CHAPTER - 7

HYDROCHEMISTRY OF GROUNDWATER

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7.1 Introduction

The quality of groundwater plays a decisive role in the sustainable development of water resources for drinking as well as irrigation purpose (Gleeson et al., 2020). In other words, significance of good groundwater potential will surface out only if it yields a good quantity and quality of water. However, during the sub-surface movements, the physicochemical characteristics of groundwater continuously change as the content of salts in the groundwater is dependent upon the place of its occurrence, path and distance which it has travelled (Todd & Mays, 2005). Also, the concentration of salts is largely governed by the climate and the source of groundwater.

The groundwater quality, often reflecting the extent of isolation from surface contaminants, is crucial for sustaining the agriculture, industrial and drinking water needs. It has a direct bearing on the human health of groundwater dependent communities. However, the natural (geo-genic) or anthropogenic sources can affect the groundwater quality adversely, which may put a constraint on its usage (Coomar & Mukherjee, 2021; Huang et al., 2023). Thus, the assessment of the groundwater quality is very important in hydrogeological studies. The groundwater quality evaluation not only provides the ionic concentrations but also its usability for groundwater-dependent livelihoods and associated ecosystems (Nikumbh, 1997). For establishing the quality criteria the physicochemical properties of groundwater should be specified along with the standard methods and comparison with recommended water quality datasets. Largely, the studies on groundwater chemistry either show quality characterization and its suitability for definite purposes or assess the rock-water interactions (Bhardwaj & Singh, 2011).

In case of Khapri watershed, the groundwater serves as the major source of fresh water for drinking and agriculture during the non-rainy periods and thus it holds the utmost importance (Dongare et al., 2022; Dongare & Deota, 2023). In such a highly groundwater dependent region, no systematic investigation exists on groundwater quality. The groundwater quality monitoring also gains importance because of increasing anthropogenic activities such as disposal of industrial effluents or extensive use of chemical fertilizers for agricultural practices (Srivastav, 2020). Fortunately, the Dangs district or Khapri watershed does not have any commercial industries whose

contaminated effluents can pollute the groundwater. However, Dangs district with major livelihood as agriculture (Nanda, 2001), the possibility of groundwater quality deterioration through use of chemical fertilizers or geo-genic contaminants cannot be neglected. Hence, in the present study, an attempt has been made to synthesize the status of the groundwater quality in terms of its suitability for drinking and agriculture purposes as well as to understand the rock-water interactions. The physicochemical parameters of groundwater such as pH, electrical conductivity (EC), total dissolved salts (TDS), total hardness (TH), total alkalinity (TA), cations (calcium (Ca^{+2}), Magnesium (Mg^{+2}), Sodium (Na^+) and Potassium (K^+)), anions (nitrate (NO_3^-), sulphate (SO_4^{2-}), chloride (Cl) and bicarbonate (HCO_3^-)) are analysed for 45 pre-monsoon groundwater samples collected in May-2022 (figure 7.1).

7.2 Sampling procedures for groundwater quality analysis

To analyse the groundwater samples for the physicochemical parameters, 45 groundwater samples are collected from the open-dug wells during the month of May 2022[1]. To collect representative water of the aquifer, the electric pumps wherever available are used and are allowed to drain water for 10 minutes so as to remove the stagnant water in the pipes (figure 7.2 a). For sampling locations where pumps are not available, the sampler (figure 7.2 b-c) has been lowered to the central bottom most part of the well. All the samples are collected in the pre-rinsed high density polyethylene bottles (HDPE) of 1000 ml capacity (figure 7.2 d). The pre-rinsed bottles are again rinsed two to three times with the same groundwater sample which is to be collected. Simultaneously, the GPS is used to record the geographical position and elevation of the sampling location. The in-situ recording of pH, EC, TDS and temperature is carried out using Hanna Portable Pen type pH and TDS-EC-TEMP meters.

7.3 Analytical procedures for physicochemical parameters

The groundwater samples are analysed for physicochemical parameters at department of environmental sciences and Department of Geology, The M.S. University of Baroda following the typical procedures of India Standards (IS), 2001. The standard procedures followed for the physicochemical parameters of groundwater is discussed in the paragraphs to follow.

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[1] The analysis of only pre-monsoon groundwater samples is presented here as the post-monsoon groundwater chemistry did not show any significant variations that can affect the use of groundwater.
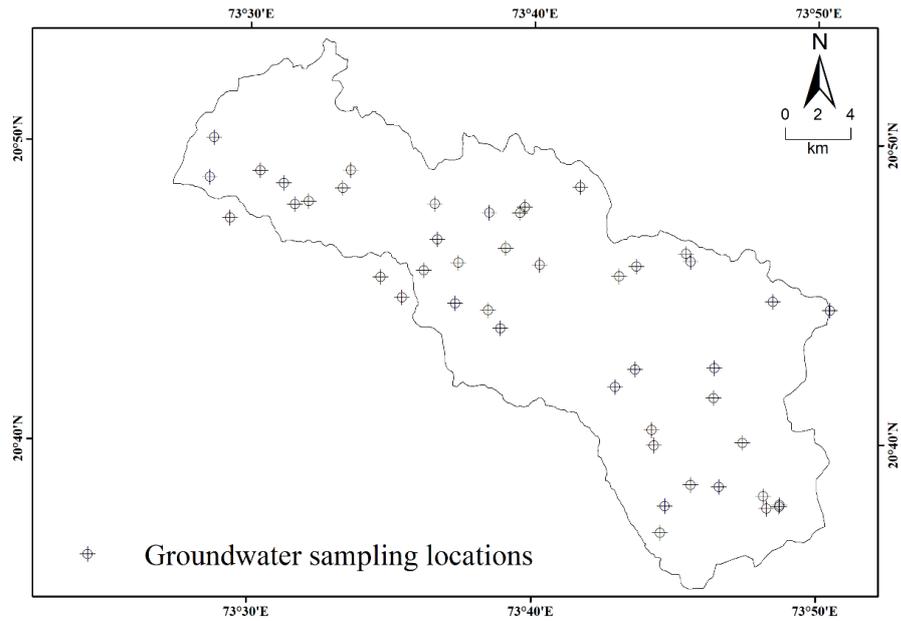
Figure 7.1 Groundwater sampling locations for water quality analysis.

Figure 7.2 Collection of groundwater samples a) after draining the stagnant water in pipes, b, c) by lowering the sampler to the central and bottom most part of well in case of absence of electric pumps, d) in high density polyethylene bottles (HDPE) and systematic labelling.

7.3.1. Total Alkalinity (TA)

The total alkalinity (TA) is the measure of neutralizing power of the water's acids, determined using IS 3025 (part 23) using methyl orange and phenolphthalein indicators. The method is based on the principle that the discoloration of phenolphthalein indicator indicates the neutralization of OH^- and $\frac{1}{2} CO_3^-$, whereas the immediate reaction in transformation of yellow to orange colour of the methyl orange indicator suggest total alkalinity. The lab apparatus such as beakers, conical flask, pipettes, burettes and volumetric flasks are utilized. The standards and reagents used are 0.02 N sulphuric acid (H_2SO_4), phenolphthalein and methyl orange indicators. Initially, 20 ml sample is taken in a conical flask and two drops of phenolphthalein are added to obtain the faint pink colour. Further the sample is titrated against the 0.02 N H_2SO_4 until the sample becomes colourless. The volume of H_2SO_4 required to change the sample to colourless is recorded. In the present study none of the samples showed faint pink colour upon addition of phenolphthalein indicator. Three to four drops of methyl orange indicator is then added to the same sample in the flask and is titrated till the yellow colour induced by methyl orange turns dark orange or pinkish orange. Correspondingly the volume of H_2SO_4 required to change the yellow colour to dark orange or pinkish orange is recorded to determine the alkalinity. It is to be noted here that when phenolphthalein alkalinity is zero then indirectly the total alkalinity is equal to the concentration of the bicarbonates and is referred as bicarbonate alkalinity. The total alkalinity calculated using equation (7.1).

$$\text{Total alkalinity (as mg/L } CaCO_3) = \frac{(A+B) * N * 50000}{V} \quad \text{……………………….. (7.1)}$$

Where, A = ml of standard sulphuric acid used to titrate to pH 8.3

B = ml of standard sulphuric acid used to titrate to pH 8.3 to pH 3.7

N = normality of acid used, and

V = volume in ml of sample taken for test

7.3.2. Total Hardness (TH), Calcium and Magnesium concentration

Total hardness of the water is defined as the sum of concentration of calcium and magnesium and is expressed in mg/l or meq/l (Saurina et al., 2002). To determine the total hardness in the water samples IS 3025 (Part 21) – EDTA method is used. The

method is based on the principle that the EDTA reagent may form EDTA-metal complexes by its reactions with the metal ions except the alkali metal ions (Batt and Aga, 2005). The reagent is capable of forming stable complexes with the alkaline earth metals such as calcium and magnesium ions in alkaline conditions (pH>9). The lab apparatus such as conical flask, burette and pipette are used. The standards and reagents used are 0.01 M EDTA, 1 N NaOH, Ammonium purpurate (Murexide) indicator, eriochrome black T (EBT) indicator and ammonia buffer solution. Using the reagents first the blank titration is performed to note the EDTA volume consumed for the blank. For sample analysis, initially 20 ml sample is taken in a conical flask. To this 1 ml of ammonia buffer solution and EBT indicator is added. The sample is then titrated against the EDTA until the colour changes from pinkish red to light black and the volume of EDTA used is noted. The total EDTA consumed for the sample is computed as C = A – B, where A is EDTA consumed for sample and B is the EDTA consumed for blank. Ultimately the total hardness (TH) is derived using the formula given in equation (7.2).

$$\text{Total Hardness (TH) as } CaCO_3 \text{ mg/L} = \frac{Volume\ of\ EDTA\ used}{Sample\ volume} \text{ X } 1000 \dots\dots\dots\dots\dots\dots (7.2)$$

To measure the concentration of calcium, the same standards and reagents as for TH are used. In the beginning 20 ml sample is taken in conical flask and 1 ml of NaOH along with murexide are added. Further the sample is titrated against the EDTA till the pink colour is changed to purple and the burette reading is noted. The total EDTA consumed for the sample is computed as C' = A' – B', where A' is EDTA consumed for sample and B' is the EDTA consumed for blank. The calcium is estimated as per the formula given in equation (7.3). The Mg^{+2} is obtained by taking the difference between the TH and the concentration of the calcium ions as per the formula given in the equation (7.4).

$$\text{Calcium (Ca) hardness as } CaCO_3 \text{ mg/L} = \frac{Volume\ of\ EDTA\ used}{Sample\ volume} \text{ x } 1000 \dots\dots\dots\dots\dots (7.3)$$

$$\text{TH} = 2.497\ (\text{Ca}) + 4.118\ (\text{Mg}) \dots\dots\dots\dots\dots\dots\dots\dots\dots (7.4)$$

7.3.3. Sodium and Potassium concentration

For determining the concentration of sodium and potassium, the IS 3025 (part 45) - flame-photometer method is used. The estimation of the sodium and potassium ions is based on the emission spectroscopy, which deals with the excitation of the electrons

from the ground state to the higher energy state and coming back to the original state by emission of light (Maiti, 2003). The instrument flame photometer and lab apparatus such as beaker is used. The reagents used for estimating sodium and potassium are the NaCl and KCl. To calibrate the flame photometer standard of sodium and potassium solutions with concentrations 20 ppm, 40 ppm, 60 ppm, 80 ppm and 100 ppm are used. Initially the flame photometer is started and the air pressure is set to 0.45 kg/cm^2. To clean the tube the distilled water is aspirated and subsequently, the standards are aspirated to calibrate the instrument. Ultimately, the samples are run to obtain the concentration of sodium and potassium. After the analysis of 15 samples, the standards were aspirated again to ensure the accuracy.

7.3.4. Chloride concentration

To determine the chloride concentration, the argentometric method is used. The lab apparatus such as amber burette, amber pipette, beakers and conical flask are used. The standards are prepared using the reagents such as silver nitrate, sodium chloride and potassium chromate indicator. Initially, 20 ml sample is taken in conical flask to which potassium chromate indicator is added. The sample is then titrated against the standardized silver nitrate solution with continuous stirring until the red silver chromate precipitates are observed. Simultaneously, the volume of silver nitrate consumed is noted down and the concentration of chloride is determined using the equation (7.5).

$$\text{Chloride (Cl}^-\text{) mg/L} = \frac{(A-B)*M*35450}{Sample\ volume} \dots\dots\dots\dots\dots\dots\dots\dots \text{(7.5)}$$

Where, A = Volume (ml) of silver nitrate consumed for the sample

B = Volume (ml) of silver nitrate consumed for the reagent blank

M = Concentration (moles/L) of silver nitrate solution

7.3.5. Nitrate and Sulphate concentration

To determine the nitrate and sulphate concentrations in groundwater samples the UV-spectrophotometric method is utilized. The method is based on the Beer-Lamberts law which indicates the amount of light absorbed is directly proportional to the solute concentration in the solution. The lab apparatus such as UV spectrophotometer set to determine the absorbance at wavelength 220 nm is required. The reagents used are potassium nitrate, concentrated hydrochloric acid, chloroform and distilled water. The stock solution of potassium nitrate (100 ppm) is prepared, from which the standard

solution of 0, 1, 3, 5 and 7 ppm are prepared. These standards are poured in a cuvette and are analysed using wavelength of 220 nm. The calibration curve is then generated by plotting graph of obtained absorption values versus concentration. For accurate calibration the R^2 value of linear regression line will be greater than 0.95. In such case, the slope and intercept are then used to determine the concentration of nitrate in the sample using equation (7.6). To analyse the nitrate concentration, 1 N hydrochloric acid is added to 50 ml sample. The sample is then transferred to cuvette and is analysed at wavelength 220 nm. The absorption value is then noted and concentration is measured using calibration curve. To estimate the sulphate ion concentration the UV spectrophotometer set to wavelength 420 nm, beakers, conical flask, magnetic stirrer, cuvettes and spatula are used. The reagents such as buffer solution (30 g magnesium chloride, 5 g sodium acetate, 1 g potassium nitrate and 20 ml acetic acid in 500 ml distilled water and has make up to 1000 ml), barium chloride and standard sulphate solution are used (Maiti, 2003 pp. 159-160). From standard sulphate solution (100 ppm) the standards of 0, 5, 10, 15, 20, 25, 30, 35, 40 ppm are prepared. The 25 ml standard solutions are analysed to generate the calibration curve. For accurate calibration the R^2 value of linear regression line will be greater than 0.95. Later the samples (25 ml) are analysed by adding 5 ml of buffer solution, small amount of barium chloride and is stirred for one minute with the help of magnetic stirrer. The sample is then transferred in cuvette and sulphate is analysed at 420 nm wavelength to obtain the absorbance. Finally, the slope and intercept values of regression line are used to determine the concentration of nitrate in the sample using equation (7.7).

$$\text{NO}_3^- \text{ (mg/L)} = \frac{Absorbance-intercept}{slope} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(7.6)}$$

$$\text{SO}_4^{2-} \text{ (mg/L)} = \frac{Absorbance-intercept}{slope} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(7.7)}$$

7.4 Significance and spatial variations in physicochemical parameters

The importance of physicochemical parameters in hydrogeological investigations is already highlighted in the beginning. The present section enumerates the significance of pH, Ec, TDS, probable sources and concentration of dissolved ions as well as their spatial variations throughout the Khapri watershed. The analytical results of all physicochemical parameters and ion balance error (IBE) for 45 pre-monsoon groundwater samples are given in annexure II.

7.4.1. Power of Hydrogen (pH)

The pH of the water can be described as the negative log of the concentration of hydrogen ions in moles per litre (Karanth, 1987 p. 146). It indicates the balance between the bases and acids in water samples. In pure water, the molar concentration of H^+ (hydrogen) and OH^- (hydroxyl) ions are equal (10^{-7} moles/litre), indicating neutral pH with a value of 7. In case of imbalance in the concentration of hydroxyl ions or hydrogen ions, the pH may accordingly exceed or decrease from the value of 7. The water typically tastes acidic when the pH value is lower than 6, bitter when pH value is higher than 8.5. For natural waters, the pH value is governed by the carbon dioxide and carbonate-bicarbonate equilibrium and remarkably affected by the changes in the temperature and pressures (Karanth, 1987).

The pH of groundwater in Khapri watershed ranges from 6.9 to 8.5 (figure 7.3), indicating the neutral to weakly alkaline nature of groundwater. The neutral pH is observed for most of the wells throughout the watershed indicating equilibrium between carbon-dioxide, carbonate and bicarbonate. The weakly alkaline pH is observed for the wells which are located near to the stream channels indicating relatively high concentration of carbonate and bicarbonate.
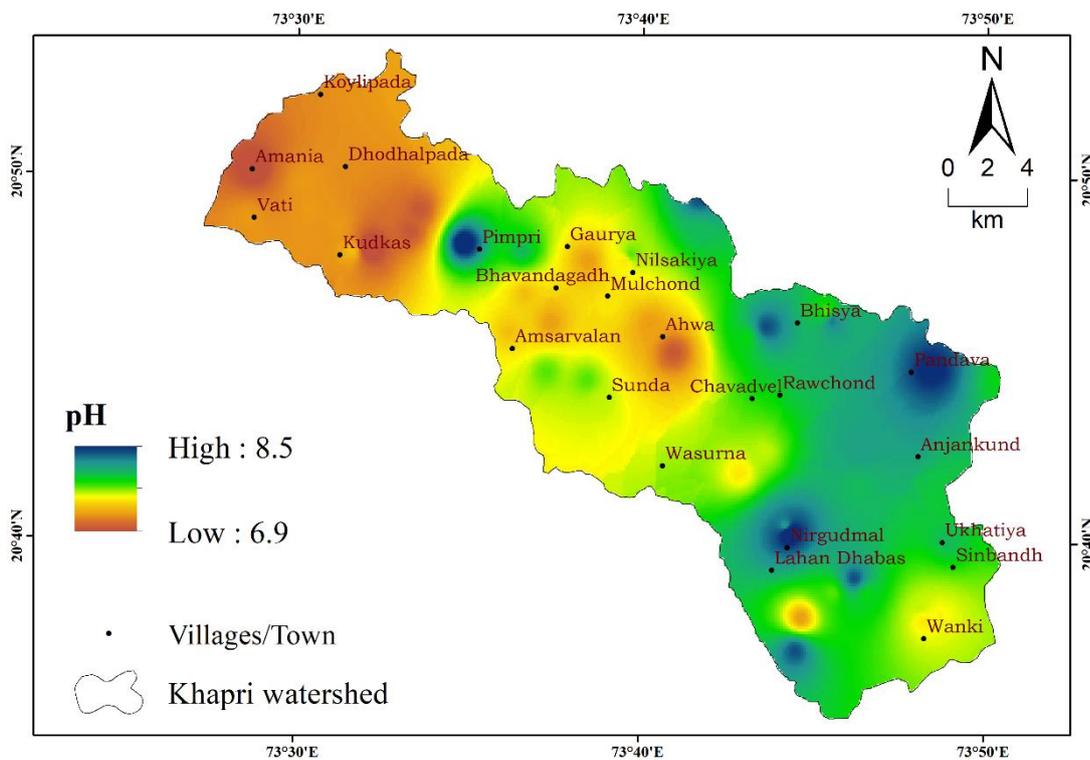

Figure 7.3 Spatial variation in pH of pre-monsoon groundwater samples.

7.4.2. Electrical Conductivity (EC)

The ability of water to conduct electric current is referred to as electrical conductivity and is expressed in micro-siemens (µS/cm). The measurement of electrical conductivity allows us to obtain the information about the extent of mineralization in the groundwater (Naudet et al., 2004). The electrical conductivity is directly proportional to the ion concentration and is indicative of the total dissolved solids in the water.

The EC of groundwater in Khapri watershed ranges from 208 to 624 µS/cm (figure 7.4). The low values of EC is indicating the lower mineralization content of the groundwater. According to the classification of groundwater based on EC, the groundwater of Khapri watershed is classified as low conductive (< 500 µS/cm) (Jagannadha Sarma & Swamy, 1981). In general, the lower EC values are observed for the wells at relatively higher elevations forming the watershed and sub-watershed divides. The relatively higher EC values are observed in the lower reaches and areas with flat slope.
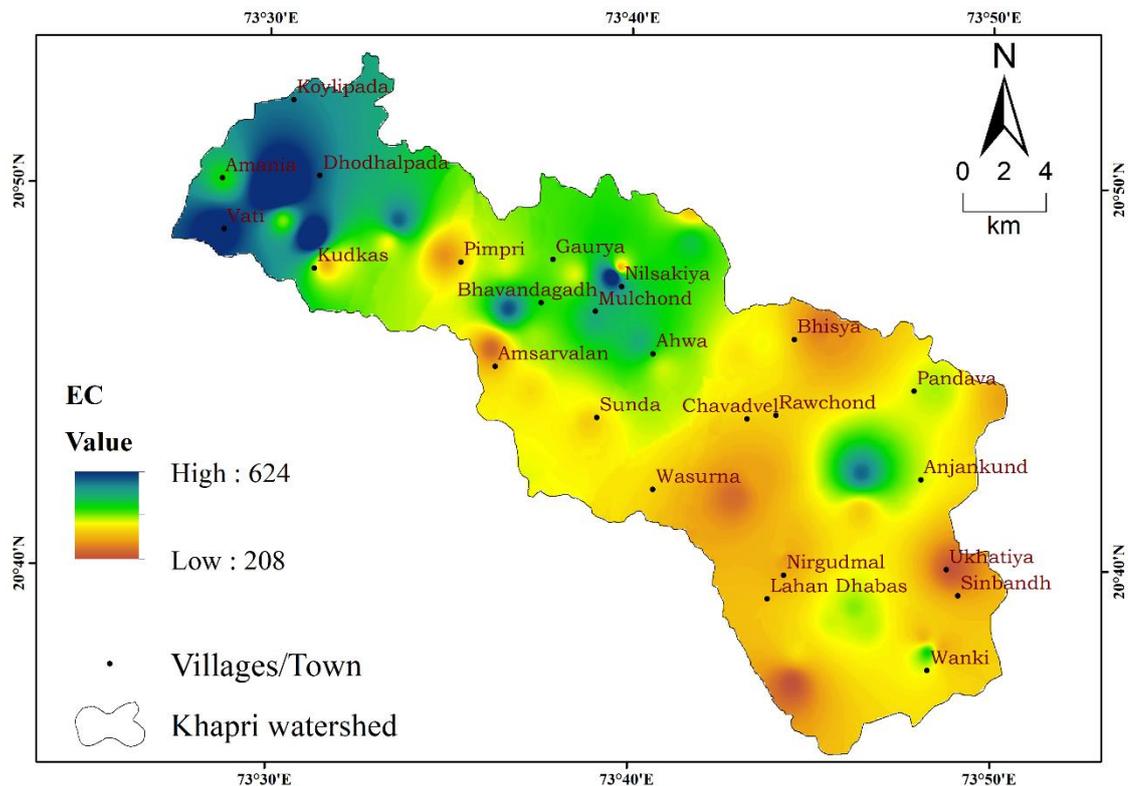

Figure 7.4 Spatial variation in Electrical Conductivity (EC) of pre-monsoon groundwater samples.

7.4.3. Total Dissolved Solids (TDS) and Total Hardness (TH)

The concentration of dissolved matter in the water is given by total dissolved solids (TDS) (Dahaan et al., 2016). The TDS of groundwater samples in Khapri watershed ranges from 112 to 285 ppm and is classified as fresh water with appropriate mineral concentrations (figure 7.5).

The hardness in the groundwater is imparted by carbonates, chlorides of calcium, magnesium and sulphate. The acceptable limit of total hardness as per BIS (2012) is 200 ppm. The total hardness of groundwater samples in Khapri watershed ranges from 88 to 245 ppm (figure 7.6).

7.4.4. Calcium

Calcium is one of the major constituents of many igneous, sedimentary and metamorphic rocks (Karanth, 1987). The calcium can enter groundwater through the dissolution of aquifer minerals, exchange of sodium for calcium by ion exchange, leaching from soil and artificial fertilizers. In case of hard rocks, the weathering of silicate minerals such as plagioclase, pyroxene and amphibole are the chief sources of calcium in the groundwater. The concentration of calcium in the groundwater is dependent on the solubility of calcium sulphate, calcium carbonate and rarely calcium chloride minerals, which is governed by the partial pressure of carbon dioxide in the air lying directly above the water. In natural conditions (partial pressure of CO_2 = 0.003 atm), the fresh water may contain 20 to 30 ppm of calcium at saturation limit. However, when water pass through thick soil-air, where the partial pressure of carbon dioxide is high as compared to atmosphere (1 to 5 atm), results into high calcium content between 70 to 110 ppm (Karanth, 1987, Hem, 1985, Nikumbh 1997).

In Khapri watershed the concentration of calcium ranges from 19.5 mg/L to 56 mg/L (figure 7.7). The spatial distribution of calcium in the Khapri watershed indicates the relative increase in the calcium content from the watershed divide towards main river channel. The high concentration of calcium observed for the well 62 is on account of the weathering of minerals such as plagioclase as well as the shallow depth of the well.
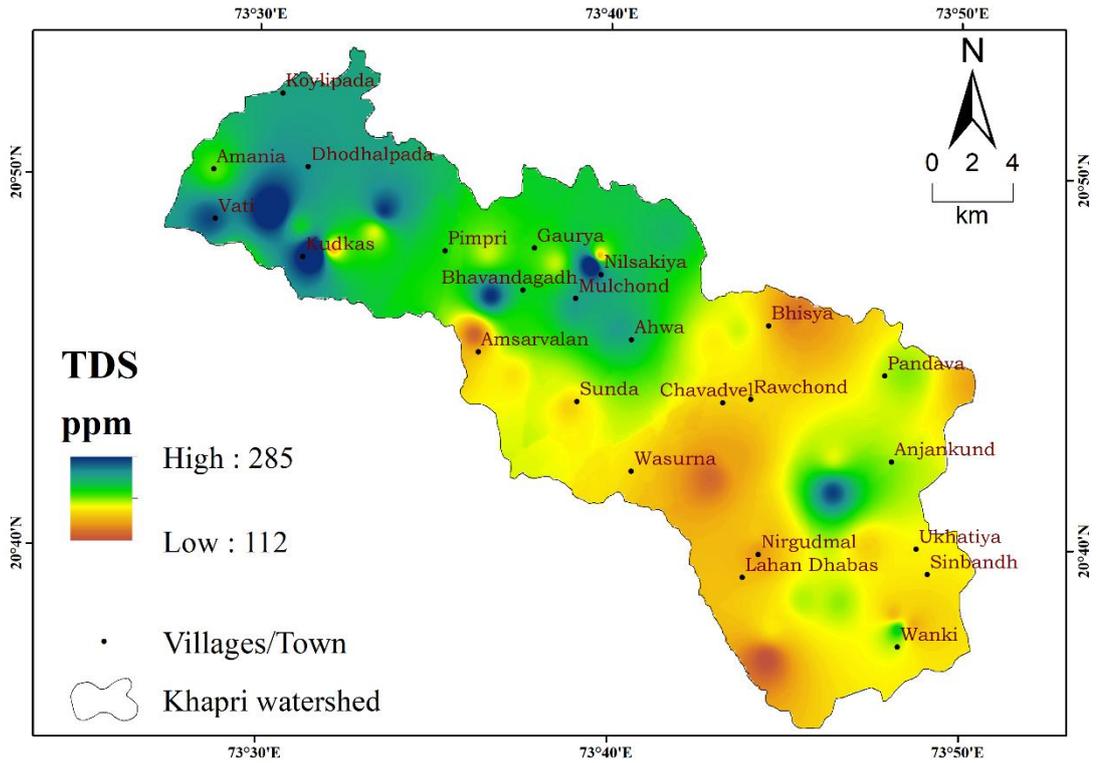
Figure 7.5 Spatial variation in Total Dissolved Solids (TDS) of pre-monsoon groundwater samples.
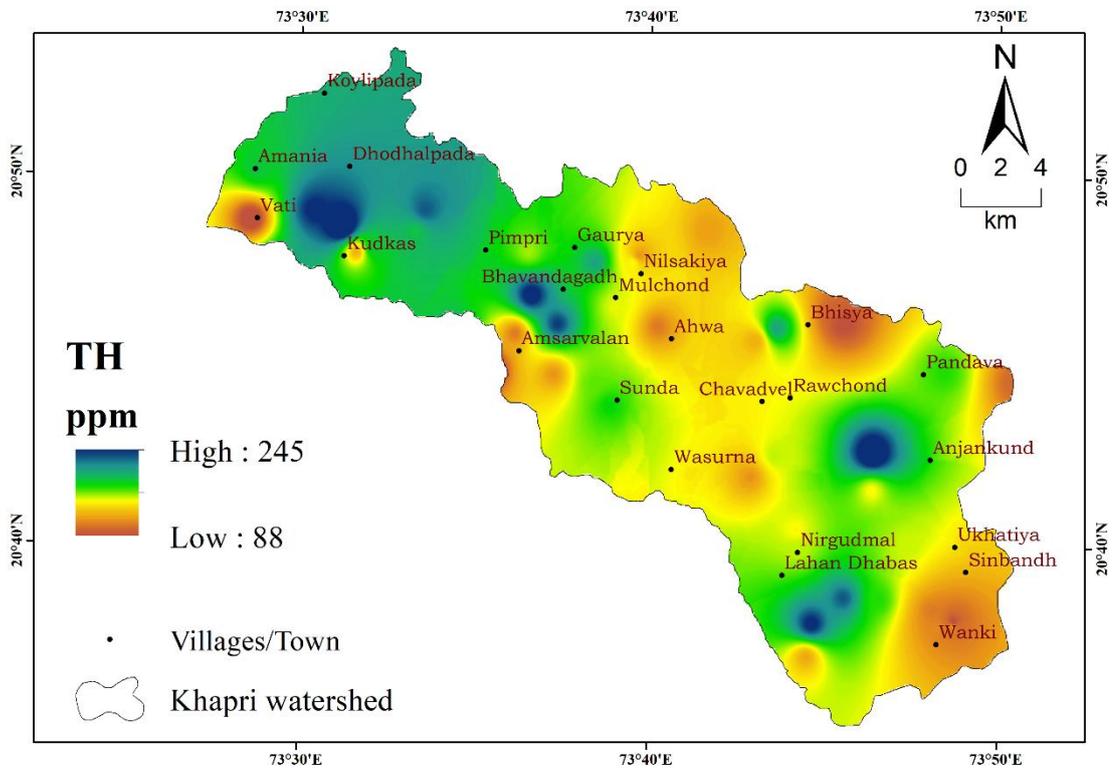

Figure 7.6: Spatial variation in Total Hardness (TH) of pre-monsoon groundwater samples.
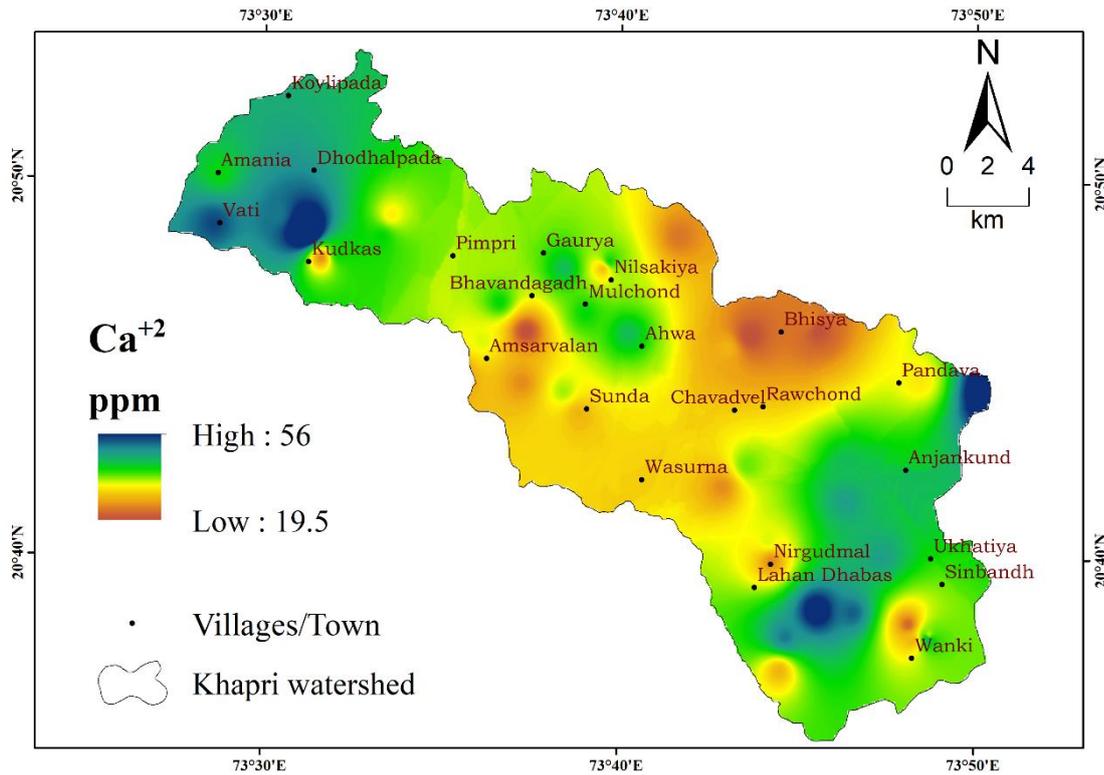
Figure 7.7 Spatial variation in Ca^{+2} of pre-monsoon groundwater samples.

7.4.5. Magnesium

The magnesium is the significant constituent of igneous rocks such as dunite, pyroxinites, amphibolites and basalts. The chief minerals that release magnesium to the water are olivine, augite, biotite, hornblende, serpentine and talc (Karanth, 1987). In igneous rocks, the magnesium is present in an insoluble silicate form, but the weathering tends to break these minerals into more soluble carbonates, clay minerals and silicates. In the ambient atmospheric conditions, the solubility of magnesium carbonate in groundwater (containing dominant sodium ions) in the presence of carbon dioxides is ten times more intense than the calcium carbonate.

In the Khapri watershed, the magnesium concentration varies from 1.1 mg/L to 40.05 mg/L (figure 7.8). The pattern of spatial variation of the magnesium concentration follows the pattern exhibited by calcium in the Khapri watershed.
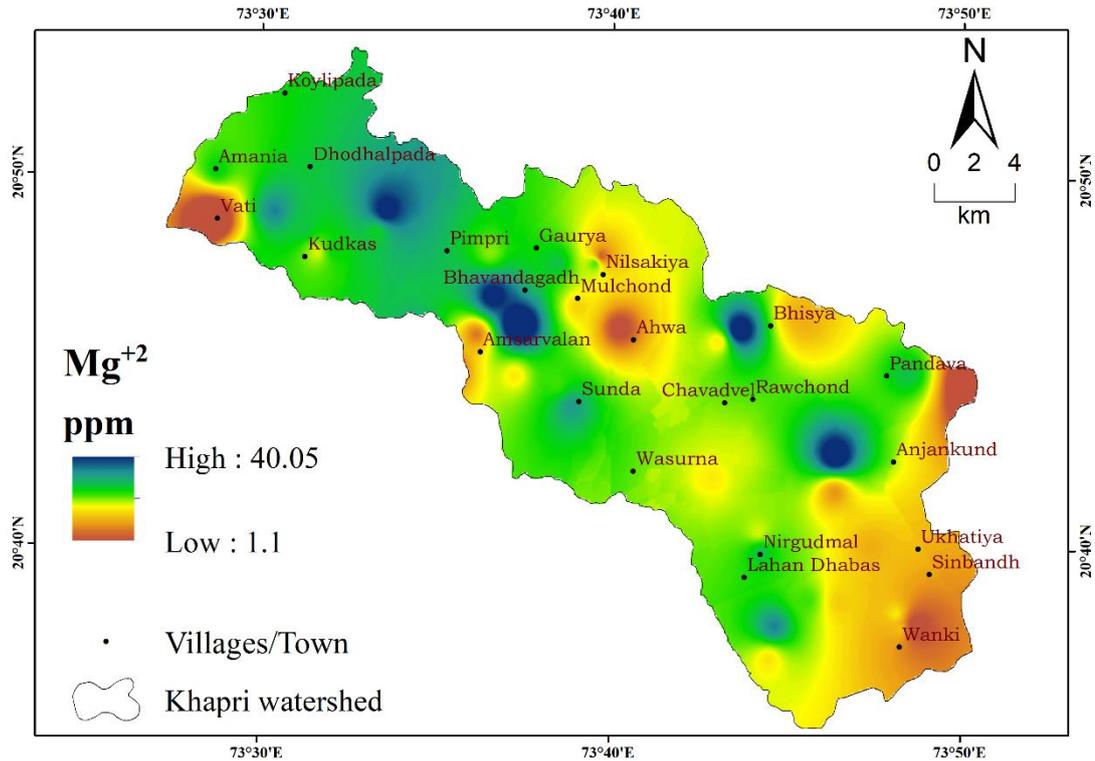
Figure 7.8 Spatial variation in Mg^{+2} of pre-monsoon groundwater samples.

7.4.6. Sodium

The sodium in the groundwater is basically on account of dissolution of evaporite deposits through meteoric water, weathering of sodium bearing minerals like albite, nepheline, sodalite, glaucophane, plagioclase feldspar and use of surface water for irrigation purposes. Additionally, the sodium precipitates in the soils, few clay minerals and certain zeolites are also the chief sources for the sodium in groundwater. However, in comparison to Ca-Mg bearing minerals, Na-bearing minerals are not very widespread (Hem, 1985). In humid regions, the sodium contents in groundwater is hardly up-to 1 ppm compared to brines having concentrations above 100000 ppm (Nikumbh, 1997). In regions with high rainfalls and well-drained soils, the sodium content in groundwater is usually up-to 15 ppm (Karanth, 1987).

The sodium concentration in Khapri watershed ranges from 1.0 mg/L to 13.89 mg/L (figure 7.9). The spatial distribution of sodium in the Khapri watershed indicates the relative increase in the concentration from the divides (uplands) towards the streams and main river channel. The overall increasing content of sodium in the downstream direction indicates the control of geology and hydrogeology on the groundwater composition.

7.4.7. Potassium

The chief geological sources of potassium in groundwater are silicate minerals such as orthoclase, microcline, nepheline, lucite and biotite present in igneous rocks. The abundance of potassium is similar to that of sodium in igneous rocks, but the concentration of potassium in groundwater is hardly one-tenth to that of sodium (Karanth, 1987). In potable water the potassium varies from 1 to 10 ppm, whereas the concentration goes from 100 ppm to several thousand ppm in brines (Hem, 1985). Other than geological sources, the agricultural activities and pollution due to uncontrolled sewage disposal are also responsible for higher potassium concentration.
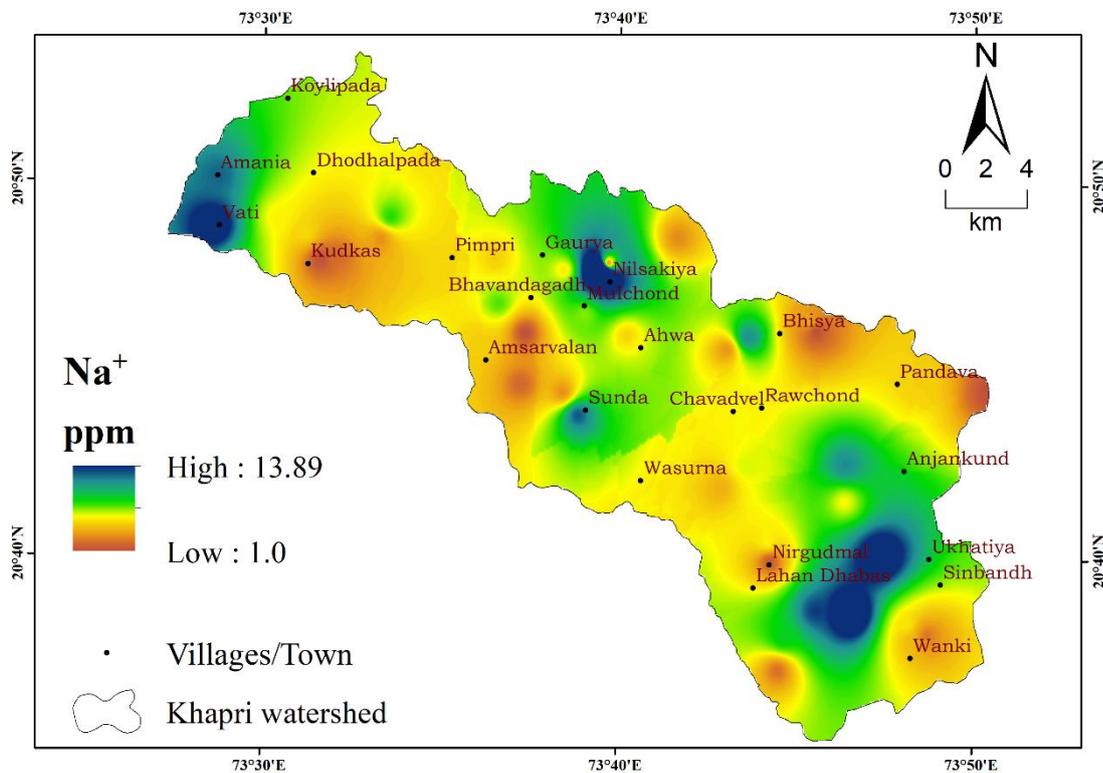

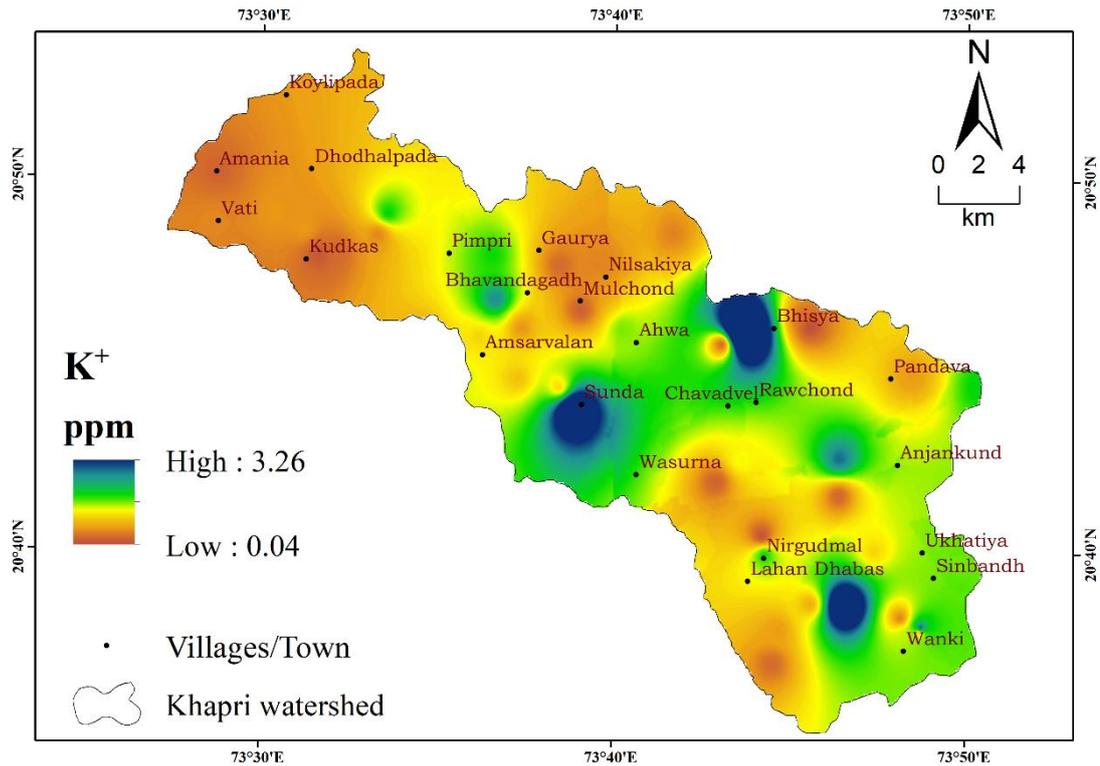**Figure 7.9 Spatial variation in Na⁺ of pre-monsoon groundwater samples.**

Figure 7.10 Spatial variation in K$^+$ of pre-monsoon groundwater samples.

The concentration of potassium in groundwater of Khapri watershed ranges from 0.04 to 3.26 mg/L (figure 7.10). The low concentration of potassium in groundwater is suggestive of geological sources and there is no significant contribution from the other anthropogenic sources.

7.4.8. Bicarbonate alkalinity

It is to be noted here that when phenolphthalein alkalinity is zero then indirectly the total alkalinity is equal to the concentration of the bicarbonates and is referred as bicarbonate alkalinity. Bicarbonate is the significant and most abundant anion in groundwater. It is the result of the complex interactions occurring between atmosphere, lithosphere and hydrosphere in two ways. It includes solubility of carbon dioxide in the water and chemical weathering of rocks by carbon dioxide saturated water (Raymahashay, 1986), Nikumbh, 1997). The natural water possesses dissolved carbonates on account of solubility of carbon dioxide from atmosphere, soil zone and oxidation of organic matter which plays a significant role in weathering of silicate and carbonate minerals. The weathering of these minerals by carbon dioxide charged water results into bicarbonate. The concentration of bicarbonate in groundwater is governed by

the partial pressure of carbon dioxide in the zone of aeration. Under regular conditions, the bicarbonate concentrations in groundwater goes up-to 200 ppm.

The concentration of bicarbonate in Khapri watershed ranges from 122 mg/L to 285 mg/L (figure 7.11). The spatial distribution map of bicarbonate indicates that the higher concentration of bicarbonate (>200 mg/L) is mainly confined to the lower reaches of the watershed. These higher concentration of bicarbonate in the downstream is attributed to the gentle topography, weathering of silicate minerals present in basalts and dissolution of carbonates present in the alluvium. Such high values of bicarbonates are more common in drainage basins with igneous rocks (Dethier, 1986).

7.4.9. Chloride

The chief sources of chloride are rainfall, chloride bearing minerals such as chlorapatite and sodalite, dry fallout in arid areas, artificial fertilizers and effluents from anthropogenic activities such as waste disposal or industries (Karanth, 1987; Hem, 1991; Nikumbh, 1997). The salinity ingression, halite solutions and presence of any evaporate minerals shows spike in the content of chloride. Unusually high concentration of chloride in groundwater could be attributed to the pollution from the sewage, leaching of saline residues from the soil and salting of coconut trees (Paulson et al., 1993, Nikumbh, 1997).

The chloride content in groundwater of Khapri watershed ranges from 9.07 to 58.98 mg/L (figure 7.12). Unlike bicarbonates, the source of chloride cannot be the weathering processes, but sea salts which are carried inland by the rainfall or the anthropogenic activities (Paulson et al., 1993). The presence of chloride in the groundwater of Khapri watershed is attributed to either precipitation or anthropogenic activities, because there is no presence of any chloride minerals in the rocks of watershed.
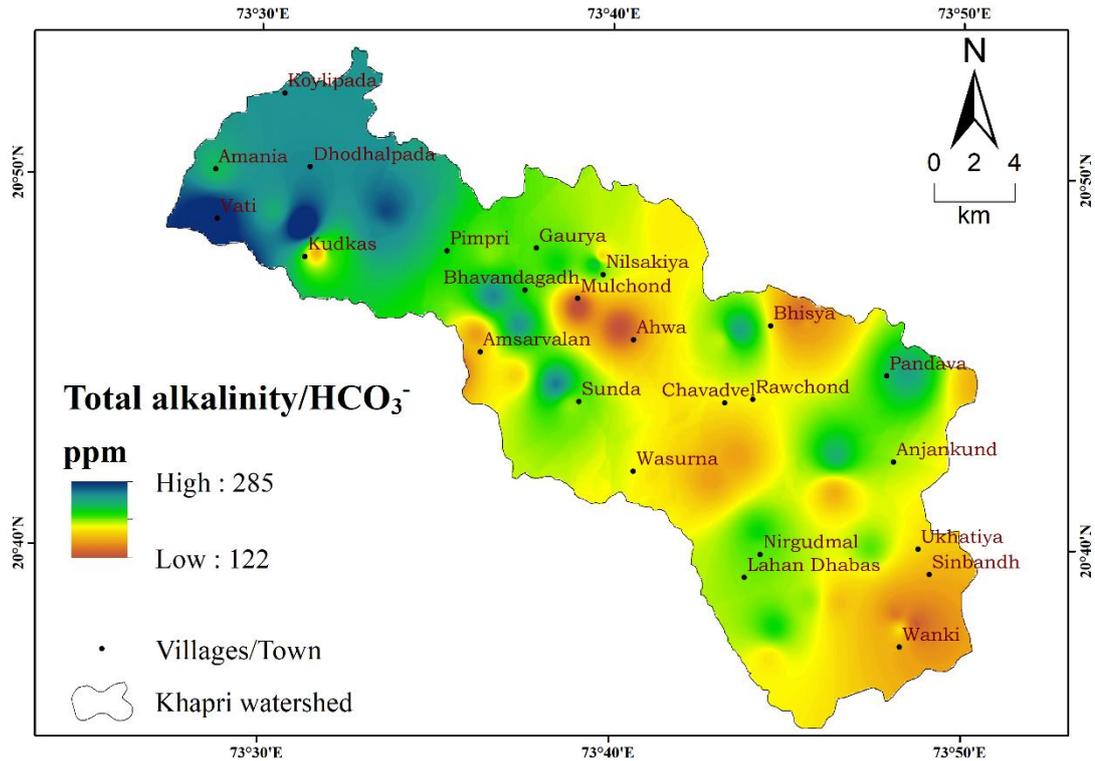
Figure 7.11 Spatial variation in Total Alkalinity (TA)/HCO₃⁻ of pre-monsoon groundwater samples.

7.4.10. Sulphate

The concentration of sulphate in rainwater is hardly 2 ppm, while it is abundantly found in most of the groundwater (Karanth, 1987). The abundance of sulphate in groundwater is due to oxidation, reduction, precipitation, solution and concentration processes as water circulates through the aquifer. The chief sources of sulphate in groundwater are sulphur minerals and sulphides of heavy metals present in igneous rocks and gypsum as well as anhydrite in sedimentary rocks, soil conditioners and artificial fertilizers (Hem, 1985, Nikumbh, 1997).

The concentration of sulphate in groundwater of Khapri watershed varies from 0.7 mg/L to 30.95 mg/L (figure 7.13). The relatively higher sulphate content found in the wells of upper reaches may be on account of improper local sewage disposals and high use of chemical fertilizers for the agriculture.
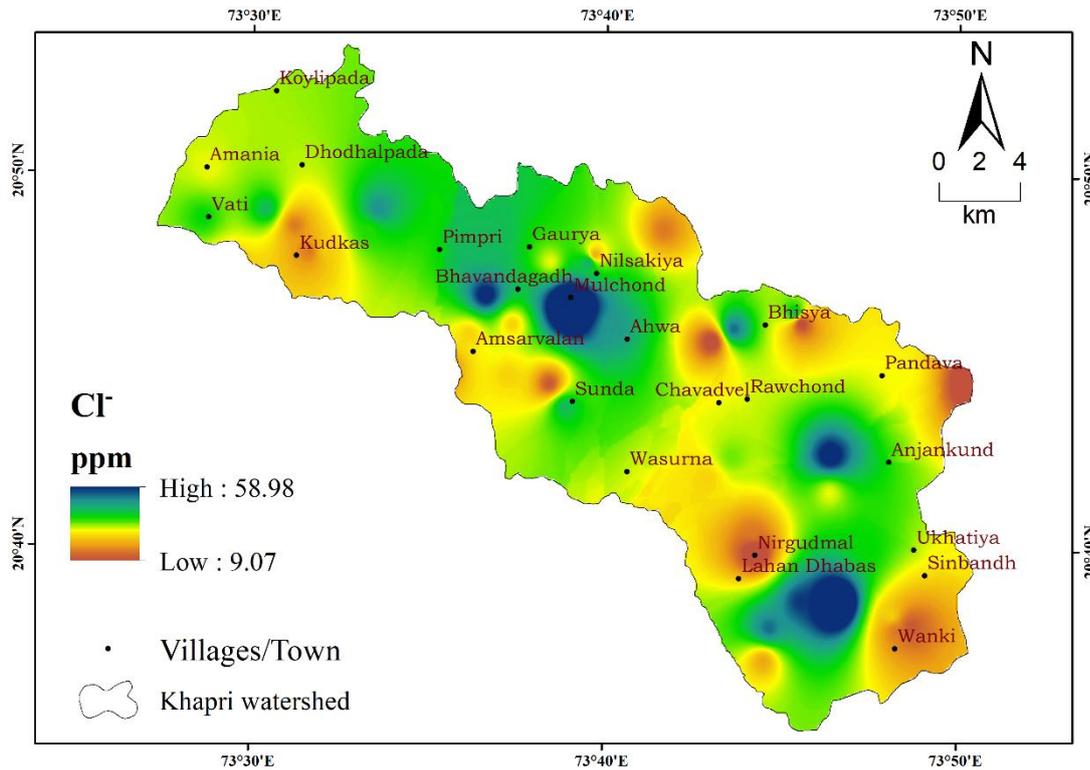
Figure 7.12 Spatial variation in Cl⁻ of pre-monsoon groundwater samples.

7.4.11. Nitrate

Around one-third of total nitrogen in the earth atmosphere is present in the gaseous form (Paulson et al., 1993). Nitrogen, in its oxide state is an essential element in the nutrition required for plants and animals and thus its concentration is of major interest in studies of natural and human influence on water chemistry. The chief sources of nitrate in the groundwater are atmospheric precipitation, geological sources, fertilizers, industrial waste sewage and animal waste (Hem, 1985). The concentration of nitrate in rainwater hardly exceed 0.2 ppm. However, due to extensive use of nitrate fertilizers and improper waste disposal systems leads to increase in the nitrate content of groundwater (Karanth, 1987). In pure groundwater the nitrate concentration goes maximum up-to 5 ppm, while polluted groundwater have concentration more than 100 ppm.

The nitrate concentration in groundwater of Khapri watershed varies from 0.1 mg/L to 6.55 mg/L (figure 7.14). The spatial distribution map reflects the relatively higher concentration of the nitrate in downstream near village Amania and in upstream near village Morzira and Jakhana. The relatively higher concentrations of the nitrate in

these regions may be the result of extensive use of nitrate fertilizers, which is not usual in the other parts of the watershed.

To assess the accuracy of analytical data of physicochemical parameters the ion balance error expressed in percentage is determined using equation 7.8.

$$\textit{Ion Balance Error } (\textbf{IBE}) = \frac{cation-anion}{cation+anion} * \textbf{100} \text{………………………….. (7.8)}$$

For the analytical data of samples in the present investigation the ion balance error is found to be below ±10% for all samples except one, indicating acceptable condition (Domenico and Schwartz, 1990) as well as the precision in the water quality analysis. However, for one sample with IBE greater than ±10%, is attributed to either omission of ionic specie with significant concentration or error observed during the analysis.
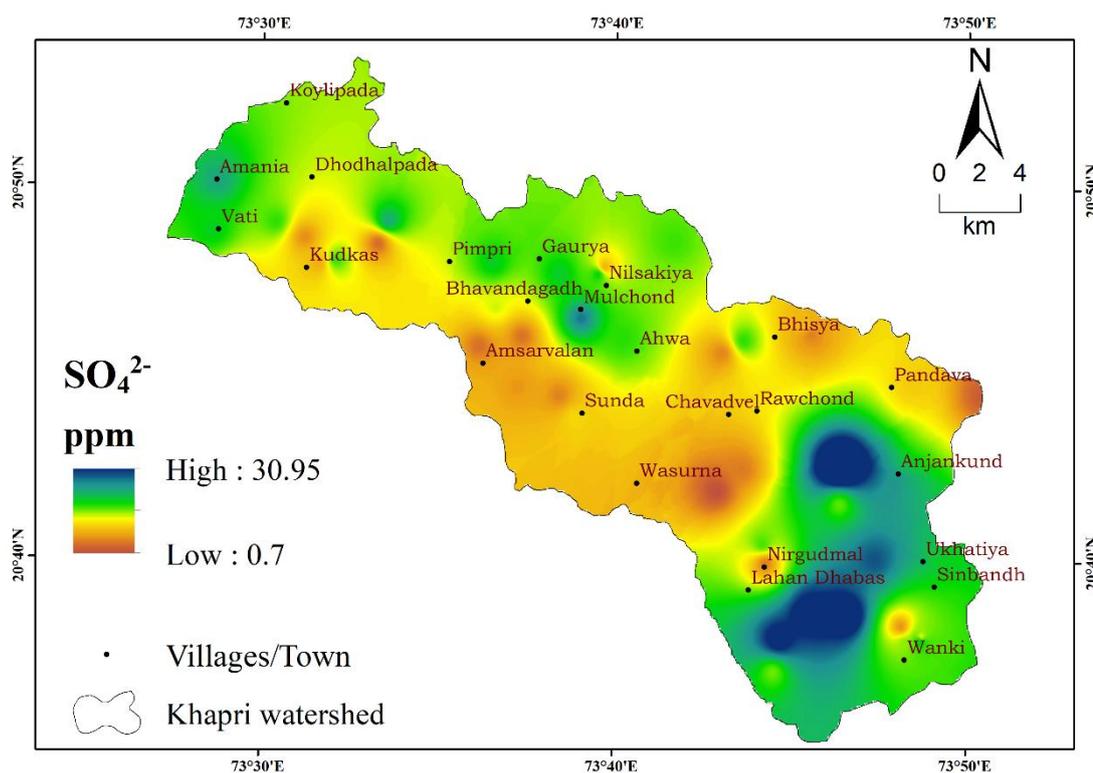

Figure 7.13 Spatial variation in SO₄²⁻ of pre-monsoon groundwater samples.
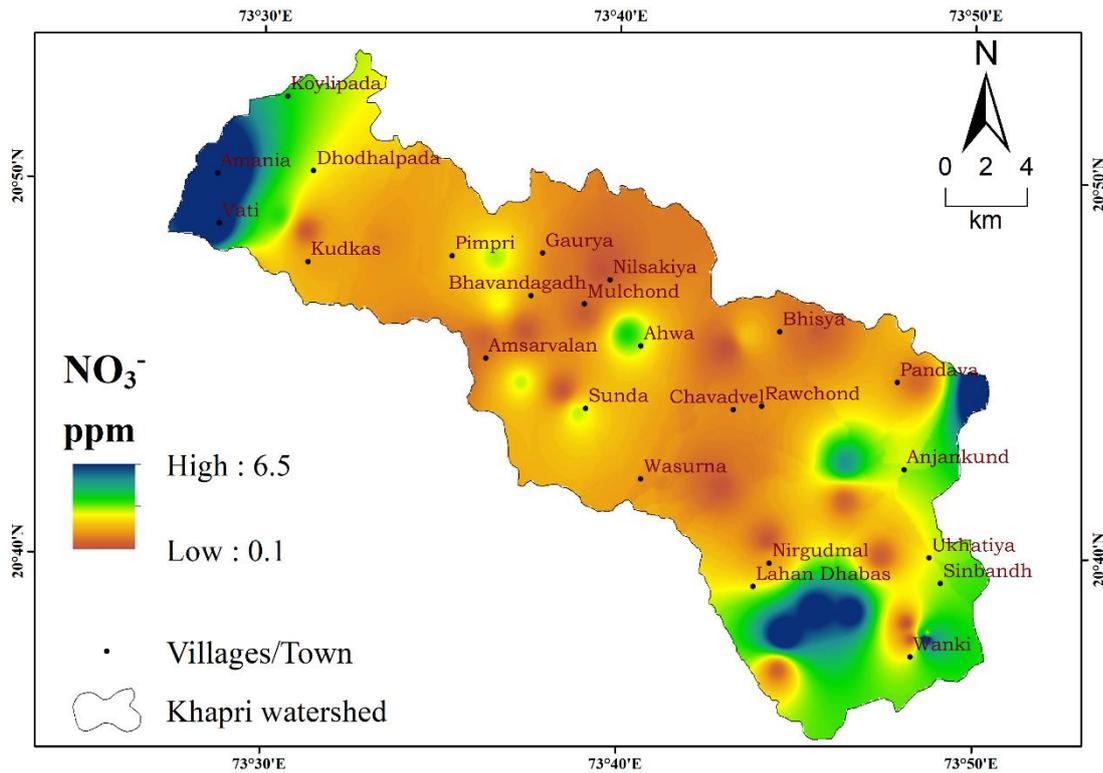
Figure 7.14 Spatial variation in NO_3^- of pre-monsoon groundwater samples.

7.5 Gibbs diagram

The source of most of the dissolved constituents in groundwater is the mineral assemblage of the country rocks through which it has passed and experienced irreversible reactions relating to dissolution of primary silicates (Rogers, 1989, Drever, 1997). The solubility of the minerals in water is not uniform and varies widely depending upon the temperature and pressure conditions. Researchers such as Gibbs, (1970) and (Hem & Steele, 1975) have attempted to study the relationship between the rock types and groundwater quality. (Gibbs, 1970)has determined a classification system which illustrates the role of three imperative natural mechanisms viz., rock-water interaction, atmospheric precipitation and evaporation, controlling the major ion chemistry of the groundwater.

The Gibbs, (1970) diagram for the groundwater samples of Khapri watershed indicates that all groundwater samples are falling in the rock dominance field indicating the control of country rock on the groundwater chemistry (Figure 7.14). The plagioclase feldspars such as labrodorite and mafic minerals such as amphiboles in basalts weather more quickly compared to the potassium feldspars. The higher abundance of calcium and

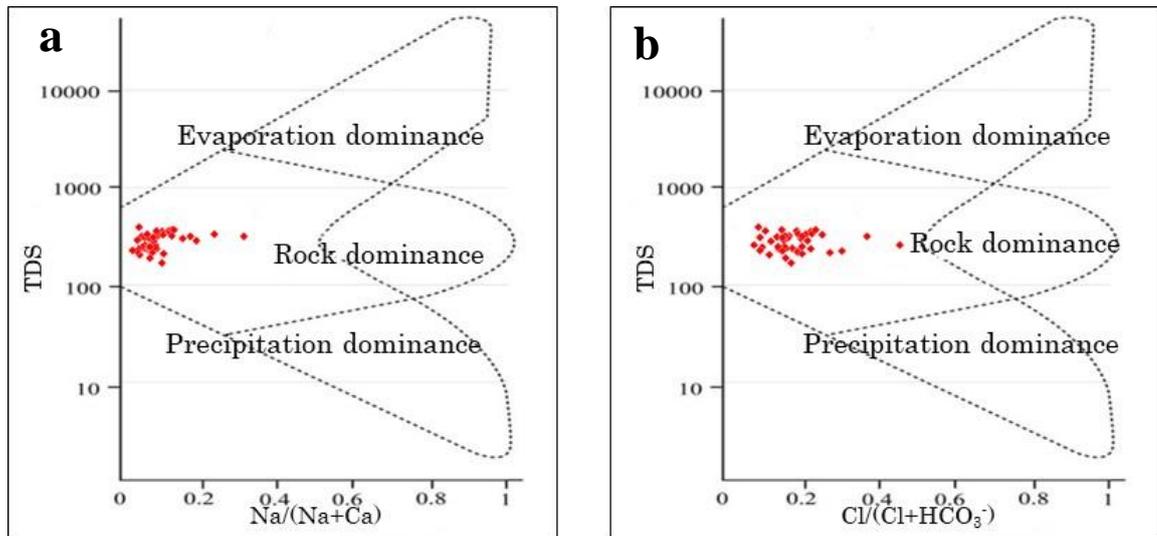bicarbonate in the groundwater of Khapri watershed is attributed to the weathering of silicate minerals.

Figure 7.15 Gibbs diagram for a) cations b) anions of pre-monsoon groundwater samples.

7.6 Hydro-chemical facies and characterisation of groundwater

The genesis of groundwater can be understood through the concept of hydro-chemical facies, where percent ionic abundance is arranged in decreasing order (Seaber, 1962 and (Mahanta et al., 2020). The concept is useful in differentiating the chemical nature of different groundwater samples. The analysis of cationic and anionic concentrations of groundwater samples of Khapri watershed, indicates the $Ca-HCO_3^-$ facies. The hydro-chemical facies for cations are Calcium > Magnesium > Sodium > Potassium, while for anions is Bicarbonate > Chloride > Sulphate > Nitrate (Figure 7.16). The dissolution of calcium containing silicate minerals such as plagioclase feldspars and pyroxenes are responsible for the higher concentrations of calcium and bicarbonate in the groundwater.
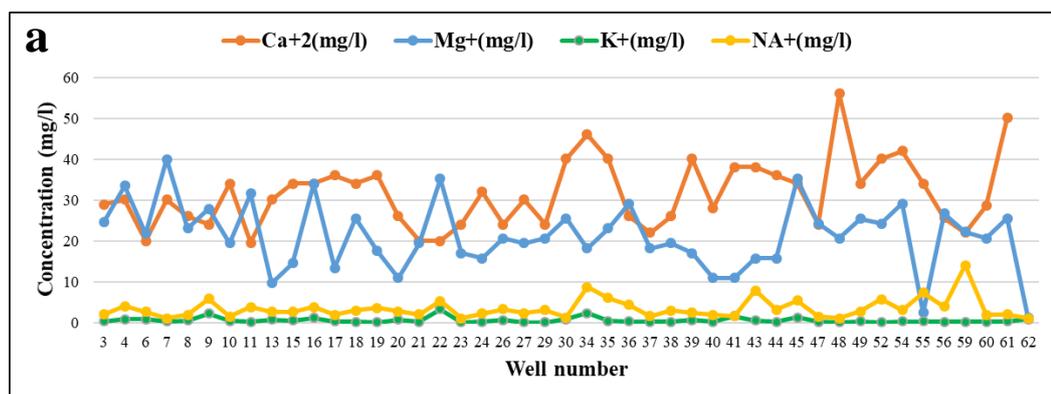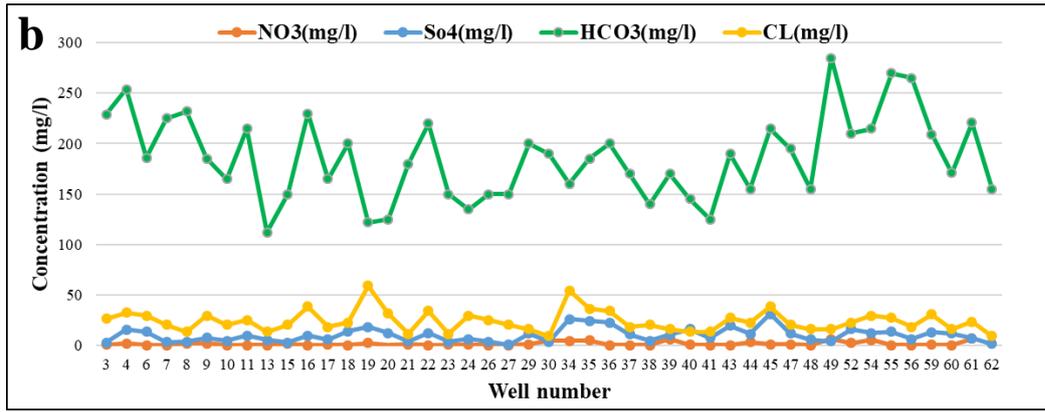
Figure 7.16 Hydrochemical facies through graphical distribution a) cations and b) anions of pre-monsoon groundwater samples.

To determine the hydro-chemical character of the groundwater the meq/L values of groups of major cations and anions are plotted on the Piper trilinear diagram (Mahanta et al., 2020; Piper, 1944). The Piper diagram have two triangular and one diamond shaped field. The percent meq/L values of cations and anions are plotted in the triangular fields and the overall character of the groundwater is derived by projecting the plots into the diamond field. The character of groundwater can be distinguished based on their position in the sub-divisions of the diamond field (Figure 7.17) as follows:

1. Alkaline earth (Ca^{+2} and Mg^{+2}) exceeds alkalis (Na^+ and K^+)
2. Alkalis exceed alkaline earths.
3. Weak acids (HCO_3^-) exceed strong acids (SO_4^{2-} and Cl^-)
4. Strong acids exceed weak acids.
5. Carbonate hardness exceed 50% i.e. chemical properties of the water are dominated by alkaline earths and weak acids.
6. Non-Carbonate hardness exceed 50%.
7. Non-Carbonate alkali exceeds 50% i.e. Chemical properties are dominated by alkalis and strong acids.
8. Carbonate alkalis exceed 50% i.e. soft waters plot in this field.
9. No one cation-anion pair exceeds 50%.

In cation triangle the groundwater samples of Khapri watershed are characterized as calcium type, no dominant type and magnesium type while, in anion triangle as bicarbonate type. All the plots in cation and anion triangle when projected in diamond field falls in sub-division 1 and 3, indicating "Alkaline earth (Ca^{+2} and Mg^{+2}) exceeds

alkalis (Na$^+$ and K$^+$)" and "Weak acids (HCO$_3^-$) exceed strong acids (SO$_4^{2-}$ and Cl$^-$)" respectively.
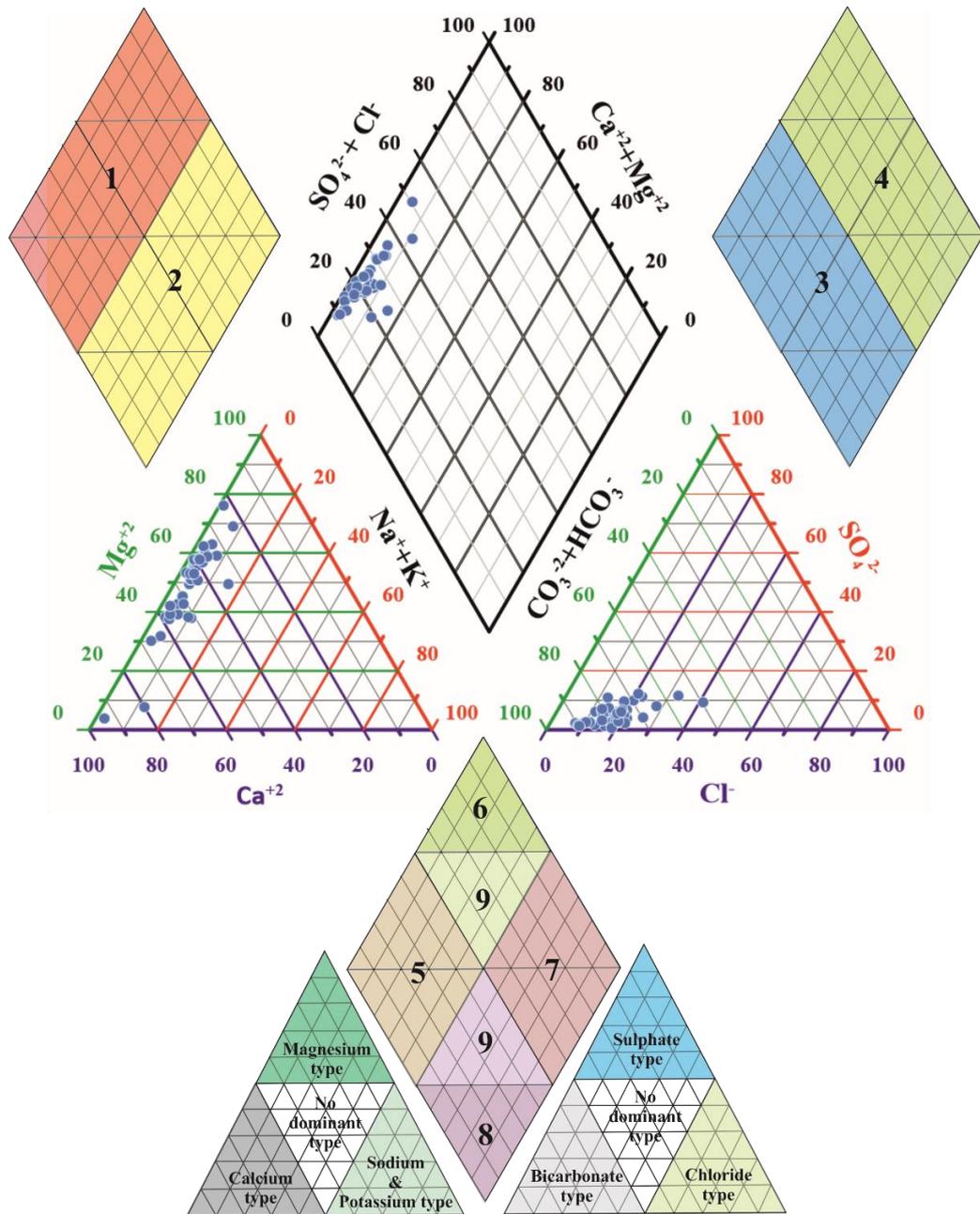
1. Alkaline earth (Ca^{+2} and Mg^{-2}) exceeds alkalis (Na$^+$ and K$^+$)
2. Alkalis exceed alkaline earths.
3. Weak acids (HCO$_3^-$) exceed strong acids (SO$_4^{2-}$ and Cl$^-$)
4. Strong acids exceed weak acids.
5. Carbonate hardness exceed 50% i.e. chemical properties of the water are dominated by alkaline earths and weak acids.
6. Non-Carbonate hardness exceed 50%.
7. Non-Carbonate alkali exceeds 50% i.e. Chemical properties are dominated by alkalis and strong acids.
8. Carbonate alkalis exceed 50% i.e. soft waters plot in this field.
9. No one cation-anion pair exceeds 50%.

Figure 7.17 Piper tri-linear plot of pre-monsoon groundwater samples of the Khapri watershed.

7.7 Suitability of groundwater for drinking purpose

The groundwater usually is consumed for direct use without any treatment considering that it is clean, clear and odour free with negligible or no suspended matter. However, certain anthropogenic actions such as improper disposal of sewage or industrial effluents may percolate and cause the deterioration of groundwater quality. As mentioned earlier, in Khapri watershed there is no threat from industrial effluents but the vulnerability due to geo-genic components and extensive use of fertilizers in agriculture cannot be overlooked. Thus, it is important to realize the suitability of chemical composition of groundwater for drinking purposes. To determine the suitability of groundwater for drinking purposes the analytical results should be compared with the set of reference values given by different organizations such as WHO (World Health Organization), USPS (United States Public Health Service), ICMR (Indian Council of Medical Research) and BIS (Bureau of Indian Standards). For Khapri watershed the analytical results are compared with the BIS, 2012. The analytical values exceeding the prescribed maximum permissible limit is a concerning issue for the potability of water.

The comparison of analytical results of groundwater samples with the BIS, 2012 reference values is presented in table 7.1. The comparison reveals that all the groundwater samples are falling within the acceptable limit as specified by BIS, 2012. This indicates that the groundwater is free from any pollutant originating due to extensive agriculturally based livelihoods or geo-genic components. Thus, the groundwater of Khapri watershed is highly suitable for the drinking purposes.

Table 7.1 Range of physicochemical parameters of pre-monsoon groundwater samples and their comparison with BIS (2012) standards for drinking water.

May 2023	Groundwater		BIS reference values for drinking water (2012)	Remark
Physicochemical parameters	Minimum	Maximum		
pH	6.9	8.5	6.5-8.5	Acceptable
Electrical conductivity (μS/cm)	208	571	≤ 750	Acceptable
Total Dissolved Salts (TDS) (mg/L)	104	285	≤ 500	Acceptable
Total Hardness (TH)	88	245	≤ 200	Permissible
Calcium (mg/L)	19.5	56	≤ 75	Acceptable
Magnesium (mg/L)	1.18	40.05	≤ 30	Permissible
Sodium (mg/L)	1.05	13.98	≤ 200	Acceptable
Potassium (mg/L)	0.04	3.26	≤ 12 (WHO)	Acceptable
Bicarbonate (mg/L)	112	285	≤ 400	Acceptable
Chloride (mg/L)	9.075	59.98	≤ 250	Acceptable
Nitrate (mg/L)	0	6.55	≤ 50	Acceptable
Sulphate (mg/L)	0.7	30.95	≤ 200	Acceptable
Total alkalinity (TA) (mg/L)	112	285	≤ 200	Permissible
Fe (mg/L)	0.005049	0.26	≤ 0.3 (WHO)	Acceptable
Mn (mg/L)	0.000275	0.0566	≤ 0.1	Acceptable
Zn (mg/L)	0.000452	0.8	≤ 5	Acceptable
Cu (mg/L)	0.000329	0.0965	≤ 3	Acceptable
Ni (mg/L)	0.000108	0.0964	≤ 0.1	Acceptable

7.8 Suitability of groundwater for irrigation purpose

The suitability of groundwater for irrigation is based on tolerance of plants, soils properties, local climate and irrigation methods (Karanth, 1987,Narany et al., 2016). The groundwater utilized for the agricultural practices shows presence of salts, usually derived from the weathering and dissolution of minerals. These dissolved salts affect the

soil properties which may eventually hinder the plant growths (Ali et al., 2014). The suitability of groundwater for irrigation purpose is evaluated with the help of three indices viz., Sodium Absorption Ratio (SAR), Residual Sodium Carbonate (RSC) and Kelly's ratio (KR).

The Sodium Absorption Ratio (SAR) reports influence of sodium concentration on stability of soil aggregates and indicates sodium/alkali hazards. It is determined using the concentrations of alkaline and alkaline earth cations such as sodium, calcium and magnesium in meq/L (Mahanta et al., 2020) and is mathematically expressed as equation (7.9). The high concentration of sodium in groundwater causes reduction in the soil permeability by displacing calcium and magnesium ions present in the soil. The sodium and potassium ions enable the dispersion of clay particles whereas calcium and magnesium support flocculation. If the irrigation water with high SAR values is used, the sodium is likely to substitute for calcium and magnesium, decreasing ability of soil to form aggregates and thereby loss of soil structure. This will lead to reduction of infiltration capacity and permeability of soil which affects the crop production. The SAR values in groundwater samples of Khapri watershed ranges from 0.02 to 0.4. The plot of SAR versus electrical conductivity (figure 7.18) indicates that the samples fall in C1S1 and C2S1 field. All the groundwater samples are regarded as "excellent" for irrigation, as per the SAR classification of Richards, 1954.

$$SAR = \frac{Na}{(\sqrt{Ca}+Mg)/2} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (7.9)$$

The Residual Sodium Carbonate (RSC) is useful in determining the suitability of groundwater for irrigation by considering anions such as carbonate and bicarbonate. The relative abundance of sodium with reference to excess of carbonate and bicarbonate over alkaline earth cations such as calcium and magnesium affects the suitability of groundwater for irrigation (Richards, 1954, Narany et al., 2016, Mahanta et al., 2020). The RSC is expressed as equation 7.10, where ionic concentration is in meq/L. In Khapri watershed, the RSC of groundwater samples ranges from -1.21 to 2.12 and falls under good and medium category. The groundwater samples with negative RSC indicate the deficiency of alkalinity over alkaline earth (Narany et al., 2016), suggesting groundwater is suitable for irrigation purpose.

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+}) \dots\dots\dots\dots\dots (7.10)$$

Kelley's ratio (1940) is a significant parameter to assess the groundwater quality for irrigation based on the concentration of sodium measured against the concentration of calcium and magnesium in meq/L. It is expressed as equation (7.11). Kelley's ratio greater than 1 indicates the excess concentration of sodium in groundwater, making it unsuitable for the irrigation purpose. The Kelley's ratio for the groundwater samples of Khapri watershed ranges between 0.011 and 0.194, indicating its suitability for the irrigation purpose.

$$\text{Kelley's Ratio (KR)} = Na^+ / (Ca^{+2} + Mg^{+2})$$

Table 7.2 Range of indices used for assessing groundwater suitability for irrigation

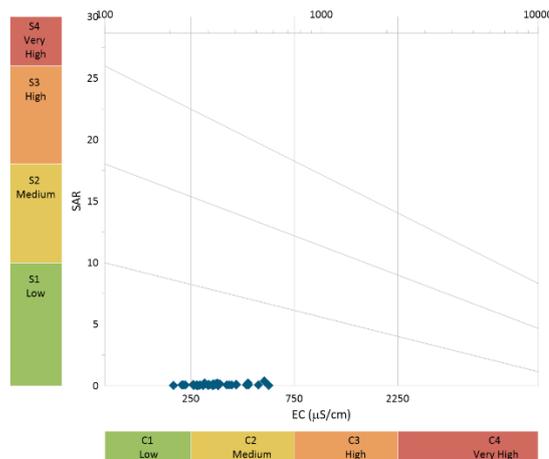| Groundwater suitability for irrigation			
Indices	*Minimum*	*Maximum*	*Suitability for irrigation*
SAR	0.02	0.40	Excellent
RSC	-1.21	2.12	Good
Kelly ratio	0.011	0.194	Suitable

Figure 7.18 USSL plot of pre-monsoon groundwater samples of the Khapri watershed.

7.9 Epilogue

In the present investigation an attempt has been made to determine the suitability of groundwater for drinking and agriculture purposes as well as to understand the dominant mechanism controlling the water chemistry.

To collect representative water of the aquifers, the electric pumps wherever available are used and are allowed to drain water for 10 minutes, to remove the stagnant water in the pipes. For sampling locations where pumps are not available, the sampler has been lowered to the central bottom most part of the well. All the samples are collected in the pre-rinsed high-density polyethylene bottles (HDPE) of 1000 ml.

capacity. The pre-rinsed bottles are again rinsed two to three times with the same groundwater sample, which is to be collected. Simultaneously, the GPS is used to record the geographical position and elevation of the sampling location. The in-situ recording of physicochemical parameters such as pH, EC, TDS and temperature is carried out using Hanna Portable Pen type pH and TDS-EC-TEMP meters. Later in lab, the parameters such as total hardness (TH), total alkalinity (TA), cations (Calcium (Ca^{+2}), Magnesium (Mg^{+2}), Sodium (Na^+) and Potassium (K^+)), anions (Nitrate (NO_3^-), Sulphate (SO_4^{2-}), Chloride (Cl^-) and Bicarbonate (HCO_3^-)) are analysed for pre-monsoon groundwater samples collected in May-2023. The range of concentration of physicochemical parameters and trace elements along with acceptable limit for drinking water as per BIS are given in table 7.1. The suitability of groundwater for irrigation purpose is determined based on indices such as Sodium Absorption Ratio (SAR), Residual Sodium Carbonate (RSC) and Kelly's ratio. To understand the dominant mechanism that govern the groundwater chemistry, Gibbs, (1970) diagram is used. The analytical results of pH indicate neutral to weakly alkaline, Ec indicate low conductive and TDS indicate fresh nature of groundwater in Khapri watershed. The chemical analysis of groundwater suggests, the calcium and magnesium are the dominant cations followed by sodium and potassium. Among anions, the bicarbonate is dominant followed by chloride > sulphate > nitrate. The higher values of bicarbonate may attribute to silicate weathering of the basalt (Dethier 1986 and Nikumbh 1997). The Piper trilinear diagram indicates the Ca-HCO3-type chemical character of groundwater (Piper, 1944). The Gibbs diagram reflects rock weathering is the dominant mechanism governing the groundwater chemistry. The comparison of the cations and anions in the groundwater with BIS (2012) standards indicates that the water is suitable for drinking. The SAR is a measure of sodium hazard of irrigation water to form exchangeable sodium in the soil (Richard 1954 and Shankar et al. 2011). The SAR value of groundwater samples ranges between 0.02-0.4 in Khapri watershed, indicating excellent groundwater quality for irrigation and negligible sodium hazard. The RSC of groundwater sample indicates the alkalinity hazard for the soil. The RSC of groundwater samples ranges from -1.21 to 2.12. The values suggest the good suitability of groundwater for irrigation. Kelly's ratio evaluates the water quality for irrigation based on the Na concentration measured against Ca and Mg (Kelly, 1940). The Kelley's ratio of groundwater samples ranges from 0.11 to 0.194. The Kelly's ratio less than 1 indicates water is suitable for irrigation purposes. The analysis of all these indices suggests that the groundwater is suitable for irrigation purposes.