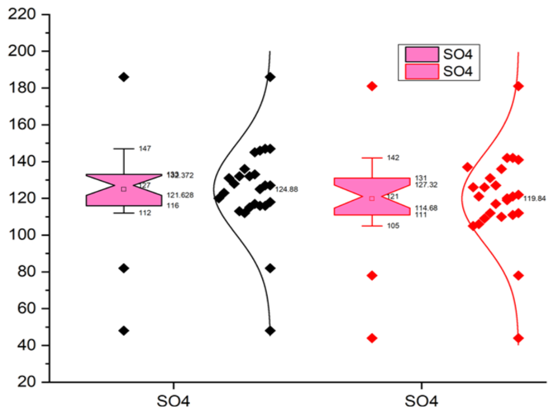


Fig5.4.7Box-Whisker graph of SO_4 in the study location.

TDS: Natural and manmade source can lead to high TDS in groundwater leading to altered taste and colour. High mineralization can be indicated in water containing high TDS. According to BIS parameter, water containing TDS level less than 500 is considered excellent for potable use. TDS level in studiedarea varied from 557 - 8480 with an average of 2554.36 in the premonsoon season and in postmonsoon season. TDS level varied from 498 - 8267 with an average of 2407.52. Kishorpur and Tatarpur recorded the minimum and maximum TDS levels respectively.

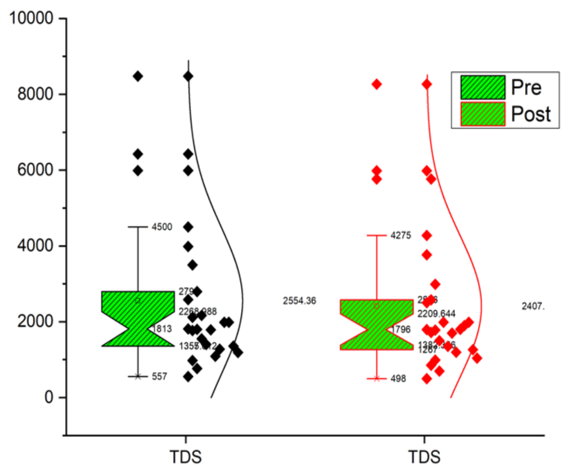


Fig5.4.8Box-Whisker graph of TDS in the study location.

TH: Hardness (CaCo3) of the water ranged from 202 mg/l to 5425 mg/l of studied region. Of all water samples analyzed- Nayagaon (22 mg/l), Gadpuri (345mg/l) had hard water and all the remaining 23 studied areas contained very hard water.

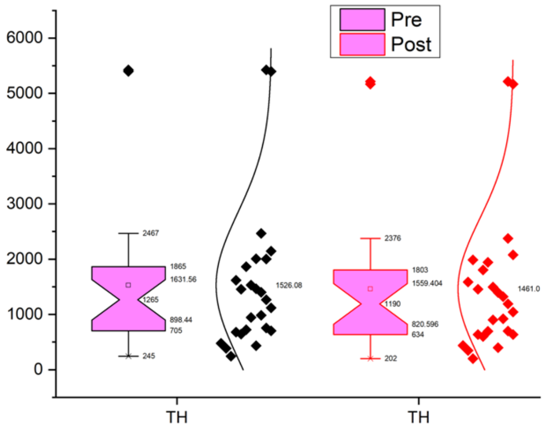


Fig5.4.9Box-Whisker graph of TH in the study location.

TA: Alkalinity in water of studied place isdue to the presence of bicarbonate of alkaline earth metals. Alkalinity above 200 mg/l in water provides it with an unpleasant taste but is not a major health threat. In the premonsoon season TA varied from 108- 845 with an average 543.92 and in postmonsoon alkalinity ranged from 98-812 with an average mean of 521.92 . Kishorpur showed minimum TA as 108mg/l while maximum value was observed in Joharkhera (845mg/l).

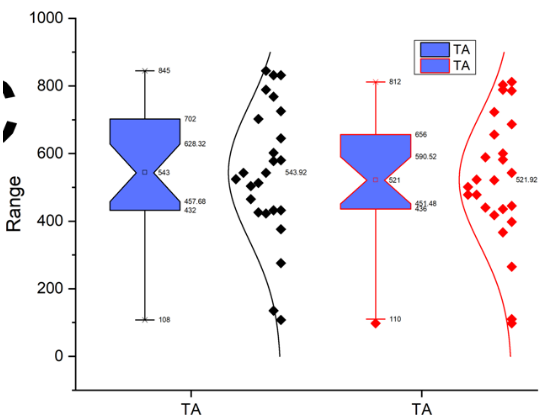


Fig5.4.10Box-Whisker graph of TA in the study location.

5.4.5Water quality index values

WQI based, drinking water can be divided into five main classifications (Kangabam et al., 2017; Uddin et al., 2021) as shown in Table 2. WQI for the study area was calculated and it reflected that during the premonsoon season none of the sample came in excellent category, 4% of groundwater samples came in good category, 28% came in poor category, 40% groundwater samples were of very poor category and 28 % groundwater samples were unfit for consumption. WQI for the post monsoon % complianceagain showed none of the groundwater samples were in excellent category, 4% groundwater samples were in good category, 32% in poor category, 36% in very poor range and 28% of the groundwater samples were unfit for consumption.

Table5.4.2Water Range based on wqi

WQI range	Water category
0-50	Excellent
50-100	Good
100-200	Poor
200-300	Very Poor
>300	Unfit for consumption

Table5.4.3Based on WQI, % Compliance of studied Location

S.No	Range	Water category	% Compliance	
			pre-monsoon	post monsoon
1	0-50	Excellent	0	0
2	50.1-100	Good	04	04
3	100.1-200	Poor	28	32
4	200.1-300	Very Poor	40	36
5	>300	Unfit for consumption	28	28

Table5.4.4Statistics of Physico-chemical parameters of collected groundwater samples

Parameter	Pre-Monsoon					Post-Monsoon				
	Min	Max	AM	MD	SD	Min	Max	AM	MD	SD
pH	6.5	7.65	6.93	6.9	0.26	6.23	7.25	6.6	6.45	0.27
Ca	30	440	104.2	81	81.21	28	438	101.64	79	81.27
Mg	10	1186	311.8	248	282.83	9	1184	308.08	244	282.45
Cl	167	4737	1455.4	1234	1132.98	123	4567	1378.4	1189	1075
F	0.12	3.12	1.33	1.34	0.81	0.1	3.07	1.214	1.25	0.79
NO3	0.37	96.7	10.71	3.3	23.55	0.32	96.2	10.41	3.1	23.45
SO4	48	186	124.88	127	23.96	44	181	119.84	121	23.93
TDS	557	8480	2554.3	1813	1908.6	498	8267	2407.5	1796	1837
TA	108	845	543.92	543	196.03	98	812	521.92	521	189.14
TH	245	5425	1526.08	1265	1289.4	202	5214	1461.04	1190	1246.35

Measurements excluding pH are in mg/l

5.4.6 Summary

High population density, expansion of industries and rapid industrialization have generated a large amount of solid and liquid effluents which has been detrimental to groundwater quality and it can be easily seen that groundwater of the studied location is highly contaminated needing some pre-treatment before it can be utilized for potability. WQI in the study area has revealed that greater than 40% of ground water samples come under very poor category, above 20% of groundwater samples were unfit for drinking. Excess groundwater extraction, shifting of people from rural to urban areas and excessive use of fertilizers are also some other causes of deteriorating water quality in the study area. At all study locations better WQI was witnessed during the postmonsoon due to rainfall percolation in the ground which recharged the aquifers. TDS of the study area is also very high which can lead to an increase in salinity of soil. Apart from assessment of water quality for consuming purposes, WQI determination can also be useful for establishing water treatment plants, choosing pipe material while laying of pipes and also it can help the town planners to select suitable places for industries, residential areas and waste disposal sites.

5.5

GROUNDWATER QUALITY EVALUATION FOR IRRIGATION SUITABILITY INSTUDY AREA

5.5.1 Introduction

Haryana is called the 'Food bowl of India' and with the commencement of green revolution in India, state has attained unprecedented economic and financial development. This unmatched growth was also possible due togroundwateravailability whichwasused for irrigating purpose thus leading toincreasedagricultural returns. This economic spurt because of high agricultural productivity led to rapid growth in industrial sector,urban area expansion and migration of people from rural to urban sector which in turn mounted pressure on natural resources.

In the past few years, this NCR region has seen unchecked growth in population,urban area expansion, boom of industrial development and modern agriculture which relies heavily on chemical fertilizers and pesticideshave killed the adjoining aquatic bodies. Much work related to groundwater quality decline has beendoneby researchers in whichpopulation growth, unplanned urbanization&misuse of landare the main factors responsible fordegradation of groundwater.

Palwal district has high population density, mushrooming industries and liberally useschemicalfertilizers and pesticides for crop yield increase which can even further decline thequality of groundwaterthereforecurrent work was done for studying use of groundwater for irrigating crops in Palwal, Haryana.

Assessing quality of groundwater for irrigation

Groundwater for agricultural activities is dependent on type ofconstituentof minerals present which can show their effect on both plants and soil which can show their effect on plants as well as soil. Various salts present in water can changestructure of soil, permeability of soil&aeration properties thus affecting plants growth. Quality of groundwater for irrigation was assessed by selected chemical parameter indices which included:

5.5.2.1Sodium Hazard (SH)

Sodium hazard was evaluated by SAR and SSP.

SSP)

Sodium is vital index to determine the usefulness of groundwater for crops by knowing permeability of soil. Excess Na+ present in water are exchanged by calcium and magnesium ions present in soil thus sodium forms chemicalbonds with soil and reduces water movementin soil. This ion-exchangedegrades the soil permeability, reduces soil drainage and over the time can harden the soil. Soluble sodium percentage (Na %) which is expressed in m Eq/l&is calculated using Todd (Todd., 2004) equation:

$$SSP = \frac{Na^+}{(Ca^{2+} + Mg^{2+} + Na^+ + K^+)} * 100$$

water used for irrigationon SSP basis,can be categorized into:

SSP< 20% (Excellent, 20-40% (Good), 40-60% (permissible), 60-80% (Doubtful), SSP>80% (water unsuitable)

(SAR)

SAR is tool which is used to estimate the effectiveness of water so that to use it for irrigation. SARisrelative ratio of Na ions to that of CaandMg ions present in groundwater. It estimates thepotential of Na^+ to pile up in the soil at the cost of $Ca^{2+}$and Mg^{2+}. High SAR value can break the physical structure of soil. SAR value is expressed in m Eq/l and calculated byRaghunath (Raghunath., 1987) equation shown below:

$$SAR = \frac{Na^+}{\sqrt{\frac{(Ca^{2+}+Mg^{2+})}{2}}}$$

On SAR basis, irrigating groundwater can be categorized in following classes:

Excellent (SAR< 10), Good(10-18) ,Doubtful(18-26),Unsuitable(SAR > 26)

5.5.2.2(RSC)

RSC denotes the $Na_2CO_3$and $NaHCO_3$salts present inwaterused for watering crops. When excess concentration of carbonate and bicarbonate ions are present in water as compared to Ca&Mg ions, they can alter soil structure by separating calcium and magnesium ions as precipitate from the soil and also increase the adsorption of sodium in soil. RSC is expressed in m Eq/l and calculatedby Eaton (Eaton et al., 1950) equation shown below:

$$RSC = (HCO_3^- + CO_3^{2-}) - (Ca^{2+} + Mg^{2+})$$

On the basis of RSCirrigationalwater can be demarcated :

Low-(RSC< 1.25), Medium- (RSC 1.25-2.5), High- (RSC>2.5),Unsuitable for irrigation-(RSC > 5)

5.5.2.3(MH)

Magnesium is an importantmacronutrientpresent in soil necessary for proper growth and development of plants but Mg^{2+} high range present in irrigational water can increase the pH of soil, make soil alkalineand also decrease thephosphorus availability to plants thus reducing agricultural returns (Machado et al., 2017). Magnesium hazard which is expressed in m Eq/l, is calculated by Szabolcs and Darab (Szabolcs., 1964) equation shown below:

$$MH = \frac{Mg^{2+}}{(Ca^{2+} + Mg^{2+})} * 100$$

On the basis of MHvalues in irrigating water,

MH < 50 (Water is suitable for irrigating crops)

5.5.2.4(PI)

PI isusedtotest suitability ofwaterforwatering crops as it focuses on movement of water in soil which is dependent on Na, Ca, Mg and HCO_3ionsconcentration present in the soil. PIis expressed in m Eq/l and is calculatedbyDoneen (Doneen., 1964) equation shown below:

$$PI = \frac{Na^{+} + \sqrt{HCO_3^{-}}}{(Ca^{2+} + Mg^{2+} + Na^{+})} * 100$$

On the basis of PI value, irrigating water can be categorized into three divisions:

Class I- PI > 75% (Suitable for irrigation), PI 25-75% (Good for irrigation), Class III PI < 25% (Unfit for irrigation)

5.5.2.5Chloro-alkaline index (CAI)

CAI reflects the ionexchange process between groundwater and water present below the ground, both during movement and resting stage of water. CAI (CAI I & CAI II) is expressed in m Eq/l and was calculatedbySchoeller (Schoeller., 1977) equation shown below:

$$CAII = \frac{Cl^- - (Na^+ + K^+)}{Cl^-}$$

$$CAIII = \frac{Cl^- - (Na^+ + K^+)}{(SO_4^{2-} + HCO_3^- + NO_3^- + CO_3^{2-})}$$

CAI is negative when ionexchange takes between NaandKionspresent in aquifer&Mg-Caions present in groundwater.

CAI is positive when reverse ionexchange occurs betweenNaandK ions present in groundwater&Mg and Ca ions present in aquifer.

5.5.2.6Kelly ratio

KIis used toassess quality of water used for irrigating crops on Na^+concentration to that Ca^{2+} and Mg^{2+} concentration. KI is expressed in m Eq/l and is calculated by Kelly (Kelly., 1940) equation shown below:

$$KR = \frac{Na^{+}}{Ca^{2+} + Mg^{2+}}$$

When value of KR > 1, it reflects excess levels of sodium ions are present in water.

KR ≤ 1 (Water suitable for irrigation), KR ≥ 1 (Water not fit for irrigation) (Rawat et al., 2016)

5.5.3 Irrigation Parameter Indices

5.5. 3.1 pH

pH of groundwater samples of the studied region varied from 6.75 to 7.56 with average mean shwing a value of 6.93. Lowest pH was found in sample S1 (6.75) while maximum pH was observed in sample S12 (7.56). Groundwater samples of the studied area belonged tosafe pHrange(6.5- 8.5) for irrigating purposes.

5.5.3.2 Salinity and Alkalinity Hazard

High salt content present in the groundwater can make the soil saline, if used for a long time for irrigation. Both EC and TDS are a measure of the salinity hazard of irrigating water (Singh et al., 2020). In the current study, EC values varied from 702 µS/cm which was seen in sample S9 to a very high EC value above 2250 µS/cm. In the current work, none of thegroundwatersamplescame in class C1, 4 % of the samples categorized in class C2, 48 % in class C3 and 48 % in class C4 as seen in Table 1.

Table 5.5.1: Groundwater quality based on EC

Parameter	Level	Range	Samples
EC µS/cm	C1	< 250 Excellent	None
	C2	250-750 Good	S9
	C3	750-2250 Doubtful	S1, S2, S5, S11, S12, S13, S15, S16, S19, S20, S24, S25
	C4	> 2250 Unsuitable for irrigation except for highly salt resistant crops.	S3, S4, S6, S7, S8, S10, S14, S17, S18, S21, S22, S23

Based on USSL classification, (Admilla et al., 2018)

TDS of the studied area ranged from 557 mg/l as seen in sample S9 to 8480 mg/l as observed in sample S10. 12% of the samples came in moderate range, 48% in high and 48% of studied samples came in the very high category of dissolved solids.

5.5.3.2 Soluble Sodium Percentage

SSP in the study area varied from 6.31m Eq/l to 73.15 m Eq/l. Lowest SSP was seen in sample S3 and highest in sample S15. Excess sodium ions present in irrigation water get exchanged with calcium and magnesium ions thus reducing the soil permeability and later causing soil hardening. In the current study, 40% of samples came in excellent category, 40% in good, 12% in permissible range, 8% in doubtful and none of the groundwater sample was unsuitable for irrigation as seen in table 2

Table 5.5.2: Irrigation water quality based on SSP

Parameter	Level	Range %	Samples
Soluble Sodium Percentage (Ahmad et al., 2020)	Excellent	< 20	S3, S6, S7, S10, S14, S17, S18, S19, S22, S23
	Good	20-40	S2, S4, S5, S8, S9, S11, S12, S13, S20, S21
	Permissible	40-60	S1, S24, S25
	Doubtful	60-80	S15, S16
	Unsuitable	> 80	None

5.5.4 Wilcox Diagram

The sodium or alkali hazard describes aboutNaions high concrelative to total Ca^{2+} and Mg^{2+}ionscopncentration. Greater thesodiumproportion(highSAR value), greater is the sodium or alkali hazard (Wilcox 1955).

Indiagrammatic representation, electrical conductivity wasplotted Vs sodium percentage. In the diagram, shown below: 40% of the water samples were in excellent category, 36% in good category, 8% in permissible, 12% in doubtful and 4% of collected groundwater were unsuitable for irrigating.

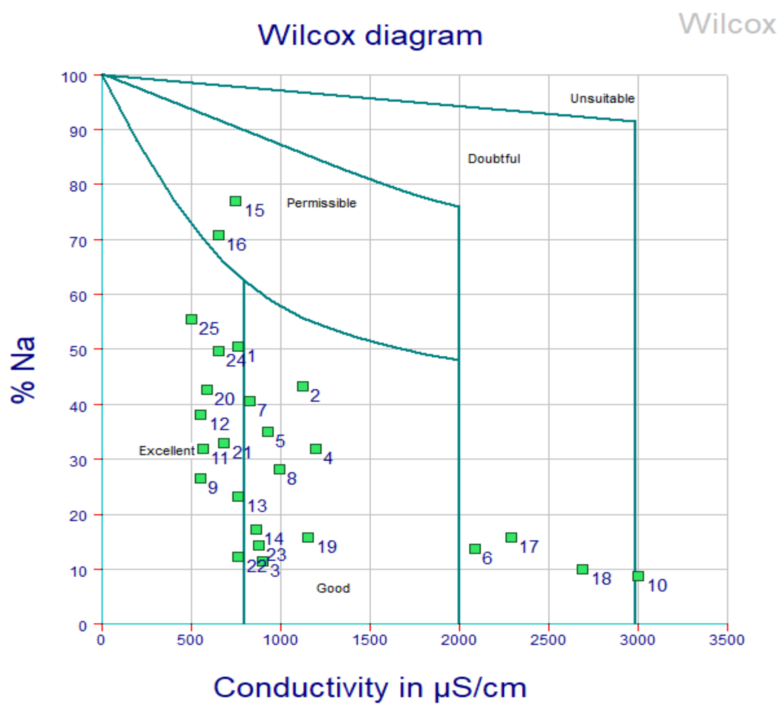


Fig 5.5.1: Wilcox diagram showingwater suitability for irrigation on the basis of EC&Na%

SAR

SAR in studied place ranged from 0.451 m Eq/l (S3) to 16.71 (S15) m Eq/l. All the locations of the study area except S15 and S16 had SAR less than 10 which categorized excellent groundwater quality suitable for irrigation whereas samples S15 & S16 had good water quality in terms of irrigating the soil. When SAR value is more than 6–9, risk of sodium which brings an undesirable effect on permeability of soil and infiltration of water in the soil is higher. (Saleh et al. 1999).

5.5.5.2 Residual Sodium Carbonate

All collectedgroundwater of studied place are in the safe quality range, show less sodium hazard (RSC < 1.25) and can be used for irrigation. The RSC of the studied area ranged from -103.3 m Eq/l to - 0.36 m Eq/l. All the samples studied show a negative sign which indicates Ca & Mg ions dissolved exceed the $CO_3$and HCO_3 ions present in water.

5.5.5.3 Magnesium Hazard

Both magnesium and calcium are necessary for maintaining an equilibrium state, any increase of these can alter the soil pH which over time can decrease the crop output. Irrigating water, having a MH > 50 is considered unsuitable for irrigation (Rahman et al., 2017). Major collected groundwater sampleshave shown high Mg content. Magnesium hazard values of the study area ranged from 22.32 m Eq/l to 93.04 m Eq/l. Lowest MH was observed in sample 20 while maximum was seen in sample 17. Only 12% of the samples (S1, S7 & S20) had shown MH less than 50 and the rest were unsuitable for irrigation based on values of MH.

5.5.5.4 PI

Concentration of Ca, Mg, Na and HCO_3 ions present in groundwater canaffectthe soil permeability (Tabbal et al., 2012) so PI is calculated using these cations and anions. PI of the study area varied from 9.76 m Eq/l found in sample S10 to 78.75 m Eq/l found in sample S30. 4% of the studied samples (S15) and 60% of the samples (S1, S2, S4, S5,

S7, S9, S11, S12, S13, S16, S20, S21, S24 and S25) were found in class one and class two respectively suitable for irrigating. Samples (S3, S6, S10, S14, S17, S18, S19, S22 and S23) were classified as class III (PI < 25) hence unsuitable for irrigation.

5.5.5.5 Chloro-alkaline index

Values of CAI I were seen between -2.39 to 0.91 as seen in sample S15 and S10 respectively. Negative value of CAI 1 was only seen in sample S15. Values of CAI II varied from -4.15 to 9.61 as seen in samples S15 and S18 respectively, this also explained how the chemical composition of groundwater can be understood with the help of exchangeable cations.

5.5.5.6 Kelly ratio

Since water which shows a KR ≥ 1 is considered unsuitable for irrigation, only three sample (12%) sites S15, S16 and S25 exceeded the permissible limits while the major portion of (88%) collected groundwater samples were within the desirable limits and were thus suitable for irrigation.

Table 5.5.3: Pre-monsoon Irrigation Parameter indices of Palwal District

Name of village	SSP	SAR	MH	KR	PI	RSC	CAI 1	CAI 2
Alahapur	46.618	4.749	48.302	0.939	56.323	-7.16	0.513	1.650
Firozpur	38.626	4.692	86.051	0.677	45.211	-16.61	0.504	1.750

Prithla	6.818	0.554	82.692	0.076	11.214	-23.2	0.872	4.275
Sikanderpur	26.762	2.844	86.666	0.392	33.158	-20.25	0.676	2.465
Asawati	32.230	2.748	79.032	0.493	40.279	-10.8	0.703	2.196
Allika	12.907	1.450	88.339	0.149	18.433	-35.96	0.944	9.097
Rehrana	19.756	2.073	49.530	0.331	33.436	-13.21	0.618	2.075
Joharkhera	25.981	2.816	79.191	0.360	31.604	-24.01	0.814	5.494
Kishorpur	25.083	1.321	57.522	0.340	34.796	-3.03	0.702	1.148
Tatarpur	7.5059	1.210	79.723	0.082	9.762	-98.5	0.911	8.195
Harfali	30.932	2.810	78.017	0.452	38.165	-13.73	0.518	1.181
Teharki	36.440	3.192	84.831	0.586	44.068	-10.23	0.373	0.849
Badha	22.058	2.260	88.739	0.286	26.316	-25.88	0.657	2.205
NagliPanchagi	15.811	1.779	90.126	0.190	19.124	-39.15	0.811	5.323
Chandpur	73.105	16.718	78.014	3.148	78.754	-8.9	-2.398	-4.158
Jaindapur	69.603	12.777	54.913	2.379	73.454	-10.21	0.085	0.468
Paltli Kalan	14.664	1.826	93.044	0.173	15.984	-54.15	0.848	15.075
Patli Khurd	9.421	1.548	89.984	0.104	11.151	-103.33	0.877	9.616
Rakhota	12.707	1.310	88.481	0.150	18.039	-29.36	0.807	2.697
Naya Gaon	35.455	1.686	22.321	0.617	55.537	-1.93	0.412	0.448

Megpur	30.411	3.053	88.149	0.452	37.034	-16.88	0.600	1.862
Jatola	11.278	1.204	87.400	0.128	15.687	-37.85	0.871	4.454
Meerapur	11.931	1.137	87.898	0.139	18.011	-26.86	0.877	4.392
Gadpuri	46.064	3.679	81.632	0.910	62.410	-0.36	0.418	0.565
Sehrala	46.680	4.584	75.520	1.046	60.787	-4.1	0.133	0.232

Table 5.5.4: Post-monsoon Irrigation Parameter indices of study location

Name of village	SSP	SAR	MH	KR	PI	RSC	CAI 1	CAI 2
Alahapur	44.996	4.350	47.489	0.877	55.417	-6.88	0.557	1.837
Firozpur	38.769	4.656	86.586	0.679	46.012	-15.38	0.512	1.671
Prithla	5.695	0.451	82.896	0.063	11.557	-21.83	0.890	3.842
Sikanderpur	26.748	2.802	86.956	0.391	32.711	-20.68	0.682	2.743
Asawati	33.248	2.821	79.734	0.514	41.809	-9.65	0.676	1.813
Allika	12.670	1.411	88.560	0.145	18.396	-35.56	0.944	8.849
Rehrana	19.643	2.017	50.341	0.322	33.640	-12.13	0.624	1.845
Joharkhera	25.935	2.775	79.298	0.358	32.512	-22.15	0.812	4.579
Kishorpur	25.687	1.304	56.220	0.349	40.168	-1.66	0.700	0.942
Tatarpur	7.315	1.172	79.687	0.079	9.650	-98.01	0.912	8.196
Harfali	31.309	2.812	77.846	0.459	39.243	-12.33	0.498	0.985

Teharki	36.686	3.165	85.365	0.590	45.216	-9.55	0.417	0.971
Badha	21.733	2.202	88.330	0.280	26.287	-25.85	0.6576	2.209
NagliPanchagi	15.344	1.704	90.258	0.183	19.172	-37.51	0.818	4.584
Chandpur	73.844	16.998	78.201	3.267	79.758	-7.63	-2.545	-3.933
Jaindapur	69.869	12.739	54.964	2.399	74.071	-9.6	0.012	0.062
Patli Kalan	14.447	1.784	93.256	0.170	17.552	-50.76	0.826	7.101
Patli Khurd	9.450	1.550	90.051	0.104	10.460	-106.16	0.8648	13.247
Rakhota	12.438	1.268	88.734	0.146	18.245	-28.68	0.800	2.445
Naya Gaon	35.126	1.599	21.126	0.600	59.772	-1.45	0.274	0.210
Megpur	30.401	3.007	88.565	0.450	37.755	-16.1	0.599	1.750
Jatola	11.119	1.174	87.581	0.125	15.846	-37.28	0.871	4.321
Meerapur	11.880	1.121	88.072	0.137	18.338	-25.71	0.878	3.954
Gadpuri	46.726	3.672	82.089	0.928	62.838	-1.016	0.38	0.539
Sehrala	47.524	4.629	75.675	1.076	62.381	-3.65	0.08	0.146

5.6Summary

The groundwater of Palwal district, Haryana varied from marginally saline to very saline in nature. Categorizing on EC basis for groundwater, 64% of groundwater samples came under doubtful to the unsuitable category of irrigation. On the basis of other irrigation indices SSP, SAR, RSC allwater samples were fit for irrigating. The Wilcox diagrams indicated that 40% of the water samples were in excellent category, 36% in good category, 8% in permissible, 12% in doubtful and 4% groundwater samples were unsuitable for irrigating crops. Classifying on MH basis, 88% of collected GW samples were not fit for irrigation while based on PI , 36% of groundwater samples were found unfit for irrigating. Demarcating onKellyRatio,88% ofwater samples collected were seen as suitable for irrigation.

5.6

ASSESSMENT OF HYDROGEOCHEMICAL FACIES OF PALWAL DISTRICT

5.6.1 Introduction

Groundwater is an important natural resource necessary for conducting various domestic, industrial and agricultural activities. As an important raw material, none of the domestic and commercial activity can run without water supply. Due to increased population growth, rapid industrialization, growing urbanization and modern agriculture which involves extensive use of fertilizers and pesticides, improved living standards and hygiene and massive construction activities the demand for groundwater has rapidly increased.

Studying the quality of groundwater for its designated use is a matter of immediate concern thus detailed and exhaustive studies related with water quality and its suitability for various uses require special attention.

Understanding the aquifer properties and studying the hydrogeochemical characteristics of groundwater is essential for long term management plans in any particular area. Cations and anions present in groundwater can reveal the groundwater quality for its various intended uses-agricultural, industrial and utilization for drinking purposes. Hydrogeochemical facies determination is used to represent the groundwater chemical composition, chemical aspects which operate in the lithologic framework and also show the pattern of groundwater flow due to groundwater and rocks interaction. Hydrogeochemical facies is influenced by precipitation quality, geochemistry of aquifers containing groundwater, infiltration of contaminants in the soil and geological processes involved in aquifers thus understanding of the hydrogeochemical characteristics of the groundwater not only help us to protect this valuable resource but also helps us to understand the changes which occur in the groundwater. Hydrogeochemical facies of an area can be explainedrepresentingvarying concentrations of positive&negativeionson a graphical representation.

Hydrogeochemical facies of the study area were understood by plotting Piper diagrams, Gibbs diagrams, Durov diagrams and Ternary diagrams. Aquachem Scientific Software Version 3.7 was used to plot Piper, Gibbs and Durov diagrams. Ternary diagrams were drawn by using triplot -a Microsoft excel spreadsheet.

5.6.2 Piper Diagrams

Piper diagrams are graphical representations proposed by Arthur M. Piper in 1994, used for understanding the dissolved constituents of various salts present in water. For plotting these graphs, both cations and anions are represented on separate triangles and there is a diamond which reflects both the cations and anions.

Calcium, Magnesium (alkaline earth metals), sodium (alkali) are the most commonly found cations whereas sulphate, chloride, bicarbonate are the most common anions in these diagrams. For these graphs, calcium, magnesium, potassium, and sodium are present at the apex of cations while anion plots are represented by chloride, carbonate, bicarbonate and sulphate. The two plots are summarized to form a diamond. Cations are found at the left side of the triangle while anions are found at the right side of the triangle. For the cation side,base of the triangle is formed of calcium, magnesium is present on the left side whereas sodium and potassium are found on the right side of the triangle. In the anion apex of the triangle, the base of the triangle has chlorides, carbonate and bicarbonate on the left side while sulphates are present on the right side of the triangle.

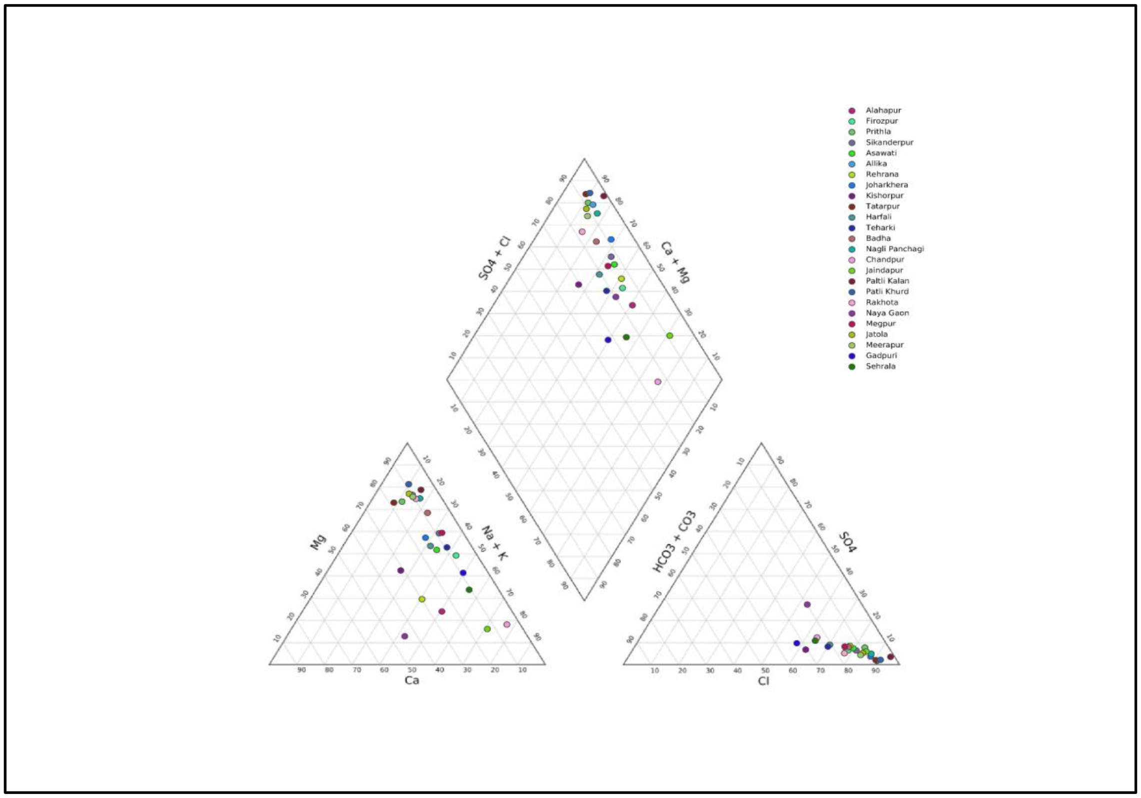


Fig 5:6:1 Piper diagram representation of the studied district inPre-monsoon Season.

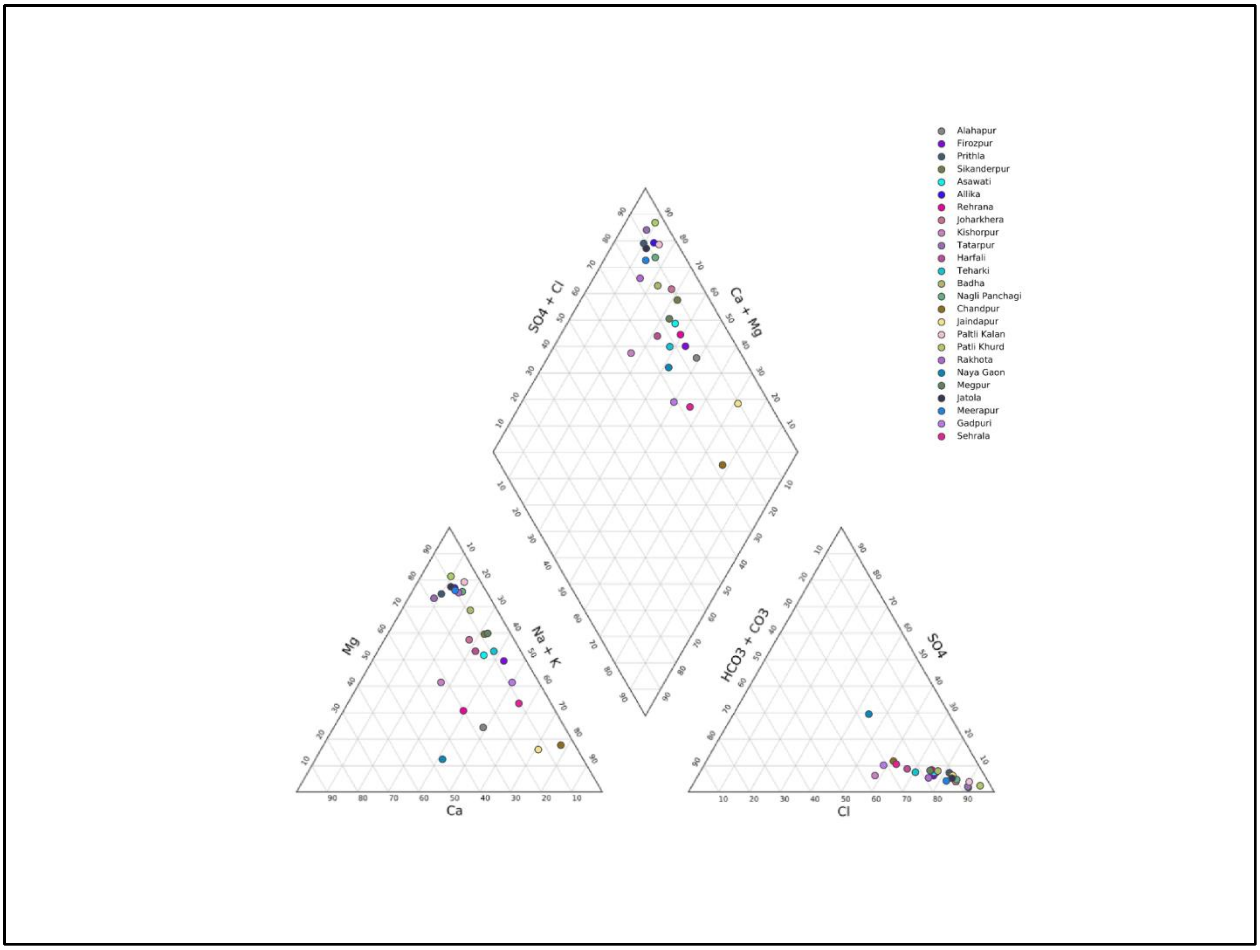


Fig 5:6:2 Piper diagram representation of the studied district inPost-monsoon Season.

Piper diagrams were drawn to study the hydrogeochemical estimation of the study area. For drawing Piper diagrams, collected and analyzed data was plotted on a diamond-shaped trilinear figure. The piper plot of studied location revealed majoritycations were represented by Mg2+(64%) then no dominant type (20%) followed by Na+ and K+ (16%) while all anions were dominantly exhibited by chloride. The results coming from the current work resonated with data on Physico-chemical analysis of groundwater in pan- India (Ravi Kumar et al., 2015) that alkaline earth metals are the abundant cations present in groundwaterwhich is an indication of anthropogenic pollution.

5.6.3Gibbs Diagram

J.R. Gibbs in 1970 had published ‘Mechanisms controlling world water chemistry’ and this article has caught such a high popularity that it has been cited more than 720 times in various web of science journals (Marandi et al., 2018). Gibbs diagrams are a representation of important processes affecting surface water chemistry. Gibbs diagrams are used to show the relationship between lithological characteristics and dissolved salts of various constituents present in water. Precipitation, rock weathering and evaporation are the three major distinct fields shown in Gibbs' diagram. It is a method for finding the groundwater ion's origin by finding the correlation between TDS and cation (Na+ and Ca2+) concentration and anion (Cl- and HCO3-) concentration.

Gibbs Diagram was drawn on the scatter plot by plotting TDS against sodium / (sodium+ calcium) ions on the X-axis and chloride / (chloride + bicarbonate) ions on the Y-axis and a boomerang shaped pattern was formed in the figure. Gibbs diagrams having the boomerang shape have been used in understanding groundwater hydrochemistry. By plotting TDS against both the cation and anion, the results can improve the understanding of various hydrogeochemical processes involved in groundwater. For anions, groundwater chemistry changes to chloride from bicarbonate ions with increasing salinity while in cations calcium ions are replaced by sodium ions.

In groundwater chemistry, a series of evolution begins from bicarbonate as mostly soil and aquifers are formed of carbonate (calcite). Change of groundwater chemistry from groundwater having low TDS and (Na+ Cl-) water type to (Ca2+ HCO3-) water type is rapid and quick progression. Fresh groundwater is generally seen in the middle part of the aquifer which is reflected as water- rock interaction.

Groundwater positioning, whether on the left or right sides of the Gibbs diagram, is dependent on both properties of the aquifer and soil. Silicate dominance will show a higher sodium/ (sodium+ calcium) ratio whereas carbonate dominance will have lower sodium / (sodium + calcium) ratio. Major portion of groundwater samples in investigated region lie evaporation dominance indicating high saline nature of soil.

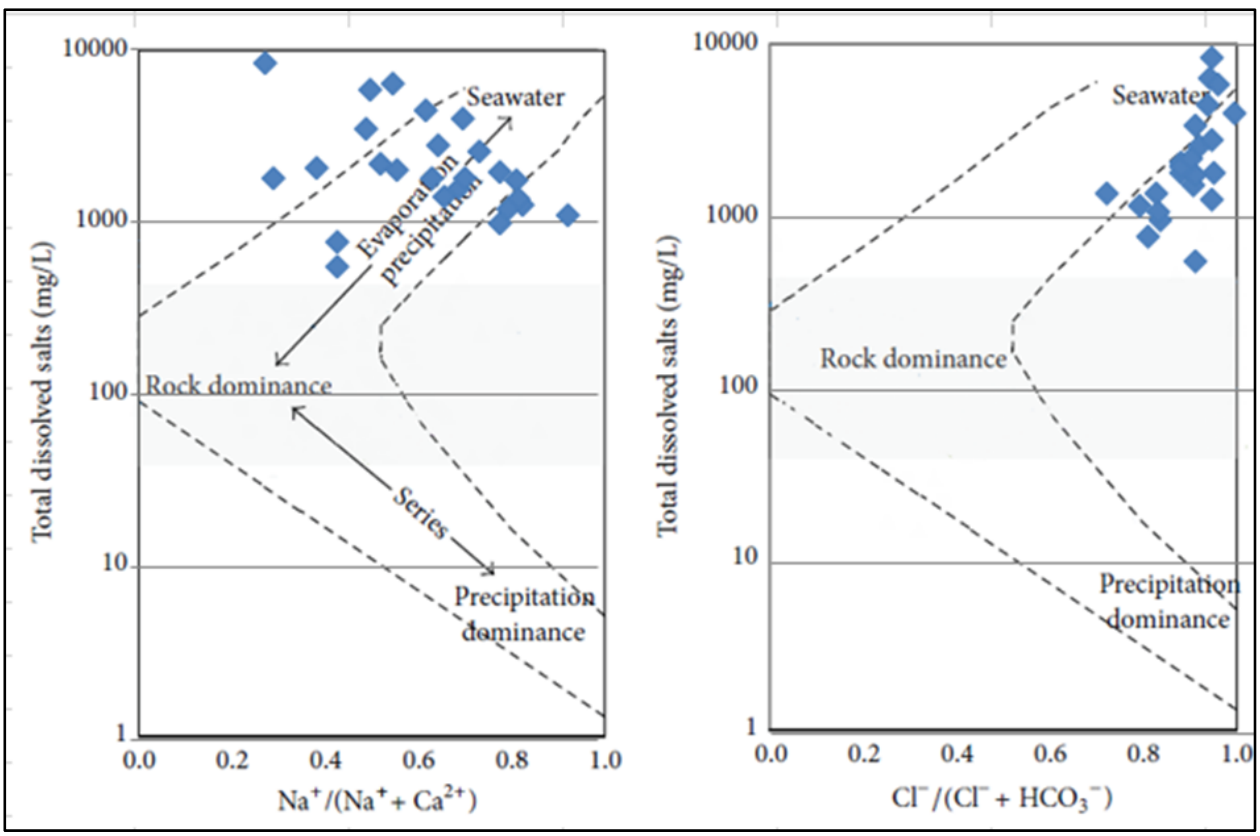


Fig5.6.3Gibbs Diagram representation before monsoon season of Palwal District

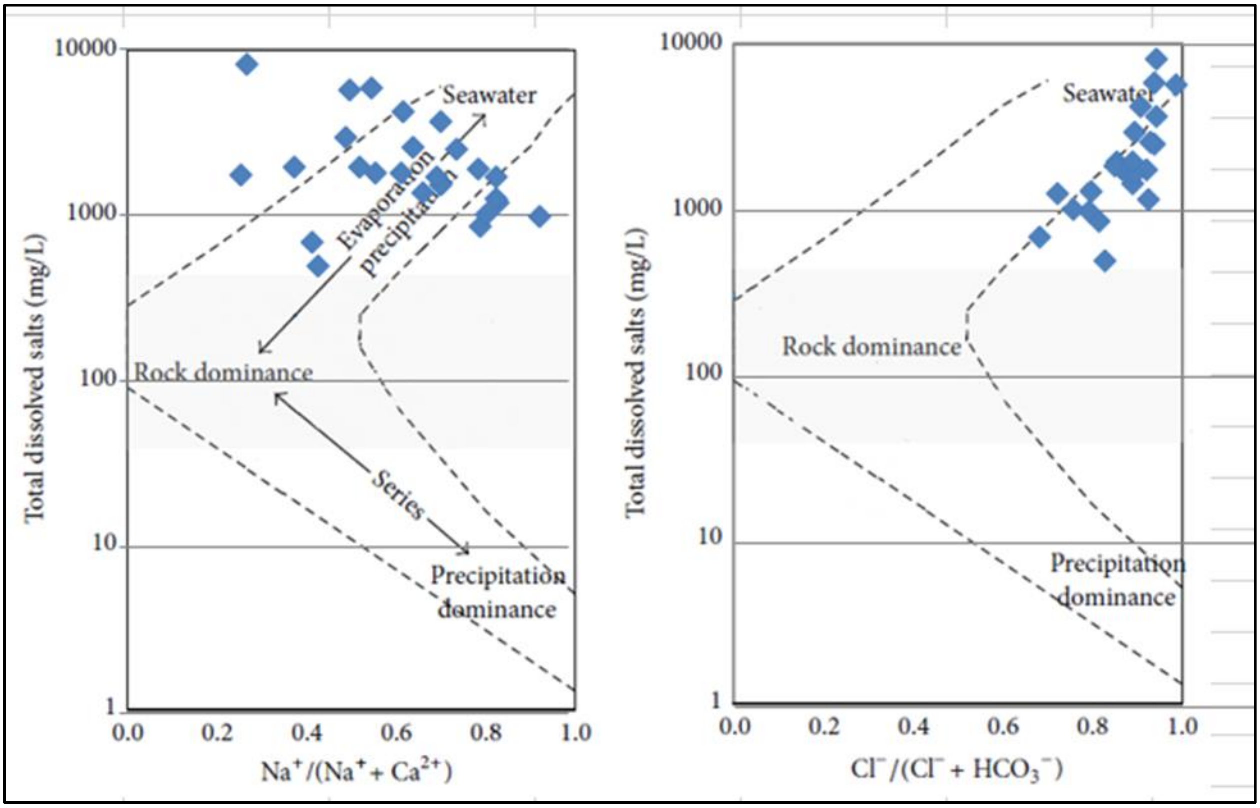


Fig5.6.4Gibbs Diagram representation after monsoon season of Palwal District.

5:6:4 Durov Diagrams

Durov diagrams are widely drawn to show the dissolved ions present in water and depict hydrogeochemical processes occurring in a particular area. Durov Diagram (Durov, 1948) which is similar to piper diagrams is an important tool to understand hydrogeochemical structure and studying the water samples chemistry. The Durov diagram represents the ions as both cations and anions are expressed as milliequivalent percentages in two trilinear graphs. In these diagrams, two triangular graphs one for cation and other for anion are drawn perpendicular to each other.Durov diagrams are used to directly compare pH and TDS or electrical conductivity which are the groundwater parameters (Al-Bassam et al., 2012).

For plotting a Durov diagram, the sum of all ions- cationic data points and anionic data points should be equal to 100%. Major cations Na+ K, Mg and Ca are drawn in the left triangle. Anions generally Cl, HCO3, So4 are drawn on the upper triangle. In an expanded Durov diagram pH is drawn at the bottom and TDS is represented on the right side of the plot.

From the Durov diagrams it is clear that Tatarpur has highest amount of TDS in both premonsoon and postmonsoon seasons. Similarly, Naya Gaon is most alkaline across both seasons. The cation and anion distribution for all studied villages remains consistent for both premonsoon and postmonsoon seasons.

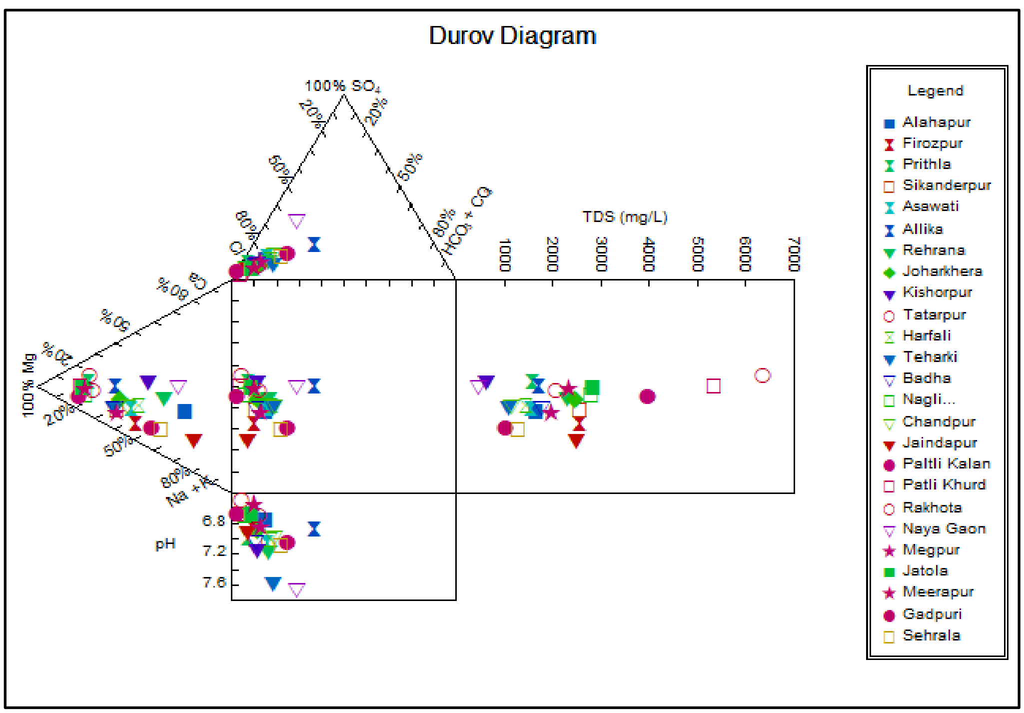


Fig 5:6:5 Durov Diagram representation in the Pre-Monsoon Season of Palwal District

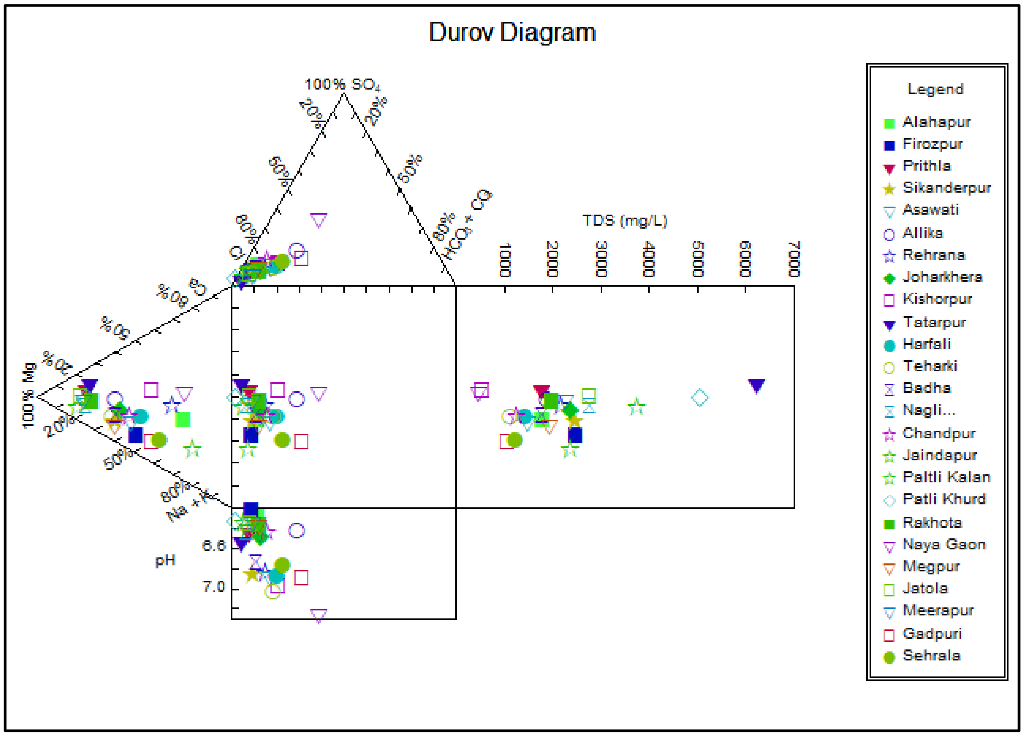


Fig 5:6:6 Durov Diagram representation in the Post-Monsoon Season of Palwal District

5.6.5 Ternary Diagrams

Ternary diagrams also called ternary graphs, ternary plots are triangular diagrams with barycentric coordinates present in three variables where the edges of the triangle are called axes and that sums to a constant. Ternary graphs are commonly used in physical chemistry and other physical sciences to showcase the composition of species, rocks and minerals forming a particular system.

In ternary graph value of three variables should sum to a constant K generally shown as 1 or 100 % and the two variables must be known to locate the third variable on the graph. Ternary plot can be suitably used for showing the chemical composition of rocks, soil and can be easily plotted on a two-dimensional graph. For drawing a ternary diagram,

- 1 or 100% point should be located on the axis
- By drawing a line parallel to the base, which is opposite to 100% point.
- Parallel lines should be followed till the axis which is the component value.
- Remaining axes should be drawn using similar steps.

The ternary diagrams show the same picture as the Durov diagrams for cation distribution. Paltli Kalan has highest Sodium distribution (~80%), Prithla has highest Magnesium percentage (~80%) and Naya Gaon has the highest percentage of Calcium(~60%).

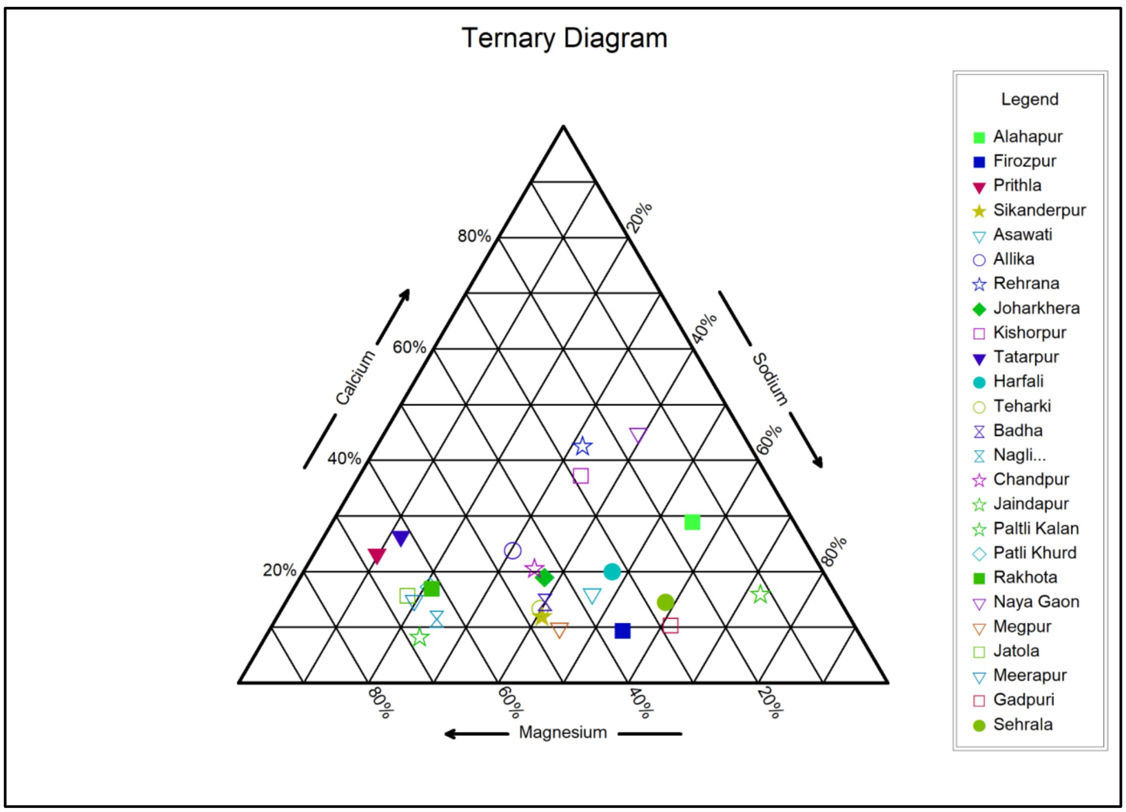


Fig 5:6:7 Ternary Diagram representation in the Premonsoon Season of Palwal District

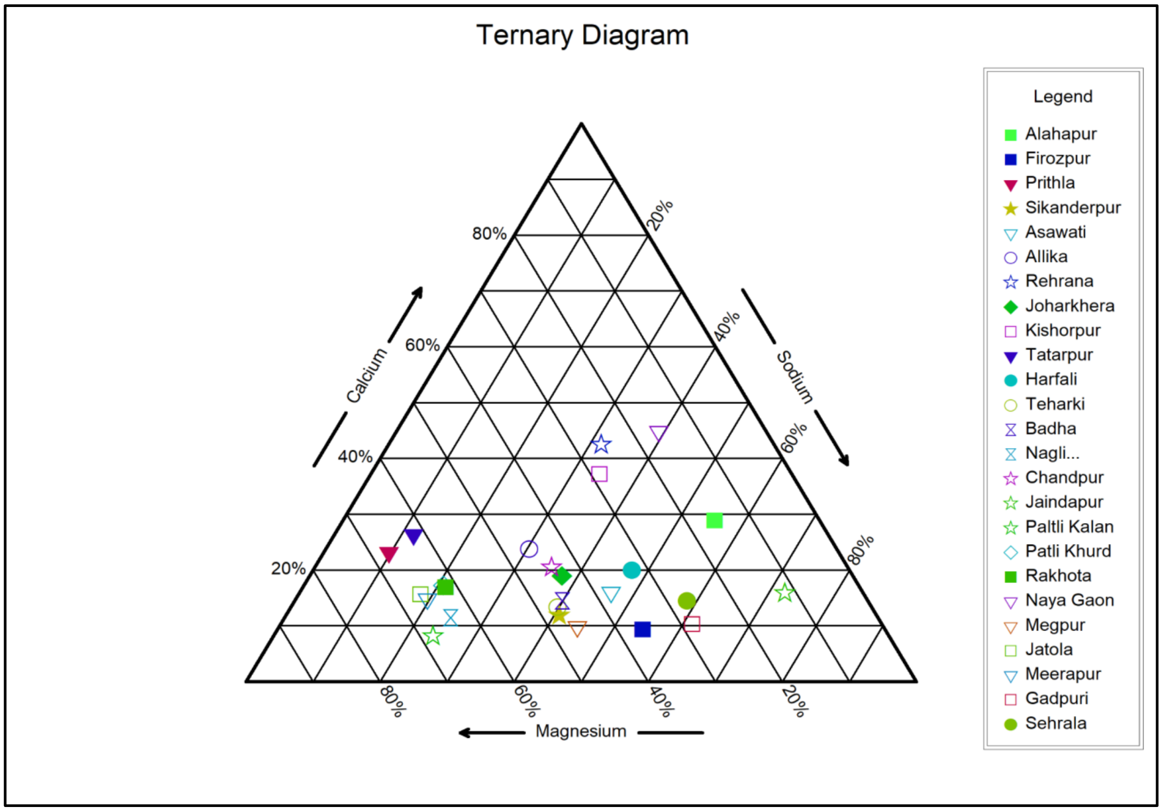


Fig 5:6:8 Ternary Diagram representation in the Premonsoon Season of Palwal District

Chapter-6

TERNARY BIONANOCOMPOSITES OF NLP/ZnO@L-CYSTEINE GRAFTED-PANI FOR MO & BG REMOVAL

6.1 Introduction

Exponential growth of population has led to rapid industrialization which has played a crucial role in proliferation of water pollution. Wastewater discharged from dye, food, textile and paper industry is a major source of dissemination of effluents in water bodies. Dyes though used in small amounts are highly observable. Around the world, nearly 700,000 tonnes of organic dyes are used in the textile industry (Tripathy et al., 2020). These effluents when released in water contain a large amount of synthetic and organic dyes which are toxic to aquatic and human life at even very low concentrations and can result in skin rashes, dysfunction of kidney and liver, neurological issues, potential mutagenic and carcinogenic effects (R. Ahmad & Ansari, 2020; R. Ahmad & Kumar, 2010; Iqbal et al., 2022). Most of the dyes released in water as effluents are non-biodegradable and quite stable (Lellis et al., 2019). Dyes released also affect the photosynthetic capability of aquatic plants by limiting the sunlight penetration in the water body (Dutta et al., 2021). In coming years as the population will continue to grow exponentially this will put a greater stress on meeting the demand of getting clean water. Ill-effects of dyes on mankind and environment have forced scientists and researchers around the world to focus their attention on dye removal from aqueous solution.

In the past few decades several processes like coagulation(Lapointe et al., 2020; Peydayesh et al., 2021), ion-exchange(Dominguez-Ramos et al., 2014), reverse-osmosis(Kaufman et al., 2010; Malaeb & Ayoub, 2011), membrane separation process("Facile Hydrophilic Chitosan and Graphene Oxide Modified Sustainable Non-Woven Fabric Composite Sieve Membranes (NWF@Cs/Gx): Antifouling, Protein Rejection, and Oil-Water Emulsion Separation Studies," 2022), flocculation (Zolezzi et al., 2018), photocatalysis (S. Ahmad et al., 2020; Danish & Muneer, 2021a, 2021b; Silvestri et al., 2019; Tanweer & Alam, 2022) methods have been used to purify water but each method has its own limitations. Purification involving reverse-osmosis is very costly and recovery of membranes need special treatment(Malaeb & Ayoub, 2011). Coagulation and flocculation work on limited capacity and produce a large amount of sludge. Among the above methods, biosorption is gaining popularity as an efficient method to treatwastewater because of high efficiency, less cost regeneration, recovery as adsorbate, no sludge formation and availability of different materials which can be used as adsorbents (R. Ahmad & Ansari, 2021a, 2021b; R. Ahmad & Kumar, 2010; Iqbal et al., 2022; Nasar & Mashkoor, 2019; Tanweer et al., 2022).

Unmodified agricultural waste materials such as vegetables peels (Asuquo & Martin, 2016), fruits peels (Aichour et al., 2019; Samet & Valiyaveettil, 2018), sago waste (Jeyanthi & Shanthi, 2007; Maheswari et al., 2008), rice husk (Lakshmi et al., 2009) and other plant waste (S. Ali et al., 2020; Bhattacharyya & Sharma, 2004; Sarma et al., 2008) have been directly employed as biosorbents for water purification. But unmodified agricultural waste materials show less adsorption capacity towards water pollutants. So, chemical modification is needed to enhance their maximum adsorption potential by increasing specific surface area, a greater number of active sites and functional groups of biosorbents. The seeds and leaves of Neem tree (*Azadirachta indica*) have enormous medicinal value and have been in use since ancient times to cure human ailments in Indian sub-continent (Bhattacharyya & Sharma, 2004). Unfortunately, neem seeds and leaves become waste after shedding during the summer months in India. Therefore, a simple idea has been exploited to chemically modify these leaves (in the form of powder) to obtain a bio-nanocomposite with enhanced adsorption capacity as compared with bare neem leaves powder. This approach may reduce the plant-waste materials from the environment and may also be efficiently used to sequestrate the water pollutants.

Several methods can be used for nanoparticle synthesis but many of these are inefficient in energy and material consumption. In chemical synthesis of nanoparticles, stabilizers (which are chemical reducing agents) are used to prevent accumulation and control growth of particles(Rashtbari et al., 2020). Thus, emphasis nowadays is being paid for the synthesis of nanoparticles which are environment friendly or using biologically prepared nanoparticles which involve the use of various parts of plants or their products which act as biosorbents (Bhattacharjee et al., 2020; Das et al., 2017).Among various nanoparticles, zinc oxide nanoparticles (ZnO NPs), a class of multifunctional inorganic nanoparticles considered ideal for having many distinct features. In addition, chemically synthesized ZnO NP do not show toxic effects on humans when exposed in small concentrations although high doses can show lethal effects (Rashtbari et al., 2020).

Polyaniline (Pani) is a conducting polymer, has been used in a variety of applications, including electrodes of lightweight battery, energy storage, sensors, electromagnetic shielding devices, and anticorrosion coatings(He., 2021; Yun., 2019). The nature of simple synthesis, stability, easy doping and suitable conductive surfacesofPanimakeitsalways an excellent choice as adsorbent for the adsorption of several dyes such as methyl orange, brilliant green, Congo red, amido black 10B, malachite green and eosin yellow from aqueous solutions (R. Ahmad & Kumar, 2010; Nasar & Mashkoor, 2019).

Researchers are focusing on nanoparticle use for treatment of water due to their efficiency in adsorption and potent catalytic activity.But due to the small size of nanoparticles, there is a problem in recovery of nanoparticles from treated water.Therefore, nanoparticle impregnation on a support to form a composite adsorbent is also gaining popularity due to easy recovery of composite adsorbent. These composite adsorbents also show a better efficiency due to presence of various active sites for adsorbate uptake (Akpomie & Conradie, 2020).

This novel study reports the synthesis of NZC-g-Pani nanocomposite and its usefor adsorption of MO and BG dye. Both these dyes arefrequent contaminants, deteriorating the environment, buthave received less research than dyes like methylene blue. Additionally, isotherm, kinetics and thermodynamics for the biosorption of MO and BG dyes by NZC-g-Pani nanocomposite were also evaluated.

6.1.2 Relevance of Current study to Palwal District

Palwal is a small district but developing progressively. Palwal is also known as ‘Cotton Town of India’. Number of cotton factories and industries are located in Palwal and a large number of local residents are employed in this sector to process cotton and cotton-based products. In most of the houses of study location, at least one member is engaged in cotton-based industries. These cotton products are sent throughout India to meet multiple utility purposes. Bansal Cotton mills, S.G. Industries dyeing mills, Shahi Dyeing

Pvt Ltd., J.B.D textiles & Sulphur dyeing services are few of the major cotton textiles mills in the study location.

Palwal dyeing and bleaching units though add colour to apparel but discharge harmful chemical effluents and dyes which have degraded the quality of surface as well as groundwater. All cotton textiles before getting dyed have to be first bleached which enhances the toxic dyeing load. These harmful effluents from bleaching and dyeing process contain many toxic dyes and salts which have seeped into groundwater thus increasing the extent of groundwater pollution.

6.2 Dyes: A threat to environment

Water is a vital resource necessary for existence of living organisms. Rapid industrialization, growing urbanization and ever-increasing population are the major reasons responsible for generating wastes into aquatic systems.

Among the above sources, the textile industry is the largest consumer and emitter of dyes. After China, India stands as the largest producer of textiles (Devaraja., 2011) in the world, 3.5 million people are earning their livelihood through the textile sector and 4% of the country's GDP is contributed through the textile industry.

Dyes used in textiles are mostly synthetic, organic compounds which are mainly used as colourants. More than 10,000 dyes are used in various industries with a world-wide production of nearly 7×10^5 tones. Various dyeing and finishing operations are responsible for loss of 200,000 tonnesof dyes annually as effluents (Chequer et al., 2013). Textile industry is responsible for consuming a large amount of water mainly during the dyeing process. Wastewater generated from dyeing units are classified among the most polluting in all industrial sectors due to large volume and as well as composition of effluents. Dyes are used in very small amounts (sometimes even less than 1 mg/l) but are highly visible, can affect the aesthetic value of the water body and hamper the transparency of aquatic ecosystems which decreases the penetration of light hence photosynthesis. Many dyes are toxic and show mutagenic effects (Lellis et al., 2013) limiting the use of water for drinking and irrigation.

Among the organic dye production, azo dyes are used in most commercial operations due to their cost effectiveness, ease of production, structural diversity and high fastness property of adhering to the substrate. Azo dyes are used extensively in textiles, cosmetics, paper, leather, paint and pharmaceutical sector but many of these azo dyes can show mutagenic effects and are carcinogenic (Chung., 2016).

Dye effluents when infilter inside the aquifers can pollute the groundwater reserves and increase the heavy metal toxicity. Dyes can alter the chemical structure and new xenobiotic compounds which are formed may show more or less toxicity than the original dye. Dyes can cause irritation in skin and eyes, respiratory trouble, allergic reactions, hemorrhage, skin ulcers, nausea and may also damage the kidneysand CNS. Long term exposure to dyes may cause cancer and is an issue of serious health concern (Lima et al., 2007)

6.3Adsorption

Adsorption technique is a process of mass transfer in which a substance from liquid phase is transferred to the solid surface and becomes attached by physical force and chemical interactions (Rasheed., 2013). The absorption process being simpler in its design, low initial cost and flexible in working is considered superior from already discussed methods. Materials providing the surface on which adsorption can occur is called adsorbent and the substance which attaches/adsorbs is called adsorbate. Depending upon the forces which hold the adsorbate to solid surface adsorption is of two kinds:

- Physisorption: Vanderwall forces are responsible for attaching the adsorbate to adsorbent which show a low rate of adsorption.
- Chemisorption: Chemical bonds are seen between adsorbate and adsorbent thus adsorption rate is higher.

6.4Preparation of NLP

Fresh Neem leaves were collected from the garden of Jamia Milia Islamia, New Delhi, India; which were washed several timesto remove dust and other soluble impurities. These washed leaves were first dried at room temperature followed by air dry in oven at 27 ± 3 °C for 2 days till the leaves became crisp. Dried leaves were then mechanically crushed ina fine powder by using mechanical grinder to procure the Neem leaf powder (NLP). The NLP sieved by sieve tray (BSS 72/ASTM70) and the 200 μ fraction was separated followed by further washing with DDW till the washing becomes clear. At last, washed NLP were air dried in oven at 27 ± 3 °C and stored in a pre-cleaned glass and kept in desiccator to avoid from environmental moisture.

6.4.1Preparation of ZnO nanoparticles

ZnO nanoparticles were prepared as reported in (Parangusan et al., 2021). Firstly, 2 g zinc acetate was dissolved in 70 ml DDW by using magnetic stirrer for an hour to get a clear solution. 0.1 % (w/v) polyethylene glycol which acted as a surfactant and 10 ml monoethanolamine was slowly poured to the solution, was stirred for another 30 minutes until the solution became clear. The content was then transferred to the Teflon capped autoclave for 3 hours at 140° C. The resultant was washed with DDW and ethanol by centrifugation and was dried at 80°C inoven for 12 hours followed by calcination in a muffle furnace for 2 hours at 400°C.

6.4.2Preparation of NZC-g-Pani nanocomposites

ZnO and NLP of a weight ratio of 1:2 (w/w/) were dispersed in 100 ml of 1 M HCl in a 250 ml beaker and was magnetically stirred for 30 min. 0.6 g L-cysteine was added ultrasonically for 1 hour to it. 1mlof aniline monomer was put to above mixture. 50ml1M HCl and 0.023 mole ammonium persulphate (APS) was added dropwise and stirred for another 12 hours. The resultant obtained after washing with DDW, methanol and acetone several times. Then filtered material was transferred in an air oven to get dry for overnight at 80°C to obtain a ternary bio-composite*i.e.*,NZC-g-Pani which was used as a biosorbent for removal of various cationic as well as anionic dyes.

6.5Characterization of NZC-g-Pani nanocomposites

The FTIR spectra of the bare NLP, bare ZnO, and NZC-g-Pani nanocomposite (before and after MO and BG dyes adsorption) were investigated in the range of 400-4000 cm^{-1}using a Perkin Elmer (Nicolet 6700, Thermo Fisher, USA).(HRFESEM) was used for recording the microstructure oftheNZC-g-Pani nanocomposite (before and after dyes adsorption) employing a Zeiss NOVA NANOSEM-450 field emissionSEM.Raman spectra of the samples was done at room temperature by aVia Reflex RamanMicroscope (Renishaw, United Kingdom) with the samples deposited on theglass slides. (XRD) measurements were performed onRigaku D/max-RA X-ray diffractometer.

6.5.1Point of zero charge

Solid addition method (Arfi et al., 2017; Chigondo et al., 2019)was used to measure the zero point charge of the adsorbent. 0.01 M of KNO_3 solution was prepared and 50 ml of prepared aqueous solution was transferred to a beaker of 100 ml capacity. 10 such beakers were prepared, and 0.15 g of NZC-g-Paninanocompositeadsorbent was added in each flask. pH of the solution wasshuffledbetween 1-10 by adding either0.1 N HCl/NaOH and the beakers were covered and stirred in intermittent duration for 24 hours. The resultant pH was noted. Difference in the initial and final pH values was calculated. InitialpH was plotted againstΔpH and the intersection point of the obtained curve was taken as pHzpc.

6.6Characterization

6.6.1 Fourier transform infra-red spectroscopy

Fig 6.1showsFTIR spectra of zincoxidenanoparticles, NZC-g-Pani and NZ-Pani (without L-Cysteine functionalized) nanocomposite. In the Fig 6.1 (a) located bandsat 3435,1542 cm^{-1} related with hydroxyl group vibrationofZnO nanoparticles (Maruthupandy et al., 2020). Furthermore,absorption peak observedat a wavenumber of 3468 and 1565 cm^{-1} also confirmZnOnanoparticles formation(Anand et al., 2015a).Plane CH bending vibrations, ZnO,NZC-g-Paniand NZ-Pani (without L-Cysteine functionalized) nanocomposite revealed a strong characteristic band about 830 cm^{-1}, which indicates para coupling,happens at 1–4 place (Anand et al., 2015b). Hence, it confirms the adherence of ZnO nanoparticles over polymer matrix. In composite (NZC-g-Pani), peak at 3440 cm^{-1} associated with O–H stretching which confirms the presence of L-cysteine(Razzaq et al., 2021). In Fig 6.1(c) short band at 674 cm^{-1} represents C–S linkage of the CysteinetoPani of NZC-g-Pani(Yslas et al., 2015). While in Fig 6.1 (b) this band found absent in the case of unmodified nanocomposite *i.e.*, NZ-Pani (without L-Cysteine). The various bands of Pani emerged at 852, 1173.2, 1280, 1381, and1680 cm^{-1}attributed to NH and CH stretching vibrations, benzenoid ring, and NH_2 bending modes. In addition to the above peaks, the spectrum of the Paniexhibitspeaks at 684 and 1581 cm^{-1} are related to NH_2 wagging and the presence of imine functional group (Ibrahim, 2017).

FTIR spectra of NLP is also found in NZC-g-Pani and NZ-Pani (without L-Cysteine functionalized) nanocomposite in Fig 6.1 (b) and 6.1(c). The bands at 1037, 1250 cm^{-1} can be due to O-H stretching while bands at 2857, and 2924 cm^{-1} owing to the C-H

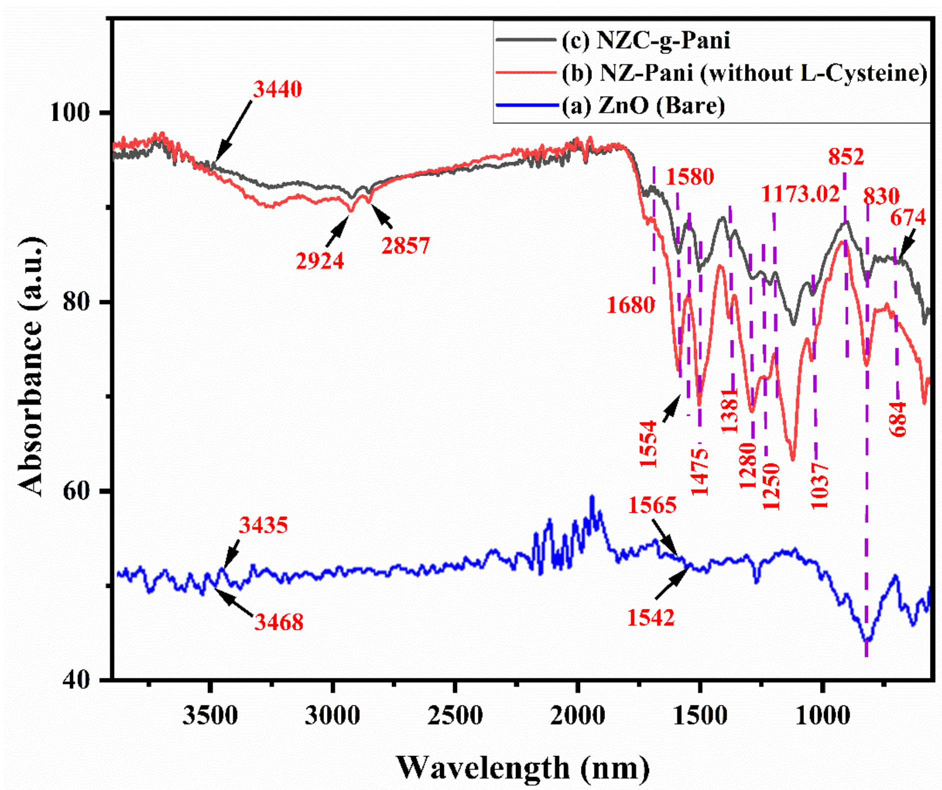


Fig 6.1 FTIR structure of Nanocomposite

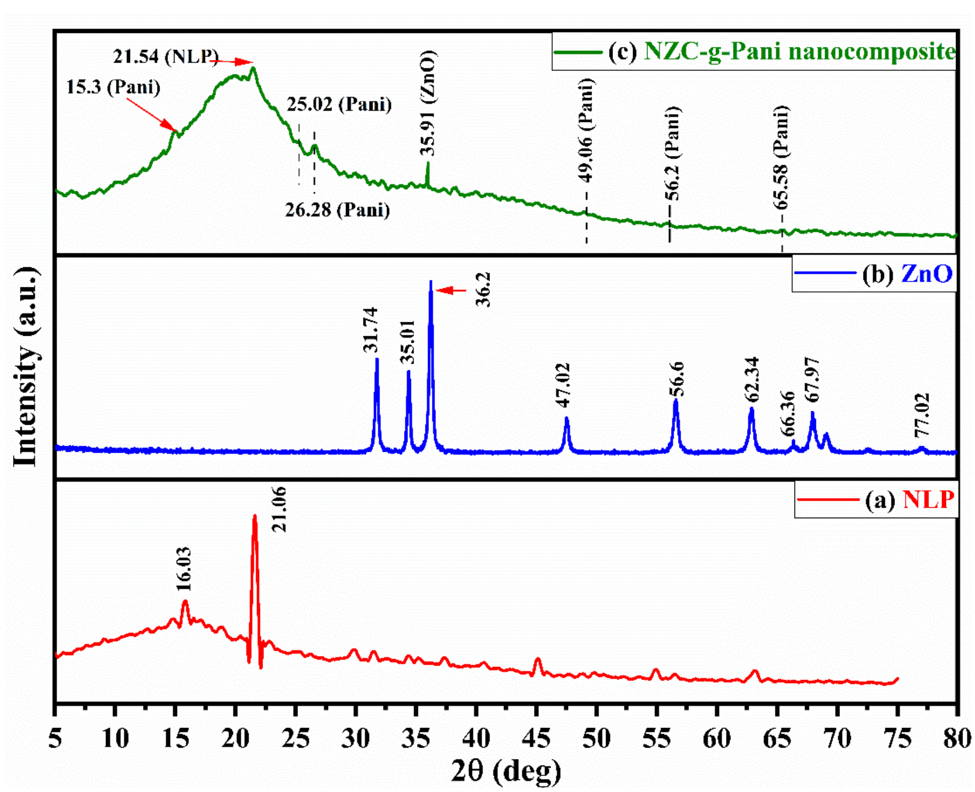
stretching of methylene groups on the NLP surface and chelates H-bridges (Alam et al., 2010).

6.6.2 High resolution X-ray diffractometer

XRD analysis of ZnOnanopartilcesFig 6.2 (b) shows high and sharp peaks with 2θ values at 31.74º, 35.01º, 36.2º, 47.02º, 56.6º, 62.34º, 66.36º, 67.97º and 77.02º which confirmed to wurtzite (hexagonal) structure of ZnO(Maruthupandy et al., 2020). The peaks of ZnOnanoparticles seen in the XRD pattern perfectly matched the JCPDS Card No: 36-1451(Chen et al., 2011) hence ZnO was successfully synthesised. Fig6.2 (a) shows the XRD pattern of NLP in which weak peaks at 16.03º, 21.026º ascribed due to presence of cellulose in NLP. The XRD pattern of NLP was characteristically amorphous in nature due to the presence of hemicellulose and lignin in the biomass(S. Ali et al., 2020).

Thediffraction peaks at2θ values31.74º, 35.01º, 36.2º, 47.02º and 56.6º correspond to planes of ZnOnanoparticles further assuredthat nanoparticles of ZnO have embedded in the matrix of Pani(Anand et al., 2015b).

Further, the XRD pattern of NZC-g-Paninanocompositefrom Fig 6.2 (c) showed



thatZnOnanoparticles and NLP got successfully incorporated inPani matrix, as visible fromFTIR spectra. The characteristics peaksPANIin amorphous state shows weak reflections at 2θ values of 49.06º, 56.2º and 65.58º, thereby confirming the report of Anand *et al*. (Anand et al., 2015b). Peaks of 2θ values at 15.3º, 25.02º and 26.28º

Fig 6.2 XRD structure of Nanocomposite

are the characteristics peaks of Pani(Patil et al., 2015). Overall, the as prepared bio nanocomposites i.e., NZC-g-Pani seems to be amorphous in nature.

6.6.3 High resolution Raman

The samplewasalso measured by Raman scattering as shown in Fig 6.3 for analyzing chemical knowledge in combining with FTIR.The Raman spectrum of bare NLP, bare ZnO and NZC-g-Pani nanocomposite has been shown in Fig 6.3.It was observed thatRamanspectrum of ZnOnanoparticles Fig 6.3 (a)was found to be in regular Raman manner and the characteristics peaks were observed at 1154 cm^{-1}, 581cm^{-1}, 437 cm^{-1}, 330 cm^{-1} confirming wurtzite structure of ZnO(Šćepanović et al., 2010; Tripathy et al., 2020).

Fig 6.3 (b) represents the Raman spectra of NLP. The spectrum of NLP did not exhibit any broad peak which probably due to existence of carbon as organic material (El-Azazy et al., 2019).

In Fig 6.3 (c), the band at 1239 cm^{-1} and 1168 cm^{-1} are assigned to C-H bending vibrations aromatic rings, C-N stretching of thesecondary aromatic amine of Pani(Ramalingam et al., n.d.; Yin et al., 2017), respectively. The absorption at about 1174 cm^{-1}, 1498 cm^{-1} and 1597 cm^{-1} were came from benzenoid ring (C-H bending), C=N stretchingin emeraldine base (imine), and quinoid ring (C=C stretching) (M. Ben Ali et al., 2019; Huang et al., 2006), respectively. Peak at 1456 cm^{-1} associated with C=N stretching mode ofquinoid units confirming the doped Pani structure. In addition, absorption at 572cm^{-1}, 607cm^{-1}, 417cm^{-1}, 811cm^{-1}, and 530cm^{-1} were associated with the

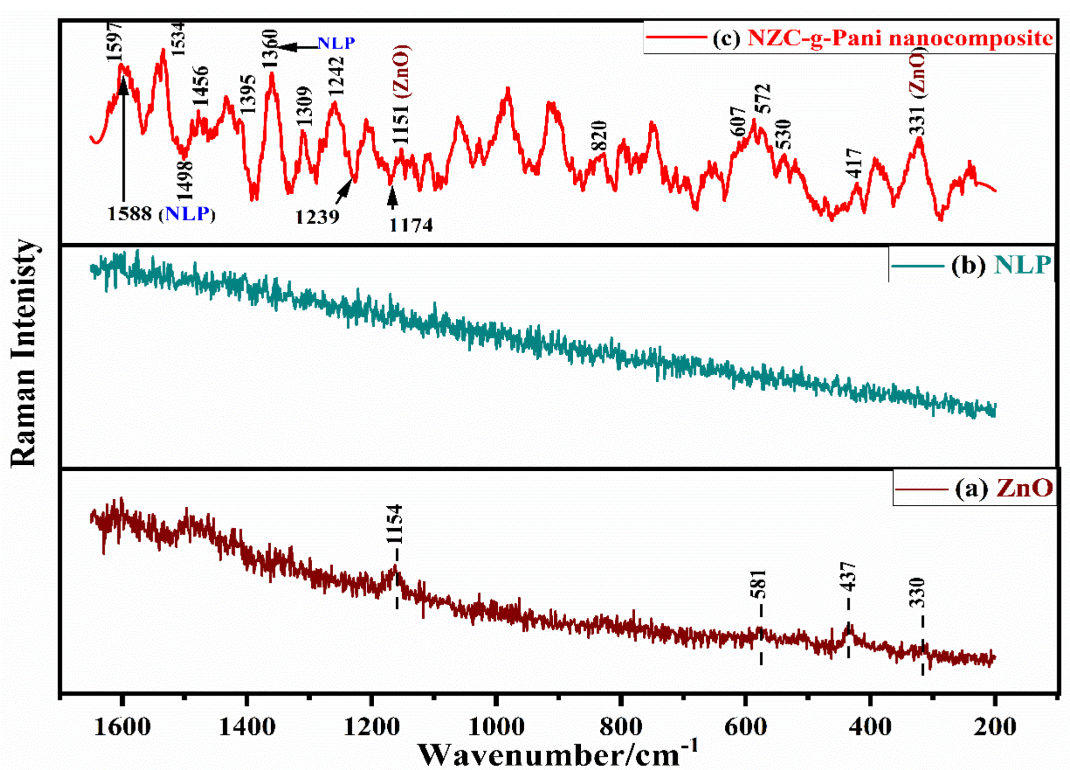


Fig 6.3 Raman spectra of bare ZnO NPs (a), bare NLP (b) and NZC-g-Pani nanocomposites (c).

doped Pani structure (Ran et al., 2012; Zujovic et al., 2010). The Raman data coupled with FTIR provide clear evidence of a large number of imine and amine groups in thePani nanocomposites. Furthermore, peaks 1360 /cmand 1588 /cm are associated with NLP (El-Azazy et al., 2019), as well as peaks 331/cm and 1151 /cm represents ZnO nanoparticles (Maruthupandy et al., 2020; Šćepanović et al., 2010) in Pani based nanocomposites.

6.6.4High resolution scanning electron microscopy

SEM has been used as a vital tool for characterization of adsorbent. Surface morphology of the adsorbent can be known through SEM. It determines the shape, porosity, particle size and pore size distribution of the adsorbent material. Surface morphology of NZC-g-Pani nanocomposite when examined with the help of SEM showed the presence of rough and porous surfaces where targeted BG and MO dyes can be trapped and adsorbed. Number of heterogeneous pores can also be seen in Fig 6.4 (a) but after biosorption significant changes can be easily observed. It is clear in Fig 6.4 (b**)** pores have been packed by dyes and lining of pores has thickened indicating the occurrence of biosorption.

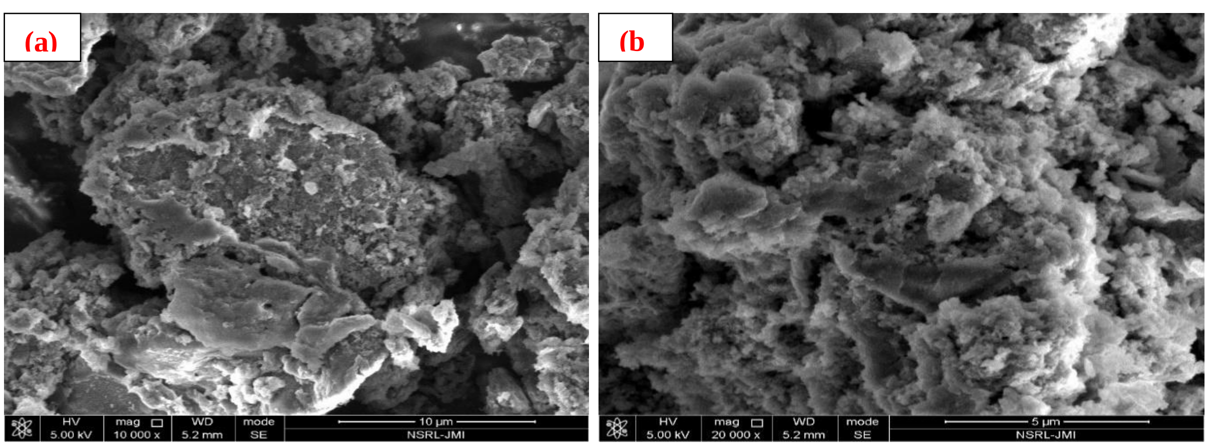


Fig 6.4 SEM of NZC-g-Pani nanocomposite (a) before, and (b) after adsorption of dye

A stockcontaining 1000 mg/L of all selected dyes such as MO, AB 10B, EBT, BG, CV and MB were prepared by dissolving 1 g of each dyein 1litersDDW.The batch adsorption experiments were done by keeping in contact 0.025 gNZC-g-Pani nanocomposites adsorbent with 30mL of 50mg/Lof each dye and shaking on a rotary shaker (250 rpm) under room temperature for one day. The residualamountsofdyein treated watersamples was conducted by measuringabsorbanceofMO, AB 10B, EBT, BG, CV and MB at 464, 630, 489.95, 625, 590, and 665 nm, respectively. The yield of removal efficiency (%)and dyes performance uptake (mg g^{-1}) was calculated by formulas (1)and (2)(R. Ahmad & Ansari, 2022; S. Ali et al., 2020).

$$\% R = \frac{Co - Ce}{Co} \times 100 \quad \mathbf{(1)}$$

$$q_e = \frac{(Co - Ce)}{m} V \quad \mathbf{(2)}$$

6.7.1 Effect of pH

pH plays a relevant parameter in adsorption techniques. Adsorption capacity of adsorbent is influenced both by surface of sorbent and degree of ionization of the functional groups present in adsorbate. In our study, pH effect on NZC-g-Pani nanocomposite was studied with the help of 50 mg/LBG and MO dyes from pH 1 to pH 10 by using 0.1 N HCl/NaOH solution to find out the most optimum pH for BG and MO dyes adsorption which can be seen inFig 6.5 (b).The pH_{zpc} of NZC-g-Pani nanocomposite is about 2.0 as seen inFig 6.5 (a).$pH > pH_{zpc}$, the NZC-g-Pani surface has -vecharge while at $pH < pH_{zpc}$ NZC-g-Pani has a positive charge. The obtained results suggested that there is adecrease in the MOpercentageremoval with increase inpH. Maximum percent removal ~ 100% of MO onto the NZC-g-Pani takes place at pH value 1. While there is an increase in BGpercentageremoval withincrease inpH. This result is in a good deal with theobtained from pH_{zpc}ofNZC-g-Paniresults.At low pH values (pH <2.0) the NZC-g-Pani nanocomposite as a positive surface charge facilitatesstronger interactions with anionic contaminants*i.e.*,MO dye. On contrary, at high pH values (pH >2.0), the NZC-g-Pani nanocomposite as a negative surface charge reveals ahigh affinity towards cationic BG dye (Eltaweil et al., 2021; Martins et al., 2017).

6.7.2 Effect of NZC-g-Pani dose

The effect of NZC-g-Pani dose on BG and MO colour removal % and adsorption capacity of biosorbents was studied. Varying amount of NZC-g-Pani sorbent (0.01g to 0.07g) was added to 50 mg/L of BG and MO dye in 100 mL Erlenmeyer flask. The flasks

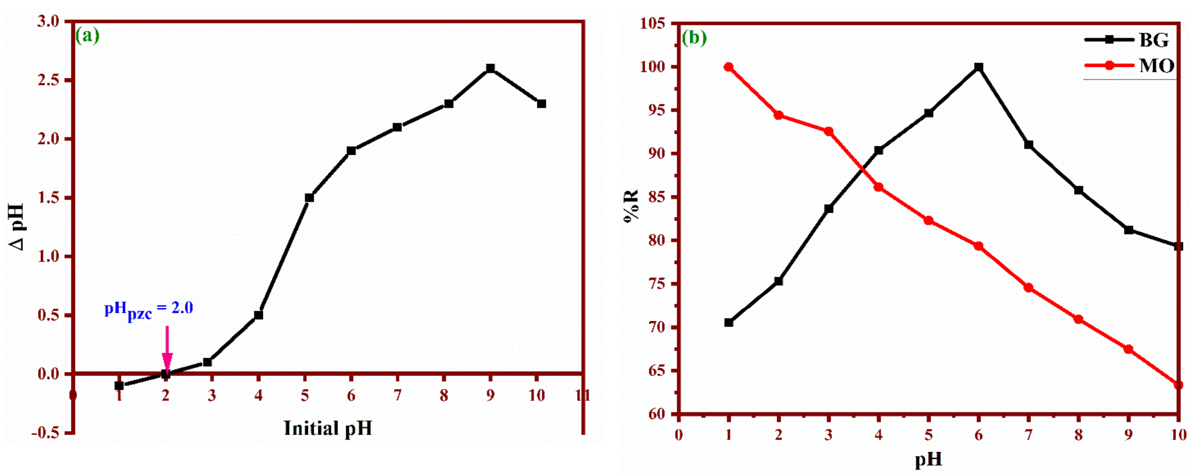


Fig 6.5 pH_{PZC} for the NZC-g-Pani nanocomposite (a), and effect of pH on adsorption of MO and BG dye in (b).

were coveredand shaked for 2 hrs in a shaking incubator to reach equilibrium. Samples were centrifuged and supernatant was placed in the U V spectrophotometer to determine the residual amount of dye in the aqueous solution.

On increasing the NZC-g-Pani dose from 0.01g to 0.04g, adsorption capacity of NZC-g-Panienhanced towards cationic BG as well as anionic MO dye due to enhancing in number of pores present on adsorbent and adsorption sites. Further increase of NZC-g-Pani dose resulted in no additional increase in BG and MO adsorption as seen in Fig 6.6 At high dosages of adsorbent, dye molecules are comparatively less to combine with all the adsorption sites present on NZC-g-Paniadsorbent gets exhausted and reduction in adsorbent per unit mass adsorption capacity(Razzaq et al., 2021). Adsorption tends to reach an equilibrium when adsorption mass reaches a particular value.Equilibrium was reached after 0.04 g of adsorbent dose for both BG and MO dyes.

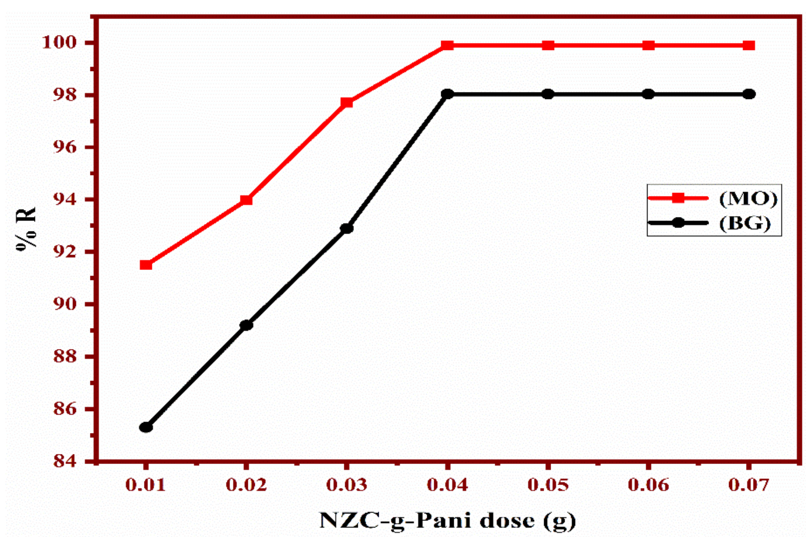
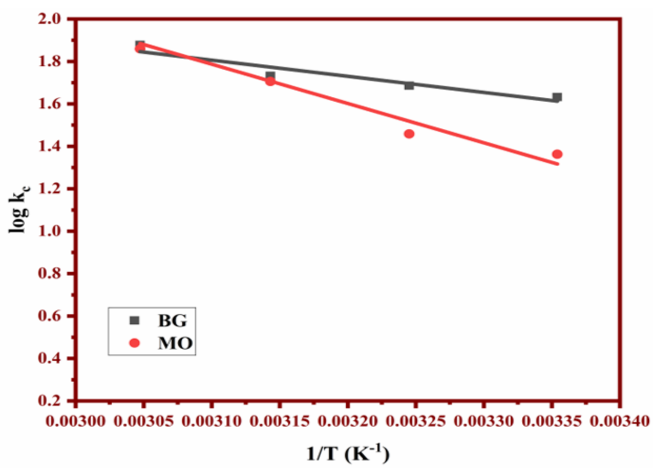


Fig.6.6 Effect of NZC-g-Pani dosages for the adsorption of MO and BG dye.

6.7.3 EffectF of time



Contacttime study was essential for designing batch experiments. Adsorption percentage of MO and BG dye on NZC-g-Paninanocomposite steadily increases with increase in contact time Fig 6.7. Constant adsorption percentage was achieved after 60 min for both MO and BG dyes.Comparative adsorption of MO and BG dye onto the NZC-g-

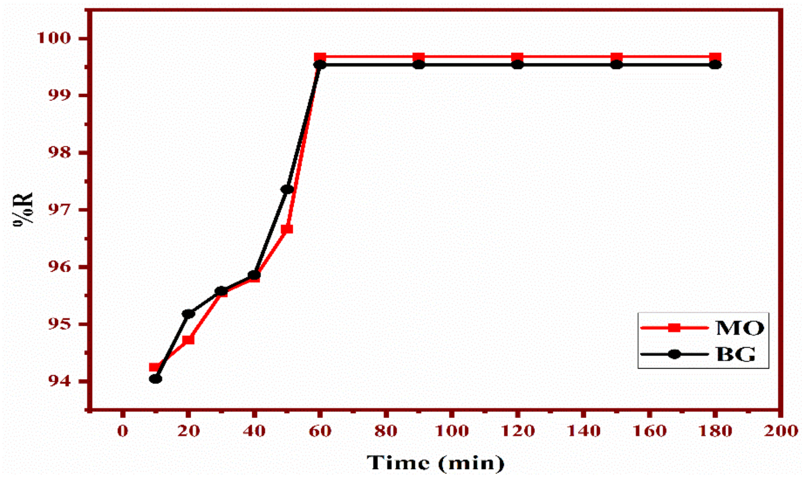


Fig 6.7.Effect of contact time for the adsorption of MO and BG dye onto the NZC-g-Pani nanocomposite.

Paniadsorbentshows that MO (%R ~100%) dye was sequestrated more than BG (%R~98.5%) dye and then the adsorption rate gradually decreased for both MO and BG, thus reaching an equilibrium.

During the initial phases of adsorption, many vacant sites are available onto the NZC-g-Pani nanocomposite which with the passage of time decrease. Left out vacant sites of NZC-g-Panibecome difficult to be occupied by BG and MO dyes due to existing repulsive forces between solute particles found on the solid adsorbent and adsorbate molecules resulting in slowing ofadsorption rate eventually(Singh et al., 2022).

6.7.4 Effect of BG and MO dye Concentration

Initial adsorbate concentration amount is an important function which controls the process of adsorption. Effect of initial adsorbate concentration was determined by preparing varying concentrations of MO and BG dyes (10-250) mg/L and comparing with % removal and keeping all other parameters (pH, adsorbent dose and time) at optimum values. It is seen from Fig 6.8 initial adsorption BG and MO dyes increase upto 50 mg/L with increase of initial dye concentration.But on further increase of dyes concentration no more dye adsorption takes place. Adsorption takes place in two phases: (a) During dye low concentration active sites present on the NZC-g-Paniadsorbent gets occupied by BG and MO dye by the process of adsorption. (b) As the concentration of targeted dye increases finite active sites present on NZC-g-Paniadsorbent decreases thus slowing the process of adsorption.

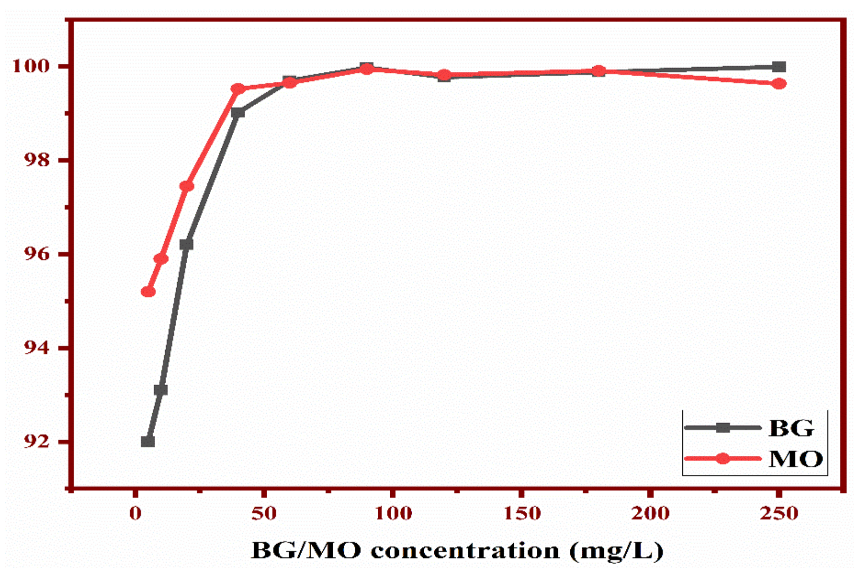


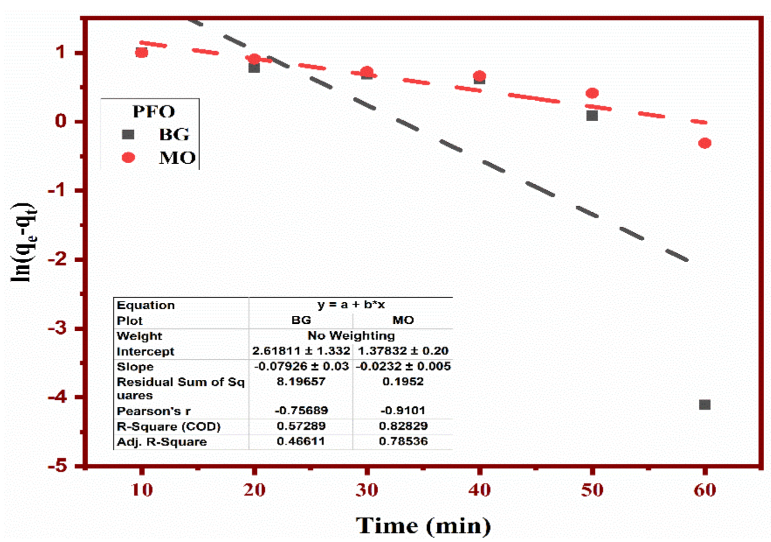
Fig 6.8 Effect of initial MO and BG concentration onto the NZC-g-Pani nanocomposite.

Adsorption kinetics are responsible for controlling adsorption rate which also determine the time needed for an adsorption process to reach equilibrium. Adsorption kinetics also give information about the path used for adsorption and the mechanism involved in adsorption. To investigate the adsorption of BG and MO on the NZC-g-Pani nanocomposite pseudo-first order (PFO) and pseudo-second order (PSO) kinetic model was used.

6.8.1Pseudo-first-order kinetics

Pseudo-first order kinetic model is the earliest known equation which describes the rate of adsorption based on adsorption capacity. It involves the reactions between functional groups which are present on adsorbent and adsorbate atoms, ions or molecules by formation of cation exchange reactions which is possible due to cation exchanging properties of adsorbents.

Graph of straight-line log ($q_e - q_t$) *vs* time was plotted as shown in Fig 6.9. Correlation



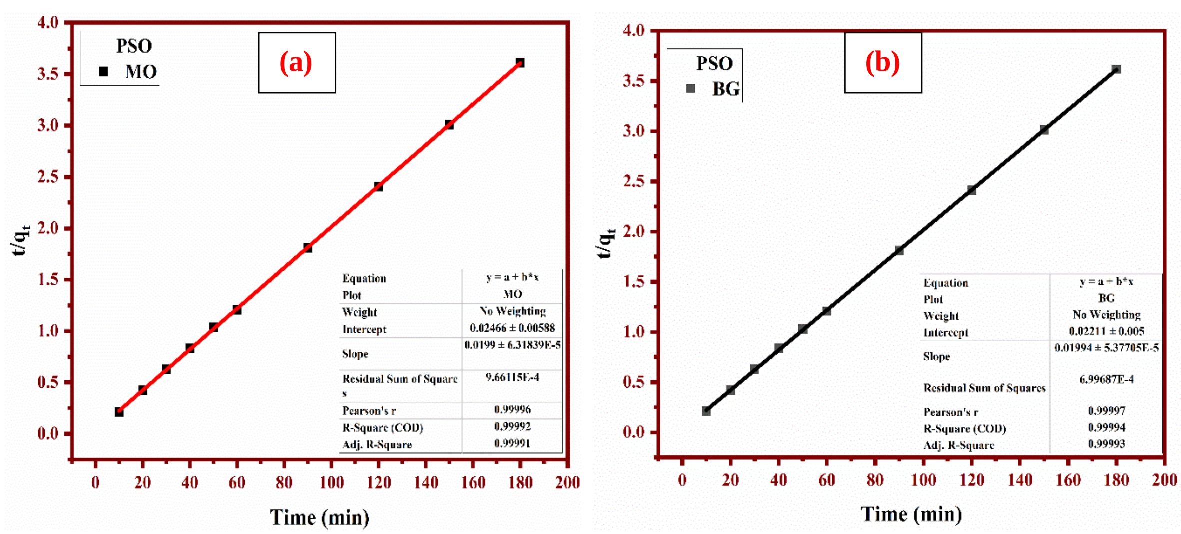
coefficient (R^2) of BG is 0.572 and MO is 0.828 from Table 6.1which depicts that adsorption of both the dyes do not follow the PFO model.

6.8.2 Pseudo-second-order kinetics

Ho and Mckay in 1997 (Ho & McKay, 1999)gave the pseudosecond order kinetic model foradsorption of divalent metals givingthe following assumptions.

- Adsorption occurs in localized areas and no interaction is seen between adsorbed molecules.
- Adsorption energy is the same for each ion and is independent of the covered surface.K_2 = (g/ mg/ min) is the rate constant for pseudo-second order kinetics.

Linear graphs of PSO kinetic model for adsorption of MO and BG dye are plotted between t / qt *vs* t as shown in Fig 6.10. Pseudo 2[nd]order rate constants K_2, $q_e$and (R^2) were observed by seeing the slope and interception of the plot. R^2 for both



the dyes in Table 6.1showed a value of 0.999 (equal to unity) showing excellent linearity which depicts adsorption of MO and BG can be illustrated by PSO kinetic model(Razzaq et al., 2021).

Table 6.1. Variables of PFO & PSO model for the adsorption of MO and BG dyes on the ternary composite.

Pollutant	PFO				PSO			
	q_e^{exp}	q_e^{cal}	K_1	R^2	q_e^{exp}	q_e^{cal}	K_2	R^2
BG	49.77	13.70	-0.00132	0.572	49.77	50.25	0.0182	0.999
MO	49.87	3.966	-0.00038	0.828	49.87	50.15	0.0163	0.999

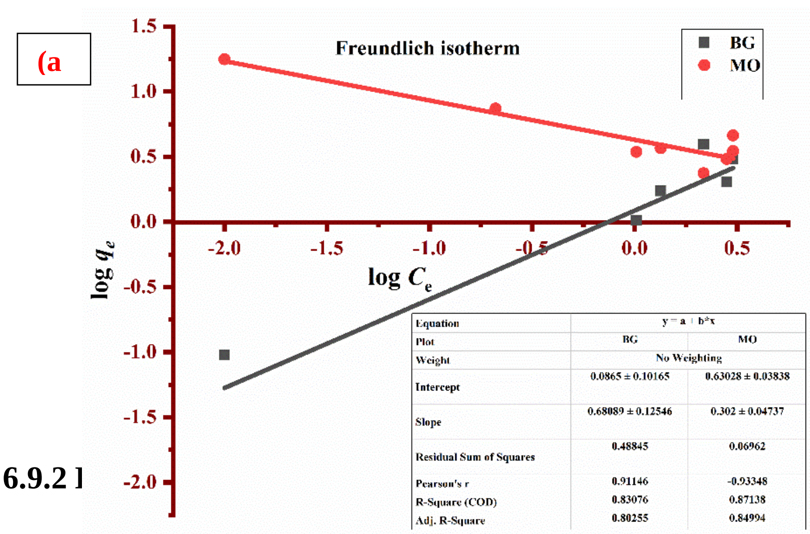
6.9 Adsorption isotherms

Adsorption isotherm states the amount of solute that can be adsorbed into an adsorbent resulting in an equilibrium concentration of solute in the solution at a constant temperature. Accumulation of any substance over solid surface is possible due to interaction or attraction of adsorbate over adsorbent. These interactions are generally electrostatic forces referred to as Vander wall forces (VWFs). Many isotherm equations have been used to study the solute adsorbed by adsorbent (per unit mass). In the current study most accepted adsorption models- Freundlich and Langmuir adsorption isotherms have been used.

6.9.1 Freundlich isotherm

Freundlich isotherm is the earliest equation describing the adsorption process.Freundlich adsorption isotherm shows the adsorption of adsorbatewhich does not confines to monolayer formation and shows various interactions which occur between adsorbed molecules(R. Ahmad & Ansari, 2021b).For many systems adsorptions heat decreases with adsorption increasing rate. This has been explained by the Freundlich isotherm which was proposed as an empirical isotherm and is explained by the linear equation which can be used to calculate the constant of K_f and n(Agarwal et al., 2017).

Graph between ln q_{eq}vs ln C_{eq} have been shown in Fig 6.11 (a). R^2 values obtained from Table**6.**2for MO and BG were 0.871 and 0.830, respectively which depicts adsorption of both the dyes did not follow this model.



6.9.2 l

Fig 6.11 (a).Freundlich isotherm plot for adsorption of MO and BG dyes.

ween adsorbate and adsorbent where adsorption of adsorbate is restricted to a single molecular layer or before a relative pressure of unity is obtained.

Langmuir isotherm which was proposed by Langmuir in 1918 (Langmuir, 1918)was considered suitable for describing the chemisorption process with covalent bonds formation between adsorbate&adsorbentbutisotherm can be used to describe the binary adsorption behaviour.

A graph of $1/q_e$ vs $1/C_e$ has been shown in Fig 6. 11 (b). Values of R^2 in Table 6.2for adsorption of MO and BG dyes are 0.992 and 0.983, respectively which specifies the high potential of the Langmuir model for adsorption of both BG and MO dyes.

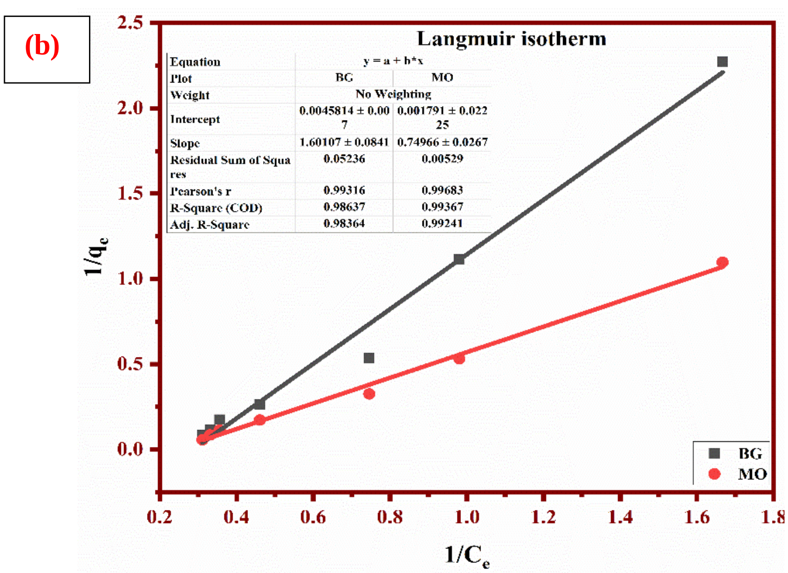


Fig 6.11 (b). Langmuir isotherm plot for adsorption of MO and BG dyes.

Table 6.2. Variables of Freundlich & Langmuir model for the adsorption of MO and BG dyes on the NZC-g-Pani.

Pollutant	Langmuir Model				FreundlichModel		
	q^{max}(mg/g)	K_l (L/mg)	R_l	R^2	$1/n$	K_f	R^2
MO	558.34	0.0023	0.893	0.992	1.468	4.26	0.871
BG	218.27	0.0028	0.874	0.983	3.311	1.22	0.830

6.10Evaluation of thermodynamicsparameters

Gibbs free energy, enthalpyandentropyarevarious thermodynamic variables were compared with adsorption of MO and BG dyes onto NZC-g-Paninanocomposite

A linear graphFig 6.12was plotted between $\ln K_c$ and 1/T for MO and BG dyes to show the thermodynamic variables as seen in Table 6.3. Negative values for BG and MO dye can be seen for Gibbs free energy and increase in Gibbs free energy (ΔG) was witnessed with increasing temperature. Enthalpy change (ΔH) is positive for both MO and BG dyes showing the endothermic nature of adsorption. Entropy (ΔS) is positive for both MO and BG dyes showing an increase in randomness during the adsorption process.

Table 6.3. Thermodynamic variables for the adsorption of MO and BG dyes on the ternary composite.

Pollutant	K_c				ΔG° ($kJ\ mol^{-1}$)				ΔH° ($kJ\ mol^{-1}$)	ΔS° (J/K mol)
	298.15 K	308.15 K	318.15 K	328.15 K	298.15 K	308.15 K	318.15 K	328.15 K		
MO	23.06	25.04	63.93	72.31	-9.29	-9.94	-10.52	-11.15	6.32	34.61
BG	42.85	48.5	53.94	59.97	-7.75	-8.24	-10.97	-11.67	15.40	62.59

6.11Summary

In the current study NZC-g-Pani nanocomposite was prepared by *in-situ* polymerization method. Synthesized nanocomposite was characterized using SEM, FTIR, Raman and XRD analysis and was used as a novel adsorbent forMO and BG dyes removal from aqueous solution. The synthesized novel adsorbent showed efficient adsorption capacitytowards both the dyes and was investigated as function of pH, initial BG/MO adsorbate concentration, contact time, NZC-g-Pani adsorbent dose. Based on the coefficient correlation (R^2) value of 0.992 and 0.983 for MO and BG, respectively, Langmuir isotherm showed a better fit. Maximum adsorptionof 558.34mg/g and 218.27mg/g were obtained towards MO and BG, respectively. Kinetic analysis revealed the PSO model executed better than the PFO model. Evaluation of thermodynamic parameter revealed endothermic and spontaneity of adsorption. Magnitude of enthalpy (ΔH) change was 6.32 kJ/mol and 15.40 kJ/mol for MO and BG, respectively, while entropy (ΔS) change values were 34.61 kJ/mol and 62.59 kJ/mol for MO and BG. From the study it can be acknowledged that synthesized nanocomposite made up of NLP, ZnO,L-cysteine functionalizedPani can be used as a potential adsorbent forMO and BG dyes removal.

Chapter-7

Summary and Recommendations

7.1 Introduction

Water is a naturalresource necessary for abidance of living organisms. Oftotal water available, only 0.5% of the earth's water can be used for quenching the thirst of humans. Groundwater - the water stored beneath the surface of earth in tiny cracks of rocks and between spaces of soil particles islargest source ofwater. With the population growing exponentially, the demand for fresh water is continuously increasing. This population growth is one of the leading reasons for contamination of surface as well as groundwater. Untreated domestic, industrial and agricultural waste in the form of fertilizers and pesticide degrades the water quality thus making it unfit for potable use and needs expensive treatment which further stresses the economy of developing countries like India.

The current study "Monitoring and Assessment of Groundwater Quality in Palwal District" was undertaken to assess and monitor the Physicochemical parameters and various heavy metals present in groundwater of study area. Samples of groundwater were collected from twenty-five villages of Palwal district, Haryana. EC, pH, TDS, TH, TA, Ca, Mg, Na, K, FCl, NO_3, SO_4, turbiditywere the Physico-chemical parameters which were assessed in Public Health Engineering Department Water Testing Laboratory, Palwal. Study on groundwater quality in Palwal district was done for three years (2019-21) in both thepremonsoonandpostmonsoon season. While quantitative analysis of heavy metals which included lead, zinc, chromium, cadmium and arsenic was done using Induction Coupled Plasma technique in Jamia Milia Islamia Lab, New-Delhi.

From the comprehensive and complete analysis of groundwater, appropriateness for collected groundwater samples for potability and irrigation purpose for agriculture was determined. Surveying of the local population in the study area was also done to know the ill-effects of drinking polluted water on the health of people.

A novel method forbrilliant green and methyl orange dye removal from water by preparing a ternary composite of neem leaf powder/ PANI/ZnO/ L-cysteine was also performed through batch experiments.

Palwal is the 21st district of Haryana which lies between western region of the Aravalli mountains and the Yamuna River eastern bank. Palwal shows tropical steppe, semi-arid climate which shows extreme dryness in air except during monsoon season. Groundwater is generally obtained from shallow and deep wells. Water percolates below the soil, collects under the ground as groundwater and gets stored below as aquifers. Water level below the ground increases with more percolation in monsoon season and reduces in dry season. Thus, water level below the ground varies in different seasons.

7.2 Physical chemical Parameters

Various Physical andchemical parameters which were evaluated during the study frame are discussed below:

- Among the selected Physico-chemical parameters,pH mean value in groundwater in the premonsoon season varied between 6.9- 7.04 while in postmonsoon time mean pH valueingroundwaterdecreased slightly due to dilution of aquifers during monsoon season. pH of groundwater samples was in the range prescribed by BIS and WHO thus indicating the usefulness of groundwater for consumption.

- Electrical conductivity valueshowed that none of the groundwater sample came in class1 (EC< 250 µS/cm), 4 % of the samples came in class 11(EC 250- 750 µS/cm) 48% of the samples came in class 111 (EC 750 - 2250 µS/cm) and 48% of groundwater samples had electrical conductivity above 2250 µS/cm. High electrical conductivity indicates a high concentration of anions and cations in water thus making it unfit for consumption and high salt content present in groundwater can make the soil saline when used in irrigation for a long time.
- BIS has fixed an acceptable limit of TDS in potable water as 500 which can be elevated to 2000 mg/l in the absence of any other alternative source. 48 % of groundwater samples in the study area had TDS level above the BIS permissible for drinking water. TDS of groundwater samples in the study area showed a mean of 2696 mg/l. 8 % of study locations in pre-monsoon and 12 % in post-monsoon were classified as fresh water while the rest of locations had brackish water. Study area samples also revealed that in post-monsoon season groundwater samples had lesser dissolved solids as compared to pre-monsoon season. Anthropogenic sources like sewage, agricultural run-off, wastewater from industries, domestic waste all contribute to high TDS in groundwater.
- Anthropogenic sources are the primary reason for the increase of chloride concentration in water. Human and animal excreta are the major source for releasing chlorides in water. BIS has set an acceptable range of chloride as 250 mg/l and 1000 mg/l in absence of any other alternative source. 52 % of the study

samples had chloride concentration above the permissible limit set by BIS with a mean of 1450 mg/l of chloride concentration in groundwater samples. Naya Gaon was the only village in the study area which showed chloride concentration of 199 mg/l which falls within the ambit of BIS acceptable limit of chloride in drinking water.

- In the present work,fluoride range in collected water exceeded permissible limit given by BIS in 48% of the samples. 36 % of the study locations had fluoride concentration within the acceptable limit given by BIS and 16% of the study locations had fluoride levels exceeding the acceptable level but within the permissible limit given by BIS. WHO has set 1.5 mg/l as the permissible limit of fluoride in drinking water and BIS has set 1.0 mg/l of fluoride as acceptable limit and 1.5 mg/l as the permissible limit for fluoride in drinking water with the remark 'Less is better'. Kishorpur (S 9) showed the maximum concentration of fluoride (3.22) in groundwater while minimum concentration (0.21) was seen in Tehraki (S12). Post-monsoon fluoride concentration in groundwater showed a decline due to dilution of aquifers due to precipitation.
- In the current investigation, mean values of 550 and 500 mg/lof total alkalinity were observed in pre-monsoon and post-monsoon seasons respectively. Post-monsoon season showed a decline in alkalinity due to aquifer recharge. Except Alahapur, Firozpur, Sikanderpur, Asawati, Allika, Rehrana, Joharkhera and Gadpuri which were 32 % of the study locations, total alkalinity in groundwater samples was within the permissible limit set by BIS.

- BIS has set 200 mg/las an acceptable range for sulphates in potable water and 400mg/l as the permittedlimit for sulphates concentration in potable water in absence of any alternative source. All the study locations were within the acceptable limit set by BIS for sulphate concentration in groundwater. Low value of sulphate concentration in groundwater was seen in the post-monsoon season due to recharge of aquifers.
- BIS has described acceptable limit of 200mg/l of TH (in form of $CaCo_3$) in drinking water and permissible limit as 600 mg/l in absence of any alternative drinking water source. 16% of the study locations in pre-monsoon and 20% of study samples in post-monsoon season were within the permissible limit set by BIS and rest samples exceeded the limit. All the water samples in the study area came in a very hard category.
- BIS has set an acceptable range of 75mg/lfor Ca in drinkable water and permissible limit as 200 mg/l in absence of any alternative source of drinking water. Tatarpur (S10) and Patli Khurd (S18) which compose 8% of the study locations had calcium concentration in groundwater above the permissible limit set by BIS. Study area showed a mean of 106 mg/l of calcium concentration in groundwater. Declining trend in calcium concentration in groundwater was seen during the postmonsoon due to aquifer recharge.

  recharging.

- BIS has setdesiredvaluefor Mg as30 mg/l in drinking water while permissible limit as 100 mg/l in absence of any alternative source. All the study locations exceeded the acceptable limit set by BIS. Alahapur, Kishorpur, Jaindpur, Nayagaon, Gadpuri, Sehrala which constitute 24% of the study samples were within the permitted limit set by BIS. Magnesium concentration in groundwater showed decline in postmonsoondue to recharge of aquifers.

- BIS has not laid any standards for presence of sodium in drinking water and WHO has given a taste threshold of 200 mg/l for sodium in drinking water. From all the study locations it was analyzed 44% of the study locations exceeded the sodium taste threshold value. Groundwater of the study area showed a mean sodium concentration value of 245 mg/l. Pre-monsoon season showed higher values of sodium concentration in groundwater which decreased in post-monsoon due to recharging of aquifers in monsoon season.
- Both BIS and WHO have not provided anypermissible limit for potassium concentration in drinking water as potassium is an essential nutrient required by humans for various metabolic processes. Potassium concentration in pre-monsoon season varied from 6 mg/l to 270 mg/l while in post-monsoon season potassium concentration in groundwater ranged from 4 mg/l to 256 mg/l. Pre-monsoon season showed higher values of potassium concentration in groundwater which decreased in post-monsoon due to aquifer recharging. 52% of the study samples had potassium concentration within the acceptable limit set by BIS. Only one study location (S7) had potassium concentration in groundwater exceeding the BIS permissible limit and 44% of the study locations were beyond the acceptable limit but were lying within the prescribed limit set by BIS.

- BIS has set a permitted limit of 45 mg/lfor nitrates in potable water with no relaxation. Sikanderpur and Asawati, which constitute 8 % of the samples in the study location, were above the limit set by BIS.

7.3 Heavy Metals Toxicity

In the current research work, concentrations of heavy metals like zinc, lead, arsenic and chromium werein the permissible limit set by BIS and WHO in groundwater meant for drinking purpose.

Cadmium variation in groundwater samples inpremonsoon season showed a mean of 0.005 mg/lwith only Joharkhera, Harfali and Patli Kalan, which constitute 12% of the study area, were within the permissible limit specified bynational& international standards. In the postmonsoon season cadmium concentration in groundwater samples showed a mean of 0.004 mg/land 40 % of samples met the permissible limit specified by BIS for cadmium concentration in drinking water thus groundwater of the studied area showedhigher concentration of cadmium as a heavy metal.

Decline in all heavy metals concentration in groundwater was seen in the postmonsoon season due to dilution of aquifers by recharging.

7.4 Relevance of groundwater for potability based on WQI and irrigation

Based on WQI range ofstudiedarea it came into light that both during the premonsoon and postmonsoon season none of groundwater samples came inexcellent category, 4% of groundwater samples were of good category while in the premonsoon season 28% groundwater samples belonged topoor category, 40% groundwater samples came in the very poor category and 28 % groundwater samples were unfit for consumption.

WQI for postmonsoon season % compliance showed that 32% groundwater came in poor category, 36% in very poor range and 28% of the collected groundwater samples were unfit for consumption.

Groundwater of the studied area varied from marginally saline to very saline in nature. Categorizing onEC basis, 64% of the collected groundwater samples came under doubtful (EC value 750-2250 µS/cm) to the unsuitable (EC > 2250 µS/cm) category of irrigation. On the basis of irrigation indices like SSP, SAR and RSC all collected samples were seen suitable for farming. Based on Wilcox diagrams it came to light that 40% of water was in excellent category, 36% in good category, 8% in permissible, 12% in doubtful and 4% of collected groundwaterwere unsuitable for irrigating crops. Classifying on(MH) basis, 88% of groundwater samples were found unfit for irrigating lands whereason the PI parameter, 36% of groundwater samples were found not fit for watering crops. Demarcating onKR basis 88% groundwater samples were seensuitable for irrigating lands.

7.5 Groundwater affecting health of local population

A health questionnaire based on groundwater quality in the study area was given to local residents to fill. Based on the questionnaire, it came to light that nearly all residents complained about the poor quality of groundwater and people also told their woes about recurrent occurrences of jaundice, tummy upset, joint problems, dental fluorosis especially in children, itching and skin rash in skin and scalp.

Many residents due to the lack of resources and their financial condition were forced to drink water from hand pumps without any treatment and complained about the bad/saline taste of groundwater.

7.6Removal of MO and BG dyes using novel biosorbent NLP/ZnO/L-cysteine grafted PANI

In the current study NLP, Zno, L-cysteine and PANI nanocomposite were prepared by in-situ polymerization. The synthesized nanocomposite was characterized using SEM, FTIR and XRD analysis and was used as a novel adsorbent for MO and BG dyes removal from an aqueous solution. The synthesized novel adsorbent showed efficient adsorption capacity towards both the dyes and was investigated as a function of pH, initial adsorbate concentration, contact time and adsorbent dose. Based on the coefficient correlation (R^2) value of 0.992 and 0.983 for MO and BG respectively, Langmuir isotherm showed a better fit. Maximum adsorption capacities of 558.34 mg/g and 218.27 mg/g were obtained for MO and BG, respectively. Kinetic analysis revealed the PSO model executed better than the PFO model. Thermodynamic studies revealed the endothermic and spontaneous nature of adsorption The magnitude of enthalpy (ΔH) change was 6.32 Kj/mol and 15.40 Kj/mol for MO and BG respectively while entropy (ΔS) change values were 34.61 Kj/mol and 62.59 Kj/mol for MO&BG respectively. From the study it can be acknowledged that synthesized nanocomposite made up of NLP/Zno/L-cysteine grafted PANI can be used as a potential adsorbent for removal of MO and BG dyes.

7.7 Conclusion

A sincere attempt was made in present research work to investigate the major Physicalchemical parameters&tracemetals present ingroundwater of the studied area and their effect onlocal people health. Efforts were also put to observe the appropriateness of groundwater for potability based on WQI values and for irrigation. Following conclusions were drawn from the research work:

- Ever increasing population and anthropogenic activities including textile industry, electroplating industry, fertilizer plants are the major threat which has led to pollution of groundwater of the study area. Textile production requires large amounts of chemicals for dyeing the fabric which needs huge amounts of water during processing thus generating excess effluents which is a source of groundwater pollution. All locations of the study area have shown over-exploitation in terms of groundwater.
- Modern agricultural practices including chemical fertilizers, pesticides, intensive irrigation practices have accelerated the rate of surface as well as groundwater contamination. Thought process of farmers- 'More fertilizer means more production' is one of the majorreason for groundwater pollution. Most ofPhysico-chemical parameters and heavy metals present in groundwater showed a seasonal variation due to recharging of aquifers present below the ground during monsoon season.
- Soil erosion, over-exploitation of water, agricultural run-off from fields, improper waste disposal both from industrial and domestic sectors have also contributed to groundwater pollution.

- Most of the local population in the study area is poor, illiterate or have just basic education. Lack of awareness, hygiene also contributes to water woes. Many people due to financial constraints do not have a proper drainage system in their homes but discharge their untreated sewage along the road-side channels and hence is a major source of groundwater contamination. Lack of sanitation has further deteriorated the quality of groundwater which plays a direct role in transmission of water-borne diseases
- Untreated waste generated from industries is dumped on land and mixes with the inefficient sewage drains. This disposal of untreated waste effluents seeps through ground and causes water pollution.
- High fluoride values in groundwater was observed in 48% of studied place. Geological strata of the research area contribute to high fluoride range.
- Waste generated from industrial units like textiles, electroplating, and plastic manufacturing units also contains toxic trace metals which is gradually increasing the concentration of heavy metals in groundwater of surveyed place. Cadmium concentration in groundwater exceeded the permissible limit set by BIS and WHO.

7.8 Recommendations

In Palwal district, the quality of groundwater is deteriorating at a distressing pace due to increasing anthropogenic interference with nature. As per the findings of various Physicochemical parameters present in groundwater samples of Palwal district, certain recommendations and proposals have been made to decrease further deterioration of groundwater reserves which will also help in conserving groundwater quality in the interest of present and future generations.

- Current study has revealed that unemployment, illiteracy, lack of health and educational facilities are the major problems faced in the villages of Palwal district.
- Villages in Palwal district are lacking even basic amenities like sanitation, drainage, concrete roads and safe drinking water therefore attention must be paid by policy makers, elected representatives to provide basic facilities to the local population. Research Scholars and scientists through their work should generate awareness among masses about the importance of safe and clean drinking water.
- Health camps should be conducted periodically for the welfare of people. NGO and health agencies should run such camps with special emphasis on the importance of clean drinking water and attention should also be focused on creating awareness regarding water borne diseases and its impact on health.
- Improper domestic waste disposal, agricultural run-off and animal excreta lying on roads are the major sources of groundwater pollution.
- Bio-fertilizers and bio-pesticides should be used as an alternative to chemical fertilizers and pesticides.
- Agricultural run-off should not be allowed to enter the nearby water bodies.
- Washing clothes, utensils, vehicles and dairy animals in water bodies should not be allowed.
- All water bodies of the Palwal district should be monitored at regular intervals and findings should be conveyed to the public through various mediums to make

people conscious how the various Physicochemical parameters&heavy metals presence in drinking water can influence human health.

- Groundwater contamination can be controlled by strict and proper management of solid waste disposal, agricultural run-off and animal excreta lying on roads.
- For feeding a large and growing population, chemical fertilizers and pesticides play an important part in modern agriculture but it is equally important to educate farmers about the optimum usage of these chemicals and also encourage farmers to switch to organic farming.
- Wherever applicable, groundwater can be recharged artificially to dilute the concentration of Physicochemical parameters present in groundwater. Percolation tanks, check dams and ponds should be constructed across all geographically suitable places for recharging of aquifers and surface storage of water.
- Water should be suitably treated before consumption.

7.8.1 Emphasis on Fluorosis

- To sensitize Gram Sabhas and Gram Panchayats about the ill-effects of excess fluoride present in drinking water so that provision of safe drinking water is made available for all people living in the studied area.
- Creating awareness between the local population about the adverse effects of excess fluoride in drinking water.
- To educate the community about increasing Vitamin C in their diet which can play a protective role and neutralize the ill-effects of excessive fluoride consumption in the body.

- The Central government along with the State government should fund and organize programs which promote and encourage defluorinated water for consumption of people.
- Current study has also revealed thatfluoriderangein groundwater samples of studied regioncrossedpermitted limit given by BIS in 48% of the groundwater samples.
- People should be made aware and given adequate information about fluorosis and its adverse effect on teeth and bones.

7.9 Scope for future study

Current study gave insight into the fact that high fluoride in the study area could be the reason attributing to dental fluorosis as the major population is dependent on groundwater for drinking. This fluoride is also an issue of concern as it leads to arthritis in elderly people. Palwal district- being the ‘Cotton City of Haryana’ also discharges many toxic dyes in surrounding water bodies. Many other Physico-chemical parameters are also much high thanpermissible limit set by BIS and WHO which has set the alarm bells ringing from local population health's point of view therefore there is a scope for future studies in the quality assessment of groundwater in the Palwal district.

- Detailed hydrogeochemical status of the study area should be prepared.
- Rain water harvesting techniques should be implemented in Palwal district to prevent the over-exploitation of groundwater.
- Detailed study of fertilizers and pesticides residue present in bore-wells and other water sources of the study area.

- Regular surveying and action -plan in areas whereconcentration of fluoride in groundwater is higher than the permissible limit set by BIS.
- Regular surveying and action -plan in those areas where cadmium concentration in groundwater ismorethan the permittedrangeset by BIS.
- Eco Friendly and low-cost biomaterials should be developed formetal ions and dyeremovalfrom the wastewater.
- Assessing the groundwater potential to recharge at regular intervals of time.

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