

Hydrochemical Characterization of Groundwater for Drinking and Irrigation in Hisar,
Haryana, India

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IN
ENVIRONMENTAL ENGINEERING

Submitted by:

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CANDIDATE'S DECLARATION

I ANTHONY NIMELY CHEA, JR. of M. Tech in Environmental Engineering, hereby declare that the project dissertation titled “Hydro chemical Characterization of Groundwater for Drinking and Irrigation in Hisar, Haryana, India” which is submitted by me to the department of Environmental Engineering, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree of Master of Technology, is original and not copied from any other source without proper citation. This work previously has not formed the basis for the award of any degree, Diploma Associateship, Fellowship or other similar title or recognition.

Place: Delhi



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CERTIFICATE

I hereby certify that the project dissertation titled “Hydro chemical Characterization of Groundwater for Drinking and Irrigation in Hisar, Haryana, India” which is submitted by ANTHONY NIMELY CHEA, JR., roll number 2KI9/ENE/17 department of Environmental Engineering, Delhi Technological University, Delhi in partial fulfilment of the requirement for the award of the degree in Master of Technology, is a record of the project work carried out under my supervision. To the best of my knowledge, this work has not been submitted in part or full for any degree or diploma to this university or elsewhere.



Place: Delhi

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Date: 29 June 2021

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ABSTRACT

Groundwater is a valuable resource. The inhabitants of Hisar, India, rely on groundwater for drinking and agricultural purposes. Consequently, thirty samples of groundwater were fetched and hydro chemically assessed for physicochemical parameters. Assessment reveals that approximately 72% of all analyzed parameters exceeded the WHO drinking water standards, and about 43% surpassed BIS standards. Water Quality Index (WQI) shows that 60% of the groundwater is unfit, 24% is poor, and 16% is good for drinking. Irrigation index from the US salinity diagram suggests the following classes: 43.33% C3-S1, 36.67% C4-S1, 13.33% C4-S2, and 6.67% C2-S1. Residual sodium carbonate depicts 50% irrigation suitability. Soluble sodium percent, Kelly's ratio, and magnesium hazard suggest 64% unsuitability for the former two, with the latter recording 97% of the water unfit. Base exchange and infiltration type show that 97% of the water is Na⁺- SO₄⁻ type and is deep meteoric. Gibb's diagrams recommend that there is a dissolution of rocks minerals in the area. Piper Trilinear classification depicts that most water is of the Mixed Ca-Mg-Cl type followed by NaCl type. The order of significant positive ions is Na⁺ > Mg²⁺ > Ca²⁺ > K⁺, and significant negative ions of the samples analyzed is Cl⁻ > HCO₃⁻ > SO₄²⁻ > CO₃²⁻ > F⁻ > PO₄³⁻. Correlation analysis reveals that EC, TDS, and salinity correlated significantly with Cl⁻, SO₄²⁻, Ca²⁺ and Li; pH negatively connected with 50% of all parameters. With a cumulative variance of 83.57%, Principal component analysis pulls out five significant components.

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LIST OF ABBREVIATIONS

BIS:	Bureau of Indian Standards
WHO:	World Health Organization
APHA:	American Public Health Association
AWWA:	American Water Works Association
WEF:	World Environmental Federation
ppm:	Parts per million
EDTA:	Ethylenediamine Tetraacetic Acid
CGWB:	Central Ground Water Board
PCA:	Principal Component Analysis
PET:	Polyethylene Terephthalate

CHAPTER

1

INTRODUCTION

Groundwater is essential to humankind. On an international gauge, humanity uses groundwater for domestic, commercial, manufacturing, and agricultural purposes. Studies have shown that 65% of the water used domestically comes from groundwater, while irrigation and industrial development carry 20% and 15%, respectively (Adimalla et al., 2018). The frequency at which groundwater infection is increasing, especially in developing countries, is a problem that has attracted many scholars' and world leaders' attention. In a country like India, which is developmentally accelerating amongst its peers, groundwater plays a vital role, especially in arid regions, where there is inadequate surface water. Most inhabitants rely on groundwater for day-to-day needs, mainly consumption purposes. There is an overuse of groundwater for local and agronomic activities on a global scale. Predicated upon the increase in the use of fertilizers and pesticides, the undiscerning dumping of solid waste and wastewater, and over-extraction, prompted by the rapid rise in population, groundwater has become prone to contamination (Subba Rao et al., 2017). The over-extraction of groundwater leads to saltwater intrusion. Goebel et al. (2017) define saline water movement as the progression in which the saltwater boundary travels inland, thereby causing saltwater to occupy portions of the freshwater aquifer due to overexploitation. The border at which saltwater and freshwater meet governs the water movement, determined by the difference in density and pressure located on both sides of the boundary and the properties associated with subsurface hydrology. Besides, infiltration rate, precipitation, runoff pattern, and under-bearing strata- which instigate the dissolution of minerals in water and alter its hydrochemical state- are other factors that lead to groundwater contamination. Therefore, groundwater quality is determined by its physicochemical state and the variation in its attribute regarding anthropogenic activities (Haritash et al., 2016).

Research on surface and groundwater concerning domestic and agricultural purposes is ongoing in various localities of the Indian subcontinent and the world in referencing hydrochemical components, major ions, trace elements, and multivariate statistical approaches. Mehra et al. (2016) conducted a study on irrigation use of groundwater in one of Haryana's districts, called Mewat. Their study concludes that the proper managerial measures to enhance groundwater sustainability are lacking; groundwater quality and quantity deteriorate with swelling susceptibility to surface and subsurface impurities, aggravating increasing exposure to climatic parameters. Ali and Ali (2018), having hydrochemically characterized groundwater quality and performed a spatial analysis in the study area, concluded that the groundwater is discreetly polluted to sternly polluted in most of Bundelkhand Massif's industrial areas; thus, the groundwater is unfit for drinking purposes.

Many latest studies have done on groundwater for drinking and irrigation uses by several researchers, in which researchers used various indices and plots (Khan et al. 2020; Kaur et al. 2019; Ravish et al. 2018, Gupta and Mishra 2016). In addition to the findings mentioned in the above preceding literature, Sheikh et al. (2017) conclude that chemical composition in groundwater found in Haryana is subjugated by monovalent cation – sodium and anion – chloride, and contains saline water. According to Sheikh et al., “groundwater is unsaturated in the case of anhydrite, halite, gypsum, and CO₂, suggesting a significant contribution of Ca²⁺, Mg²⁺, and other ions in the groundwater”. Therefore, this research was carried out with the following objectives:

- To assess the quality of groundwater for drinking and agricultural purposes in Hansi, Hisar District
- To compare findings with drinking water quality standards set by the Bureau of Indian Standard (BIS) and World Health Organization (WHO)
- To characterize groundwater-based weathering type, base-exchange, meteoric type, Piper trilinear diagram, etc.

CHAPTER
2
REVIEW
OF
LITERATURE

Though water is abundant on the earth, the rate at which industries, population growth, and urbanization are increasing have sparked groundwater shortage worldwide. Many studies have been done – with a lot more ongoing – to address groundwater scarcity and propose remediation measures of the contaminated groundwater on the Indian subcontinent. [Kaur et al. \(2019\)](#) classified groundwater from a hydrogeochemical perspective in the river Yamuna – one of India’s famous rivers, found on alluvial plains north of the subcontinent. Their study, done in the Panipat district of Haryana, aimed to investigate the significant aquifer chemistry and the hydrochemical developments that influence the study area. The researchers collected Forty-five groundwater samples in the post-monsoon season of 2015. They executed conventional methodology and carried out the hydrochemical analysis. [Kaur et al. \(2019\)](#) conclude that the aquifer I Panipat is influenced by carbonate and silicate weathering. Hydrochemical facies from Chadha’s and Piper’s diagrams suggest that the groundwater in the area is permanently hard, represented by $\text{Ca}^{2+} + \text{Mg}^{2+} - \text{Cl}^- + \text{SO}_4^{2-}$; chloro-alkaline indices discovered reverse ion exchange and dominance ion exchange is ongoing in the aquifer. They went further by asserting that “The anthropogenic influx from agricultural and industrial sources may pose a significant threat to groundwater resources in the region.” Their investigation demonstrated that the significant hydrological, chemical, geochemical, and human-induced processes control aquifer chemistry, which may aid in sustainable groundwater quality supervision and policy decision-making in the Panipat.

A case study of groundwater susceptibility in some remote urban agricultural regions and the industrial district around Haryana regarding contaminated irrigation waters was also assessed by [Rosina et al. \(2013\)](#). The research objective was to test the application of a field-scale decision support system (DSS) named IMPASSE. The IMPASSE was used to analyze groundwater contamination in the outskirts of the Faridabad district. The study was segregated into two classes, agricultural and non-agricultural area – based on land use maps. The land use maps

of the study area-produced site were digitized in Arc View Spatial Analyst – GIS software. In an attempt to comprehend land and water management practices and their contribution to heavy metal leaching and surface water percolation, groundwater samples were collected and testing in triplicate for EC, pH, Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , F^- , CO_3^{2-} and HCO_3^- Cu, Fe, Mn, Zn and Cr, Ni, Pd, Cd were analyzed as per the standard procedures using flame atomic absorption spectrometer – model ECILA AS4141 and polarographic TraceLab Analyzer model POL150. Results revealed that the primary cause of salinity in groundwaters in the region was geogenic. The findings also authenticated and established an enthusiastic method for assessing saline and trace metal that make groundwater vulnerable in any area with different soil profiles, agricultural patterns, and water management strategies.

In addition to the preceding, [Khan et al. \(2020\)](#) conducted a study in which they hydrochemically characterized and assessed groundwater quality in Tamil Nadu and Puducherry's coastal areas. In their study, an effort was made to establish groundwater aptness for human ingestion and irrigation purposes. Sixty-six groundwater samples were fetched from wells. After analysis, the results disclose that dominant ions are in the sequence $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-}$. Hydrochemical facies from Piper's diagram unveils that most of the groundwater is Ca-H- CO_3 , Na-H- CO_3 , CaCl, mixed Ca-Na-H- CO_3 , NaCl types, notwithstanding of time of the year, and show two different paths of origin. The samples' pH, EC, and TDS readings are within the acceptable limit, with some exceptions, which cross the limits.

Generally, groundwater along the coastal tracts was appropriate for domestic use except for some places. [Khan et al. \(2020\)](#) accessed groundwater aptness for irrigation uses for permeability index, soluble sodium percent, sodium adsorption ratio, and magnesium adsorption ratio. The SAR index suggests low sodium hazard for most samples. As for salinity hazard, the groundwater varies in this regard – low to high. Soluble sodium percentage results depict that most of the

groundwater in the area is fit for agronomic purposes. Magnesium hazard findings display that groundwater at some places was inapt for agricultural use. Gibb's diagram was used to hydrochemically categorize the process and mechanism governing water chemistry; the authors deduce that chemical constituents found in the rocks and soils are dissolving, and rock minerals are, as well, weathering.

Haritash et al. (2008) assessed groundwater's domestic, industrial, and agricultural quality in some North Indian villages. The scholars prepared and tested their samples for physicochemical constituents, having fetched thirty-four groundwater samples from an area – Rewari town, primarily used for cropping. The physicochemical classification results disclose that many sources, which supply irrigation water of the city and its perimeter was unsafe for consumption due to rising volume of Ca^{2+} , Mg^{2+} , TH, and F⁻. When the samples were assessed for irrigation suitability, SAR was high; RSC, SSP, and MH were moderate to high. The industrial evaluation suggests that the water in the area was unsuitable for industrial activities since its readings were high for Ca^{2+} and CO_3^{2-} , which can precipitate very quickly. Besides, **Haritash et al. (2008)** conclude that the principal ions found in the samples are Na^{2+} , SO_4^{2-} , and Cl⁻. Most groundwater samples are Na^+ - SO_4^{2-} and NaCl type predicated upon cations and anions' profusion and their relationship type. The dense accumulation of chemicals in the area is associated with rocks and minerals' physical characteristics.

To assess the accumulation of salt in Haryana's groundwater, **Sheikh et al. (2017)** use a hydrochemical toolbox related to GIS. Their research was geared toward identifying the aspects influencing groundwater quality in the Sonipat. They conclude that silicate weathering is a governing factor; besides, carbonate rocks – “Reh” and “Kankar” underlying the area indicators of mineral dissolution. According to the study, the most critical aspects affecting the quality of water in Sonipat are reverse ion exchange processes. The researchers further elaborated expanded their conclusion, stating: “The majority of the samples had a chemical composition dominated by sodium and chloride ions and was saline. The saturation

index showed that the groundwater is unsaturated in the case of anhydrite, halite, gypsum, and CO₂, suggesting a significant contribution of Ca²⁺, Mg²⁺, and other ions in the groundwater.” They finally asserted that salinity in shallow aquifers of the study area occurs through diverse sources, amplified by climatic conditions. “Intensive agriculture in the area, irrigation by canal water, and tube wells have triggered salts’ mobilization and dissolution.”

In furtherance to the groundwater studies which have ongoing, [Vishal and Rachna \(2020\)](#) embarked on a study titled “A multivariate statistical approach for monitoring of groundwater quality: a case study of Beri block, Haryana, India.” Their study’s priority was to examine groundwater quality in Beri Block and its perimeter and some adjacent Jhajjar District villages. The authors summarized their research to conclude that “the current state of Beri block’s water quality and its nearby villages is not good; leaching and capillary action of water may be the contributing factors. Few parameters, viz. hardness, alkalinity, chlorides, sodium, and TDS, were higher than the prescribed limits suggested by BIS. Total hardness showed a significant positive correlation with Ca, Mg, Cl, SO₄²⁻, Na, K, Fe, Cr, and Zn. TDS showed a significant positive correlation with EC, TH, Ca, Mg, SO₄²⁻ and Cl⁻. EC shows a significant positive correlation with Ca, Mg, SO₄²⁻ and Cl⁻.”

WQI results show that the study area’s water quality classification comprises three classes: poor, very poor, and unfitting. Principal Component Analysis (PCA) extracted five variables of sixteen variables. The samples’ alarming concentration is probably due to weathering of rocks under redox environment, human-induced effects, and the natural percolation or infiltration of water during rainfall. The findings from PCA converged with that of cluster analysis. Their research provided essential details on drinking water quality in Beri, which can improve public health. Their employed methodology exemplified the practicality of multivariate statistical procedures for scrutinizing and explaining outcomes of multifaceted data set, evaluation of water quality, and intricate interactions among variable quantity.

Integrated Groundwater assessment for agricultural purposes was studied by Mehra et al. (2016). With the aid of GIS, the objective was to understand groundwater resources for irrigation in the Mewat district of Haryana, India. The study reveals a combination of groundwater potential, quality, and susceptibility using a multivariate clustering method to interpret an integrated groundwater map. Their joined evaluation of groundwater resources in the study shows that groundwater resources are affected by trilinear variables, i.e., groundwater quality, potential, and vulnerability. These factors' connections can impact farming communities' decision-making concerning their cropping pattern and groundwater resource use. The review also provides the strength and challenges in each of the identified zones. The researchers conclude that the complications would exacerbate when the excellent quality zones get vulnerable surface and subsurface contaminants. The worsening of the situation would further depreciate the quality of groundwater in those compartments.

With the quest to understand groundwater chemistry in some regions of Bundelkhand Massif, India, Ali, and Ali (2018) studied the hydrochemical faces and spatially analyzed groundwater quality in that area. Their findings revealed that groundwater is under the influence of alkaline earth species, increasing total hardness in all samples and categorizing them as moderately complex to strenuous. In some vicinities, chloride's alarming concentration could increase saltiness in water and affect consumers' health. Hydrogeochemical characterization was done with the help of Durov, Piper, and Gibb's diagrams. Several irrigation water classification determinants, such as SAR, RSC, and % Na, exposed that most groundwater in the research location is inappropriate for agriculture. Besides, water in manufacturing and agricultural vicinities of the research location was not fit for domestic use.

Due to the relevance of agriculture in the Haryana, scholars are continuously endeavoring to evaluate groundwater. A study in Bhaskara Hansi – Butana Branch – on the Multipurpose link Channel (Mpl) in Haryana, for domestic and

agricultural purposes, was done by [Singh et al. \(2015\)](#). They concluded that overall groundwater quality along the MPL channel is suitable for domestic consumption and irrigation purpose, provided that there is no alternative source (s).

Two years later, [Kumar and Sharma \(2017\)](#) embarked on studying the removal fluoride concentration in groundwater quality in Hisar. They assessed several water quality indicators concentrating on fluoride in the ground and surface water of the city. In furtherance, a comparison of all parameters checked was made with the Indian and WHO standards. At the final analysis, the scholars concluded that surplus fluoride concentrations were found in most water samples. They asserted that fluoride is unevenly distributed across Haryana. The unequal supply of fluoride in groundwater located in Hisar is a consequence of the random distribution of rocks, such as fluorite, apatite, biotite, etc., containing fluoride. Also, their work highlighted that the aggressive exploitation of groundwater in the area is exhausting groundwater, thus generating excess fluoride from fluoride-containing minerals. Fluoride did not show a strong relationship with any of the analyzed water quality variables. They recommended that, because the extra fluoride concentration is not unique to Haryana, both state and federal authorities need to consider remediation.

To supplement the previous studies done in Haryana and other parts of India, [Singh et al. \(2011\)](#) initiated Chemometric Analysis of Groundwater of Few Villages of Narwana Block in Jind District, Haryana, India. They carried out the physicochemical analysis of twenty samples for various water quality parameters such as pH, EC, and TDS. TA, TH, Cl⁻, Ca²⁺, Mg²⁺, and F⁻ were also analyzed. The study shows that groundwater of the Narwana block, Jind District, is suitable for drinking and domestic purposes. It is necessary to treat the infected water to reduce contamination, particularly for hardness, chloride, and fluoride.

Additionally, the need to assess, monitor, check, remediate, and manage groundwater has proven essential to many research scholars in India. This desire

continues with a recent study done by Herojeet et al. (2017). In Nalagarh Valley, Himachal Pradesh, India, Herojeet et al. (2017) characterized water quality and identified litter source of surface water. The researchers' main intention was to examine the dominant ions prompting the water types and the key factors affecting the water quality, using different statistical approaches. The summary of their results shows that physicochemical parameters are within the acceptable limits of BIS (2012) and WHO (2011), except for EC (both seasons), Mg^{2+} , Na^+ , and K^+ (pre-monsoon), respectively. The biological indicators, namely BOD and TC, surpass most of BIS's acceptable limits (2012), indicating pollution from organic sources. EC values' suitability falls moderately to high saline for agricultural classification, whereas TDS values belong to the freshwater class. The result of the Piper Trilinear diagram validates that the area is under the influence of $Ca - Mg - HCO_3$ - water type signifying temporary hardness, with the remaining samples belonging to $Ca^{2+} - Na^+ - HCO_3$ - or $Na^+ - HCO_3$ - forms by base ion exchange processes. According to Herojeet et al., "hydro chemical faces, ion exchange processes' influence attributes to alkaline earth metals' dominance over the alkali metals and weak acidic anions over strong acidic anions in the study area. PCA and CA identify the surface water chemistry is strongly controlled by natural factors such as weathering of minerals, ion exchange processes, and anthropogenic factors like agricultural runoff and discharge of industrial and domestic effluent. Thus, PCA and CA modeling's holistic approach will help plan future design through optimal sampling locations based on seasons without losing any outcome significance and develop remedial measures to restore water resources".

A survey of the groundwater in Delhi based on the area's hydrochemistry was carried out by Alam et al. (2009). The study focused on the extent to which groundwater in the research lo. According to Alam et al., "twenty groundwater samples were collected from tube wells, boreholes, and hand pumps. The samples were analyzed for significant ions chemistry, employing the standard methods of the American Public Health Association (APHA). Hydrogen ion concentration

(pH), total dissolved solids (TDS), and conductivity were measured using pH, TDS, and conductivity meters, respectively. Total alkalinity (TA) was estimated using HCl titrimetry. Total hardness (TH) and calcium (Ca^{2+}) were analyzed titrimetric using standard EDTA. Magnesium (Mg^{2+}) was computed, taking the difference between total hardness (TH) and Calcium (Ca^{2+}) concentrations. For copper, chromium, cadmium, cobalt, zinc, and nickel, determination in water samples and air acetylene flame was used. The determination of heavy metal was done using Atomic Absorption Spectrophotometer (AAS), Perkin Elmer model 3100. They concluded that the quality of water samples subjected to the study was acceptable for most parameters. It was within the maximum permissible limits of BIS's drinking water standards. Among heavy metals, Zinc, Nickel, and Cobalt were found more than Copper, Chromium, and Cadmium. The findings inferred that the groundwater samples are fit for human consumption without prior treatment".

[Acharya et al. \(2008\)](#) assessed groundwater properties in North Gujarat. They analyzed EC, pH, TDS, K^+ , and F^- . TDS and EC were above the BIS allowable limits. However, HCO_3^- , K^+ , and F^- were within the boundaries while 53%, 61.53%, and 46% of Cl^- , SSP, and SAR, respectively, exceeded the limits.

A similar study was done by [Wu et al. \(2015\)](#). The paper is titled; "Chemical Characteristics and Quality Assessment of Groundwater of Exploited Aquifers in Beijiao Water Source of Yinchuan, China: A Case Study for Drinking, Irrigation, and Industrial Purposes." The study's goals, conducted by Wu et al., were directed to understanding groundwater chemistry, establishing those factors that control it, and understandably assessing the groundwater in the area. Wu et al.'s conclusion from their assessment revealed from the statistical analysis carried out that the quality of the water in a confined environment is better than the phreatic water samples. As per the Piper diagram, the hydro chemical study showed a series of chemical constituents and composition comparing phreatic water and confined water and suggesting the indicators which control the groundwater chemistry. The

outcome also indicates mixed phreatic water and excess anions of bicarbonate in the water.

Moreover, the groundwater assessment of the groundwater suggests magnesium hazard, but no harm can be caused by sodium in the study area's phreatic water. The magnesium hazard has the propensity to depreciate soil quality upon activated alkalinity. Therefore, the phreatic water in the study area is inappropriate for agricultural activities. Finally, suitability assessment of groundwater for industrial use points out that confined water in the study area has no coating harm to boilers. However, the confined water can cause a slight foamy response and are slightly acidic.

A study on WQI was conducted in Tumkur Taluk, Karnataka State, by [Ramakrishnaiah et al. \(2009\)](#). A study in which samples 269 samples of groundwater were collected in February 2006 revealed that WQI for all samples has its minimum and maximum values at 89.21 and 660.56, respectively. About 99 % of the groundwater samples surpassed 100, the maximum bound for domestic water. The exceeding WQIs were recorded from samples with higher Iron II, Nitrate, Total Dissolved Solids, Total Hardness, Fluoride, Bicarbonate, Chloride, and Manganese values the groundwater.

[Rajankar et al. \(2009\)](#) embarked on a related assessment titled: "Water Quality Assessment of Groundwater Resources in Nagpur Region (India) Based on WQI". The researchers collected their groundwater from the Khaperkheda in Maharashtra, India, between 2005 and 2006. The samples represented three seasons: winter season, post-monsoon, and summer. The results obtained from their study suggested that the water quality in the study area was poor.

A study titled "Evaluation of Groundwater Quality and Suitability for Drinking and Irrigation Purposes Using Hydrochemical Approach: The Case of Raya Valley, Northern Ethiopia" was carried out by [Gebrerufael et al. \(2019\)](#). To test and analyze, they collected 30 groundwater samples from Raya valley in 2015 and

2018. The groundwater samples collected from Raya valley showed the groundwater types as Mg-HCO₃ and Ca-Na-HCO₃ from the water's hydrochemical classification. Based on the total hardness classification, 46% of the groundwater from the study area is classified as hard water. Simultaneously, type based on TDS values indicates that 95% of the study area's water is acceptable for domestic use. The groundwater quality for drinking exceeds the guidelines permissible limits of Ethiopian standard by Mg²⁺ in 49%, Ca²⁺ in 33%, and K⁺ in 54% of analyzed water. Of the analyzed water samples' parameters, total hardness, total dissolved solids, and electrical conductivity also surpass the Ethiopian standard's permissible limits for drinking - 46%, 5%, 18%, respectively. Water quality assessment for irrigation suitability based on Na%, SAR, Mg ratio, and PI indicate that the water quality can be ranged from acceptable to good.

Nevertheless, increasing salinity and sodium concentration due to cations and low permeability index have hampered its irrigation suitability, mainly at south-central and southeastern discharge areas of Raya valley. Wilcox diagram depicts 98% of the study area's analyzed samples are classified as medium to high salinity range. In comparison, 97% of the groundwater from Raya valley contains low sodium.

In addition to the above studies done on groundwater, [Wotany et al. \(2014\)](#), in a South Western Cameroonian division of Ndian, researched the "Hydrochemical attributes of groundwater in sedimentary, metamorphic, and volcanic aquifers". Their study's objective was to find out the types of rocks that constitute the aquifers and assess the physical properties and hydrochemistry of groundwater used by communities as potable water sources. Thirty-eight (38) groundwater samples, including twenty samples (sedimentary aquifer), eleven samples (metamorphic aquifer), and seven samples (volcanic aquifer), were collected, tested, and analyzed for physicochemical parameters. From their analysis, the authors concluded that the range of pH of groundwater collected from sedimentary, metamorphic, and volcanic formations are 5.55 – 8.0, 6.10 – 7.4, and 5.80 – 7.6, respectively, reflecting 60% acidic and 40% neutral and basic. For TDS and EC, most

mineralized waters were found in the sediments, followed by volcanic and least mineralized water in metamorphic aquifers. They went further by stating that 37 samples were suitable for drinking, while 1 sample was unsuitable due to excess nitrate (77.28 mg/l) and bromide (0.08 mg/l). Irrigation-wise, the water was appropriate based on EC readings.

Besides the above studies, [S. Singh et al. \(2012\)](#) studied drinking water supply and their sources in some of the Safidon and Julana blocks, India. [S. Singh et al.](#) collected thirty-five and thirty-six groundwater samples from Safidon and Julana, respectively. They tested the groundwater and analyzed the samples' physicochemical parameters. The pH values were 7.2 to 9.3 for Safidon and 7.16 to 8.73 for Julana. The EC of all samples was 1.1 mS to 5.7 mS/cm for the Safidon block and 1.12 mS to 8.07 mS/cm for Julana. The readings obtained for the Safidon block for TDS concentration were 704 mg/L to 1752 mg/L, while Julana block had 1018 mg/L as its minimum concentration and 5165 mg/L as maximum. In the Safidon block's water samples, the total hardness ranged from 190 mg/L to 508 mg/L. The Ca^{2+} content was from 24 mg/L to 96 mg/L and 7 mg/L to 109 mg/L for Safidon and Julana. In study locations of Julana block, Na^+ varied from 50 mg/L to 200 mg/L. Additionally, Cl^- was found in the range of 67 mg/L to 376 mg/L in Safidon, with its lowest and highest reading being 31.5 mg/L and 379.9 mg/L, respectively. The SO_4^{2-} content in all samples was lower, kept below the acceptable limit; Fluoride content, 0.11 to 2.93 mg/L in the Safidon block's groundwater, had its average of 1.37 mg/L. Fluoride in Julana was in the range of 0.47 to 2.72 mg/L. Following the results obtained from their study, they concluded that "out of thirty-five samples of groundwater from Julana area, all samples require one or another kind of treatment before drinking. Special attention for removing hardness is required as all the samples are found to be of very hard category. Considering hardness, about 93% of the groundwater in Safidon and Julana blocks of Jind district is not fit for human consumption".

Singh et al. (2011) conducted a study titled, “Hydrochemical Analysis and Quality Assessment of Groundwater in Noida Metropolitan City, Uttar Pradesh”. This paper dealt with groundwater hydrogeochemistry, identified potential contaminants, and assessed water’s suitability for domestic and agricultural uses. The researchers used conventional water testing methodologies by BIS and APHA after collecting 33 and 14 water samples in pre-monsoon and monsoon seasons of 2006 -2007. After testing and analyzing all metadata for significant ions, pH, EC, TDS, and irrigation factors %Na, SAR, RSC, and MH, they concluded that “groundwater in the investigated area is alkaline and fresh brackish in nature”. More so, their study resolved that specific significant “ions and heavy metal concentrations in groundwater exceed the desirable limits for drinking water at many places. Concentrations of TDS, Cl, Na, SO₄, TH, Fe, Mn, Pb, Ni, Al, and B at many sites are beyond the safe limits of drinking water, indicating contamination by untreated industrial, domestic waste effluents. The different hydrogeochemical processes like dissolution, mixing, ion exchange processes, and the weathering of silicate and carbonate minerals control groundwater chemistry. The calculated values of SAR, RSC, and sodium percentage indicate water quality for irrigation uses as good to permissible category. However, a high salinity value restricts its suitability for agricultural purposes, and plants with good salt tolerance should be selected for such an area. A detailed hydro-geochemical investigation and integrated water management are suggested for sustainable development of the water resources of the area for better plant growth as well as maintaining human health”.

In their quest to evaluate the “causes of groundwater quality deterioration in Puttalam, Sri Lanka, using isotope and hydrochemical tools”, Edirisinghe et al. (2016) collected seventy-five (75) groundwater samples analysis of isotopes and significant ions during two seasons: dry and wet seasons. According to Edirisinghe et al. (2016), “the composition of all waters (surface, shallow and deep) in the Puttalam area’s dry season is mainly the Na–K–Cl type. During the wet period, the

deep groundwater is mostly in Na–K–Mg–Cl type, and surface and shallow waters are of NDC–NDA type. Generally, groundwater salinity in the Puttalam area originates from the dissolution of salts, which may be precipitated in the soil through the seawater spray over time, leaching of salts from salterns, and the dissolution of minerals in the geological matrix. There is no evidence from isotope or hydrogeochemical evaluation for seawater intrusion, causing salinity increase in groundwater in the Puttalam area wells.”

A study was conducted by [Azizi et al. \(2019\)](#) in which a new groundwater quality index was proposed, using standard water quality parameters. The proposed Groundwater Quality Index of Saltwater Intrusion (GWQI_{SI}) helps understand the extent of groundwater salinity.

[Nag and Lahiri \(2012\)](#) conducted a study on Dwarakeswar Watershed Area, intending to assess groundwater’s hydrochemical attributes for farming and drinking uses. Having collected twenty-seven samples from a varying depth of 30 to 50 meters in Dwarakeswar, the researchers analyzed the groundwater to establish the concentrations of physical parameters to include EC, pH, TDS, and TH, the chemical characteristics such as SO_4^{2-} , Cl^- , Fe^- , K^+ , Ca^{2+} , HCO_3^- , and Na^+ . The metadata analyzed also accounts for irrigation water parameters, including MHR, SSP, KR, SAR, TH, and RSC were determined. The study concluded that the water is fresh and drinkable except for some areas where TDS concentration surpassed the acceptable standards of 500 mg/L. As for irrigation water assessment, from the metadata analysis, SAR values, recorded in meq/L, were between 0.09 - 0.54 during the pre-monsoon season and 0.01 - 0.24 in the post-monsoon season. Results indicated that the sodium adsorption ratio’s calculated values were below 3 in all the samples, and other irrigation parameters were below the standards. The scholars, therefore, infer that groundwater in the study area groundwater is suitable for irrigation. Meanwhile, the analyses for groundwater’s physicochemical characteristics in Dwarakeswar Watershed Area established that

all parameters, in almost all samples, were within the allowable limits of WHO and BIS limits for drinking water.

Based on the extensive literature review done herein, only one study has been found on the study area. Consequently, more research needs to be done on different Hisar District blocks and Haryana in general to monitor groundwater status. The current study was formulated to hydrochemically classify groundwater for drinking and irrigation purposes in Hisar District, Haryana.

CHAPTER

3

MATERIALS

&

METHODS

of the most overcrowded districts in Haryana, next to Faridabad. According to Central Ground Water Board (CGWB) reports, Hisar is the largest producer of galvanized iron in India. As per India census 2011, the district contains 1,742,815 inhabitants, thus acquiring a rank of 276th in India out of 640 sections. The community has a populace of 438 residents per square kilometer, with an inhabitants' progress rate during the era, 2001 to 2011, 13.38%. The ratio of males to females is put at 1000 to 871, with 73.2% of the literate residents. Haryanvi is widely spoken in that part of India. Religiously, 98% of its inhabitants are Hindu, with only approximately 40,000 Muslims, and the rest comprises mostly Jain and Sikhs.

3.1.2 Geomorphology of Hisar

Considering the Central Ground Water Board (CGWB 2017) report, the Hisar district's geomorphology can be classified into two significant categories: fluvial and aeolian. Older subterranean alluvial plains, palaeo-channels, etc., are of fluvial morphology, while complex dunes, straight deep eolian, interdunal flat, and dunes are of eolian origin. The details of the Hisar district's landforms are shown on the map (Fig. 3.2).

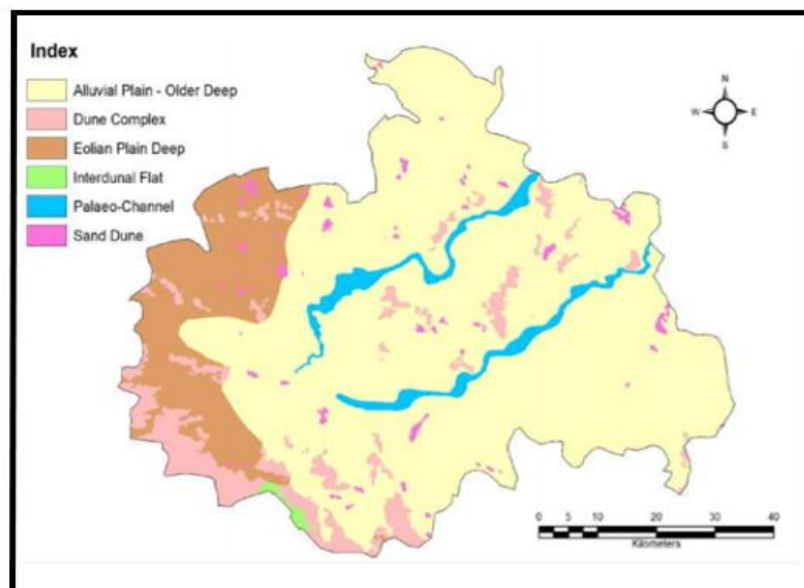


Fig. 3.2 Geomorphology of Hisar District, Haryana (adapted from CGWB 2017)

3.1.3 Hydrogeology of Hisar

Except for western Hisar, which is underlain by aeolian deposits, the district's northern, southern and eastern regions consist of alluvium formation. Besides, there are both shallow and deep aquifers. On the one hand, tube-wells are primarily used to tap the unconfined shallow aquifers for irrigation in the area. While on the other hand, boreholes are used to tap deeper aquifers that contain impermeable clays both on top and beneath them (CGWB, 2017). The geological formation of the Hisar district is on the map (Fig. 3.3).

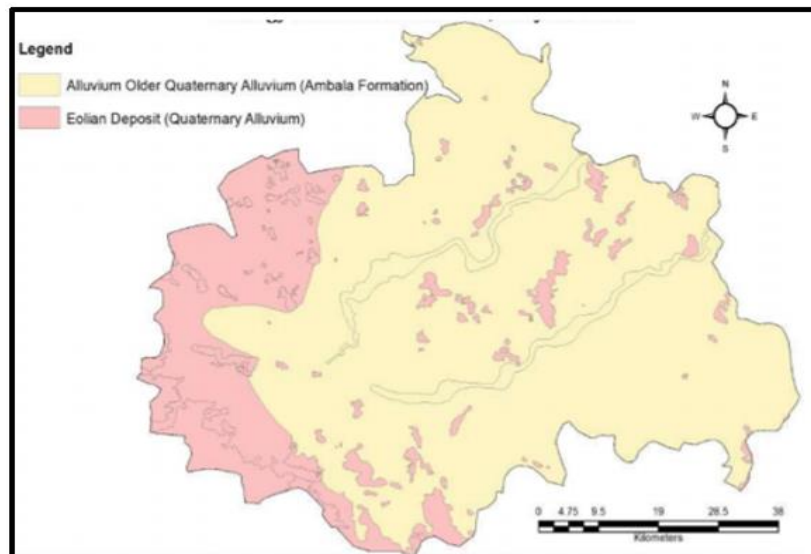


Fig. 3.3 Geological map of Hisar District (adapted from CWGB 2017)

3.2 Sampling

In the post-monsoon season of 2020, thirty (30) groundwater samples were collected to test and analyze physicochemical characteristics for drinking and irrigation purposes in Bhatol Jattan and its surrounding villages in Hisar District. The sites from which the samples were collected are situated about 1 km apart. The groundwater was supplied either by tube-well or handpump. The water samples were collected in December 2020, from an average depth of 7.59 m (Table 3.1), during the winter seasons. Table 3.1 contains information on the source (tube-well or handpumps), the original's age, and

the purpose for which the water is used. Before collecting the samples from the tube-wells or handpumps, the water was drawn for about 5-10 minutes to remove motionless water. The samples were garnered in ultra-pure water rinsed polyethylene terephthalate bottles, stored at 4°C in the laboratory, awaiting testing.

Table 3.1a Source, age, depth, and usage of groundwater from Hansi District

S. No	Source of groundwater sampling	Age	Supply Line	Depth	Use
1	Hand pump	2 yrs.	PVC pipe	7.62m	Drinking
2	Hand pump	10yrs.	PVC pipe	0.67m	Drinking
3	Hand pump	15yrs.	PVC pipe	7.62m	Drinking
4	Tube well	5yrs.	PVC pipe	9.75m	Agriculture
5	Hand pump	5yrs.	Steel pipe	7.62m	Drinking
6	Tube well	12yrs.	Steel pipe	11.58m	Agriculture
7	Tube well	7days	PVC pipe	9.15m	Agriculture
8	Tube well	2yrs	PVC pipe	8.54m	Agriculture
9	Hand pump	2yrs	PVC pipe	6.10m	Drinking
10	Tube well	5 months	PVC pipe	9.15m	Agriculture
11	Tube well	20 yrs	PVC pipe	12.19m	Agriculture
12	Hand pump	25 yrs	PVC pipe	7.62m	Drinking
13	Hand pump	15yrs	PVC pipe	7.32	Drinking
14	Hand pump	30 yrs	Steel pipe	6.71m	Drinking

Table 3.1b Source, age, depth, and usage of groundwater from Hansi District

S.No.	Source of groundwater	Age	Supply Conduit	Depth	Use
15	Hand pump	4years	PVC pipe	6.10m	Drinking
16	Hand pump	8years	Steel pipe	7.62m	Drinking
17	Hand pump	5years	PVC pipe	6.10m	Drinking
18	Hand pump	6months	PVC pipe	7.01m	Drinking
19	Hand pump	12years	PVC pipe	6.71m	Drinking
20	Hand pump	8years	PVC pipe	7.32m	Drinking
21	Hand pump	6years	PVC pipe	9.76m	Drinking
22	Tube well	25years	PVC pipe	10.67m	Agriculture
23	Hand pump	6years	PVC pipe	7.62m	Drinking
24	Hand pump	10years	PVC pipe	7.93m	Drinking
25	Hand pump	12years	PVC pipe	7.01m	Drinking
26	Tube well	10years	PVC pipe	7.62m	Agriculture
27	Hand pump	12years	PVC pipe	7.01m	Drinking
28	Hand pump	6years	PVC pipe	6.71m	Drinking
29	Hand pump	10years	PVC pipe	7.62m	Drinking
30	Hand pump	5years	PVC pipe	7.93m	Drinking

3.3 Processing and Analytical Procedures

After collecting and processing the groundwater, the samples were tested for EC and salinity, in $\mu\text{S}/\text{cm}$ and ppt, respectively; pH (unit less), total dissolved solids (TDS), calcium (Ca^{2+}), total alkalinity (TA), as CaCO_3 , and total hardness (TH) as CaCO_3 , all in mg/L. Besides, concentrations of phosphate (PO_4^{3-}) lithium (Li), sulfate (SO_4^{2-}), carbonate (CO_3^{2-}), as CaCO_3 , bicarbonate (HCO_3^-), as CaCO_3 , all in mg/L were checked. Additionally, nitrate (NO_3^-), magnesium (Mg^{2+}) sodium (Na^+), and potassium (K^+), expressed in mg/L were measured. And lastly, chloride (Cl^-), fluoride (F^-), and silica (SiO_2) in mg/L were measured, following the standard procedures proposed by the American Public Health Association, American Water Works Association, World Environment Federation (APHA, AWWA, WEF, 2017) and Bureau of Indian Standards (BIS 2012). Benchtop multiparameter water quality meter was used to measure EC, pH, salinity, and TDS. Volumetric analysis (acid-base titration), a conventional method, was applied to determining TH concentration in the groundwater, TA, and Cl^- contents. Other anions, such as SiO_2 , PO_4^{3-} and SO_4^{2-} were analyzed by microprocessor UV-VIS single-beam spectrophotometer, Labtronics model-LT-290. While NO_3^- was analyzed using a microprocessor LABINDA analytical UV-VIS double-beam spectrophotometer – UV 3092. Fluoride was measured using a portable digital multipara meter Orion Star A329 model. Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Li were analyzed using a flame photometer, Systronics model 128 μc . The results of all parameters that were studied are in Table 3.2a, 3.2b, and 3.2c.

3.3.1 Procedures for Analysis

Hydrogen ion concentration, represented by pH, measures the acidity and alkalinity in water. pH is expressed on the logarithmic scale, and its inverse represents the concentration of hydrogen ion. The colorimetric method can measure the pH by employing different indicators or using a hydrogen ion-sensitive electrode. pH, in this study, was measured using a pH meter, and the pH meter was standardized using an

aqueous solution of weak acid and base of pH 4, 7, and 9.2, and then the pH of the sample is determined.

3.3.2 Total dissolved solids (TDS)

TDS come about by organic and inorganic matters dissolved in water. They contain no gas or colloids. The TDS in the samples were measured using a Benchtop Multiparameter Water Quality meter.

3.3.3 Electrical Conductivity (EC)

EC represents the ability of a material or solution to allow the flow of electricity through it. In this study, EC was measured using a Benchtop Multiparameter Water Quality meter. The application of this technique gives the concentrations of major ions or common ions present in the water. The EC meter was calibrated with standard KCL solution (0.10N). The KCL solution was made ready by liquifying 0.7474g of KCL in 100ml of water. The EC of the stock solution was set at 12.88 mhos/cm at 25°C. Having calibrated the instrument for the measurement of EC, the EC of all samples was then measured.

3.3.4 Hardness

All polyvalent cations in the water cause hardness, and it is called hardness of the water. Scholars also define hardness as the totality of calcium and magnesium expressed as calcium carbonate in mg/L. Hardness may be carbonate or non-carbonate. Suppose the total hardness is the same as total alkalinity, it is called carbonate hardness, but if total hardness is more than the total alkalinity, the hardness is called non-carbonate hardness. If the sample's hardness is below than or the same as the total carbonates and bicarbonates, then the hardness in that water is carbonate hardness.

Requirements

- 0.01M Ethylenediamine Tetraacetic Acid solution: Dissolve 3.732gm of EDTA disodium salt to form volume 1 liter.

- Ammonium acetate buffer solution: 1 ml
- EBT indicator

Procedure

- Sample taken in conical flask for titration: 25ml
- Add 1ml of ammonium acetate solution to the sample in the flask, and then a pinch of EBT indicator
- It was titrated against EDTA standard solution until there was a change of color from reddish-pink to blue

Calculations

Where,

M_2 - Molarity of standard of EDTA solution

V_2 - Volume of EDTA solution used (ml)

V_1 - Volume of the sample taken (ml)

3.3.5 Alkalinity

The concentration of all the ions present in the water, capable of neutralizing the acids, is referred to as the water's alkalinity. Or, it may also be defined as the ability of water to neutralize the acid. Significant alkalinity types are carbonate, bicarbonate, and caustic alkalinity caused by inorganic mineral salts or by the biological decomposition of organic matter or dissolved gases in water.

Procedure

- 25ml of groundwater sample water was collected
- 2-3 drops of phenolphthalein were show make visible the color change of the solution. After the addition of phenolphthalein, the sample will change from colorless to pink. If there is no color change, then the alkalinity due to phenolphthalein is zero. If, however, the opposite occurs, then the alkalinity can

be determined by titrating the pinkish solution with HCl until the color vanishes. Whether or not the pink color shows, proceed with the titration process using the water sample that phenolphthalein was added to before the color disappearance.

- At this point, add 2-3 drops of methyl orange as an indicator and titrate the sample till the yellow color shown after the addition of methyl orange changes to orange.
- Now the solution has change to range, one can calculate the total alkalinity at this point.

Calculation

Where, A = volume (ml) of HCl used only with phenolphthalein

B = volume (ml) of HCl; total HCl use with both indicators that was used with both phenolphthalein and methyl orange

3.3.6 Cations (Na, K, Mg, Li)

Cations concentration in this study is calculated using Flame photometry – a division of atomic spectroscopy – which focuses on electromagnetic radiation captivated and formed by atoms. The atomic species, which are investigated, are thrilled by the illumination.

Procedure

- Open the lid, insert a suitable filter, and close the lid
- Next, enclosure the PVC free end and remove the duct in distilled or ultrapure water.
- Adjust the instrument. Make sure that the device has 00 after adjusting it
- To get an on-screen readout display of 100, ensure you adjust each channel until it reads 100

- Replicate the 3rd and 6th steps until 00 and 100 are shown only when the blank solution and the standard solution, which has the top most concentration, are aspirated into flame.
- Remove the PVC and the duct in distilled or ultrapure water for 2 – 3 minutes to wash the chamber carefully.
- Again, the PVC was put into it, and capillary actions absorbed some sample; the concentration of the parameter being checked was recorded from the displayed on the screen.
- Intermittently insert the standard solutions whose concentrations are known from the calibration of the instrument. Verify the 00 with the blank solutions.

Sodium

Sodium is one of the essential cations that naturally occur. Sewage from residential places, which supply sodium to freshwater, is one source of sodium. The sodium salt contains high solubility in water. Irrigation waters do not need high sodium concentration since water with high sodium is not suitable for agricultural use because of chlorides and sulfide.

Calcium

Ca²⁺ is a silvery species, light in weight, and an alkaline earth element. It is a fundamental part of natural substances – minerals, rocks, and ores. The solubility of minerals in water is a determinant of weathering rate—besides, the disproportionate suspension of calcium salt instigates the rise of water’s total hardness. When Ca²⁺ occurs in the water or soil water line, it regulates the soil’s ability to exchange positive ions and absorb nutrients from the ground. Moreover, the water or salt line’s occurrence impacts positive ions exchange regarding its contents in water and deteriorates the irrigation water quality. Whenever pH is high, the Ca²⁺ amounts often get deposited in the form of CaCO₃. In this research, the Ca²⁺ concentration was determined by using the Systronics make Flame Photometer 128μC model.

Potassium

K^+ is also one of the elements that exist naturally. But unlike sodium, calcium, and magnesium, the amount of K^+ is often lower than the Na^+ , Ca^{2+} , and Mg^{2+} . If K^+ is not precipitated, its impacts are somehow minor, like sodium. In this research, the K^+ concentration was determined by using the Systronics make Flame Photometer 128H model.

Lithium

Lithium is said to be the lightest metal and the lightest solid element found on the periodic table. Li is a soft element found in group one on the periodic table. Like other alkalis, the Li can be found in mineral oil and is very flammable. It does not occur freely in nature; however, it seems like ionic compounds. The species, in its ionic form, is soluble in ocean water and gotten from seawaters. The concentration of lithium was determined using the Systronics made Flame Photometer 128 μ C model.

Magnesium

Mg^{2+} occurs in natural water bodies; however, its concentration in those natures is usually lower than Ca^{2+} . Mg^{2+} is also a critical species as regards its contributions to total hardness. Magnesium concentration in this study was determined as the difference between total hardness and calcium hardness.

3.3.7 Anions (SO_4^{2-} , PO_4^{3-} , NO_3^- , SiO_2^{4-} , Cl^-)

Sulfate

The technique by which sulfate is measured is predicated upon the concept that Ba and SO_4^{2-} will form solids with nanometer size. The precipitate form by Ba and SO_4^{2-} is heightened in HCl acid, NaCl, and $C_3H_8O_3$.

The concentration of sulfate was determined using a microprocessor UV-VIS single-beam spectrophotometer, Labtronics model-LT-290 at 420mm.

Requirements

- Gelatin
- BaCl₂
- HCl
- Na₂SO₄

Preparation of reagents

1. Conditioning reagent

- Dissolve 0.3 gm gelatin in 100ml distilled water, warm, and dissolve. Cool and keep in the refrigerator for 12 hours.
- Allow it to come to room temperature and add 3gm of BaCl₂ and dissolve.
- Allow standing for 2 hours.

2. Stock solution

- Dissolve 0.14gm anhydrous sodium sulfate in 1L of distilled water.
- Take 1L of concentration HCl and add to 9L of distilled water.

Procedure

- To make standard solutions, prepare dilutions from the stock solution from concentration varying to 5 to 100ml.
- Take a 20ml sample.
- Add 1 ml of HCl
- Add 1ml of conditioning reagent and mix for 30 seconds.
- Wait for 30 minutes and read absorbance.
- By plotting a graph, obtain the data (concentration vs. percentage absorbance).
- Trace the points for the sample against measured absorbance.

Total Phosphate

The digestion of sulphuric acid (H₂SO₄) and nitric acid (HNO₃) was applied as a technique used to determine total PO₄³⁻. The concentrated HNO₃ converts bound PO₄³⁻ to a boundless form. So, using ammonium molybdate and stannous chloride (SnCl₂ ·

2H₂O) method, the total PO₄³⁻ in the sample digested with concentrated acid can be precipitated, detected, and read directly by spectrophotometer.

PO₄³⁻ is a critical nutrient in the growth of algae. The augmentation of phosphate subsidizes significantly to the development of algae. The most significant source of PO₄³⁻ is the release of sewage, detergents, and agricultural runoff.

Procedure

- 10 ml sample was taken, 0.4ml of concentrated H₂SO₄ and 2 ml of concentrated HNO₃ were added.
- Set for 5-10 minutes at 200Kw, the sample was kept in the digestion unit, and the microwave was turned on.
- After digestion, the solution was neutralized with NaOH. The solution turned pink – a color that appeared after the addition of two drops of phenolphthalein.
- Then, NaOH was added to the digested samples.
- 10ml of the sample was measured, and 0.4ml of ammonium molybdate was added and mixed well.
- Five drops of SnCl₂ · 2H₂O were added to the solution. The resulting solution was thoroughly mixed with the solution obtained in the previous step.
- After a wait for 5 minutes, the solution appeared blue.
- 690 nm was the wavelength at which the test was conducted using the spectrophotometer.

Nitrate

Nitrate is a significant nutrient for eutrophication. It has essential sources, such as domestic sewage, natural runoff, and agricultural wastes. NO₃⁻ in water is not harmful as it serves as an indicator of the decomposition of living things. However, if nitrate is present in surplus, it affects babies and results in methemoglobinemia or blue baby.

Nitrate was measured by using the nitrate electrode by a multiparameter meter. Firstly, the nitrate electrode was calibrated, and then the concentration of nitrate was measured by dipping the electrode in each water sample.

Silica

Silicon is the second most abundant naturally occurring element on the earth. It looks like SiO_2 and is united with metallic elements in many complex silicate mineral deposits when rocks containing silica weather, groundwater, and surface water get affected, provided that the weathered material contained excess silica. Volcanic and polymeric states and silicic acids or waters heated with the earth are often rich in silica. The SiO_2 concentration in natural water bodies most generally lies between 1 - to 30mg/L. However, high amounts - 100 mg/L of SiO_2 are typically seen; besides, concentration SiO_2 above 1000mg/L are often seen in brines or brackish waters. SiO_2 is objectionable in many industries because it forms silica and silicate scales. These silica and silicate scales that developed in metal conduits and equipment are challenging to remove. Silica is detached by distillation or by reverse osmosis in some industries.

The concentration of SiO_2 was determined using Molybdosilicate Method.

Requirements

- Sodium bicarbonate – NaHCO_3
- H_2SO_4
- 1.0 N – HCl 1 +1

Ammonium molybdate reagent Procedure

1. Developing color
 - Collect 50.0 mL sample
 - Add 1.0 mL HCl and 2.0 mL ammonium molybdate reagent to the sample.

- Mix the resulting solution obtained from the previous step and wait for 5 - 10 minutes.
 - Then, add oxalic acid - 2.0 mL solution and mix thoroughly.
 - Observe the color between 2 – 15 mins to obey Beer's law; ensure that the solution shows yellow color.
2. Detecting molybdate reaction with silica, digest sample with NaHCO_3 color development
- Omit the digestion process if only all the SiO_2 reacts with molybdate.
3. Preparation of standards
- About 45 mL, of which NaHCO_3 is 200 gm, and 1.0 N H_2SO_4 is 2.4 mL, must be added to the standard solutions, only if NaHCO_3 pretreatment is used.
 - Dilute to 50.0 mL
4. Correction for color or turbidity
- To correct color or turbidity, measure equal volumes of two different blank samples in the test tubes and carry out the regular procedure, including sodium bicarbonate treatment.
 - Add all reagents as directed to one of the blanks and add HCl and oxalic acid to the other blank without adding ammonia molybdate.
 - Use the blank sample, which contains no molybdate.
 - Read molybdate absorbance to adjust the photometer to zero absorbance.
5. Prepare a calibration curve from a series of approximately six standards to cover the optimum ranges.
- Foremost, use distilled water to set the instrument at zero absorbance with
 - Read all standards, including a reagent blank, against distilled water.
 - Graph micrograms silica in the final (55 mL) developed solution against photometer readings.

- Run a reagent blank and at least one standard with each group of samples to confirm that the calibration curve previously established has not shifted.

Calculations

$\text{SiO}_2 \text{mg/L} = \mu\text{g SiO}_2 (\text{in } 55\text{mL of final volume}) \text{ mL of sample}$

Chloride

The presence of chloride in water in high concentration designates its pollution due to industrial waste or sewage. In natural freshwater, its concentration is low.

Reagents

- 0.02 N silver nitrate solution
- 5% potassium chromate solution

Procedure

- 25 mL sample was taken in a conical flask
- 2-3 drops of K_2CrO_4 indicator were added to the sample
- The resulting solution was titrated against AgNO_3 until the yellow color obtained after adding K_2CrO_4 changed to light brick red. The titration was done in duplicate

Calculations

$$\text{Cl}^-(\text{mg}) = N_2 V_2 \times 35.5 \times 1000 V_1$$

Where,

N_2 = Normality of standard AgNO_3 solution (0.0141 N)

V_2 = Volume of AgNO_3 solution used (in mL)

V_1 = Volume of the sample taken (25 ml)

CHAPTER

4

RESULTS

&

DISCUSSION

4.1 Groundwater consideration for drinking purposes

4.1.1 Hydrogen ion (pH)

Results indicate that the groundwater pH values vary from 6.5 to 7.4 (mean, 6.98) (Table 4.1). Though the average pH value represents slightly acidic groundwater, all the samples' readings are within the prescribed limits (6.5 -8.5) (BIS, 2012). The water's slight acidity may be due to the presence of acidity-causing substances such as Cl^- and SO_4^{2-} and lowering concentrations constituents like Ca^{2+} and Mg^{2+} (Haritash et al., 2017). Besides, the low pH readings are, to some extent, due to the impact of fertilizers such as superphosphate and ammonium sulfate in agricultural fields (Appelo and Postma, 2005). Compared to international standards, 6.5 - 9.5 (WHO, 2017) (Table 4), all groundwater samples obeyed the standards.

Table 4.1 Minimum, maximum, and mean concentrations of physicochemical parameters of groundwater

Parameters	Min.	Max.	Range	Mean	Std. Dev
pH	6.5	7.3	0.8	6.98	0.17
TDS mg/L	308	5530	5222	1668.67	1321.93
EC, $\mu\text{s}/\text{cm}$	617	11260	10643	3324.17	2650.99
Salinity, ppt	0.23	6.15	5.92	1.72	1.49
Cl^- , mg/L	100	4400	4300	878.43	994.12
PO_4^{3-} , mg/L	0.05	0.25	0.19	0.1	0.05
F^- , mg/L	0.49	5.5	5.01	2.412	1.44
NO_3^- , mg/L	0.21	23.22	23.01	3.73	4.56
SO_4^{2-} , mg/L	156.88	371.59	214.71	305.44	56.71
SiO_2 , mg/L	34.09	65.89	31.8	48.92	8.66
TH, mg/L CaCO_3	58	3160	3102	1239.93	832.99
Ca^{2+} , mg/L	3.94	318	314.06	137.49	90.26
Mg^{2+} , mg/L	46.6	540	494.4	175.49	349.59
TA, Mg/L CaCO_3	390	1160	770	665.67	162.6
CO_3^{2-} mg/L CaCO_3	0	180	180	59.33	39.82
HCO_3^- mg/L CaCO_3	350	980	630	607	140.47
Na^+ , mg/L	36.1	1061.25	1025.15	384.67	298.35
K^+ , mg/L	2.5	383.7	381.2	28.55	70.29
Li, mg/L	0	1.5	1.5	0.54	0.45

*Not Detected

4.1.2 Electrical Conductivity (EC)

EC varies from 617 to 11,260 $\mu\text{S}/\text{cm}$ (mean, 3,324.17 $\mu\text{S}/\text{cm}$). EC surpasses the (BIS, 2012) maximum acceptable limit in approximately 37% of the samples. Salinity and phosphate values range from 0.23 to 6.16 ppt and 0.05 to 0.25mg/L, respectively, with the mean values being 1.71 ppt for salinity and 0.1 mg/L for phosphate (Table 4.1).

4.1.2 TDS

TDS is an essential determinant of groundwater water portability for domestic use. High TDS in water may be due to inorganic species' presence, specifically high-level anions and soluble salts. Livestock waste, dissolved minerals, manganese, and irons from landfills and agricultural land may also contribute to the high TDS. The concentrations of TDS in the samples range from 308 to 5,530 mg/L. Eight (8) representatives (~27%) exceed the permissible limit, 2,000mg/L (BIS, 2012) (Table 4.2). Almost all sampling locations that have high EC contain high TDS.

4.1.3 TA

The ability of water to neutralize strong acid is known as total alkalinity. Bicarbonate, carbonate, and hydroxyl ions are the species responsible for total alkalinity in water. The values of TA vary from 390 to 1,160mg/l, with a mean equivalent of 665.67mg/l. About 70% of the samples exceed the prescribed standard of 600mg/l (BIS, 2012), and approximately 83.4% exceed the 500mg/l standard (WHO, 2017) (Table 4.2). HCO_3^- was in the range of 350 to 980 mg/L (mean, 607 mg/L), while CO_3^{2-} has its minimum, maximum and average reading as 0, 180, and 59.33mg/L, respectively.

4.1.4 Cations chemistry

The cations present in groundwater with high concentrations (> 1mg/L) are calcium, magnesium, potassium, and sodium (Younger 2007), and the primary cause of hardness in water is polyvalent cations – calcium and magnesium. TH vary from 58 to 3,160 mg/L, with average concentration 1239.93mg/L. Comparing TH to TA, roughly

80% of the former samples are higher than the latter. According to Jain et al. (2010), Ca^{2+} concentration generally surpasses Mg^{2+} content due to their presence in rocks.

Table 4.2 Comparison of groundwater quality parameters with the Indian (BIS) and International (WHO) standards

Parameter	Units	Min.	Max	Mean±	Std.Dev	BIS	WHO	Source No. exceeding Max. Permissible limit	
						Standards (Max Permissible limit)	Standards (Max Permissible limit)	As per BIS standards	As per WHO standards
pH	-	6.5	7.3	6.98±	0.17	6.5-8.5	6.5-9.5	-	-
TDS	mg/L	308	5530	1668.67±	1321.93	2000	1200	4,6,7,8,9,10,11,26	4-11,17,18,22,24,
EC	µS/cm	617	11260	3324.17±	2650.99	3000	-	4-11,18,26,29	26,29,30
Salinity	ppt	0.23	6.15	1.72±	1.49	-	-	-	-
Cl ⁻	mg/L	100	4400	878.43±	994.12	1000	300	4,6-8,10-11	4-20,22,24-26,30
PO ₄ ³⁻	mg/L	0.05	0.25	0.1±	0.05	-	-	-	-
F ⁻	mg/L	0.49	5.5	2.412±	1.44	1.5	1.5	1,2,6-8,11-13,15,16,18-21,29	1,2,6-8,11-13,15,16
NO ₃ ⁻	mg/L	0.21	23.22	3.73±	4.56	45	50	-	18-21,29
SO ₄ ²⁻	mg/L	156.9	371.59	305.44±	56.71	400	250	-	-
Silica	mg/L	34.09	65.89	48.92±	8.66	-	-	-	-
T.H	mg/L	58	3160	1239.93±	832.99	600	500	1,4-12,14,17-19,22-24,26-30	1,2-14,16-19,22-30
Ca ²⁺	mg/L	3.94	318	137.49±	90.26	200	300	4,6-11	4,8
Mg ²⁺	mg/L	46.6	540	175.49±	349.59	100	-	1,4,6,8,10-13,16,17,19,22-24,26,30	-
T.A	mg/L	390	1160	665.67±	770	600	500	1,4-8,10-16,18,22-24,27-30	1,4-8,6-19,22-24
CO ₃ ²⁻	mg/L	0	108	34.45±	108	-	-	-	26-30
HCO ₃ ⁻	mg/L	427	1195.6	740.81±	768.6	-	-	-	-
Na ⁺	mg/L	36.1	1061.3	384.67±	384.67	-	200	-	4-8,10-15,17,19,22,24
Li	mg/L	0	1.5	0.54±	0.54	-	-	-	26,28-30
K ⁺	mg/L	2.5	383.7	381.2±	28.55	-	-	-	-

Observations from the data analysis in this study show that only 43% of the samples' calcium concentration exceeds the study area's magnesium content. Besides, 50% of the samples outdo the maximum Mg^{2+} standard of 100 mg/L as per BIS. Eight samples (8), representing about 27%, transcends the permissible value - 200mg/L (BIS, 2012) - of calcium content in drinking water. The calcium content ranges from 3.94 to 318mg/L (mean equivalent, 137.49mg/L). As for sodium and potassium, their concentrations in the study area vary from 36.1 to 1,061.25mg/L (mean, 384.67mg/L) and 2.5 to 381.2mg/L (mean, 28.55mg/L) respectively. As indicated by Naidu et al. (1985) and Singh et al. (2006), a high sodium concentration in the samples results from the soil's mineral. With about 84% of the samples exceeding the maximum permissible limit of 200mg/l (WHO, 2017), it can be noted that there is high weathering of felspar and montmorillonites in the study area (Naidu et al., 1985; Singh et al. 2006).

4.1.5 Anions chemistry

According to Young (2007), the main anions with the highest concentrations (>1 mg/L) in groundwater are chloride, sulfate, and bicarbonate, an assertion that validates the findings of this study. Of All anions checked in the study area, chloride, sulfate, and bicarbonate recorded the maximum averages as 878.43, 305.44, and 59.33, respectively.

Six (6) samples of chloride surpass the permissible limit of 1000mg/L of the BIS standard; for the WHO standard (300mg/l), twenty-two (22) samples (~ 74%) exceed it. Halite and related sedimentary bedrock minerals may cause leaching of chloride during groundwater infiltration or recharge. High Cl^- concentration may also be derived from rainfall and dryfall (windblown dust containing salt). It could also be due to the irrigation—return flows and chemical fertilizers (Subba Rao et al. 2012). The samples' nitrate was in the range of 0.21 to 23.22 mg/l (mean 3.73mg/l) (Table 4.1). Observation shows that nitrate was within the prescribed limits of both BIS and WHO, 40 and 50mg/l, respectively. Though sulfate was also within the permissible limits of 400mg/l

as per the Indian standards, twenty-six (26) samples (~ 87%) exceeds 250mg/l (WHO, 2017). SiO₄⁴⁻ had 34.09mg/L as its minimum value and 65.89 mg/L as maximum.

4.1.6 Water Quality Index (WQI)

To further assess the samples for drinking, the Weighted Arithmetic Water Quality Index (WQI) values were also calculated based on Cl⁻, total hardness (TH), total alkalinity (TA), NO₃⁻, SO₄²⁻, Ca, Mg and F⁻. The equation used to calculate the WQI was employed by Brown et al. (1972).

$$WQI = \frac{\sum W_n Q_n}{\sum W_n} \dots\dots\dots \text{Eq. 1}$$

where Q_n - quality rating for each parameter [$Q_n = \frac{(v_n - v_o)}{(s_n - v_o)} * 100$]; v_n is the mean concentration of the nth parameter, and s_n is the nth parameter's desirable standard, v_o is the ideal value of the parameter in pure water (it id 0 for all parameters, except pH is 7.0); W_n is the unit weight of each parameter – (W_n = K/S_n); K=1/(Σ/1S_n).

Results generated from Eq. 1 show that 60% of the water in the study area is unfit (WQI > 100) for drinking, 23.33% is poor (51 < WQI < 75), and only 16.67% is good (26 < WQI < 50) for drinking.

Predicated upon the results from the analysis conducted in this study, and remembering that almost all samples exceed both BIS and WHO standards, it can be inferred that groundwater was found unsafe for drinking.

4.2 Groundwater consideration for irrigation purposes

The use of groundwater for irrigation is somewhat essential for the survivability of man. This importance makes irrigation water supply cardinal develop and maintain viable irrigation projects; however, the farmers and agricultural institutions cannot achieve the project's development and maintenance without controlling the soil's alkali and salt (Haritash et al., 2008). According to Haritash et al. (2008), groundwater characteristics for agriculture that are essential in defining its quality include the

following: (1) concentration of different elements that may be toxic to plants (2) total concentration of soluble salts; (3) relative proportion of sodium to other principal cations (magnesium, calcium, and potassium) and (4) the bicarbonate concentration, under some conditions, related to the contents of calcium and magnesium. The paper considers the classification and assessment of groundwater for irrigation purposes using various indicators from this backdrop. The assessment indices are sodium adsorption ratio (SAR), residual sodium carbon (RSC), percent sodium (%Na), soluble sodium percent (SSP), permeability index (PI), and Kelly's ratio (KR). Others include hydrochemical facies, base-exchange, and meteoric genesis indices.

4.2.1 Sodium Adsorption Ratio (SAR)

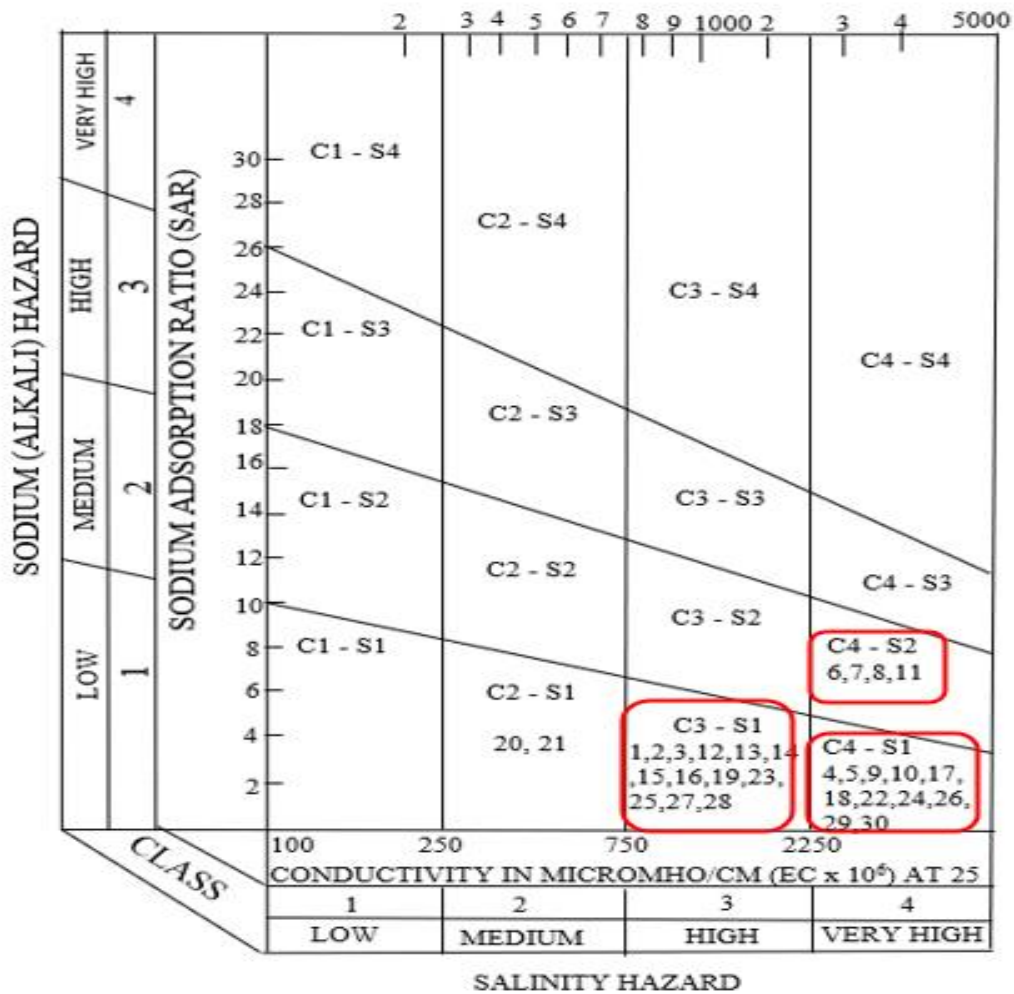
SAR is one of the indices that researchers often use to assess water's suitability for irrigation purposes. It measures the sodium concentration in the water. It expresses the fraction of sodium ions in the water to the sum of calcium and magnesium ions in the water sample. Soil alkali, also known as sodium hazard, is typically expressed as SAR (Kumar et al., 2014). Singh et al. (2006) asserted that high sodium concentration in water is unsuitable for soil irrigation since excess sodium may deteriorate soil quality. The sodium adsorption ratio values were calculated using the below equation (Richards 1954; Kalra and Maynard 1991).

$$\text{SAR} = \text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+}) / 2 \dots\dots\dots \text{Eq. 2}$$

The Na^+ , Ca^{2+} , and Mg^{2+} can be expressed in meq/l (Kalra and Maynard 1991) and mg/l (Richards 1954). Groundwater samples are classified based on the following SAR values (Singh et al., 2006). In class I, if $\text{SAR} < 3$, there is no sodium problem. Class II has SAR in the range of 3 – 6 for the low sodium class and having few problems, except with sodium-sensitive crop. The increasing concern with medium sodium is in Class III of SAR between 6 – 8. Class IV is not generally recommended since it contains a high sodium range of 8 – 14. And the final class, V, with very high sodium, is unsuitable and must therefore be disregarded. The SAR was in the range of 1.03 – 12 meq/l (mean, 6.05meq/l) (Table 5). The samples' classification for irrigation shows that 30% of the

samples are from class I, 23.33% are found in Class II, and 16.66% are from class III. Nine (9) samples (30%) are from class IV and no class V samples. Besides using Eq. 1 to calculate the SAR and classify groundwater for irrigation, Fig. 4.1 was also used to determine irrigation suitability and classify samples. Thirteen (13) samples (43.33%) are of C₃ – S₁. Eleven (11) samples (36.66%) are of C₄ – S₁. Four (4) samples (13.33%) are of C₄ – S₂, and finally,

Fig. 4.1 US salinity diagram for calculated values of SAR



two (2) samples (6.67%) are of C₂ – S₁. These results confirm the findings obtained from calculating SAR. Based on the preceding indices, it is visibly evident that the water is not recommended for irrigation.

4.2.2 Residual Sodium Carbonate (RSC)

It is likely for calcium and magnesium to precipitate as carbonate in natural waters with high bicarbonate concentration. If the total calcium and magnesium concentrations are less than total carbonate concentrations, excess carbonate may reduce the water quality (Singh et al., 2011). This study considers using RSC (Eaton 1950) to calculate the residual sodium carbonate and check the samples' suitability for irrigation. Eq. 3 can be used to calculate RSC.

$$\text{RSC} = (\text{CO}_3^{2-} + \text{HCO}_3^-) - (\text{Ca}^{2+} + \text{Mg}^{2+}) \dots\dots\dots\text{Eq. 3}$$

where CO_3^{2-} , Ca^{2+} , HCO_3^- and Mg^{2+} are expressed in mEq/L. Based on the RSC, irrigation water may be suitable, moderately suitable, and unsuitable. If RSC is less than 1.25 meq/l, the water is suitable. The water is slightly suitable if $1.25 < \text{RSC} < 2.5$ meq/L, and if RSC is greater than 2.5, the water is inappropriate for irrigation. From Table 5, RSC ranges from -20.78 to 8.41 (mean, -2.78). Additionally, 50% of the samples' values were < 1.25 , satisfying condition one. The RSC values of 14 samples (~47%) are negative. Only 33.33% of the samples satisfy the condition, which has RSC values greater than 2.5, with 16.66% of the samples RSC values found between 1.25 to 2.5. As per the above index, the groundwater samples can be considered safe for irrigation purposes.

Table 4.3 Computed values of physicochemical parameters to assess suitability for irrigation

S. No.	SAR	%Na	RSC	SSP	KR	PI
1	1.03	30.42	4.98	19.16	0.24	51.85
2	2.57	45.14	1.88	44.41	0.79	70.49
3	2.05	39.79	2.78	38.65	0.63	69.38
4	9.49	54.7	-17.45	54.64	1.2	59.38
5	7.64	55.08	2.14	54.76	1.21	64.11
6	9.72	58.21	-9.53	57.97	1.38	64.19
7	11.43	59.75	-18.11	59.55	1.47	63.98
8	12	61.12	-15.73	60.97	1.56	65.64
9	1.97	42.66	-13.62	22.88	0.29	49.57
10	5.98	47.67	-11.58	47.29	0.89	54.86
11	11.36	64.2	-5.53	63.97	1.78	70.51
12	7.45	60.87	2.45	60.49	1.53	72.13
13	4.78	54.89	3.27	53.85	1.17	71.58
14	4.17	56.51	3.13	50.01	1	72.71
15	6.75	63.99	8.41	63.46	1.74	80.94
16	2.69	40.92	3.62	37.17	0.59	60.11
17	6.23	53.87	-3.88	53.73	1.16	63.58
18	1.33	15.45	-20.78	14.13	0.16	23.61
19	4.78	51.45	-1.1	50.72	1.03	63.91
20	4.06	58.01	4.42	57.69	1.36	83.92
21	1.54	44.83	5.651	43.08	0.75	112.11
22	9.62	65.58	-1.07	65.44	1.89	74.22
23	2.79	38.99	1.5	38.05	0.61	58.13
24	9.53	65	-0.61	64.63	1.83	73.53
25	2.59	42.99	1.06	41.53	0.71	64.62
26	10.75	68.92	-2.35	68.66	2.19	76.95
27	4.18	53.88	3.56	53.46	1.15	76.14
28	5.88	65.95	6.65	65.79	1.92	88.96
29	9.68	66.36	-1.54	66.2	1.96	74.77
30	7.58	60.58	1.85	60.34	1.52	71.99
Min	1.03	15.45	-20.78	14.13	0.16	23.61
Max	12	68.92	8.41	68.66	2.19	112.11
Mean	6.05	52.93	-2.78	51.09	1.19	68.26

4.2.3 Soluble Sodium Percentage (SSP)

Many researchers use Wilcox (1955) index to determine the SSP and classify water for irrigation. As proposed by Wilcox, SSP values were calculated using Eq. 4.

$$SSP = Na^+ / (Ca^{2+} + Mg^{2+} + Na^+) \times 100 \dots\dots\dots Eq. 4$$

SSP < 50 signifies good irrigation water quality, and SSP > 50 implies that the water is unsuitable (Wilcox 1955; USDA 1954). From the SSP computation for all samples, the minimum and maximum values are 14.13 and 68.66, respectively, with a mean of (51.09) (Table 4.3). Additional results reveal that nineteen (19) samples (63.33%) exceed 50. One sample - (#14) was neither less nor more than 50, with the remaining ten (10) samples (33.33%) observed to be below 50. Thus, the quality of groundwater is unsuitable for irrigation.

4.2.4 Kelly's Ratio (KR)

Like SAR, SPP, etc., KR is also used to classify groundwater for irrigation. If KR < 1, there is an excess of Na, and if KR > 1, then the water is short of Na (Raju et al., 2013). KR < 1 indicates good water quality for irrigation (Karanth 1987). Kelly's ratio can be computed using Eq. 5.

$$KR = Na / Ca + Mg \dots\dots\dots Eq. 5$$

The KR range for all samples is 0.16 to 2.191 (mean, 1.19). The results depict that 63.66% of the samples are > 1, 33.33% are < 1 (Table 4.3), and one sample – 14 is equal to 1—these outcomes provide additional confirmation that the water quality is unsafe for irrigation since it is short of Na (See Fig. 4).

4.2.5 Permeability Index (PI)

Soil or rock permeability is defined by its capacity to convey liquid. It is governed by sodium, soluble salt, magnesium, calcium, and bicarbonate concentrations in the rock or soil, which may harm the water quality. Doneen (1964) formulated PI as in Eq. 6.

$$PI = \{[(Na + K) + (HCO_3)^{1/2}] / [(Ca + Mg + Na + K)] \times 100\} \dots\dots\dots Eq. 6$$

where Na⁺, K⁺, Ca²⁺, Mg²⁺, and HCO₃⁻ ions are measured in mEq/L. All samples' PI values range from 23.61 to 112.11 (mean, 68.26) in this study.

4.2.6 Magnesium Hazard (MH)

Magnesium and calcium, also known as alkaline earth, often sustain a state of groundwater steadiness. (Adimalla and Venkatayogi 2018). The presence of excess magnesium concentration in water deteriorates the soil quality, thereby making the soil alkaline. MH for all samples was calculated using Eq. 7.

$$MH = [Mg / (Ca + Mg)] \times 100 \dots\dots\dots Eq. 7$$

where Mg²⁺ and Ca²⁺ ions are in mEq/L.

Results depict that 93.3% of the samples are > 50 (unsuitable) and only 7.7% are < 50 (suitable) for irrigation.

4.3 Hydrochemical classification of groundwater by type

4.3.1 Base-exchange and meteoric genesis indices

According to Soltan (1998), groundwater may be classified on base-exchange and meteoric genesis indices. The groundwater was classified based on base-exchange and meteoric genesis using Eq. 8 and Eq. 9 (Soltan 1998).

$$r_1 = (Na^+ - Cl^-) / SO_4^{2-} \dots\dots\dots Eq. 8$$

where r₁ = base-exchange index, and Cl⁻, Na⁺ and SO₄²⁻ are expressed in mEq/L. The water type is a factor of r₁. If r₁ < 1, the water type is Na⁺- SO₄²⁻, while if the r₁ > 1, the water type is Na⁺- HCO₃⁻. Predicated upon the results generated from Eq. 8, twenty-nine (29) samples ~97% are of Na⁺- SO₄²⁻ type, r₁ < 1 and only one (1) sample is Na⁺- HCO₃⁻, r₁ > 1 (Table 4.4).

$$r_2 = [(K^+ + Na^+) - Cl^-] / SO_4^{2-} \dots\dots\dots Eq. 9$$

where r_2 = the meteoric genesis index, and K^+ , Na^+ , Cl^- and SO_4^{2-} are concentrations expressed in mEq/L. The water may be classified as deep meteoric infiltration type or shallow meteoric infiltration type as per the index. The water is deep meteoric percolation type if $r_1 < 1$; otherwise ($r_1 > 1$), it is a shallow meteoric percolation type. Similar to base-exchange, all samples are of deep meteoric infiltration type, except one (sample 29) with a shallow meteoric infiltration type.

Table 4.4 Groundwater classification according to r_1 and r_2 readings

S. No.	Base-exchange index (r_1)	Water type	Meteoric genesis index (r_2)	Water type
1	-0.09	Na ⁺ - SO ₄ ²⁻	0.19	Deep meteoric
2	-0.06	Na ⁺ - SO ₄ ²⁻	-0.04	Deep meteoric
3	0.05	Na ⁺ - SO ₄ ²⁻	0.08	Deep meteoric
4	-11.32	Na ⁺ - SO ₄ ²⁻	-11.03	Deep meteoric
5	0.07	Na ⁺ - SO ₄ ²⁻	0.11	Deep meteoric
6	-2.28	Na ⁺ - SO ₄ ²⁻	-2.23	Deep meteoric
7	-5.41	Na ⁺ - SO ₄ ²⁻	-5.36	Deep meteoric
8	-5.01	Na ⁺ - SO ₄ ²⁻	-4.97	Deep meteoric
9	-1.34	Na ⁺ - SO ₄ ²⁻	-0.07	Deep meteoric
10	-4.28	Na ⁺ - SO ₄ ²⁻	-4.24	Deep meteoric
11	0.36	Na ⁺ - SO ₄ ²⁻	0.41	Deep meteoric
12	0.19	Na ⁺ - SO ₄ ²⁻	0.23	Deep meteoric
13	-0.26	Na ⁺ - SO ₄ ²⁻	-0.18	Deep meteoric
14	-1.32	Na ⁺ - SO ₄ ²⁻	-0.9	Deep meteoric
15	-0.08	Na ⁺ - SO ₄ ²⁻	-0.02	Deep meteoric
16	-1.03	Na ⁺ - SO ₄ ²⁻	-0.82	Deep meteoric
17	-0.83	Na ⁺ - SO ₄ ²⁻	-0.81	Deep meteoric
18	-1.19	Na ⁺ - SO ₄ ²⁻	-1.12	Deep meteoric
19	-1.31	Na ⁺ - SO ₄ ²⁻	-1.25	Deep meteoric
20	-0.89	Na ⁺ - SO ₄ ²⁻	-0.88	Deep meteoric
21	-1.13	Na ⁺ - SO ₄ ²⁻	-1.1	Deep meteoric
22	-0.21	Na ⁺ - SO ₄ ²⁻	-0.19	Deep meteoric
23	-0.23	Na ⁺ - SO ₄ ²⁻	-0.19	Deep meteoric
24	0.79	Na ⁺ - SO ₄ ²⁻	0.85	Deep meteoric
25	-2.01	Na ⁺ - SO ₄ ²⁻	-1.95	Deep meteoric
26	0.94	Na ⁺ - SO ₄ ²⁻	0.98	Deep meteoric
27	0.15	Na ⁺ - SO ₄ ²⁻	0.17	Deep meteoric
28	0.67	Na ⁺ - SO ₄ ²⁻	0.68	Deep meteoric
29	2.57	Na ⁺ - HCO ₃ ⁻	2.59	Shallow meteoric
30	0.35	Na ⁺ - SO ₄ ²⁻	0.38	Deep meteoric

4.3.2 Silicate and carbonate weathering

Silicate weathering or carbonate weathering tends to influence groundwater as regards the source of ions. The ratio of $(Ca + Mg) / (Na + K)$ is used as a factor of reference as regards ions sources present in groundwater. Computation shows that the equivalent ratio is 1.07. The equal proportion depicts that the majority of the groundwater chemistry is under the influence of silicate weathering. Moreover, the mean equivalent fraction between Ca/Na , Mg/Na and HCO_3/Na are 0.53, 0.72 and 1.09, respectively. These ratios validate the hydrochemical process under which the study area is going considering that soil of dominant carbonate has Ca/Na , Mg/Na and HCO_3/Na ratios around 50, 10, and 120, respectively (Negrel et al. 1993). The results in Fig. 4.2 suggest that all of the samples are influenced by silicate weathering, and non is governed by evaporating dissolution and carbonate weathering. Additionally, Gibbs plots (1970), found in Fig. 4.3, indicate that the groundwater in the study area is impacted by rock dominance – a confirmation of the results obtained from Fig. 4.2.

Fig. 4.2 Weathering type based on sodium normalized calcium and magnesium

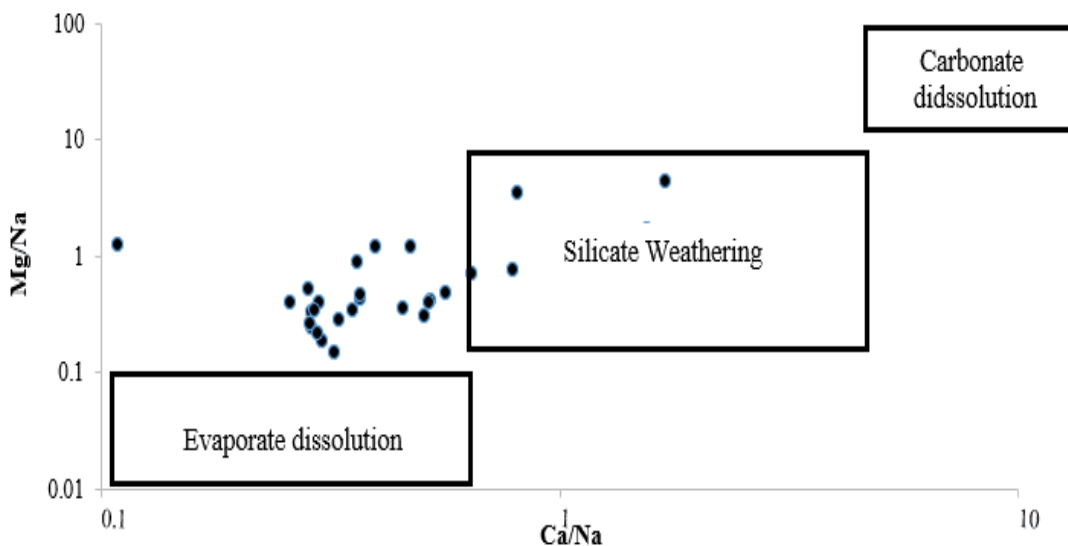
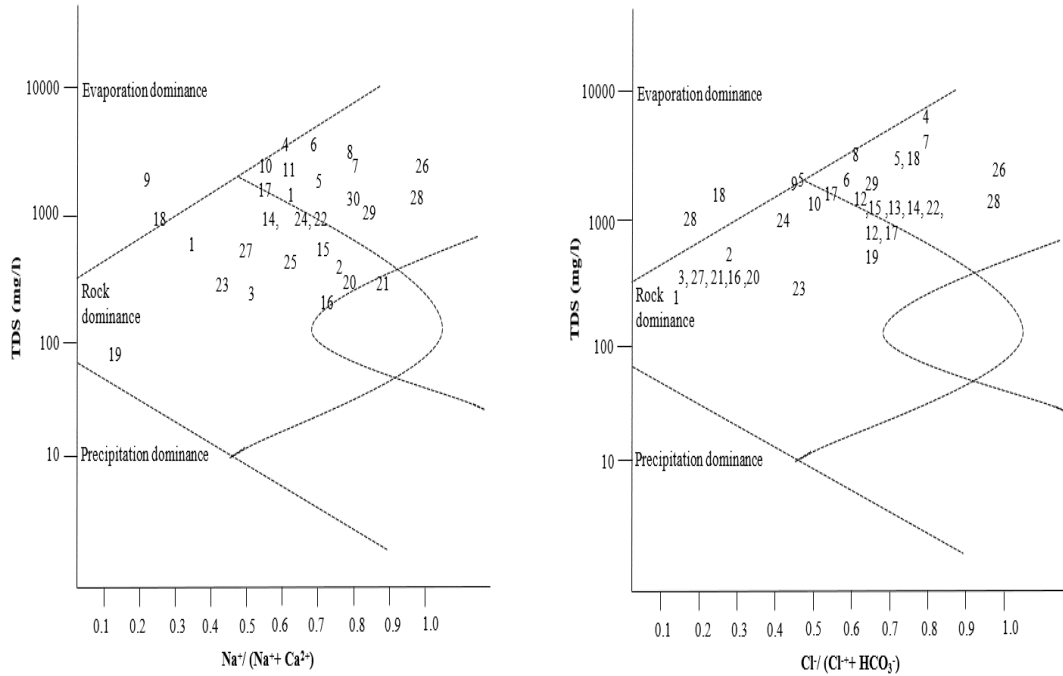


Fig. 4.3 Gibbs plot for classification of water quality dominance

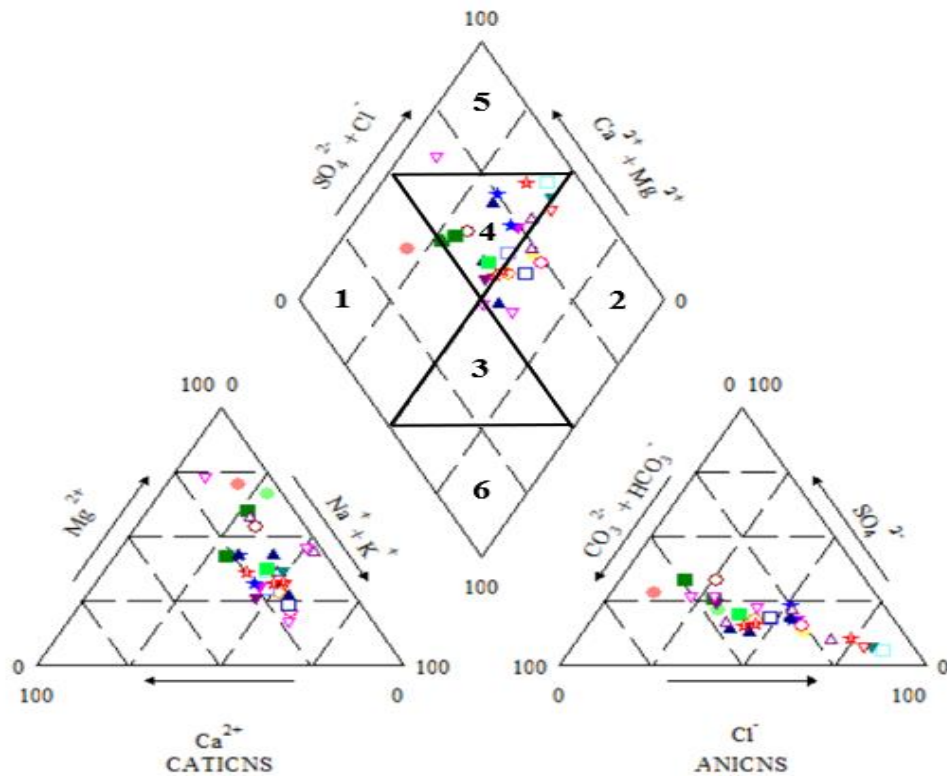


4.3.3 Hydro chemical faces

Researchers have used Piper trilinear diagram (Piper 1953) for explaining the hydro-chemical faces and the distribution of groundwater as per its origin. Further, the groundwater calibration chart is also used to classify groundwater using significant cations (Fig. 4.4) and anions generated. The diagram depicts that most groundwater samples are of the Mixed Ca-Mg-Cl type followed by NaCl type. Two samples were observed to be of CaCl and CaHCO₃ types, respectively. The examination of the graph (Fig. 7) suggests that alkaline earth (Ca²⁺ and Mg²⁺) dominates alkalies, and strong acid (SO₄²⁻ and Cl⁻) outweighs weak acid (CO₃²⁻ and HCO₃⁻) in the study area (Haritash et al. 2017).

Fig 4.4 Piper Trilinear diagram for hydro-chemical classification of groundwater type

- 1-CaHCO₃ Type
- 2-NaCl Type
- 3-Mixed CaNaHCO₃
- 4-Mixed CaMgCl
- 5-CaCl Type
- 6-NaHCO₃ Type



4.4 Correlation Analysis

The correlation analysis is an analytically numerical tool that shows the affiliation between two or more arbitrary variables. In this study, EC, TDS, and salinity positively correlated with Cl⁻, SO₄²⁻, Ca²⁺, Na⁺, and Li (Table 4.5). The significant relationship between TDS and EC is a consequence of total dissolved solids being a conductivity

factor (Singh et al., 2011). Cl^- positively correlated with SO_4^{2-} , SiO_2 , TH, Ca^{2+} (as CaCO_3), Na^+ , Ca^{2+} and Li. Besides, TA shows a significant correlation with SiO_2 and Ca^{2+} in a positive direction; however, a strong negative relationship between TA and Mg^{2+} was observed. HCO_3^- positively correlated with SiO_2 but strongly correlated with Mg^{2+} in a negative sense. Furthermore, Ca^{2+} was noticed to be in significantly positive correlation with SO_4^{2-} , SiO_2 , TH, Ca^{2+} (as CaCO_3), Mg^{2+} (as CaCO_3), TA, HCO_3^- , and Na^+ (Table 7). Also, Na^+ generated a strong positive correlation with SO_4^{2-} , SiO_2 , TH, Ca^{2+} , TA, and HCO_3^- . Finally, pH negatively correlated with 50% of the parameters - including a strong negative correlation SO_4^{2-} and Mg^{2+} , but strongly correlated with PO_4^{3-} positively.

4.5 Principal component analysis (PCA)

Many scholars have used PCA as an analytical tool for recognizing essential parameters that influence water quality (Akbal et al. 2011, Varol and Daraz 2014, Ahmad et al., 2020). The study intends to investigate the principal component of groundwater quality in the Hansi Block II using SPSS software. The results in Table 4.6 suggest five (5) extracted components with a cumulative variance of 83.57%. The first component one has a strong correlation with TDS, EC, Salinity (0.95), Ca^{2+} (0.92), TH, and Cl^- (0.88), Na^+ (0.83) Mg^{2+} (0.82), SO_4^{2-} (0.79), Li (0.65) and SiO_2 (0.53); and accounts for 53.42% of the cumulative variance. Principal component (PC) two accounts for 18.88% of the cumulative variance and shows a strong relationship with SiO_2 (0.50), TA (0.83), HCO_3^- (0.79), CO_3^{2-} (0.58), and F^- (0.54). PC three displays a robust correlation with PO_4^{3-} (0.75) and pH (0.62), accounting for 10.85% of the components' cumulative variance. PC four and five represent 8.88 and 7.96%, respectively, of the cumulative variance, with the fourth PC demonstrating cohesive correlation with Li (0.51) and K^+ (0.65), and the fifth PC signifying a solid connection with NO_3^- (0.80)

Table 4.5 Correlation matrix of physicochemical parameters of groundwater in Hansi Block II, Hisar District

	pH	TDS	EC	Salinity	Cl ⁻	PO ₄ ³⁻	F ⁻	NO ₃ ⁻	SO ₄ ²⁻	SiO ₂	TH	Mg ²⁺	Mg ²⁺	TA	CO ₃ ²⁻	HCO ₃ ⁻	Na ⁺	Ca ⁺	K ⁺	Li	
pH	1.00																				
TDS	-0.08	1.00																			
EC	0.20	1.00	1.00																		
Salinity	-0.08	1.00	1.00	1.00																	
Cl⁻	-0.06	0.93	0.94	0.94	1.00																
PO₄³⁻	0.44	-0.22	-0.22	-0.22	-0.30	1.00															
F⁻	0.22	0.09	0.08	0.09	0.04	-0.02	1.00														
NO₃⁻	-0.03	0.21	0.20	0.20	0.22	-0.36	-0.09	1.00													
SO₄²⁻	-0.42	0.70	0.69	0.69	0.50	-0.23	-0.11	0.23	1.00												
SiO₂	-0.02	0.38	0.37	0.37	0.39	-0.09	0.18	0.05	0.34	1.00											
TH	-0.18	0.87	0.87	0.87	0.73	-0.22	-0.02	0.14	0.78	0.38	1.00										
Mg²⁺	-0.60	0.29	0.30	0.30	0.22	-0.17	-0.11	-0.06	0.35	-0.11	0.30	1.00									
Mg²⁺	-0.19	0.35	0.35	0.34	0.30	-0.15	-0.10	0.07	0.43	-0.02	0.45	0.11	1.00								
TA	0.17	0.31	0.31	0.30	0.27	-0.03	0.34	0.30	0.33	0.66	0.23	-0.38	0.11	1.00							
CO₃²⁻	-0.01	0.14	0.14	0.14	0.12	-0.28	0.46	0.04	0.16	0.44	0.16	-0.03	0.03	0.63	1.00						
HCO₃⁻	0.20	0.32	0.31	0.31	0.26	0.05	0.26	0.34	0.34	0.66	0.22	-0.41	0.10	0.97	0.46	1.00					
Na⁺	0.09	0.85	0.85	0.85	0.80	-0.09	0.17	0.19	0.60	0.38	0.59	0.01	0.26	0.50	0.12	0.54	1.00				
Ca²⁺	-0.07	0.83	0.83	0.82	0.79	-0.16	-0.01	0.22	0.70	0.43	0.78	0.14	0.40	0.37	0.04	0.38	0.75	1.00			
K⁺	-0.01	0.07	0.07	0.07	-0.09	-0.07	-0.13	0.16	0.23	-0.21	0.30	0.26	0.00	-0.18	-0.03	-0.21	-0.21	0.15	1.00		
Li	-0.07	0.57	0.57	0.57	0.42	-0.17	0.31	0.03	0.65	0.21	0.66	0.16	0.25	0.20	0.11	0.19	0.52	0.62	0.33	1.00	

Correlation in boldface is significant at 0.05 level (2 tail)

Table 4.6 Principal component analysis (PCA) of groundwater samples

Parameters	Component 1	Component 2	Component 3	Component 4	Component 5
TDS	0.95	-0.16	0.15	-0.10	-0.05
EC	0.95	-0.16	0.14	-0.11	-0.05
Salinity	0.95	-0.16	0.15	-0.11	-0.05
Ca ²⁺	0.92	-0.18	0.15	0.04	0.04
TH	0.88	-0.31	-0.07	0.18	-0.01
Cl ⁻	0.88	-0.13	0.13	-0.32	-0.11
Na	0.83	0.18	0.34	-0.19	0.00
Mg ²⁺	0.82	-0.12	-0.22	0.12	-0.14
SO ₄ ²⁻	0.79	-0.28	-0.15	0.14	0.12
Li	0.65	-0.17	-0.14	0.51	-0.07
SiO ₂	0.53	0.50	-0.18	-0.09	-0.17
TA	0.47	0.83	-0.12	0.02	0.20
HCO ₃ ⁻	0.46	0.79	0.02	-0.03	0.27
CO ₃ ²⁻	0.24	0.58	-0.54	0.16	-0.16
F ⁻	0.21	0.54	-0.13	0.38	-0.37
PO ₄ ³⁻	-0.28	0.17	0.75	0.32	-0.05
pH	0.14	0.45	0.62	0.36	0.29
K	0.04	-0.46	-0.20	0.65	0.42
NO ₃ ⁻	0.24	0.05	-0.25	-0.27	0.80
Eigenvalues	8.48	3.00	1.72	1.41	1.26
% of Variance	44.65	15.78	9.07	7.42	6.64
% Cummulative Variance	44.65	60.43	69.50	76.92	83.57

CHAPTER

5

CONCLUSION

Groundwater in the study area varied from one place to another. High values of conductivity, total dissolved solids, total alkalinity, chloride, sulfate, fluoride, and sodium were found in groundwater samples collected from Hansi Block II, Hisar District, Haryana. Approximately 72% of all analyzed parameters in samples exceeded the WHO drinking water standards, and about 43% surpassed BIS standards. Results generated from WQI, considering parameters such as TH, TA, Cl⁻, Ca²⁺, Mg²⁺, NO₃⁻, SO₄²⁻, pH and F⁻, depict that 60% of the water is unfit for drinking (WQI > 100), 24% poor (51 < WQI > 75) and 16% good (26 < WQI > 50). Therefore, it is likely that agricultural activities significantly impact groundwater in the study area. As such, groundwater must be treated using low technology for hardness and fluoride remediation before domestic usage.

Other parameters assessed are SAR, RSC, SSP, KR, and MH since the block is notable for agricultural activities. The groundwater characterization outcome for such activities indicates that about 80% of the groundwater in the study area is high in EC but low in Na; 13% is high in EC with medium Na and 7% contains medium Ec and low Na. As per RSC, 50% of the groundwater is suitable for irrigation, 16% is slightly eligible, and 33% unsuitable regarding Residual Sodium Carbonate. In the same vein, approximately 64% of the water in Hansi Block II is unsuitable for irrigation (SSP > 50). In furtherance, about 64% of the groundwater samples, KR > 1, are unsuitable for agricultural activities, validating the results obtained from SAR regarding Na shortage in groundwater. It is glaring that excess ions and soluble salt found in the soil have deteriorated groundwater, thus generating high PI values with an average of 68.26. Magnesium Hazard, MH, is high in the study area, with about 94% of the samples unfit for farming purposes.

Hydrochemical characterization was done based on water type (based-exchange and ion classification), infiltration type, rock weathering, rock dominance, precipitation dominance, evaporation dominance, or dissolution. Based on base-exchange and infiltration type, approximately 97% of the water in the research area is Na⁺-SO₄⁻ type

and deep meteoric percolation type. Similarly, Gibb's boomerang diagram suggests that the groundwater in the study area is dominated by rock-water interaction rather than evaporation dominance or precipitation dominance. The findings gathered from Piper's graph depict that most groundwater samples are of the Mixed Ca-Mg-Cl type followed by NaCl type. The relative abundance of cations and anions in the groundwater is of the order $\text{Na}^+ > \text{Mg}^{2+} > \text{Ca}^{2+} > \text{K}^+$ and $\text{Cl}^- > \text{HCO}_3^- > \text{SO}_4^{2-} > \text{CO}_3^{2-}$. More so, the determination of weathering processes that influence groundwater in the study area indicates that most of the water in the area is under the influence of silicate weathering rather than carbonate weathering.

Additionally, the correlation matrix reveals that EC, TDS, and salinity correlated significantly with Cl^- , SO_4^{2-} , Ca^{2+} and Li; Ca^{2+} strongly correlated with SO_4^{2-} , SiO_2^4 and Na^+ . Hydrogen ion (pH) connected considerably with 50% of all parameters – though in a negative sense. As for PCA, five components, having a cumulative variance of 83.57%, were extracted. PC 1, 2, and 3 accounts for 53.42, 18.88, and 10.85%, respectively, of the total cumulative variance. PC 4 and PC recorded the lowest of 8.88 and 7.96%, respectively, of the total cumulative variance.

As per these findings, more studies need to be done to determine the source(s) of groundwater contamination in the study area. The inhabitants must switch to an alternative source to fetch drinking water. Otherwise, the water supply's current source(s) must be treated for hardness and fluoride before domestic use to avoid fluorosis and gastrointestinal infections.

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