CHAPTER -IV

HYDROGEOCHEMISTY

4.1 Introduction

Almost all groundwater originates from rain hence gets partly influenced by the atmospheric conditions during precipitation. On reaching ground it gets divided into surface and subsurface flow and in that process gets further modified. The infiltrating water from the partially saturated soil zone to the water table gets altered chemically. One of the major causes of alteration is the uptake by the water of soil zone CO_2 to form H_2CO_3, HCO_3^- and CO_3^{--}. Finally after reaching the water table, the water moves through various geologic units that commonly have different mineral assemblage. The composition of the assemblages and the order in which they are encountered by the water control the chemistry of the groundwater. The most important reactions that are governing chemical alteration of groundwater are mineral dissolution and precipitation, redox reactions and cation exchange, wherein temperature play important role.

Broadly the quality of groundwater dependent upon factors like mineral composition of the water bearing formations/host rock, residue time in aquifer, recharge and discharge within the basin and salinity ingress which can be grouped in contamination caused by natural processes. There are anthropogenic contaminations caused by different types of pollutants like industrial, agricultural and sewerage. Ground water quality in the study area is highly diverse and complex due to influence of sea water intrusion (coastal salinity), inherent sediments' salinity, quality deterioration due to overexploitation and pollution.

The study area is characterized by diverse lithologies having varied chemical composition and physical properties. As a result there is variation in its water bearing properties both in quality and quantity. Precipitated water while traveling through soil, vadose zone and finally to water table (in case of unconfined aquifer) dissolve and precipitate various geochemical constituents. This overall process develops a chemical nature to water 'now groundwater' which again alters depending upon the residence time of chemical constituents.

Groundwater while passing through igneous rock dissolves only very small quantities of mineral matter because of the relative insolubility of the rock composition. On the contrary sedimentary rocks being more soluble dissolve more constituents. Among cation Sodium and Calcium are most common while among anions it is bicarbonate and sulfate. Chloride occurrence in groundwater is by and large from connate water and partly from intruded sea water and sewage as a surface pollutant (Todd, 1980).

The groundwater salinity in coastal tracks is through airborne salts which originates from the air-water interface over the sea and are deposited on land both by precipitation and by dry fallout. Another important anion in coastal region is chlorine which is an indicator of salinity ingress. Chloride abundance in coastal groundwater range between 4 to 20 kg Cl/ha and it decreases inland, varying exponentially with distance from the sea (Todd, 1980).

4.2 Methodology for Data Appraisal

The study area fall with in the jurisdiction of two important districts namely Vadodara and Bharuch. Hydrogeologically these districts have been studied in detail by various government and non government organizations. Long and short term seasonal monitoring of groundwater regime through number of observation wells has been carried out by the departments like CGWB and GWRDC. The available secondary data for 1985 has been used to compare with the authors own analyzed results to infer long term geochemical behavior of groundwater. The author has carried out groundwater sampling for both pre and post monsoon seasons from different geomorphic regions on a well spaced grid pattern. For this entire area was divided into 10 x 10 km grid. From the grid, center point was picked up as the nodal village for water samples collection. From each village one open well sample, one hand pump sample (shallow change in aquifer) and tube/bore well (Deeper aquifer) samples were collected for evaluating the chemical content pre and post monsoon seasons (Fig-4.1 & 4.2). Samples were analyzed in the laboratory for their major and minor chemical constituents. Apart from major cation and anions some trace elemental analysis and oxygen isotope studies have also been attempted. Details on seasonal collection of groundwater samples and their analytical attributes are given in Table 4.1.

Table-4.1 Detail of the Groundwater Sample Collected for Geochemical Analysis

Sr. No.	Season	Total No of Samples	Sample Analyzed for
1	June 2002	52	Major Cations and Anions
2	Oct-Nov 2002	145	Major Cations and Anions & Isotope
3	May-June 2003	101	Major Cations, Anions & Trace elements
4	Oct-Nov 2003	101	Major Cations, Anions and Trace elements

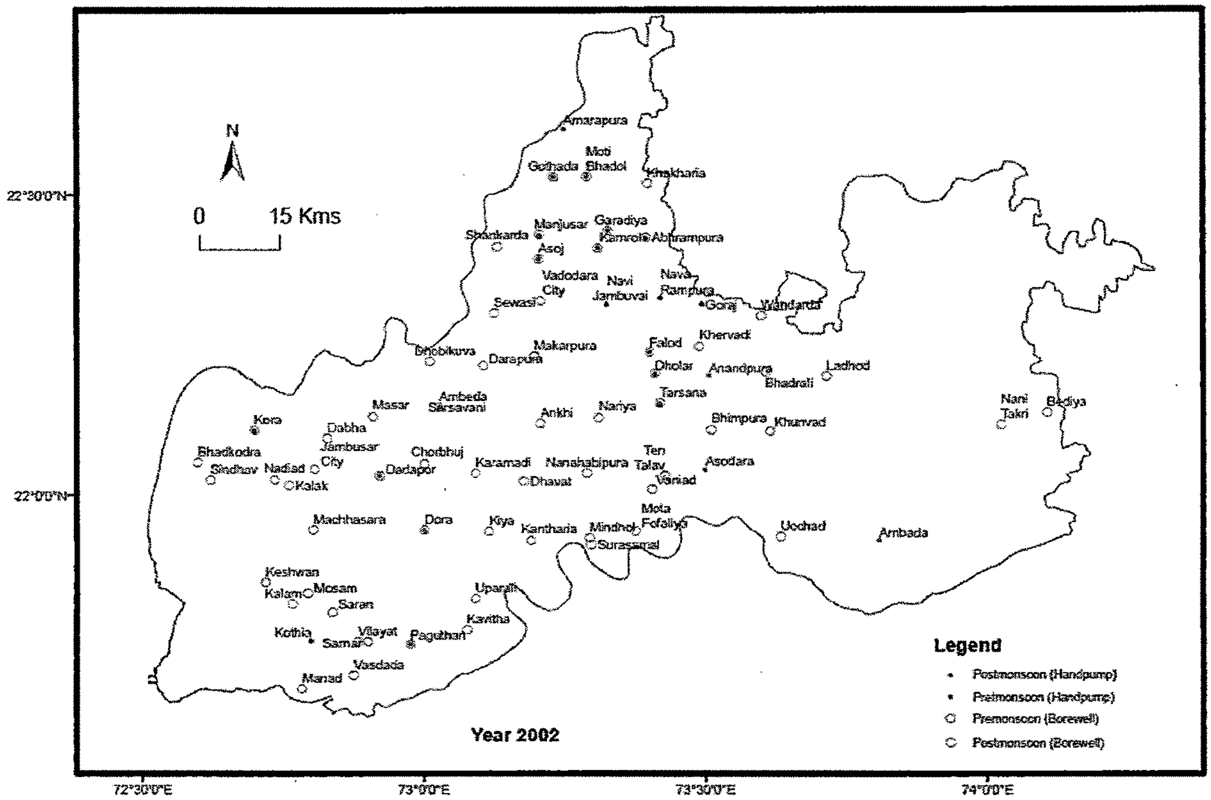


Fig-4.1 Locations of Water Samples in the Study Area (Pre and Post-monsoon 2002)

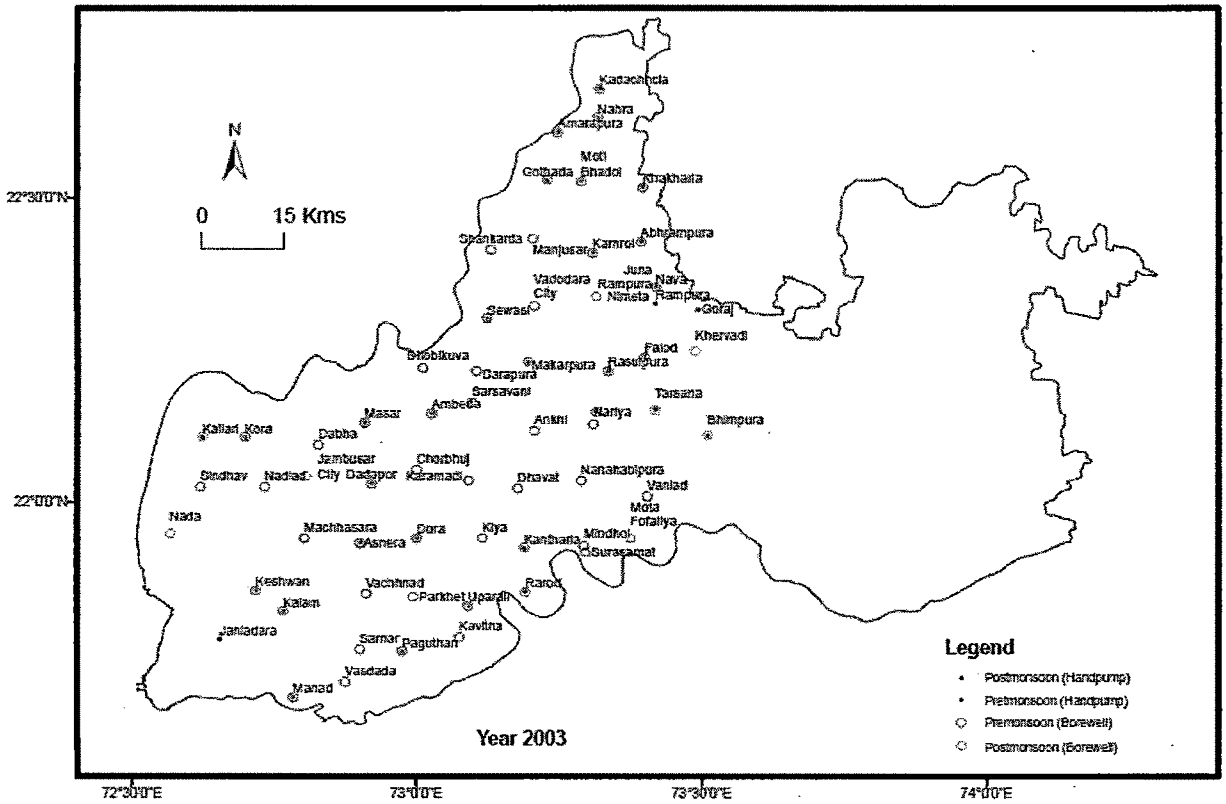


Fig-4.2 Locations of Water Samples in the Study Area (Pre and Post-monsoon 2003)

Hydro chemical Analysis Approach: The American Public Health Association (APHA, 2000) has prescribed standard analytical techniques for determining the dissolved chemical content in groundwater. The water analysis was carried out using standard methods given in *"Standard methods for the examination of water and waste water"*. Parameters like Alkalinity, Total hardness, Calcium hardness, Magnesium hardness, Chloride were analyzed using titration method however, calcium hardness was cross-checked with Flamephotometer. Major cations like sodium, potassium, and calcium were analysed with systronics 128-Flamephotometer. Sulfate and Nitrate were analysed with UV-spectrophotometer. All values are expressed in milligram/liter (mg/l), except pH and conductivity.

For TDS measurement groundwater samples were filtered using Whatman grade 934 AH filter paper having 12.5 cm diameter. Out of filtered volume 50 ml of measured sample was transferred to evaporating dish (oven dried at 108° C) and evaporated to dryness in steam bath. Later samples were dried in an oven at 180 ±2° C, cooled in desiccators and finally weighted on an electronic balance.

In order to determine the geochemical behavior of groundwater in the study area the analysis has been divided into the following parts.

- **Physical Characteristics**
- **Chemical Characteristics**
- **Geochemical Characteristics**
- **Oxygen Isotope Behaviour**
- **Groundwater Quality Characterization**
    - **Drinking Water Quality Assessment of Groundwater Samples**
    - **Classification of Groundwater for Irrigation Purpose**
    - **Trace Element Analysis for Assessment of Toxicity**
- **Application of correlation analysis for evaluation of hydro-geochemical Parameters**

4.3 Physical Characteristics

Colour, odour, turbidity and temperature are the main physical properties for water quality determination especially for drinking and industrial purpose. Unlike surface water, ground water is generally clean, colourless and odourless, with little or no suspended matter and has relatively constant temperature (Karanth, 1987). In the study area none of the sample was found showing any colour development, giving any odour or having any turbidity. The samples collected during the entire period were free from physical impurities. The temperature of shallow groundwater is controlled to a large extent by atmospheric temperature (Karanth, 1987). Temperature of the groundwater in most of the part of the study area was found to be more or less constant except for open well water (Table-4.2). In open wells the average water temperature was found to be ±23°. Whereas deeper wells average temperature comes out to be 29.3. Detail data information on temperature as physical parameter for various locations is given in Annexure 4.1 to 4.4.

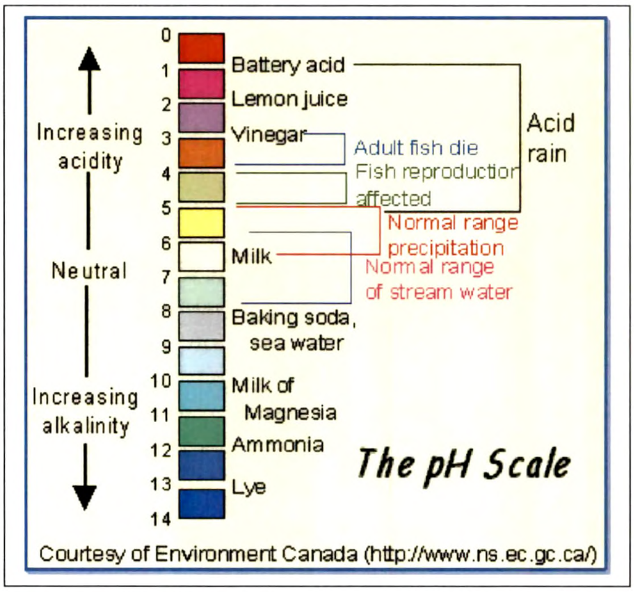
Table-4.2 The Statistical Analysis for Temperature Distribution in Groundwater's of the Study Area

Sr. No.	Year	Mean	Min	Max	Std. Dev.
1	Pre Monsoon 2002	28.3	26.7	29.7	0.44
2	Post Monsoon 2002	28.1	23	32	1.4
3	Pre Monsoon 2003	30.4	27.6	32.8	0.99
4	Post Monsoon 2003	29.3	23.4	31.6	1.4

4.4 Chemical Characteristics

4.4.1 Hydrogen Ion Concentration (pH)

pH in water indicates the concentration of hydrogen ions and is expressed as the negative logarithm of the concentration of hydrogen ions. As the ionic product of water is 1.01×10^{-14} at 25° C. Therefore, a neutral solution will have 1×10^{-7} ions of H^+ and OH^- each. The pH scale for aqueous solution ranges between 0 to 14 (Fig.-4.3). At 25° C, pH 7.0 is neutral, the activities of hydrogen and hydroxyl ions are equal and each corresponds to an approximate concentration of 1×10^{-7} moles/l. the neutral point is temperature dependent and is pH 7.5 to O° C and pH 6.5 at 60° C. the pH below 7.0 is acid and above 7.0 is being alkaline.



Courtesy of Environment Canada (http://www.ns.ec.gc.ca/)

Fig-4.3 The pH Scale

Measurement of pH is one of the most important and frequently used parameters in water chemistry. Most chemical and biological reactions occur at a narrow range of pH. Higher values of pH hasten the scale formation in water heating apparatus and also reduce the germicidal potential of chlorine. pH below 6.5 starts corrosion in pipes, thereby releasing toxic metals. In general pH of natural water ranges between 6.0 to 8.0 and the variation is mainly due to presence of dissolved CO_2 and hydrogen carbonate ions. High pH >8.5 are associated with sodium-bicarbonate-carbonate water, medium pH (5.5-8.5) are associated with water having high bicarbonate concentration and presence of free acids causes low pH <5.5 values in water (Garrels and Christ, 1966; Schwille, 1976).

pH was measured in the field itself during groundwater sampling with the help of portable instrument. The pH probe was calibrated with standard pH solutions. All necessary precautions were taken to avoid any contamination of samples. For in field direct measurement of pH, groundwater sample was taken in 100 ml beaker (HDPL plastic) and pH reading was taken. Average of three values was taken as final pH.

Evaluation of pH through available secondary data (mainly from Govt. reports) suggests predominately alkaline nature. However, the alkalinity tends to increase from eastern hilly zone to western coastal plains (E to W) as well as with depth. pH values on comparison with the pre and post monsoon seasons indicates no significant change due to rainfall recharge (Fig 4.4). Overall statistical analysis over the observed seasonal range of pH values is given in the Table 4.3.

Table-4.3 Statistical Analysis for Range of pH Distribution Pattern in Study Area

Sr. No.	Year	Mean	Min	Max	Std. Dev.
1	Pre Monsoon 2002	8.14	7.61	8.87	0.2
2	Post Monsoon 2002	7.56	7.07	8.6	0.34
3	Pre Monsoon 2003	7.68	7.06	8.71	0.29
4	Post Monsoon 2003	7.66	6.65	8.48	0.36

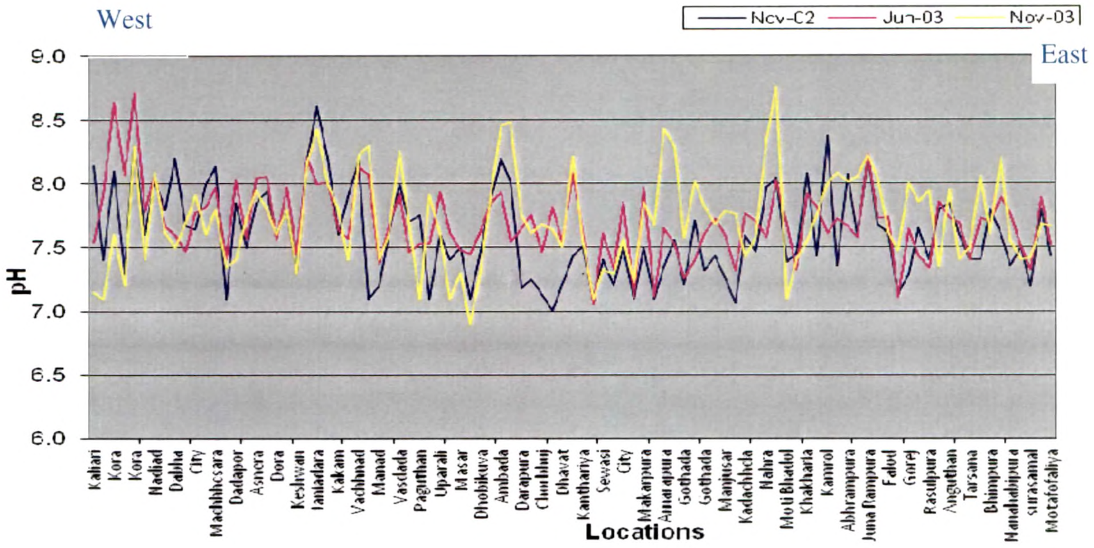


Fig-4.4 Comparison of pH in the Water Samples of the Study Area for Three Seasons

4.4.2 Specific Electrical Conductance (EC)

The ability of an aqueous solution to carry an electric current is Conductivity 'k' which in turn depends on the presence of ions and on the temperature of the solution and is expresses as 1/ohm-cm or mho per centimeter. Conductivity is normally reported in micromhos per centimeter (μmho/cm).

The conductivity of groundwater samples were measured in the field using portable field instrument. For this samples was taken in 100 ml HDPL beaker and EC was measured. The instrument was duly calibrated using standard KCl solution.

Temporal and Spatial Variations in Specific Conductance in the Study Area: In the study area the EC tends to increase from east to west. This is mainly due to the coastal influence and inherent salinity of aquifers. In Vagra Taluka coastal aquifers are highly saline therefore it is mainly utilized for salt production. EC values obtained for five seasons does not show any significant change (Table 4.4).

Table-4.4 Statistical Analysis for Electric Conductivity Distribution Pattern in Study Area

Sr. No.	Year	Mean	Min	Max	Std. Dev.
1	Pre Monsoon 2002	3486	829	13500	2844.63
2	Post Monsoon 2002	21812	415	19600	2583.33
3	Pre Monsoon 2003	2677	451	13300	2521.37
4	Post Monsoon 2003*	2730	448	15700	2608.1

*With an exception of brine Tube well sample at Nada village (Jambusar Taluka).

4.4.3 Total Hardness (TH)

Hardness is a result of presence of divalent metallic cations, of which calcium and magnesium are the most abundant in groundwater (Todd1980). The hardness in natural water seldomly exceeds 200 mg/l unless and until water comes in contact with limestone or gypsum bearing formations (Hem, 1959). Public acceptability of the degree of hardness of water may vary considerably from one community to another, depending on local conditions and availability of resources (USPEA, 1976). Permissible limit for the Total Hardness in groundwater for drinking purpose is 600 mg/l (**BIS 10500**). Classification of groundwater hardness is given in the Table 4.5.

Table-4.5 Classification of Groundwater Based on Hardness

Category	Types of Water	Klut-Olszewski (1945) meq/l	Kass (1965) meq/l	Sawyer and McCarty (1967) mg/l
I	Very Soft	0-1.43	0 – 1	<60
II	Soft	1.43-2.86	1 – 3	
III	Average Hardness	2.86-4.28	3 – 5	60 - 120
IV	Moderate Hardness	4.28-6.42		
V	Hard	6.42-10.72	5 – 10	120 – 180
VI	Very Hard	>10.72	>10	>180

The spatial profile of TH for pre-monsoon 2002 gives an idea on the behavior of TH in the study area (Fig-4.5). About 40% of the samples are within the permissible limit of 600mg/l while 30% are unfit for drinking purpose. Mainly samples from coastal plains (west) have high concentration and it decreases towards landward (east). However, in alluvial plains (central part) few localities observed TH is high. Majority of samples fall in Very Hard Category.

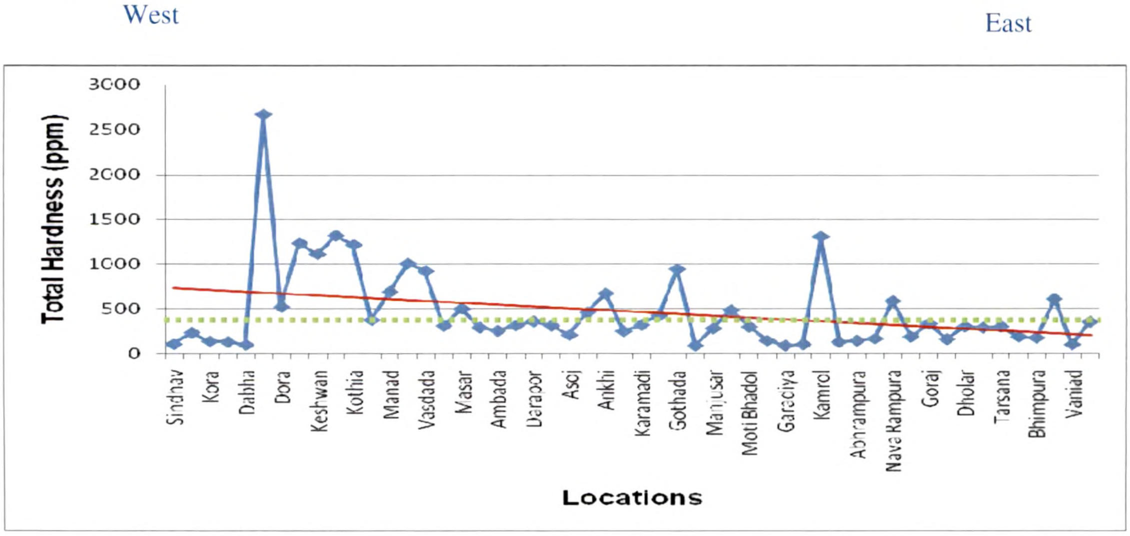


Fig-4.5 Total Hardness Distribution in the Study Area of Pre-monsoon 2002 Samples

During post monsoon 2002 about 75% of samples were found to be unfit as they show very high total hardness (Fig- 4.6). Most of the samples from the coastal region were found to have high concentration except those wells which are supported by surface water pond. The infiltration from these ponds dilutes the ionic concentration of water but this effect is at very local level.

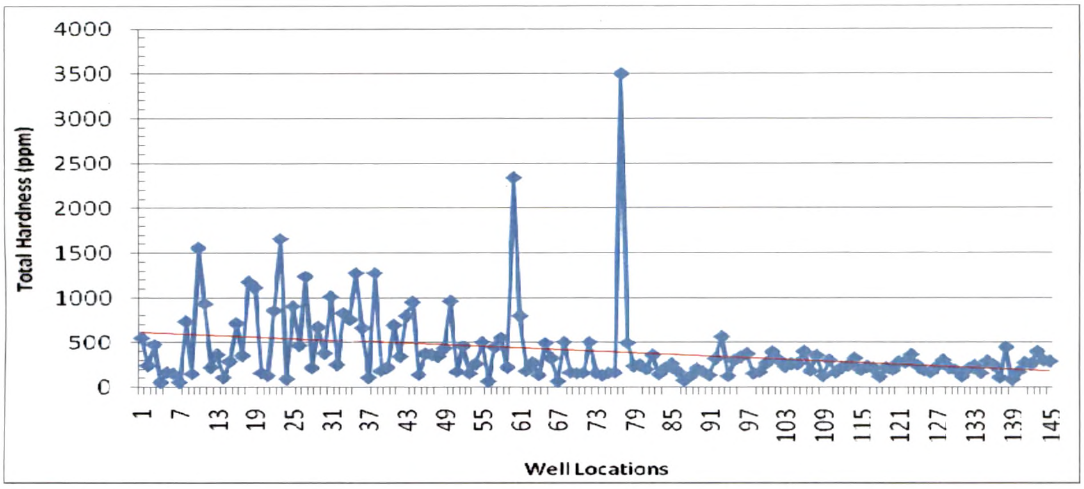


Fig-4.6 Total Hardness Distribution in the Study Area for Post-monsoon 2002 Samples

During Pre-monsoon 2003, samples were collected from coastal plains, alluvial plains and piedmont zone. The plotted spatial distribution profile west to east suggest a minor decrease in total hardness (Fig- 4.7). About 70% of the samples are within the permissible limit while remaining 30% samples are unfit as they show high concentration of TH.

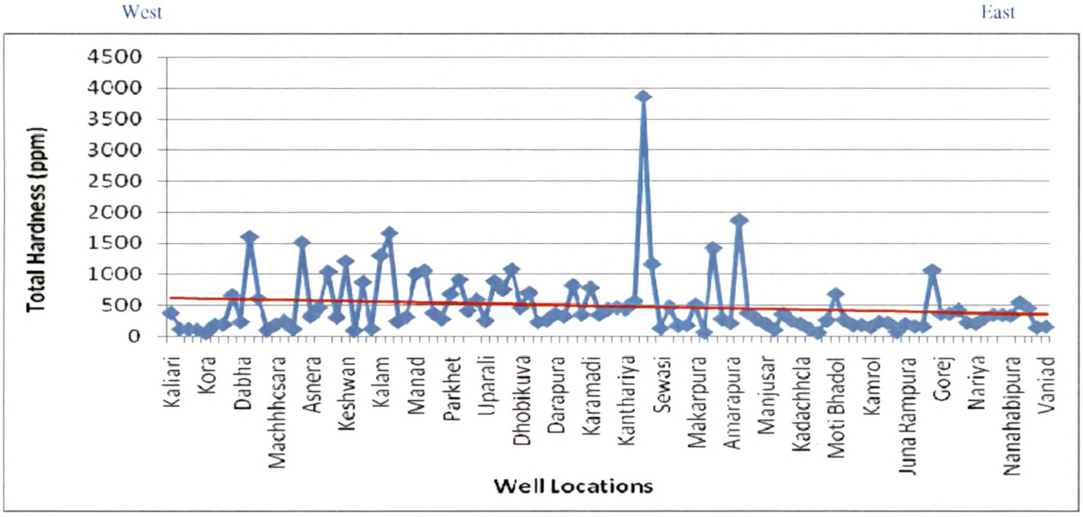


Fig-4.7 Total Hardness Distribution in the Study Area for Pre-monsoon 2003 Samples

Similarly post-monsoon 2003 samples indicate slight increase in TH concentration after getting recharge from rainfall. About 71% of the samples fall below 600 pm concentration while 29% of the analyzed samples fall above the permissible limit of drinking water. The Fig-4.8 represents variation in the groundwater concentration in the study area.

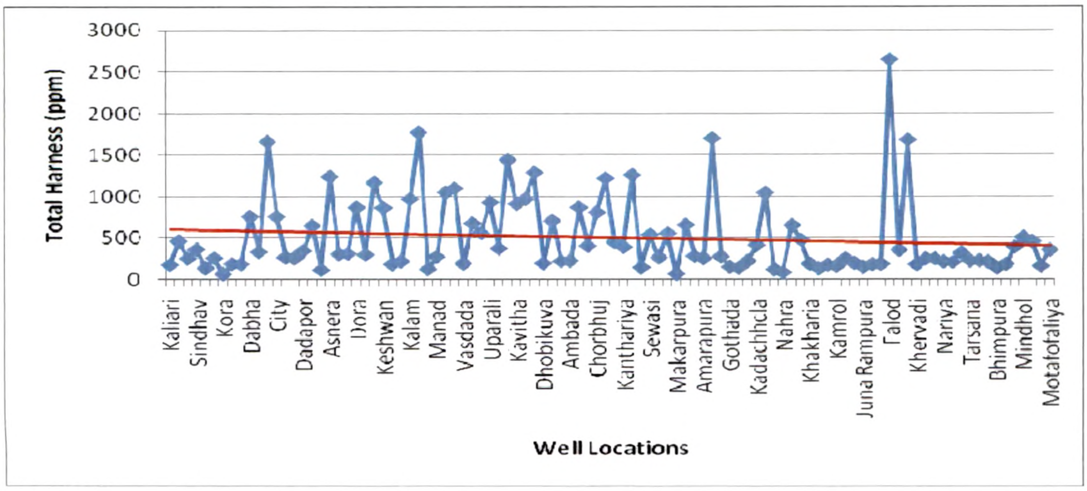


Fig-4.8 Total Hardness Distribution in the Study Area for Post-monsoon 2003 Samples

The Table 4.6 show details on number and percentage of samples falling in different category for different seasons. During post-monsoon 2002 samples were collected from highland area therefore the number and percent of sample is comparatively more. From five set of samples for pre and post-monsoon period it appears that overall the concentration of TH remain more or less constant. After monsoon slight increase in TH concentration has been observed in some of the villages.

Table-4.6 Sawyer and Mc Carty Classification of Water Hardness in the Study Area

TH Category	Pre Monsoon 2002	Post Monsoon 2002	Pre Monsoon 2003	Post Monsoon 2003
No. of Samples	52	145	101	101
I	0	0	2/2	0
II &III	5/10	11/7	10/10	4/4
IV & V	8/15	30/21	10/10	13/13
VI	39/75	104/72	79/78	84/83

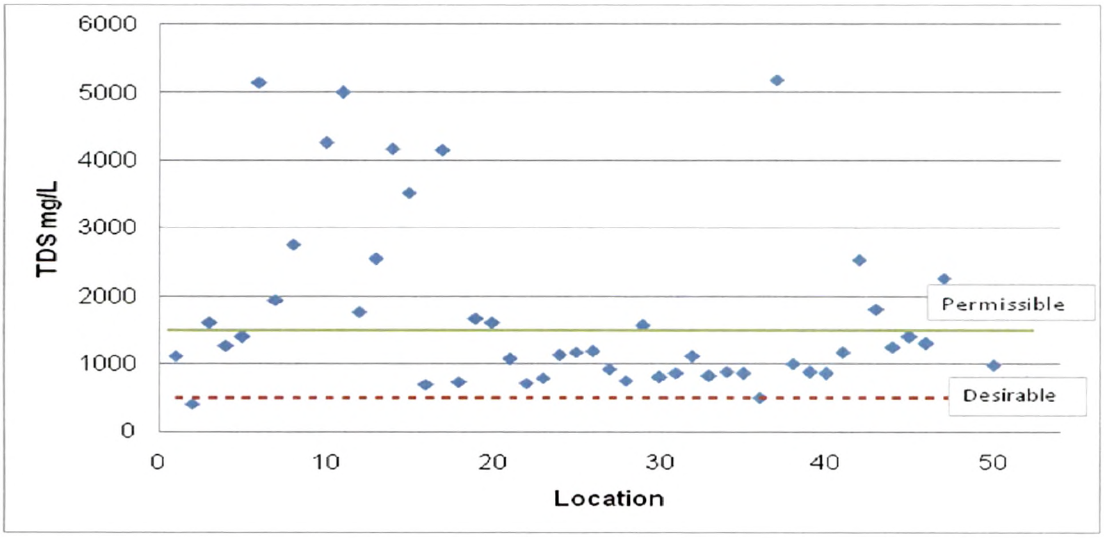
39/75-No. of samples/percentage

4.4.4 Total Dissolved Solids (TDS)

Total Dissolved Solids are determined by weighing the evaporated residue of a known volume of water. Bicarbonate, sulphates and chlorides of calcium, magnesium, sodium and silica forms major constituents whereas potassium, chloride, nitrate and boron forms a minor part of the dissolved solids in groundwater. Heavy metals and radioactive constituents occur in trace quantities. There are several processes that may cause an increase in the dissolved solids content of groundwater. These include movement through rocks containing soluble mineral matter, concentration by evaporation, and contamination due to influx of sea water and industrial and municipal waste water disposal. The amount and character of the dissolved solids depend upon the chemical composition and physical structure of rocks, temperature, residence time, pH and Eh conditions (Hem, 1959). Generally, the TDS is indicative of an overall suitability of water. Water that contains too much dissolved solids is not satisfactory (McKee & Bacon, 1953). Concentration of TDS can amount to less than 10 mg/l in rain and snow, less than 25 mg/l in groundwater in humid regions with relatively soluble rocks and more than 300,000 mg/l in brines (Hem, 1970; Davis & De Wiest, 1967).

Spatial and Temporal Behaviour of T.D.S.

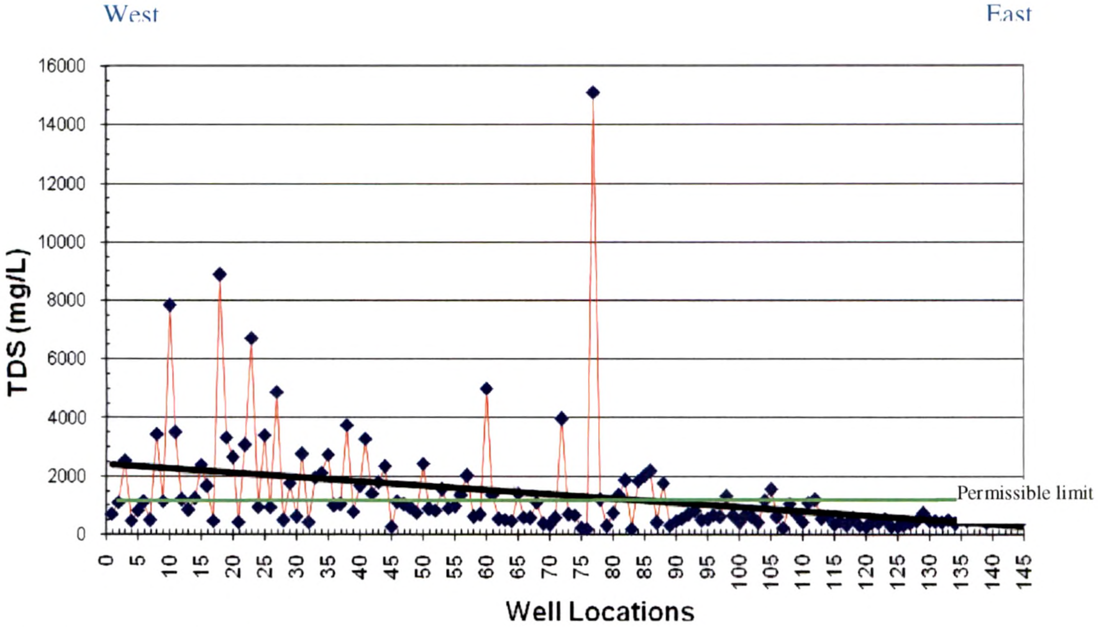
Most of the samples show high concentration of TDS in the study area. Sample analysis of pre-monsoon 2002, indicated that 40 samples fall below the permissible limit i.e. 2000 mg/l (**BIS 10500**) while only two samples i.e. Bhadkodara (Jambusar Taluka) and Vaniad (Sinor taluka) both bore well samples falls under desirable limit with low concentration. Rest 12 samples are unfit for drinking purpose (Fig-4.9).



(Note: Location Number (Annexure-4.1))

Fig-4.9 Pre-monsoon 2002 TDS Distribution in the Study Area

The post monsoon 2002 groundwater samples show wide variation in TDS content varying both laterally and vertically. In comparison to pre-monsoon, post-monsoon groundwater samples shows decrease in TDS concentration and most of the samples are within the permissible limit but above desirable limit. This effect is due to dilution by infiltrating rainwater. The highest peak in the graph (Fig-4.10) is from hand pump sample at Falod village (Waghodia Taluka). It has exceptionally high concentration of 2530 mg/l. While other minor peaks are from the coastal plains wherein due to sea water influence the groundwater is saline. About 84% of the samples falls below the permissible limit of drinking (N=122) while 16% are unfit for drinking purpose (N=23).



(*Refer Annexure 4.2)

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Fig-4.10 Post-monsoon 2002 TDS Distribution in the Study Area

From post monsoon period to pre-monsoon of 2003 there has been an increase in TDS concentration. This increase in TDS is mainly due to withdrawal of groundwater that has caused removal of less TDS concentric water charged during rainfall, leaving behind the high concentrated water. During pre-monsoon season about 79% (N=80) of the samples are below the permissible limit of drinking water criteria (IS, 1983; **BIS 10500**) while 21% (N=21) are samples are above prescribed limit (Fig-4.11).

An Iso-TDS contour map was prepared for post-monsoon 2002 to evaluate spatial distribution pattern (Fig-4.11). The distribution pattern of TDS is low in eastern part while increase as we moves towards western part. The TDS for shallow and deeper aquifers have more or less similar pattern except in shallow wells there is a maxima in Waghodia Taluka which shows very high concentration of TDS (Fig 4.12 a & b).

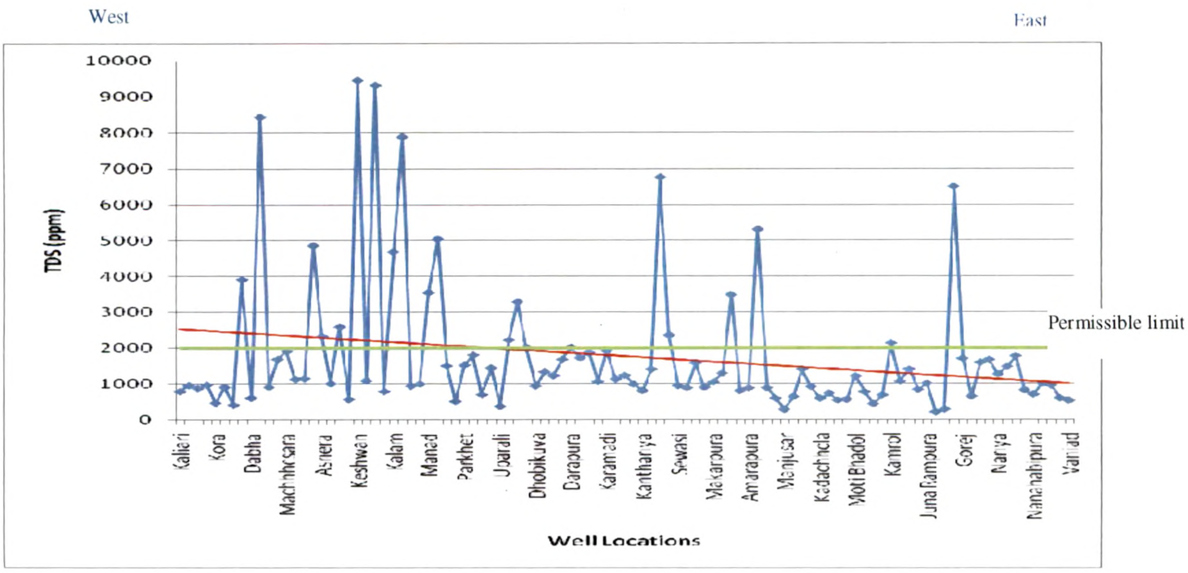


Fig-4.11 Pre-monsoon 2003 TDS Distribution in the Study Area

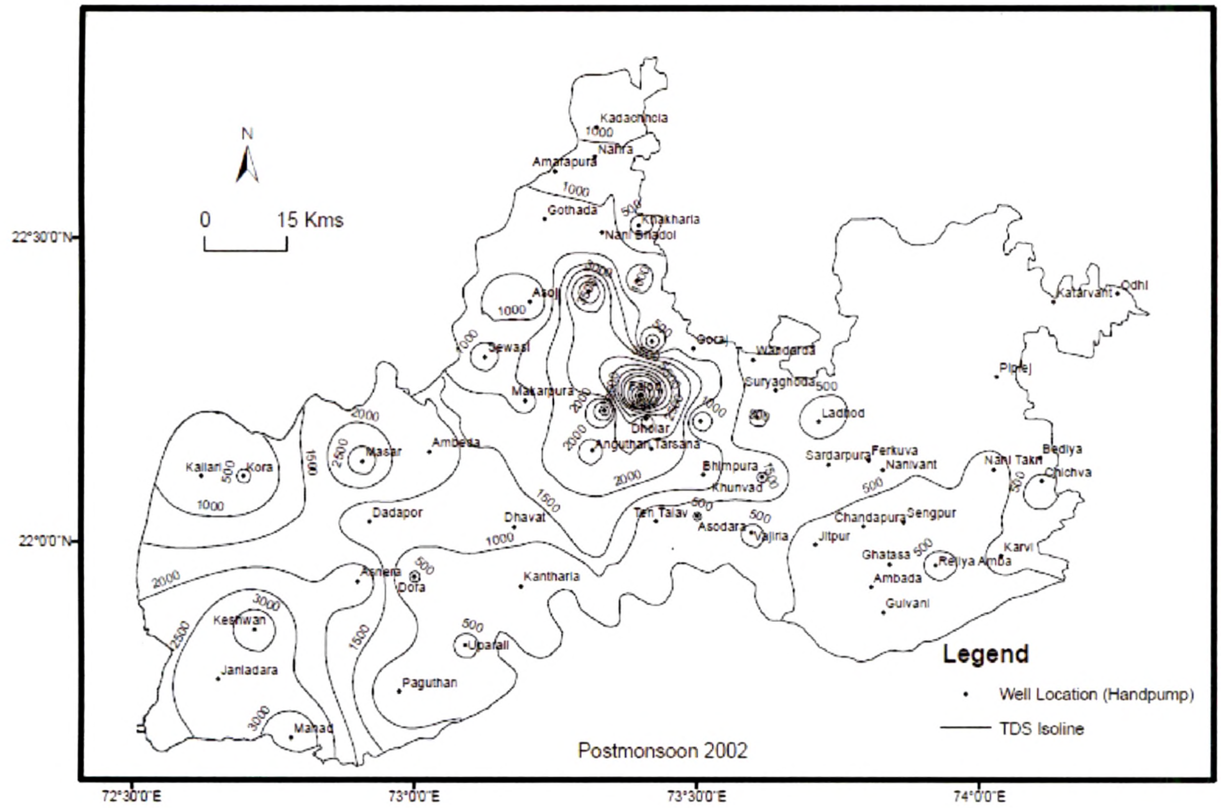


Fig4.12(a). Iso-TDS (mg/l) Contour Map in Shallow Aquifers of Study Area

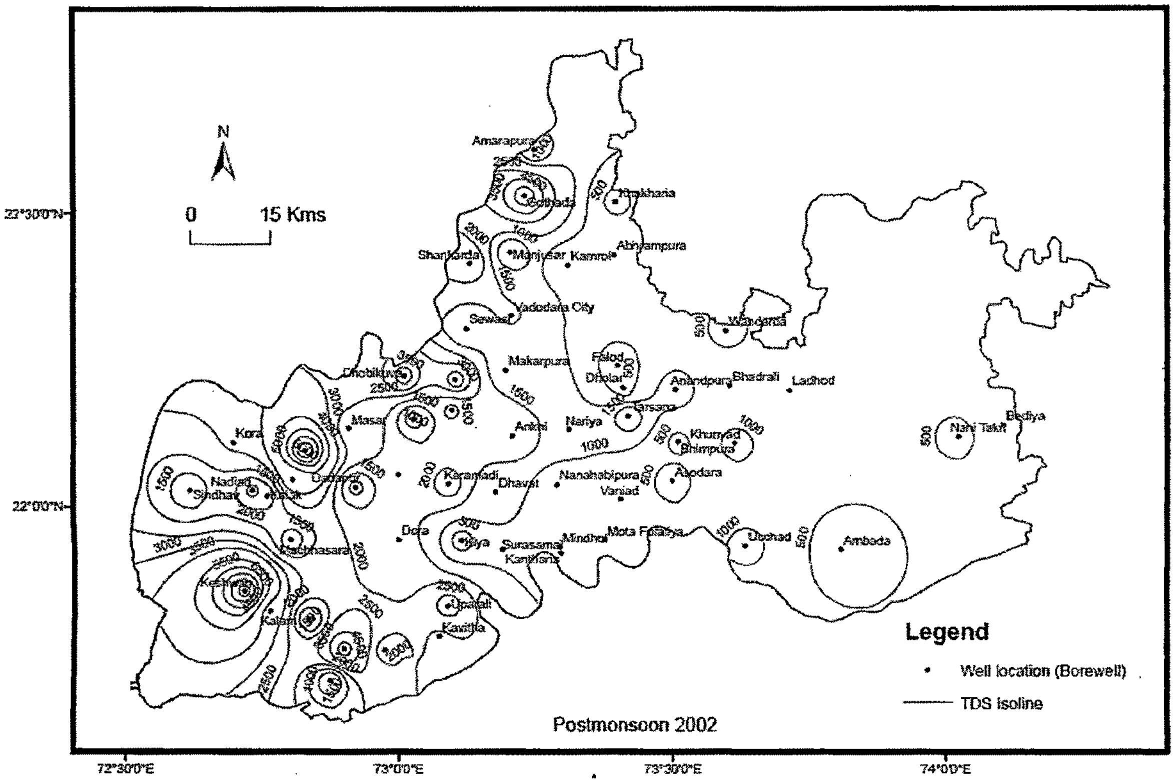


Fig4.12(b.) Iso-TDS (mg/l) Contour Map (Deeper aquifers) of Study Area

About 70% of the samples fall below the permissible limit of TDS while 30% of the samples are unfit for drinking purpose. In case of shallow phreatic aquifers, particularly from coastal plains TDS show high concentration while the concentration tends to decrease towards piedmont zone. The Falod village sample from alluvial plain shows very high TDS (>10,000 mg/l) value even during post monsoon season (Fig-4.13). This exceptionally high T.D.S. in inland aquifer may be attributed due to lack of lateral continuity therefore; groundwater may be classed as connate type.

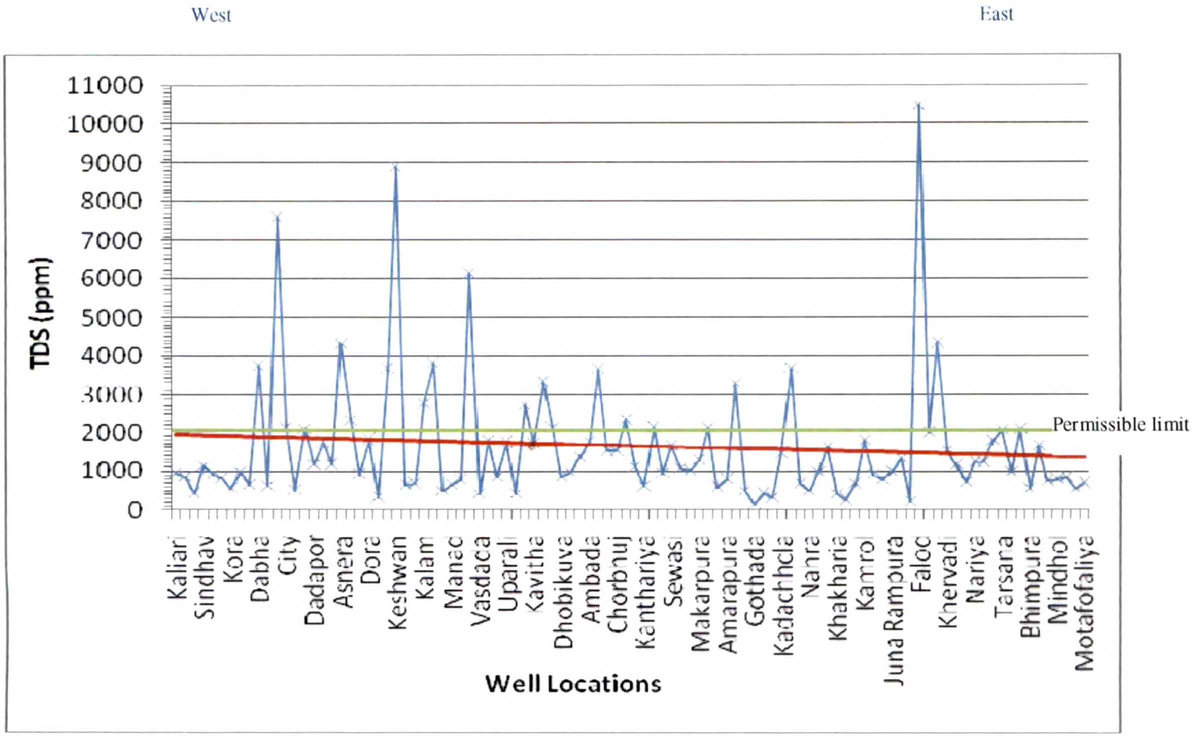


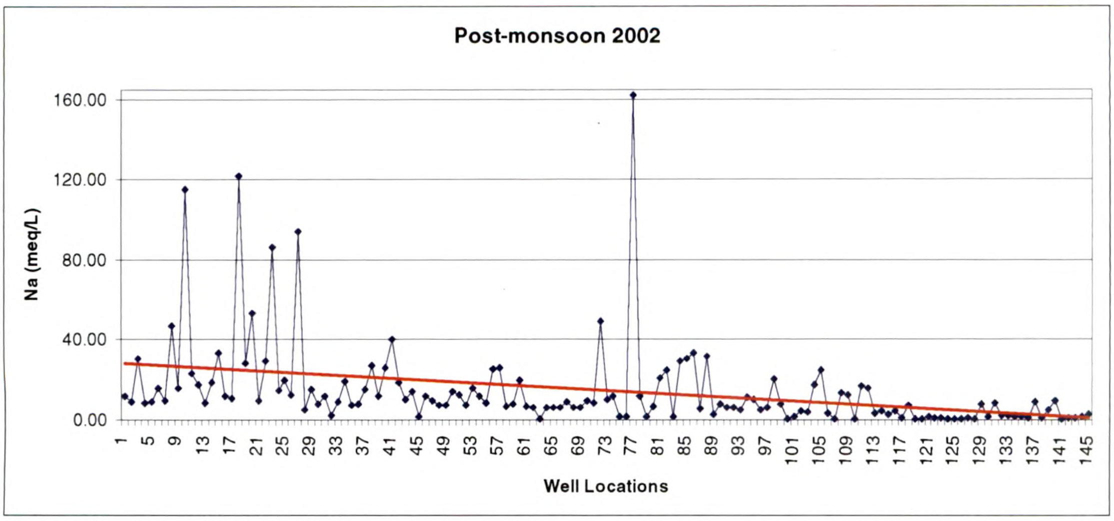
Fig-4.13 Post-monsoon 2003 Total Dissolved Solids Distribution in the Study Area

4.4.5 Sodium (Na^+)

Sodium is the most abundant member of the alkali-metal group (Hem, 1971). It is one of main constituents of igneous rock and rock salt. Moreover, it is also present in minerals like plagioclase feldspar, nepheline, sodalite, glaucophane, aegerine etc. Na+ is released into groundwater during weathering of these rocks and minerals.

Na^+ form of sodium occurs in dilute water (dissolved solids constituents below 1,000 mg/L) whereas in more concentrated solutions variety of complex ions and ion pairs is possible. The sodium content in groundwater of well drained areas with good amount of rainfall unusually has 10 to 15 mg/l concentration whereas it ranges from 1 mg/l in humid region to over 100,000 mg/l in brines (Hem, 1991). Irrigation water with excess sodium makes soil unproductive by increasing the alkalinity. It is considered to be the most injurious cation in irrigation waters (Glover, 2000).

The sodium concentration in the study area is on higher side and shows an overall decreasing trend towards highlands. The higher concentration is on the coastal plains then in alluvial plains and comparatively lower in piedmont and highlands. In alluvial plain one of shallow depth sample (HP) from Falod village shows exceptionally high concentration of sodium (3724 mg/l). This may be on account of some local saline aquifer, otherwise BW sample of the same locality at 36 m depth show 34.1 mg/l sodium concentration. Other samples show minor fluctuation within a given range. The sodium distribution in the study area for post-monsoon 2002 season is shown in Fig- 4.14.



(Note: Well Location Wides Annexure 4.1)

Fig-4.14 Distribution of Sodium in Groundwater Samples of Study Area

In the study area concentration of sodium is very high, shallow and deeper aquifers are enriched in Na content. Detail of sodium distribution in the study area is given in Table 4.7.

Table-4.7 Statistical Values for Sodium Concentration in Groundwater of the Study Area

Sr. No.	Year	Mean	Min	Max	Std. Dev.
1	Pre Monsoon 2002	508.1	69.3	2699	470.7
2	Post Monsoon 2002	335.9	16.6	3727	513.2
3	Pre Monsoon 2003	430.53	19.1	2846	497.05
4	Post Monsoon 2003	685.29	12.6	27730	2762.43

The rise in Na content in localized pockets within the study area can be attributed to the following reasons.

i. Evapotranspiration of groundwater leads to increase in concentration, though there is no direct indicator of this phenomenon.

ii. The increase in Na^{++} concentration is mainly due to inherent sediment salinity causing base exchange reaction between groundwater and aquifers that are medium rich in clay content. The coastal tract and area under vast alluvium cover, shows higher Na content.

iii. Increase in water table cause enrichment of dissolved salts rich in sodium content.

iv. Lack of lateral continuity of aquifers hampering annual flushing and groundwater accumulates in connate form i.e. brine

4.4.6 Calcium (Ca^{++})

Calcium is one of the most abundant cation in groundwater and generally occurs less than 100 mg/l in fresh water but brines may contain concentration as high as 75000 mg/l (Todd, 1980; Sharma & Chawla, 1977). Calcium is present in almost all types of water because of its solubility but do not occur in free form. Minerals like plagioclase feldspar, pyroxene, and amphibole group in igneous and metamorphic varieties and limestone, dolomite and gypsum in sedimentary sequence are the chief source of Ca^{++} (Davis, 1967). Presence of large amount of calcium and bicarbonate in solution is attributed to abundance leading to hydrolysis of carbon dioxide .

$$CaCO_3 + H_2O + CO_2 = Ca^{++} + 2HCO_3$$

Calcium is essential to normal plant growth (Sharma & Chawla, 1977). Moreover, water with high concentration of Ca^{++} & Mg^{++} ion is good for irrigation (Mathess, 1982). However, Calcium rich hard water is not desirable for domestic purpose.

The permissible limit of calcium for drinking water is 200 mg/l (BIS, 10500). During pre-monsoon 2002 there are 43 (83%) samples which are below the desirable level of drinking criteria while 4 samples have concentration above the permissible level and 5 samples have high concentration which is undesirable for drinking (Fig-4.15).

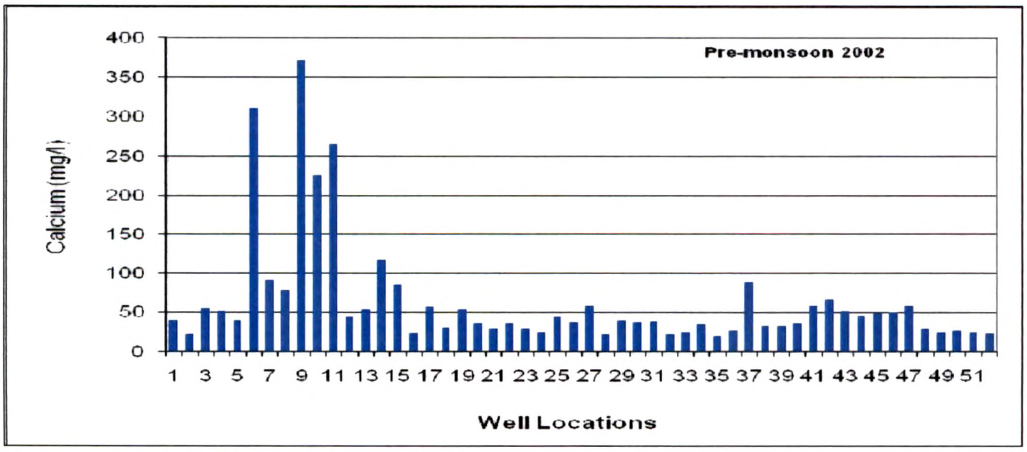


Fig-4.15 Distribution of Calcium in Groundwater Samples of Study Area (Pre-monsoon 2002)

Calcium concentration for post-monsoon 2002 season indicates that about 140 samples are with in the permissible limits while 5 samples are above the prescribed limit of drinking water. About 126 samples are within the desirable limit which is 87% of the total samples. As we move towards highlands the concentration of calcium decreases, more no of samples show less concentration which is attributed to flushing effect in rocky domain (Fig-4.16).

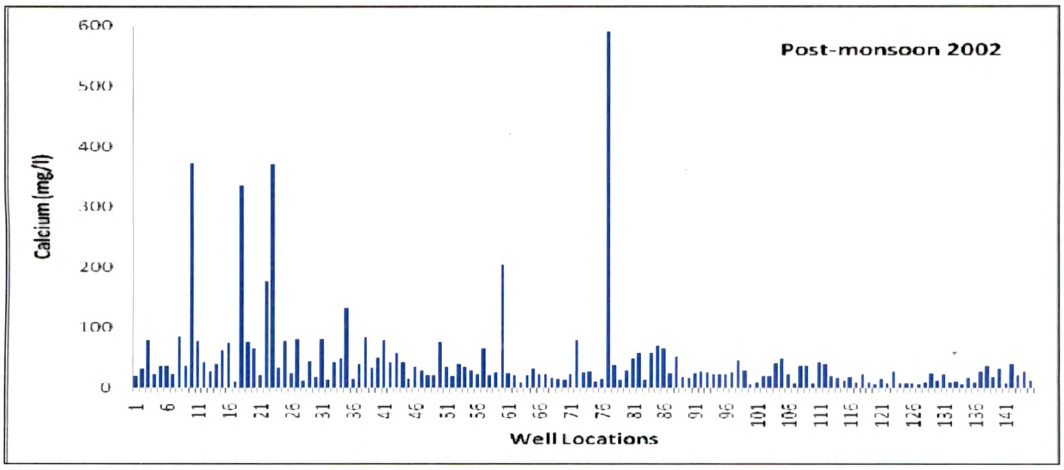


Fig-4.16 Distribution of Calcium in Groundwater Samples of Study Area (Post-monsoon 2002)

The pre-monsoon 2003 analysis has indicated that 95 no. of samples are within the permissible limit prescribed for drinking water which has gone to 83 no in post-monsoon 2003. The high concentration in post monsoon 2003 samples has been observed at Dabha TW (615.8 mg/l), Nada TW (6115 mg/l), Kalam HP (319 mg/l), Sarnar TW (388.6 mg/l), Masar TW (322.4 mg/l) Kadachhachla HP (387.8 mg/l), Falod HP (967.7 mg/l), Nimeta BW (446.8 mg/l) and others (Fig-4.17).

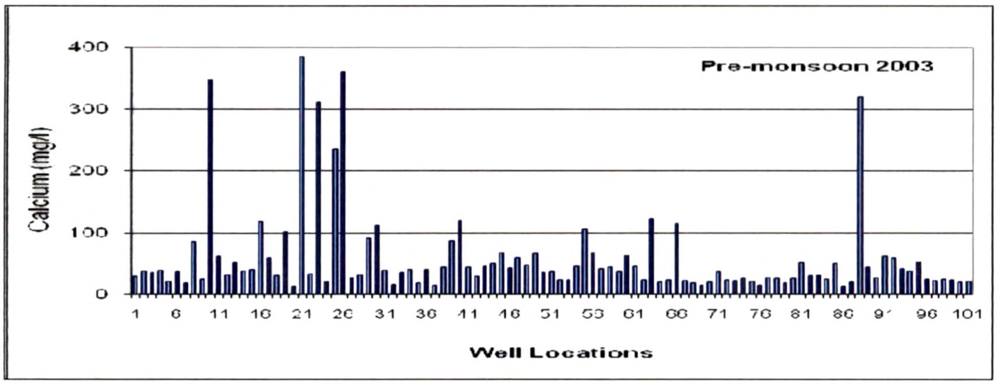


Fig-4.17 Distribution of Calcium in Groundwater Samples of Study Area (Pre-monsoon 2003)

The range of concentration of calcium content in the groundwater over a period of two years is given in Table 4.8. The high mean and standard deviation in post-monsoon 2003 is due to 18 no of samples with high concentration including one brine sample from coastal plain (Fig-4.18).

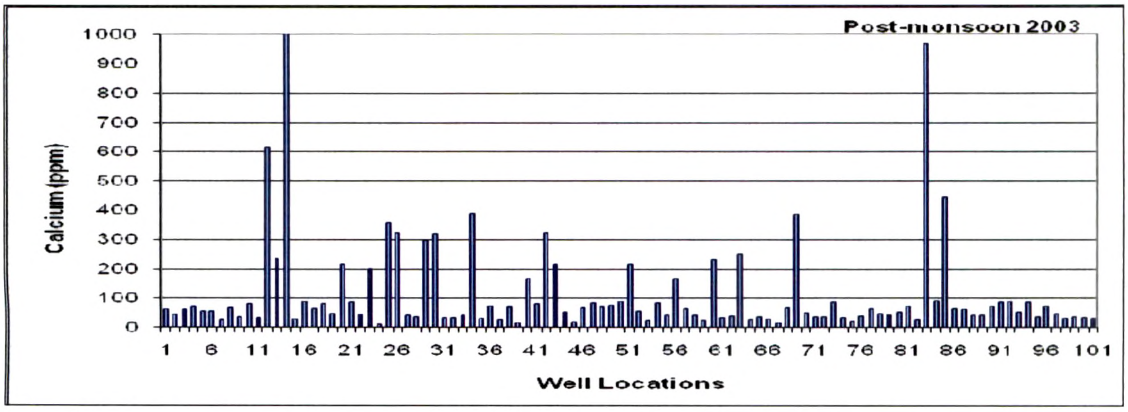


Fig-4.18 Distribution of Calcium in Groundwater Samples of Study Area (Post-monsoon 2003)

Table-4.8 Statistical Values for Calcium Concentration in Groundwater of the Study Area

Sr. No.	Year	Mean	Min	Max	Std. Dev.
1	Pre Monsoon 2002	61.97	18.5	370.6	71.83
2	Post Monsoon 2002	44.53	5	589.5	71.15
3	Pre Monsoon 2003	58.53	12.8	384.2	72.96
4	Post Monsoon 2003	164.8	10.1	6115	613.6

Calcium content in the study area display wide range because of the following reasons.

Seasonal change due to:

i. The rise in concentration from pre to post may be attributed to the increase in water table that results in enrichment of the salts.

ii. The lowering can be attributed due to flushing action (particularly in highland and piedmont zone) as well as replacement by other ions in Base Exchange reaction in clay minerals.

4.4.7 Magnesium (Mg^{++})

Magnesium is one of the main constituents of rocks and minerals. It occurs in biotite, hornblende and augite in basic igneous rocks, talc and tremolite schist in metamorphic rock and dolomite, limestone in sedimentaries rocks. Magnesium carbonate under the influence of carbonic acid and water converts into more soluble bicarbonate (Sharma & Chawla, 1977; Hem, 1959).

$$MgCO_3 + CO_2 + H_2O = Mg\ (CO_3)_2$$

Mg^{++} is essential to plant nutrition and is an important constituent of the chlorophyll of green plant (Sharma & Chawla, 1977). The reaction of Mg^{++} is much like that of Ca^{++} ion and has essentially the same effect on the physical and chemical properties of the soil. Magnesium concentration is generally less than 50 mg/l in groundwater, 1000 mg/l in ocean and brines may contain as much as 57000 mg/l (Todd, 1980).

The study area shows higher concentration of Mg^{++}, at times value is higher than Ca^{++} because like Ca, Mg is normally present in ionic form in solution and once in solution it has greater tendency to remain in that state (residence time) than does calcium. Distribution of Mg^{++} in the study area during various seasons is given in Fig-4.19 and their average concentration is given in Table 4.9.

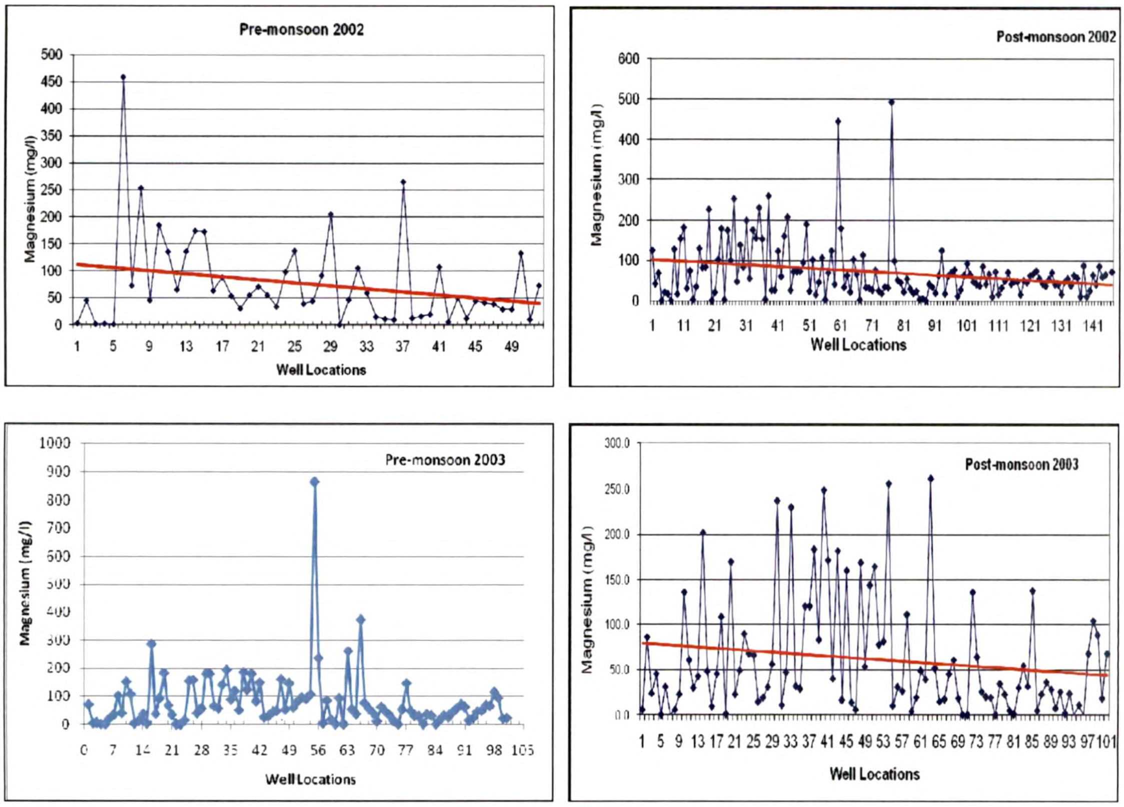


Fig 4.19 Seasonal Levels of Magnesium Concentration Over a Period of Two years

Table-4.9 Statistical Analysis for Magnesium Concentration (mg/l) in Groundwater of the Study Area

Sr. No.	Year	Mean	Min	Max	Std. Dev.
1	Pre Monsoon 2002	76.24	0.55	459.62	84.4
2	Post Monsoon 2002	71.44	0.01	492.8	72.87
3	Pre Monsoon 2003	79.26	0	863.37	104.21
4	Post Monsoon 2003	61.5	0	260.9	65.8

4.4.8 Potassium (K^+):

Igneous rocks compared to sedimentaries are rich in potassium. Major natural source of potassium are the feldspar (Orthoclase, microcline), leucite and biotite from igneous rock & metamorphic rocks sylvite, niter from sedimentaries rocks (Hem, 1970; Todd, 1980). The potassium in high concentration is seldom found in groundwater due to lower geochemical mobility (Mathess, 1982). The concentration in groundwater is less than 10 mg/l as much as 10 mg/l in hot springs and as high as 25,000 mg/l in brines (Todd, 1980; Hem, 1970). Due to excessive use of potassium in agriculture fertilizers some cultivated areas may have high concentration (Harth, 1965). Plants use potassium by removing from soil solution or from exchange medium in the soil. The potassium in the plant structure is returned to the soil, unless the plant is removed (Hem, 1959).

Distribution of potassium in groundwater of the study area in time and space is shown in Fig-4.20 for four different seasons.

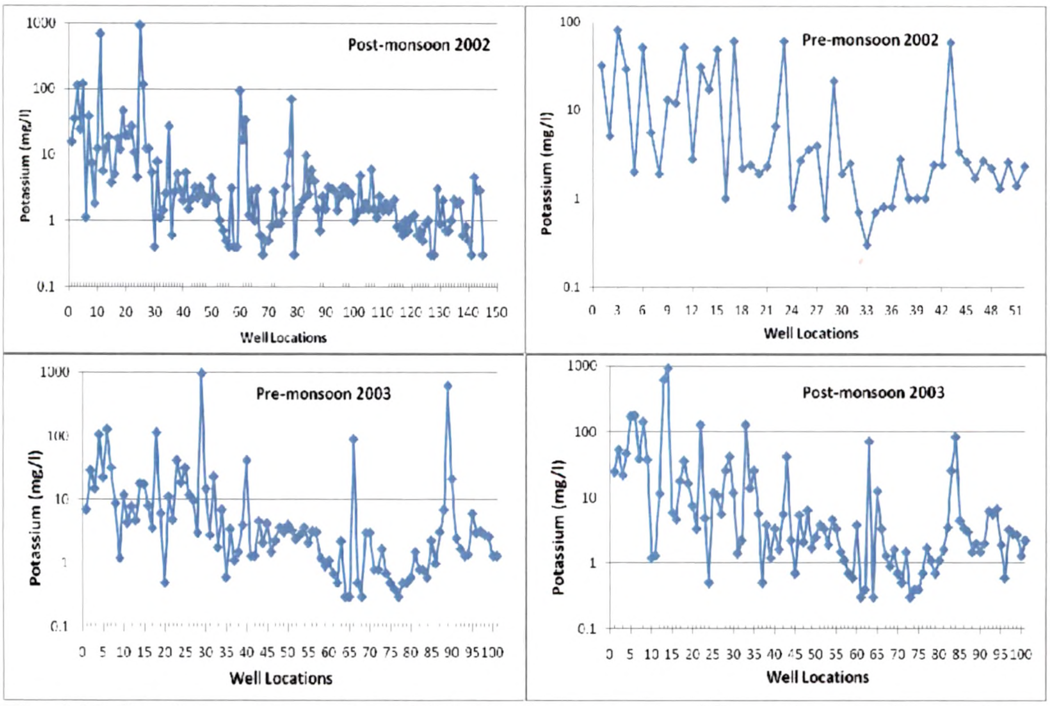


Fig-4.20 Spatial and Temporal Distribution pattern of Potassium in Groundwater Study Area

The coastal aquifers have high concentration of potassium in groundwaters showing perceptible decrease from coastal zone to highland region. Some of the aquifers in alluvial and piedmont zones show groundwater enriched in potassium content. Such aquifers are saline in nature. The range of potassium concentration in groundwater during different seasons is given in Table 4.10.

Table-4.10 Statistical Values for Potassium Concentration in (mg/l) Groundwater in the Study Area

Sr. No.	Year	Mean (mg/l)	Min (mg/l)	Max (mg/l)	Std. Dev.
1	Pre Monsoon 2002	12.53	0.3	81.8	20.29
2[#]	Post Monsoon 2002	19.43	0.3	937.6	97.6
3[#]	Pre Monsoon 2003	25.45	0.3	956	112.5
4[@]	Post Monsoon 2003	31	0.3	920	112.7

[#] The singly very high concentration to the order of 937.6 mg/l (pre-monsoon) and 956 mg/l (post-monsoon) is from Manad Village in coastal plains of study area.

[@] The high concentration of 920 ppm is from brine well and it is used mainly for salt production. The site is at coastal village 'Nada'.

The exceptionally high concentration of potassium in few localized pockets may be attributed to the following reasons:

i. Excessive use of potash fertilizers in agricultural fields is added to the groundwater regime as returned irrigation seepage.

ii. Due to its lower geochemical mobility few pockets show high concentration.

iii. Presence of brines (connate water) in the coastal aquifers.

4.4.9 Alkalinity

Alkalinity of water is its acid neutralizing capacity and it is primarily a function of carbonate, bicarbonate and hydroxide.

Carbonate (CO_3^{--}): Carbonate as limestone, dolomite and iron carbonate is widely present on the earth surface (Davis & De Wiest, 1967). In acidic medium (pH < 4.3) carbonate exist as H_2CO_3 while with pH >8.5 carbonate changes to bicarbonate (Hem, 1970). On application of soluble carbonate (Alkali) rich water in the irrigation, the response given by soil may be of two types:

i. When soluble calcium or magnesium is absent in the soil, the soil becomes alkaline and takes on the unfavorable characteristics.

ii. If excess soluble calcium is present such as gypsum, calcium carbonate is precipitated and little adverse effect on the soil is noted. Alkali carbonate such as sodium carbonate is undesirable in irrigation water and the soil solution is extremely toxic to plants.

Bicarbonate (HCO_3^-): Bicarbonate in groundwater occurs in solution form. It is generally derived from complex atmosphere-hydrosphere-lithosphere interactions by two different processes viz. i) solubility of CO_2 in water and ii) chemical weathering of rocks by CO_2 saturated water (Davis & De Wiest, 1967). Carbon dioxide released through plants root system and decaying organic matter adds to bicarbonate content when dissolved in the soil water (Sharma & Chawla, 1977). The concentration of bicarbonate ions in rainwater is below 10 mg/l, often below 1 mg/l while in normal groundwater it ranges from 50-400 mg/l (Davis & De Wiest, 1967). The estimation of these anions has been done using standard titration method.

The geochemical distribution of bicarbonate (HCO_3) in the study area exhibits a declining trend from coast to highland during 2002. However, during 2003 there is upward trend. This is attributed to non collection of water samples from high land region and in 2003 groundwater samples were collected upto alluvial plain only (Fig-4.21).

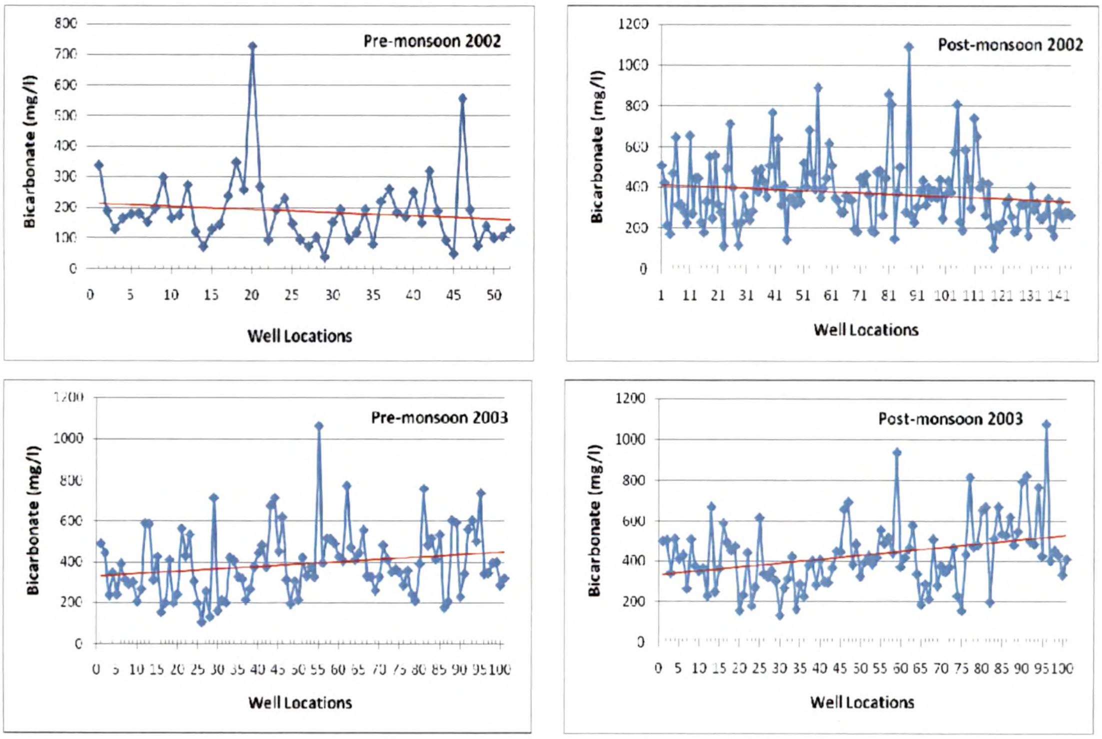


Fig-4.21 Spatial and Temporal Distribution of Bicarbonates in Groundwater of Study Area

Though carbonate concentration in groundwater of study area is low (Table-4.11) but few higher values can be attributed to the release of the carbon dioxide under the higher water table condition and or the presence of large amount of sodium in proportion to calcium and magnesium (Hem, 1959).

Table-4.11 Statistical Analysis for Alkalinity Concentration in Groundwaters of Study Area

Sr. No.	Year	Mean		Minimum		Maximum		Standard Deviation	
		CO_3	HCO_3	CO_3	HCO_3	CO_3	HCO_3	CO_3	HCO_3
1	#Pre Monsoon 2002	186.9		38		728		118.8	
2	*Post Monsoon 2002	19.8	371.7	6	105	72	1089	15.8	167.2
3	Pre Monsoon 2003	25.2	390.8	5	105	130	1064	17.6	162.2
4	Post Monsoon 2003	26.2	432.4	8	134	52	1076	11.7	169.3

During investigation of pre monsoon 2003 samples, carbonate analysis was not done hence the values are for total alkalinity.

4.4.10 Sulphate (SO$_4^{-}$)

The sources of Sulfate in the groundwater system are from sulphur minerals, sulfides of heavy metals from igneous and metamorphic rocks; gypsum and anhydride from the sedimentary rocks (Hem, 1959). Considerable amount of Sulphate is added to the hydrologic cycle through precipitation (Goreham, 1955; Rankama & Sahama, 1960). A wide variation in the sulfate content of groundwater is on account of various ongoing geochemical reactions like reduction, precipitation, solution and concentration (Hem, 1959). Moreover, sulphate is also added through leachable sulphate in fertilizers and other anthropogenic factors (Matthess, 1982). Sulphur is an essential element in plant nutrition and in the form of sulphate in groundwater it is readily available to plants (Sharma & Chawla, 1977).

The graphs below (Fig-4.22) provide a view of sulfate distribution in the study area. The pattern indicates that in the coastal plains the concentration range between 100-10000 mg/l while in alluvial plains and piedmont zone the concentration is between 100-1000 mg/l while few samples in alluvial plains shows above 1000 mg/l concentration. In highlands the sulphate concentration ranges between 10-1000 mg/l. Similar trends are shown in contour maps of post-monsoon period of 2002 and 2003 (Fig 4.23a & 4.23b). Overall the concentration level is same and hence the trend.

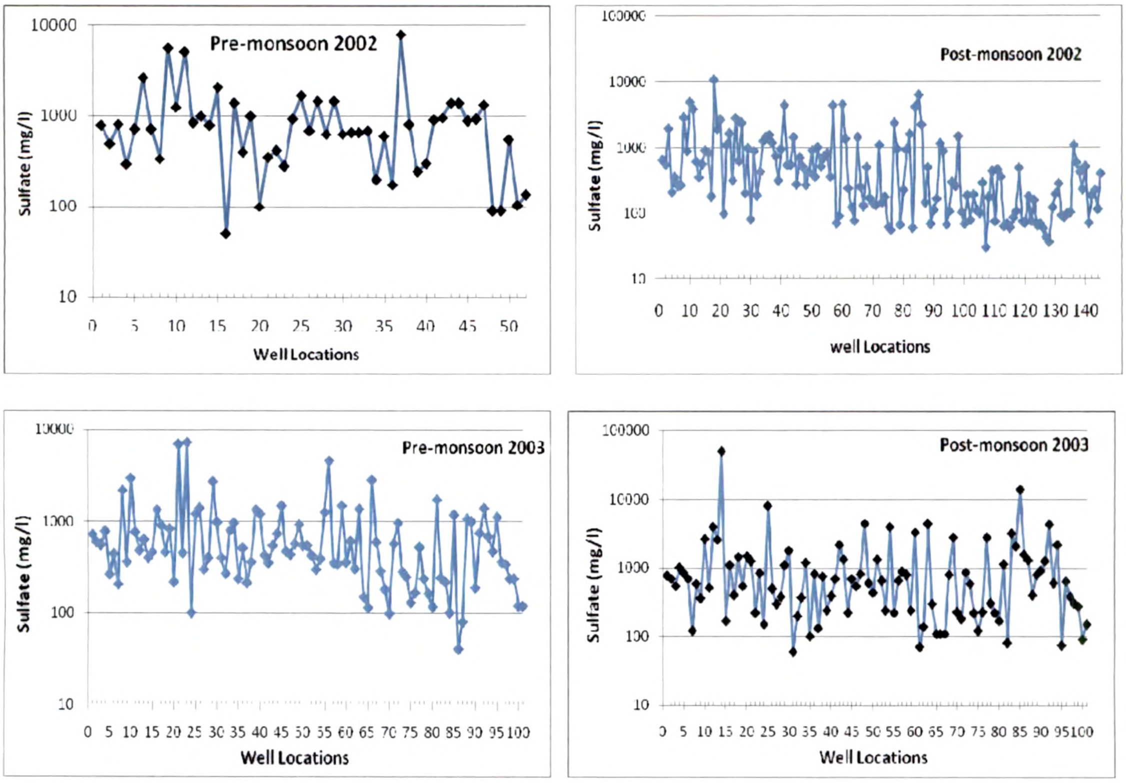


Fig-4.22 Spatial and Temporal Distribution Pattern of Sulphate in Groundwater of Study Area

Variation in the concentration of sulfate in groundwater for different seasons is given in Table-4.12. On an average the concentration is on the higher side which is due to inherent salt concentration in coastal and alluvial aquifers and upto some extent land use pattern. Presently 12.6% of the total land is under cultivation wherein sulfate in fertilizer form is excessively used in agriculture. Moreover, increase in sulfate content may also be attributed to the enrichment of salts due to evaporation, leading to calcium sulfate, magnesium sulfate salts etc.

Table-4.12 Statistical Analysis for Sulphate Concentration in Groundwaters of Study Area

Sr. No.	Year	Mean	Min	Max	Std. Dev.
1	Pre Monsoon 2002	1076.6	50	7800	1405.5
2	Post Monsoon 2002	813	30	10770	1367.6
3	Pre Monsoon 2003	811.6	40	7300	1135.8
4#	Post Monsoon 2003	1624.3	60	50000	5184.8

The high value of standard deviation is due to one sample brine sample from coastal plains

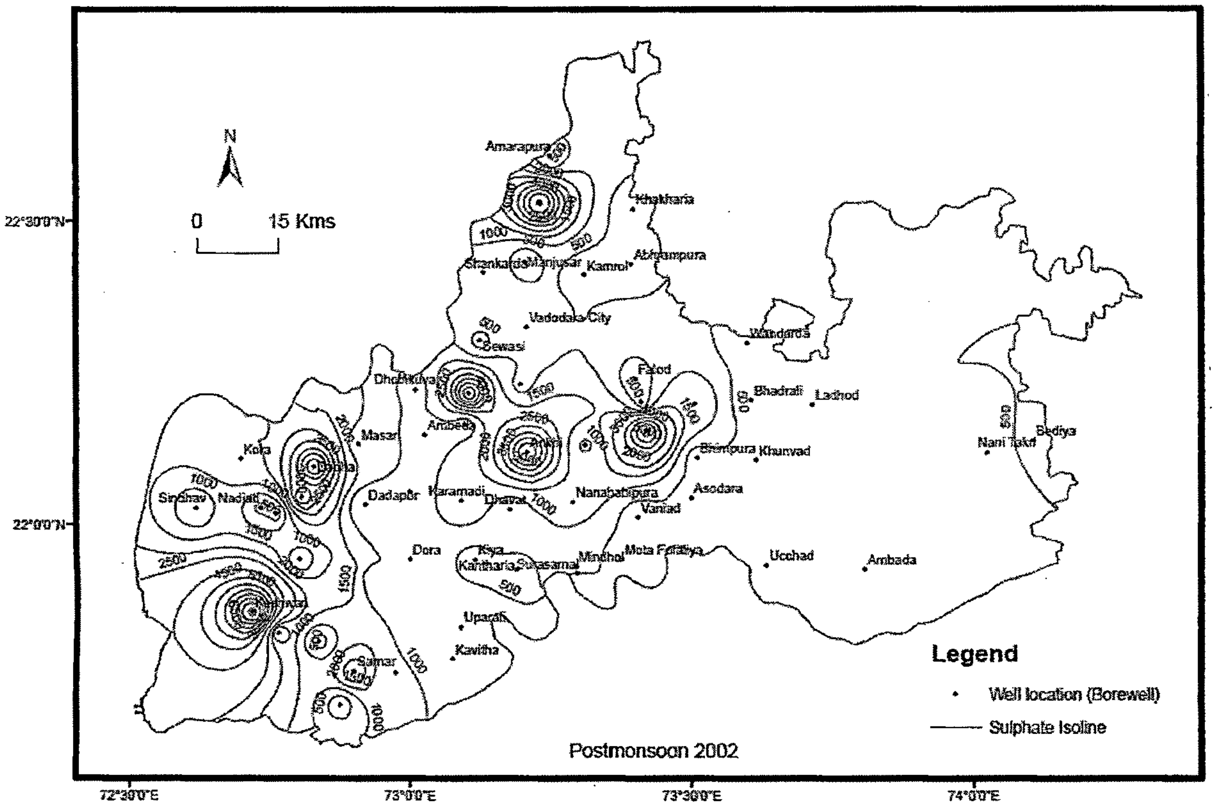


Fig- 4.23(a) Iso-Sulfate contour Map of the Study Area (Post-monsoon 2002)

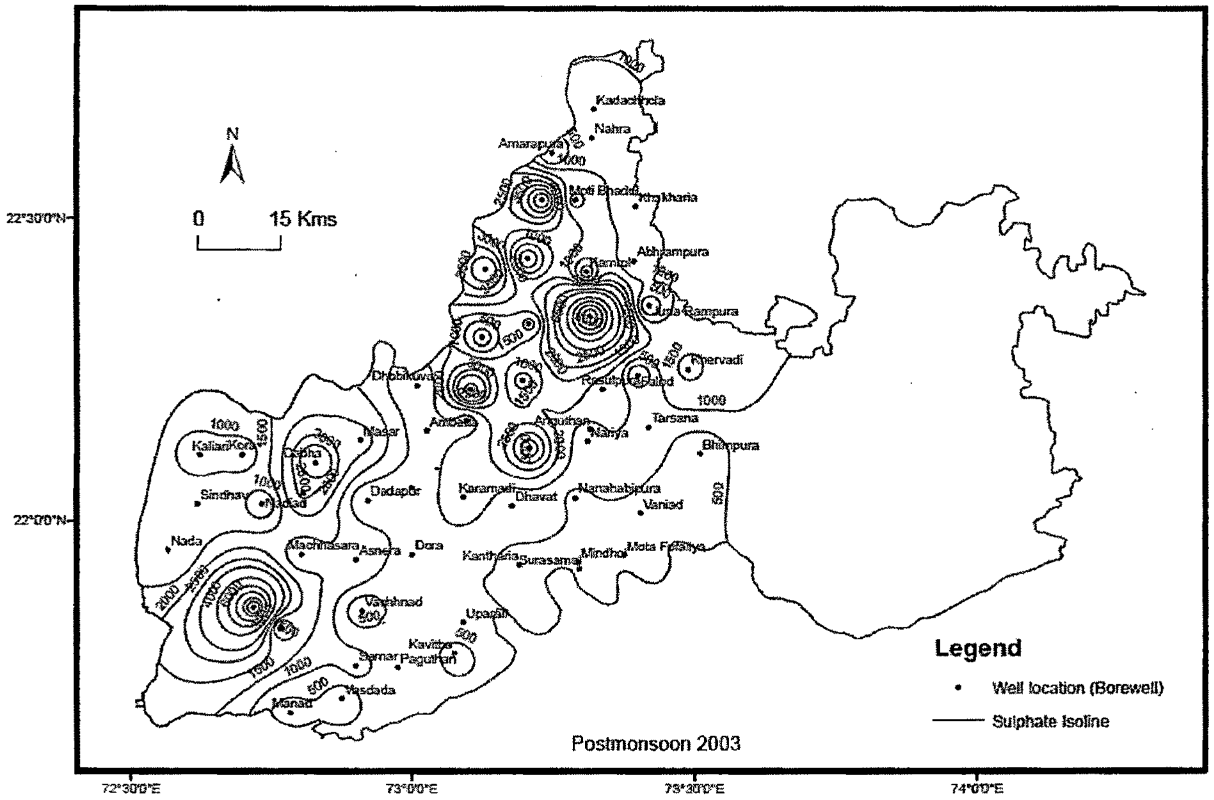


Fig 4.23(b) Iso-Sulfate contour Map of the Study Area (Post-monsoon 2003)

4.4.11 Chloride (Cl^-)

Chloride is present in all natural water. The source of chloride in water could be because of many reasons. Presence of chloride bearing minerals viz. sodalite, chlor-apatite, occurring as constituents of igneous and metamorphic rocks may contribute in groundwater. Solution of halite and other evaporite minerals also give rise to high chloride content in the groundwater (Walton, 1970). Concentration in groundwater can also be ascribed to atmospheric sources or seawater contamination (Matthess, 1982).

The chloride concentration in rainwater is normally less than 10 mg/l while in groundwater varies from a few mg/l to several thousand mg/l in desert brines and upto 13000 mg/l in the seawater. Therefore, in the groundwater the availability of chloride can be as high as the seawater or very less like the rainwater (Hem, 1959; Matthess, 1982).

Chloride is an essential element for plants and animals in a very limited amount or as traces in the soil solution. It inhibits the growth of most plants at the higher concentration and for some plants has definite toxic effects (Sharma & Chawla, 1977).

The chloride concentration in the study area increases from east to west specifically in the domains recharge and discharge area. The eastern hilly zone show overall low chloride concentration in shallow and deeper aquifers. The chloride concentration increases in the central part and that is mainly due to high use of chloride containing fertilizers in agriculture fields. As we move westward to alluvium plain and coastal plain chloride concentration further increases. Variation in the distribution of chloride content in space and time is given in Fig-4.24.

In order to assess the spatial and temporal change in chloride content the post-monsoon contour diagrams for the year 2002 and 2003 have been prepared (Fig.4.25 a & b). The coastal plains show very high concentration levels with close spacing of contours. The localized pockets of high concentration around Gorej village (Waghodia taluka) indicates a declining trend from 1000 mg/l level contour to 600 mg/l contours in post monsoon period of 2002 to 2003. Otherwise more or less the contour pattern indicates a similar trend of high concentration in the coastal plains and to some extent in alluvial plains.

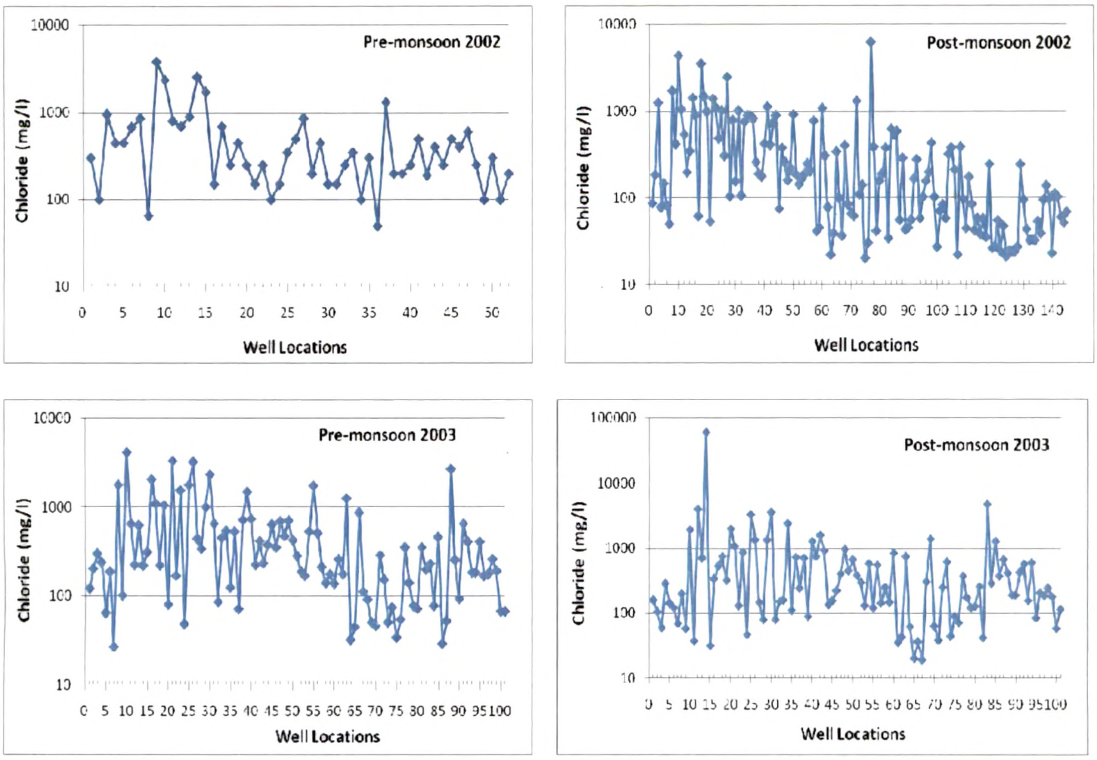


Fig-4.24 Spatial and Temporal Distribution Pattern of Chloride in Groundwater of Study Area

The geochemical data of pre and post-monsoon period of 2002 and 2003 indicates that in alluvial plains the concentration varies in the range of 100-1000 mg/l. From coastal plains, pond supported wells show less Cl^- concentration compared to wells where fresh water recharge is not available throughout the year. Lower concentration is measured in piedmont and highlands except few local pockets where high concentration has also been recorded. The statistical level of chloride concentration in the study area is given in Table-4.13.

Table-4.13 Statistical Analysis for Chloride Concentration in Groundwaters of Study Area

Sr. No.	Year	Mean	Min	Max	Std. Dev.
1	Pre Monsoon 2002	548.5	49.9	3798.8	688.4
2	Post Monsoon 2002	405.9	20	6240	767.6
3	Pre Monsoon 2003	527.79	27	4099	741.47
4	Post Monsoon 2003	1131.7	19	59189	5894.1

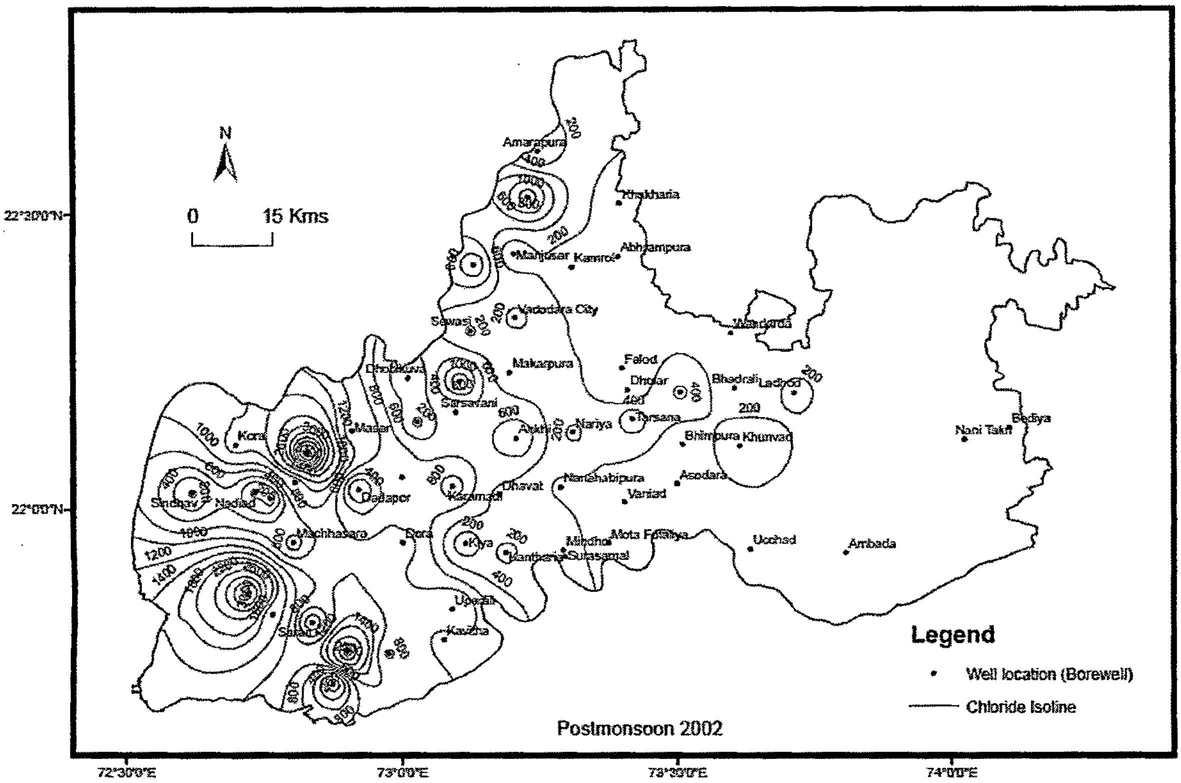


Fig-4.25(a) Spatial Distribution of Chloride in Groundwater of Study Area (Post-monsoon 2002)

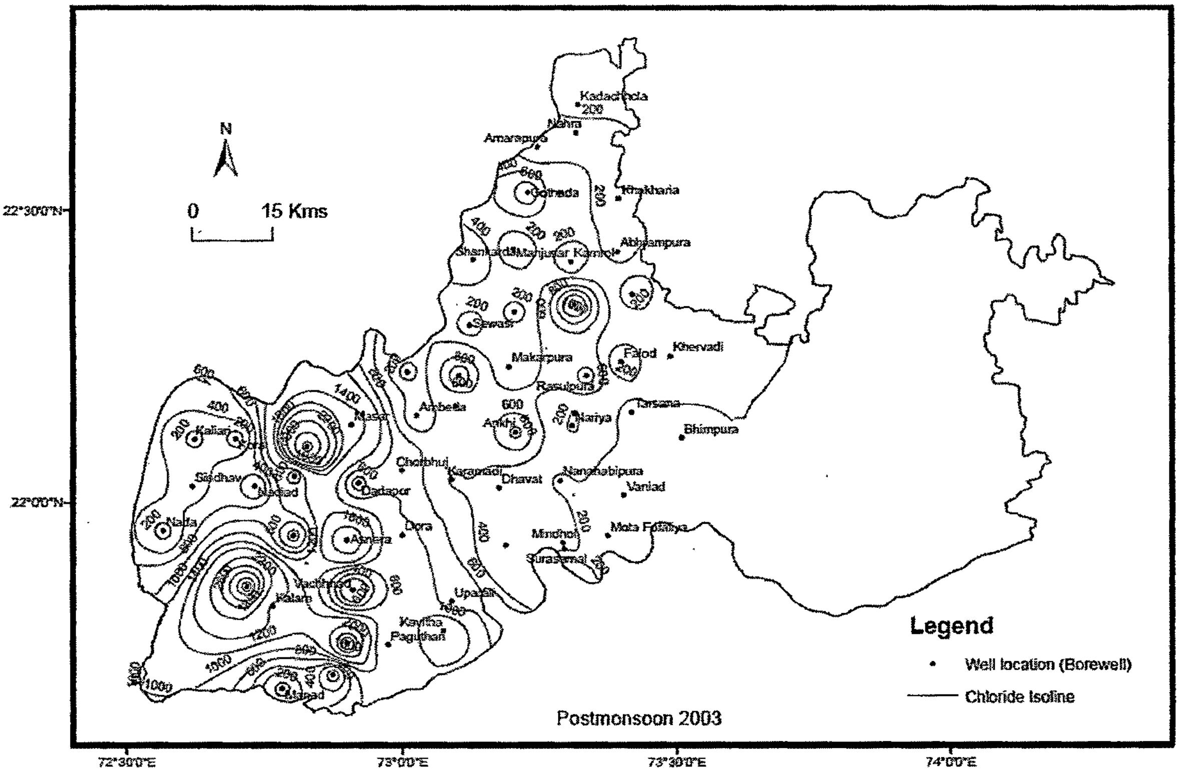


Fig -4.25(b) Spatial Distribution of Chloride in Groundwater of Study Area (Post-monsoon 2003)

4.4.12 Nitrate

The element nitrogen is present in rather small quantities in igneous rocks and in the oceans. It is essential part of living organisms in the structure of proteins. The nitrogen content of the sub-soil is increased much more by nitrogenous bacteria on plant roots which take nitrogen from the air and fix it in soil as nitrate. In addition to that added by plants, nitrogen is added to soil from animal excrement and inorganic nitrate fertilizers. Nitrate content in groundwater have wide range from practically zero to nearly 1000 mg/l. Nitrate concentration near 100 mg/l may occur in irrigated regions (Hem, 1959).

The permissible limit of Nitrate in groundwater for drinking purpose is 45 mg/l (BIS 10500). The nitrate concentration in groundwater varies in pre and post monsoon season with a wide range. During pre-monsoon 2003 groundwater samples show a range of minimum of 4.8 mg/l to maximum of 265 mg/l with 16.1 mg/l average. Four samples show high concentration and they are at Keshwan BW (265 mg/l), Rarod HP (240 mg/l), Kadachhchla HP (120 mg/l) and Falod HP (215 mg/l).

The post-monsoon season also shows a wide range of nitrate concentration from a minimum of 0.2 mg/l to a maximum concentration of 325 mg/l. Out of 101 samples 96 shows concentration below permissible limit of 45 mg/l (BIS 10500). The five samples with high nitrate concentration have been observed at Keshwan BW (245 mg/l) & HP (165 mg/l), Kadachhcla BW (325) & HP (120 mg/l) and Falod HP (295 mg/l). The pre and post monsoon HP samples of Keshwan village were taken from two different places therefore, the pre monsoon period shows a lower concentration (0.9 mg/l). Though the places were different but the depth was almost same of ±30m. This indicates that even at same depth there exist different aquifers having varied properties. Comparison of pre and post-monsoon concentration of Nitrate in groundwater is given in Fig. 4.26 and along with aerial distribution is shown in Fig-4.27 a & b.

The observed high concentration of nitrate on specific locations may be attributed to use of inorganic nitrate fertilizers.

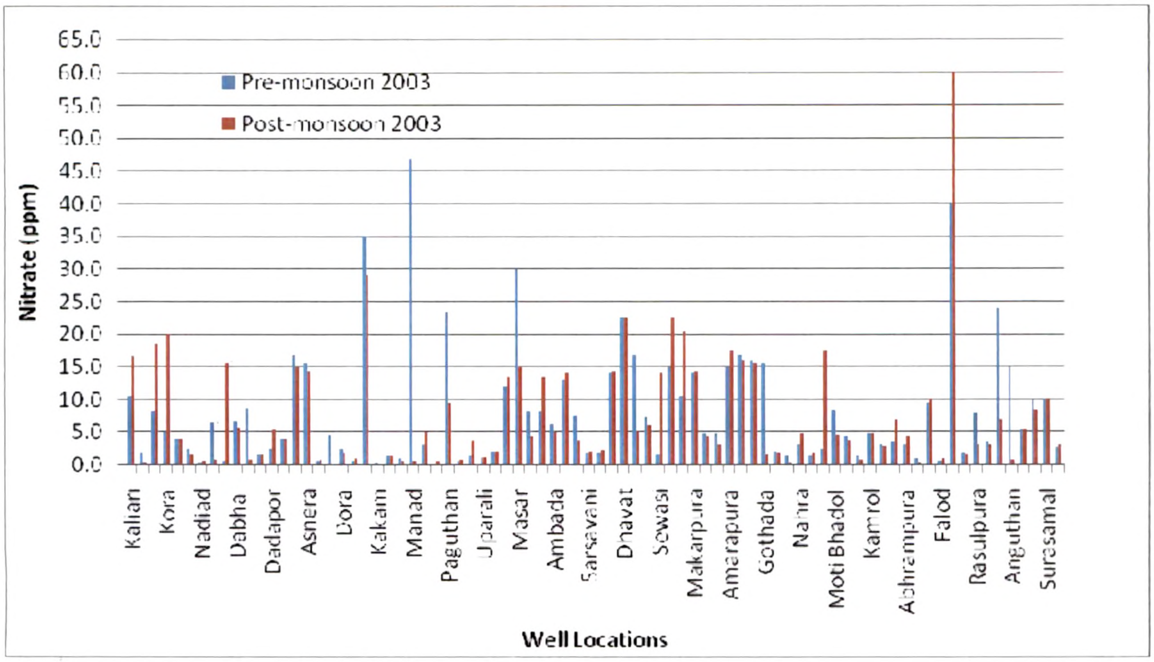


Fig-4.26 Comparison of pre and post-monsoon Nitrate Concentration in Groundwater Samples of the Study Area

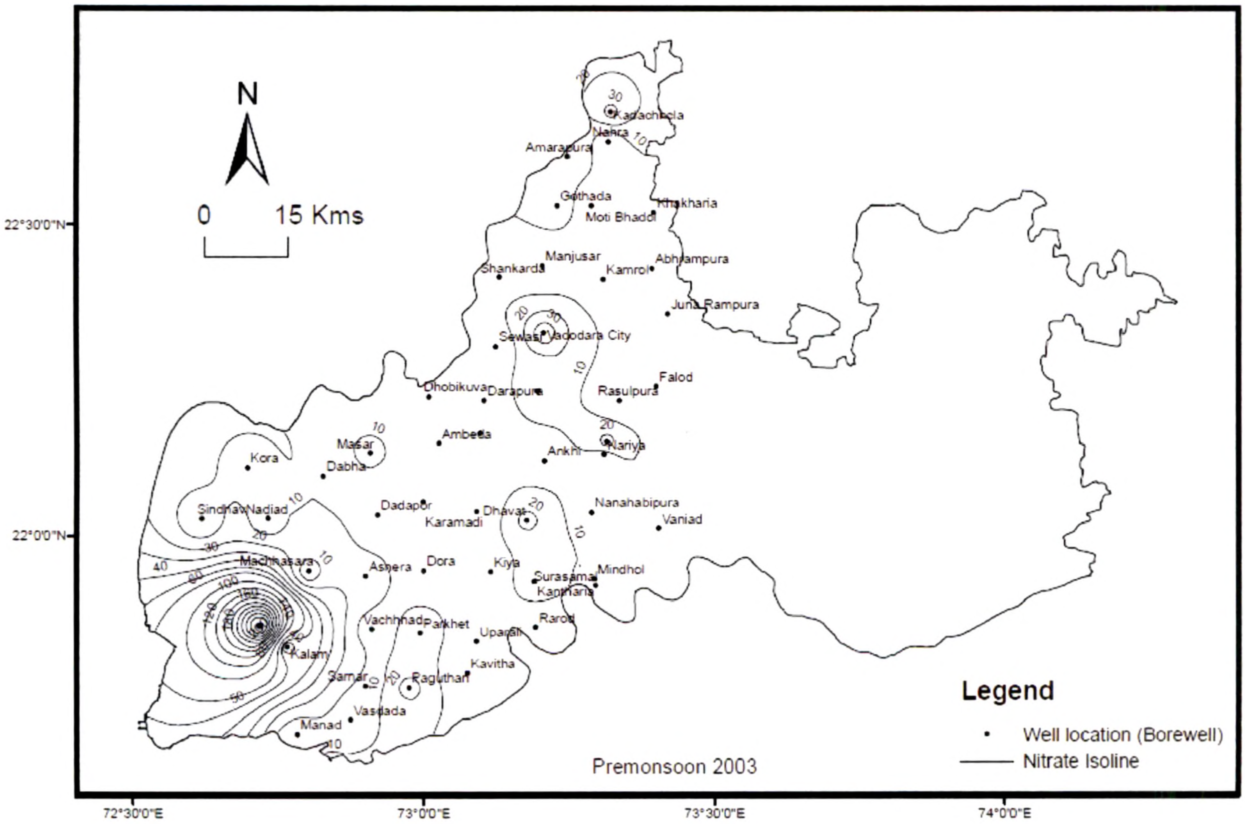


Fig4.27 (a) Spatial Distribution of Nitrate in Groundwater of the Study Area

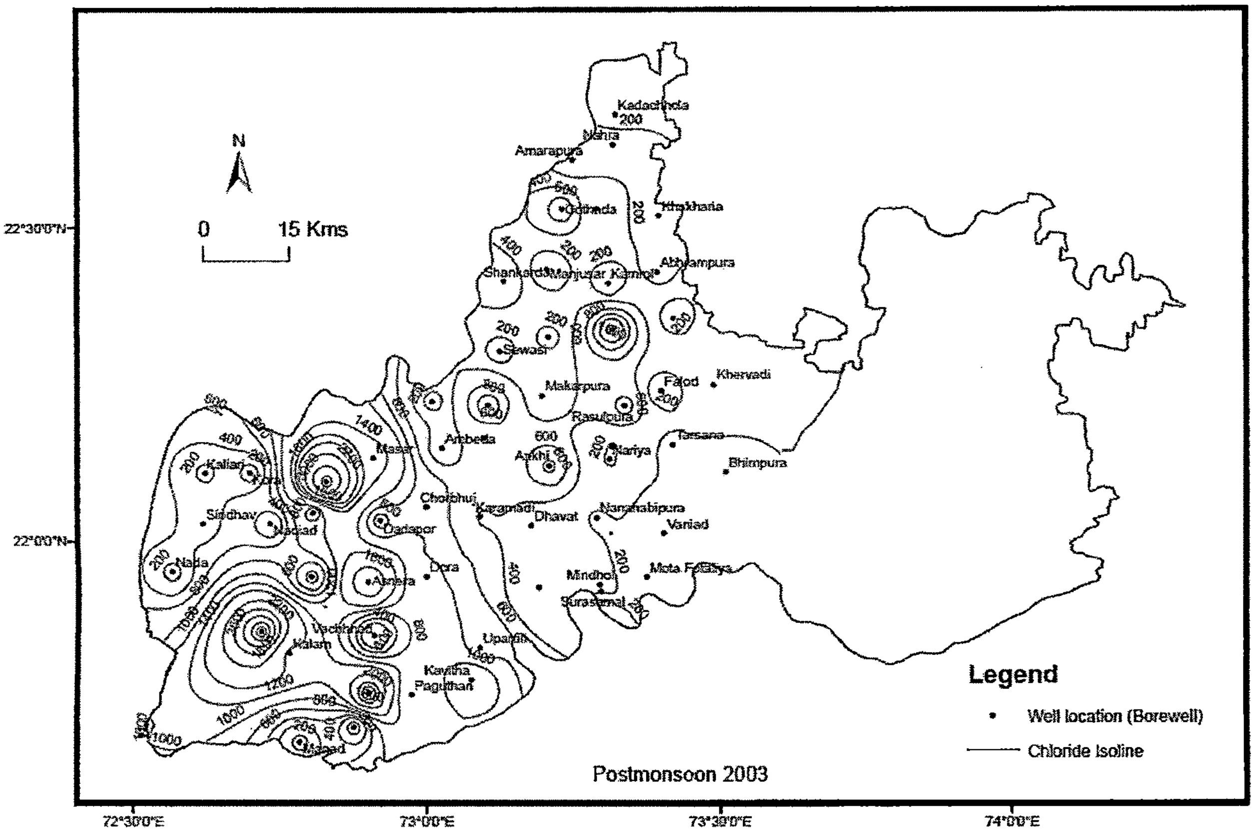


Fig-4.27(b) Spatial Distribution of Nitrate in Groundwater of the Study Area (Post-monsoon 2003)

4.4.13 Fluoride (F^-)

Introduction

Fluorine is the lightest member of the Halogen group of elements. In number of respects, its chemical behaviour is different from that of other halogens, and some of these differences are evident in its behavior in natural waters. Fluorine is the most electronegative (relative tendency of an atom to acquire negative charge) of all the elements. In solutions, it forms F^- ions.

Fluoride (F^-) concentration is an important aspect of hydrogeochemistry, because of its impact on human health. The recommended concentration of F^- in drinking water is 1.50 mg/l (WHO, 1984). Low F^- content (<0.60 mg/l) causes dental caries, whereas high (>1.20 mg/l) fluoride levels results in fluorosis. Hence, it is essential to have a safe limit of F^- concentration of between 0.60 to 1.20 mg/l in drinking water. The Bureau of Indian Standards (BIS) prescribed a limit between 1.0 and 1.5 mg/l (BIS, 1991). Fluoride in groundwater poses a great problem in most part of the states of India and about 62 million people are at risk of developing fluorosis from drinking high fluoride water (Andezhath et al., 1999). The problems are most pronounced in Andhra Pradesh, Assam, Bihar, Gujarat, Madhya Pradesh, Punjab, Rajasthan, Tamil Nadu and Uttar Pradesh (Pillai, K.S. and Stanley, V.A., 2002; Chakraboti, D., 2002). High concentration of fluoride has been reported by Mishra et al. in Unnao, Kanpur, Agra district and three blocks i.e. Baldeo, Saidabad & Shahpur of Mathura district. These areas fall in the Ganga alluvial plain of Uttarpradesh.

The fluoride problem is normally associated with groundwater since surface water does not carry significant levels of fluorides. Dissolved fluoride in water is derived by mineral water interaction. The trend of fluoride concentration in groundwater is on the higher side in many part of the Indian subcontinent. The highest fluoride concentration is in some wells in Nagaur district of Rajasthan showing 44 mg/l while Nalgonda district of Andhra Pradesh also shows high values around 20mg/l. Type of rock i.e. lithology is very important since source of fluoride is from the minerals in these rocks. Fluorite can occur in small quantity in minerals such as mica and amphiboles or there can be specific fluoride mineral such as fluorite (CaF_2). Fluorite is not a common mineral but when it reacts with water, it dissociates and releases fluoride ions to water.

$$CaF_2 \leftrightarrow Ca^{++} + 2\,F^-$$

Similarly any other fluoride bearing minerals mentioned above can also release fluoride to the surrounding water bodies. Hence weathered rocks such as basalt or sediments overlying such rocks and biotite rich rock as in Nagaur district of Rajasthan shows high values of fluoride leading to weakening of the bones and fluorosis. Since most phosphate minerals such as apatite contain some amount of fluoride as per the above reaction, use of phosphatic fertilizers leads to accumulation of excess fluoride in soils that may eventually get into the groundwater as well as soil run off to surface waters. Igneous rocks are a common source of fluoride. Fluoride is also used in industrial processes as a strong acid. Fluoride is added to many municipal water systems to prevent tooth decay.

Methodology for Fluoride Analysis

For fluoride measurement, water samples were collected in PET bottles of 2 liter size and closely fitted. Fluoride content was determined by SPADNS (2-(*p*-Sulphophenylazo)-1,8-dihydroxy-3,6-naphthalein disulphonate) method as described in APHA-2000. All reagents were obtained from E-Merck of AR grade.

Fluoride standards were prepared in the range of 0 to 1.4 mg F^-/L. In each sample 5ml of SPADNS solution and zirconyl-acid reagent was added and mixed well. Thereafter, spectrophotometer was set to zero absorbance with the reference solution and readings of standards were taken. Spectrophotometer was set at 570 nm wavelength by providing a light path of 1 cm. After obtaining results, graph of concentration versus absorbance was plotted and standard curve was obtained. Similarly reading for samples was taken by diluting the samples by adding appropriate distilled water.

Status of Fluoride in Study Area

In study area the fluoride concentration in groundwater beyond the permissible limit is found in limited number of samples while others are within the safe limit. The concentration ranges between 0.1 and 13 mg/l, details on statistical analysis of fluoride is given in Table -- 4.8. During pre-monsoon 2003 out of 101 samples analyzed for fluoride only six samples were found to be exceeding the upper permissible limit of 1.9 mg/l (BIS 10500). This includes Kora BW (3.45 mg/l), Makarpura HP (6.0 mg/l), Nariya BW (5.4 mg/l), Anguthan BW (6.65 mg/l) & HP (5.6 mg/l). Maximum fluoride concentration during pre- monsoon is observed in Dabhoi Taluka. This high concentration may be attributed to the source of water and geological formation of the area. Area is underlined by basaltic rocks and the presence of fluoride in groundwater is attributed mainly due to presence of fluoride bearing minerals in these rocks. Also, source of flouride may be attributed from the upstream located fluorspar mine at Ambadongar, as sub-surface flow accumalation.

During post monsoon 2003, 10 no. of samples were found to exceed the permissible limit and rests were within the permissible range. This includes Kaliari BW (2.1 mg/l), Nada BW (3.8 mg/l), Ambada BW (2.2 mg/l), Vadodara city BW (1.9 mg/l), Makarpura HP (3.8 mg/l), Khervadi BW (2.8 mg/l), Nariya BW (2.2 mg/l), Anguthan BW (7.0 mg/l) & HP (2.6 mg/l) and Bhimpura HP (13 mg/l). A comparative account on fluoride concentration during pre and post-monsoon periods is given in Table-4.14, Fig-4.28 and their spatial distribution pattern is given in Fig-4.29 a & b.

Table-4.14 Statistical Analysis for Fluoride Distribution in Study Area

Sr. No.	Statistical Input	Pre Monsoon 2003	Post Monsoon 2003
1	Mean	0.80	0.94
2	Median	0.48	0.50
3	Minimum	0.11	0.10
4	Maximum	6.65	13
5	Standard Deviation	1.15	1.5

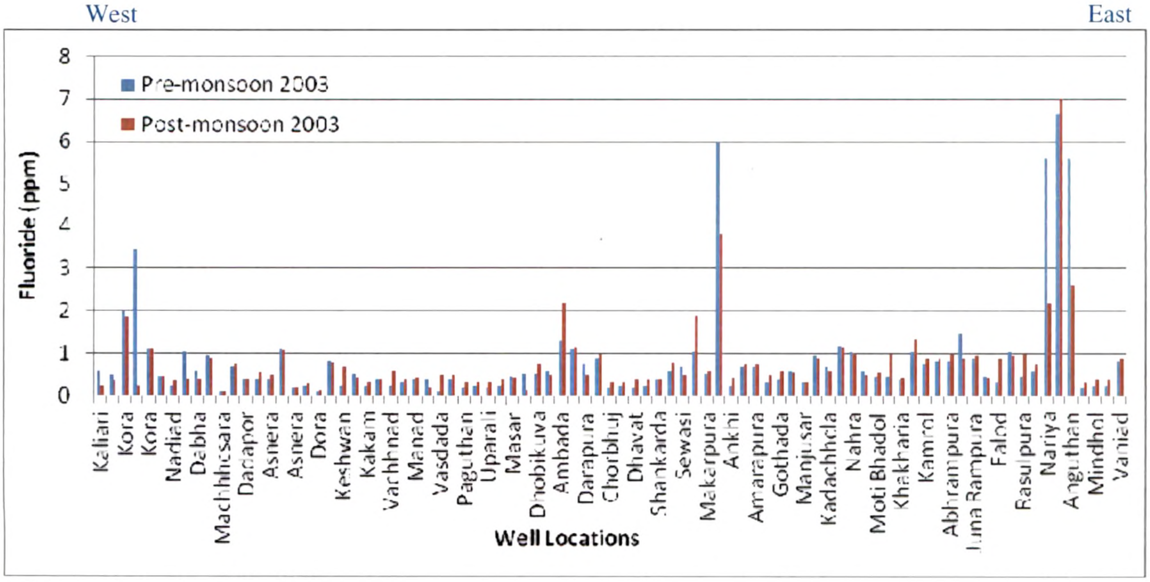


Fig-4.28 Comparison of Pre and Post-monsoon Fluoride Concentration in Groundwater of the Study Area

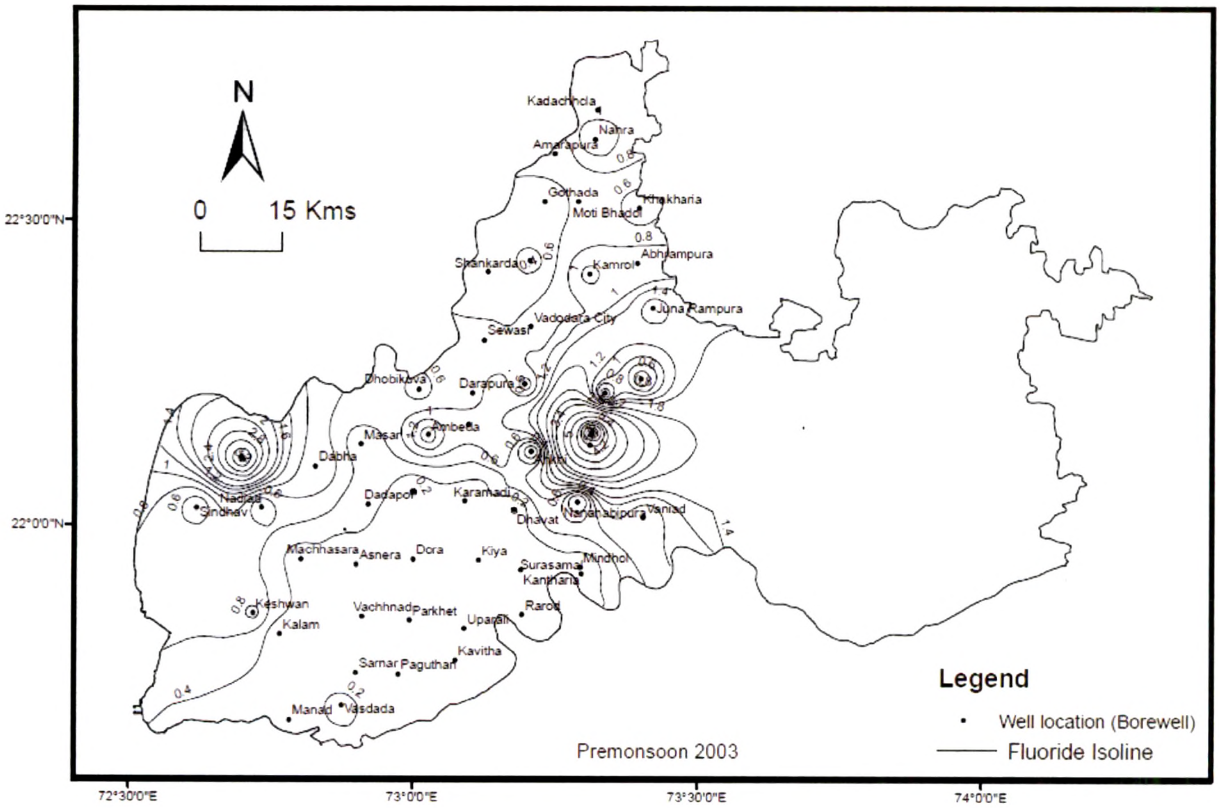


Fig-4.29(a). Iso-Fluoride Concentration Map of the Study Area (Pre-monsoon 2003)

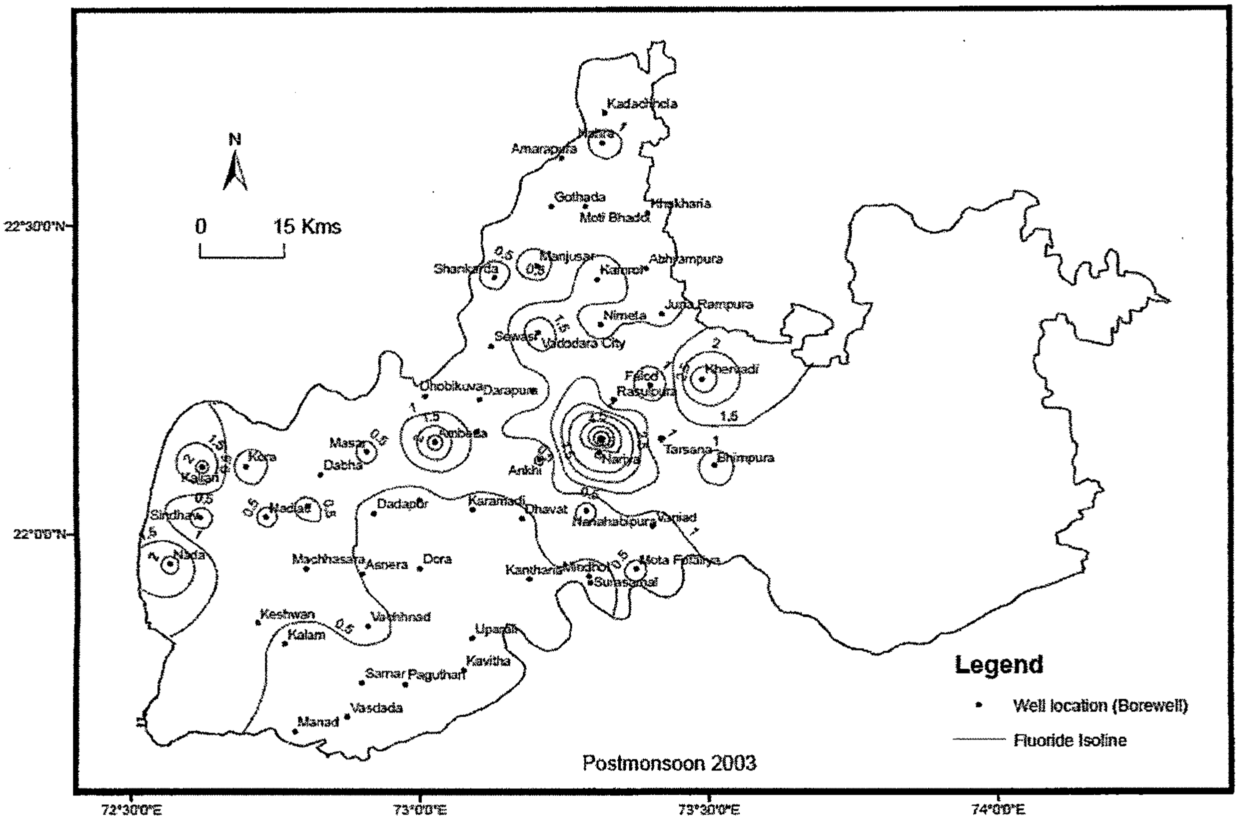


Fig-4.29(b). Iso-Fluoride Concentration Map of the Study Area (Post-monsoon 2003)

4.5 Hydrochemical processes

The groundwater chemistry is resultant outcome of groundwater with the reservoir rocks while its movement from recharge to discharge point. Following processes are dealt in detail to understand the groundwater chemistry in the above referred context

4.5.1 Evaporation

Evaporation causes strong influence on the groundwater chemistry compared to the other processes. The process can be identified from the plot between sodium to chloride ratio and sodium to chloride ratio versus electrical conductivity (EC). The Na vs. Ca ratio remains unchanged if the groundwater is experiencing strong evaporation compared to the hydrochemcial processes (Jankowski and Acworth, 1997).

The ratio of sodium and chloride has been plotted for four seasons and in that the ratio has remained more or less same and therefore exhibits linear relationship (Fig-4.30).

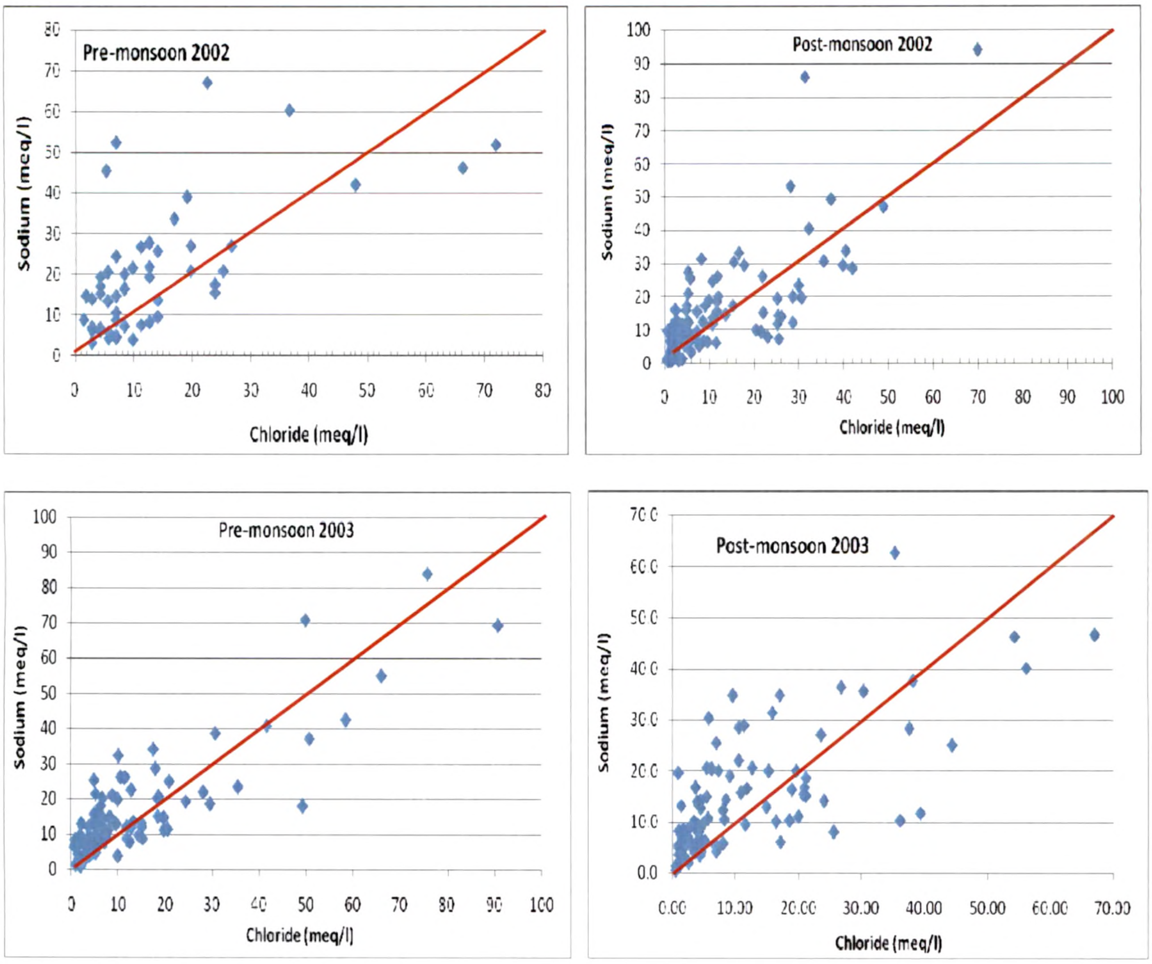


Fig-4.30 Na-Cl Variation in the Pre and Post Monsoon Water Samples for the Year 2002-2002

Overall the plots suggest the dominance of sodium concentration as majority of samples lie above the 1:1 equiline.

The Na vs. Cl plot of pre-monsoon 2002 indicates that with the increase in sodium content there is slight decrease in chloride content otherwise samples fall in unity line. Similar trend is also prominent in post-monsoon 2003 samples where lower values of chloride have higher sodium content.

There is a good correlation observed between Na/Cl vs Ec, pre and post monsoon samples have shown strong inverse relationship between these parameters (Fig-4.31a-d). The dominance level of evaporation is possible to be assessed by these plots.

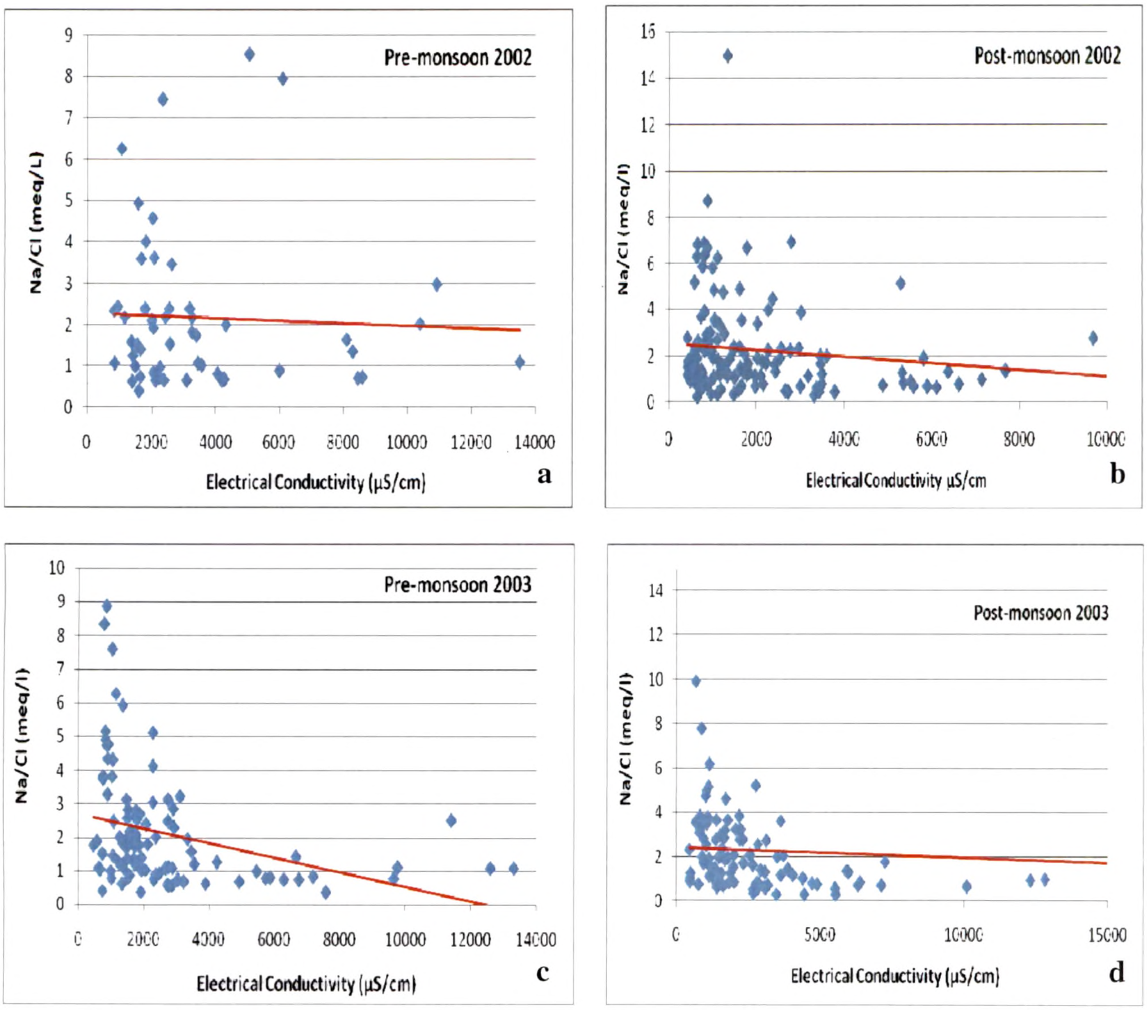


Fig-4.31 (a-d) Na/Cl vs. Ec Plots for the Pre and Post Monsoon Period (2002-2003)

4.5.2 Cation Exchange Reactions

The occurrence and distribution of ions in groundwater to some extent is controlled by cation exchange reactions. Such reactions can be identified using a plot of sodium versus chloride. Another indicator of cation exchange reaction is depletion of sodium with respect to chloride (Jankowski and Acworth, 1997; Salama, 1993). The unusual high or low levels of Na compared to the Cl in all probability result due to the cation exchange reaction. This is possible to be assessed by comparing sodium concentration with respect to cation like Ca etc. (Fig-4.32 a-d).

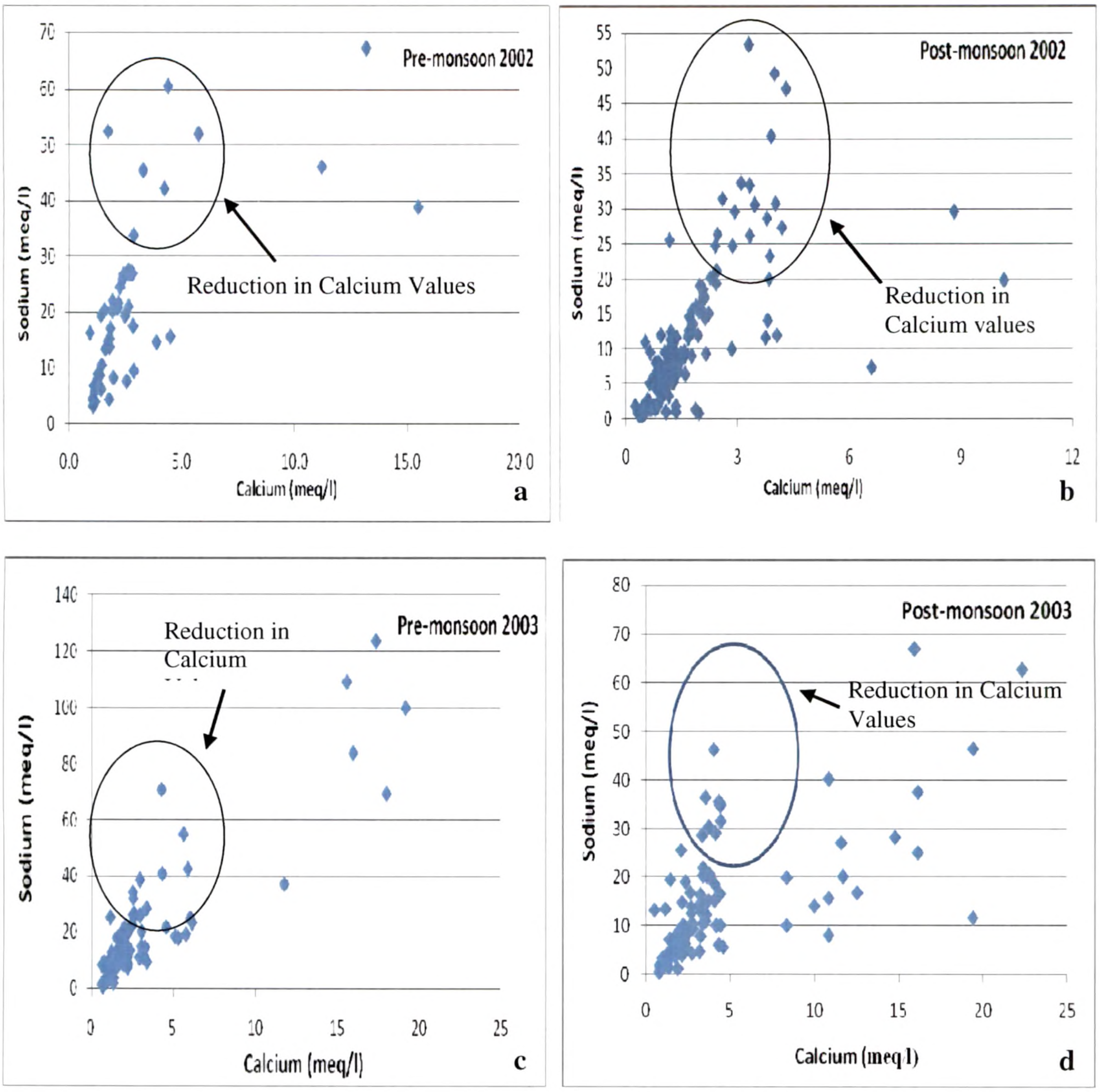


Fig-4.32 (a-d) Sodium vs. Calcium variation for Pre and Post monsoon Groundwater Samples for the Year 2002-2003

4.5.3 Silicate Weathering Processes

The silicate minerals of the aquifers react with the groundwater and the extent of these reactions can be assessed by measuring the relation between (Ca + Mg) vs. (HCO^{-}_3 + SO^{-2}_4). The Ca, Mg and HCO^{-}_3 plots show that the samples point falling above the equiline are due to the carbonate weathering and points falling along or below the equiline suggest strong silicate mineral weathering (Datta and Tyagi, 1996).

The scatter diagram of (Ca +Mg) vs. (HCO^{-}_3 + SO^{-2}_4) for the study area for four seasons shows that most of the samples lie below the equiline with few above and along the equiline.

This indicates that silicate weathering may be pronounced in the area compared to carbonate weathering (Fig.4.33 a-d).

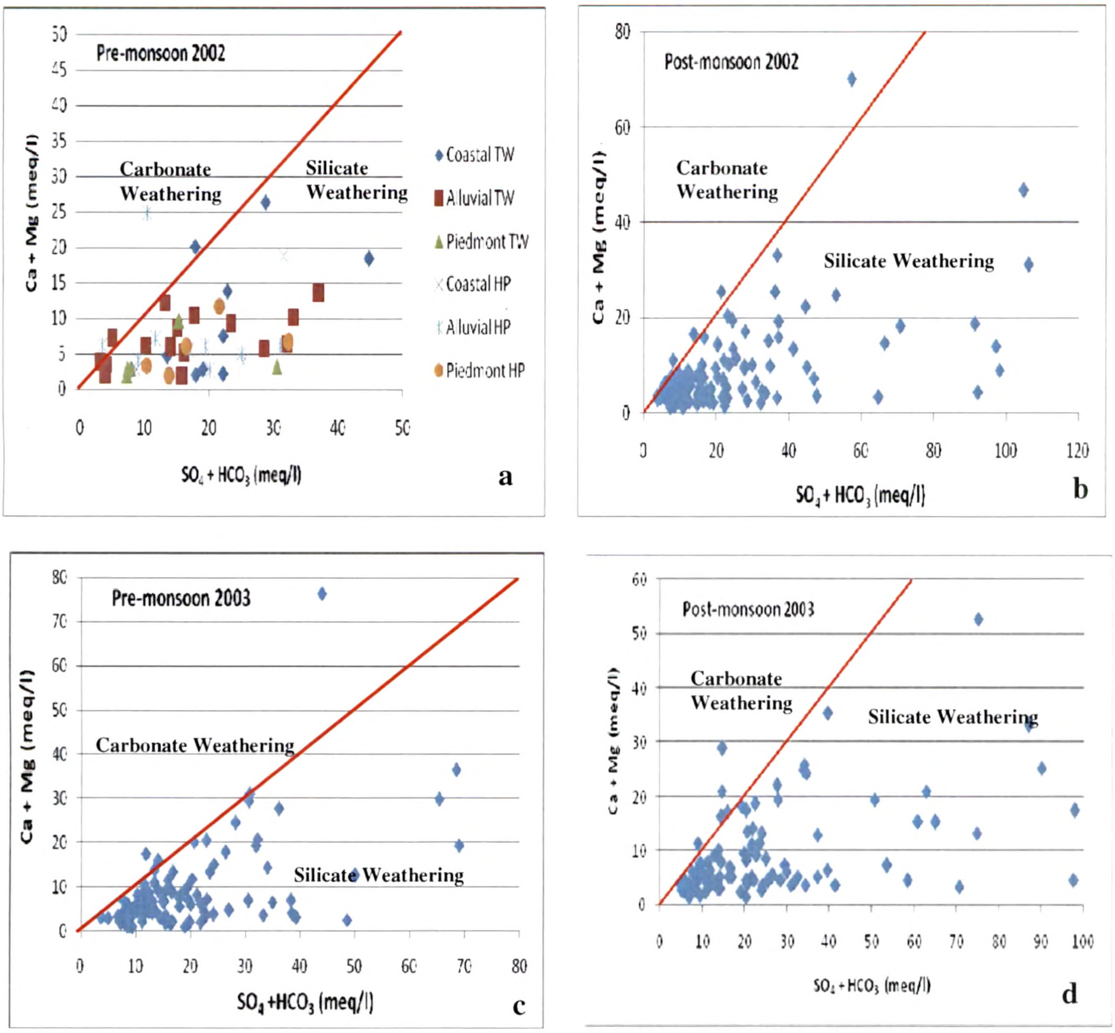


Fig-4.33 (a-d) Plot of (Ca +Mg) vs (HCO_3 + SO_4) showing carbonate dissolution and silicate weathering

In groundwater increase in concentration of HCO_3 compared to Na concentration suggests that silicate weathering. This may imply that Na concentration is reduced from the ground water because of the ion exchange process (Elango, 2003). Lavitt et al. (1997) indicated that slightly rise in concentration of calcium compared to sodium also confirms this. In order to identify the process scatter diagram of Na vs. Ca has been plotted for the four seasons (Fig-4.32a-d). The scatter diagram clearly indicates increase in concentration of Na compared to Ca which implies that silicate weathering process is not dominant in the study area. The scatter plot of Na vs. HCO_3 (Fig4.34a-d) indicates the dominance of Na compared to HCO_3 again support that silicate weathering is not prominent.

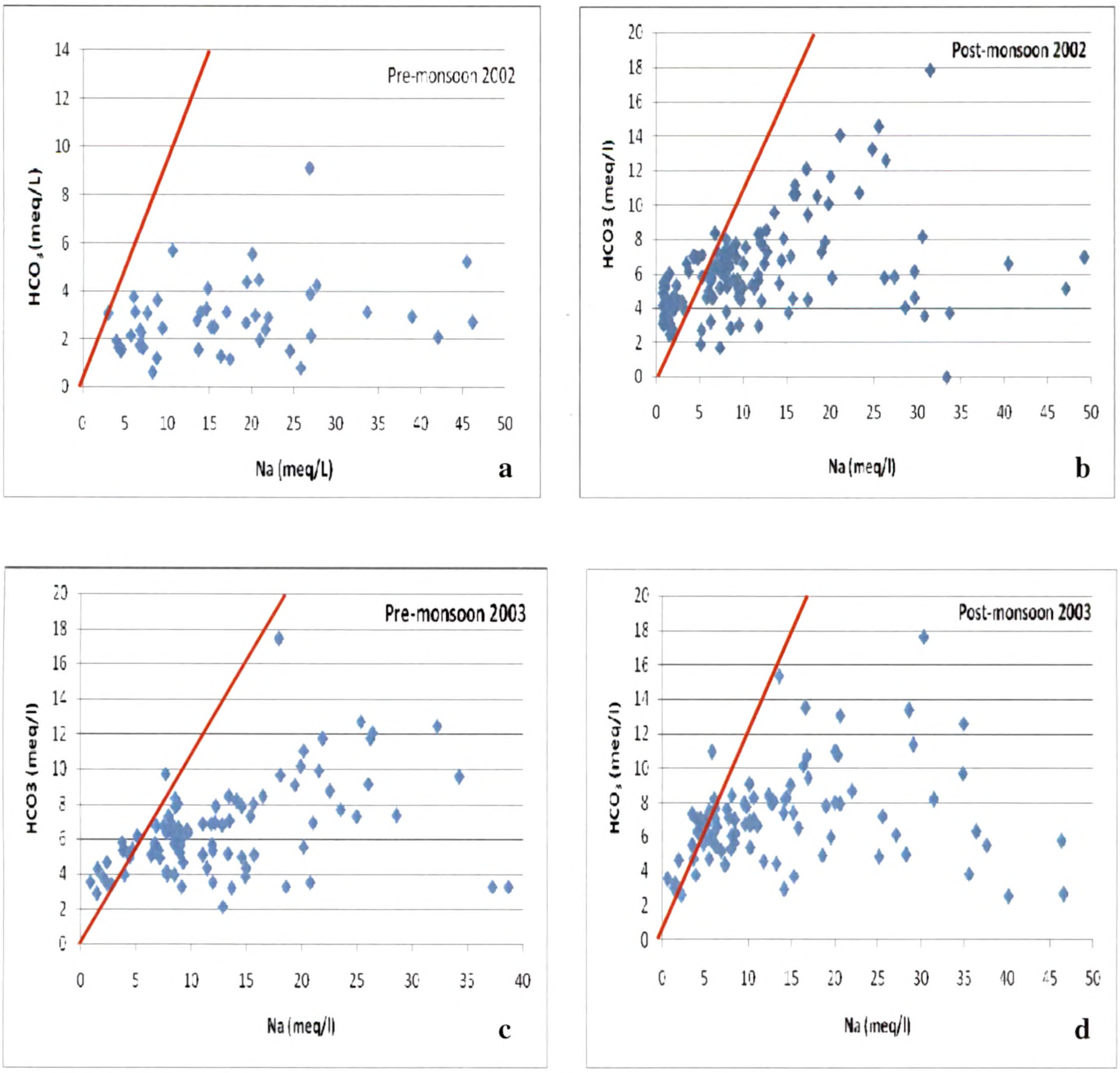


Fig-4.34 (a-d) Plot of Na vs. HCO_3 showing increased concentration of Na compared to HCO_3

In the study area, the ratio of Na/Cl for groundwater samples of the study area generally ranges from 0.39 - 8.53 (Pre-monsoon 2002); 0.25 – 15.0 (Post-monsoon 2002); 0.36 – 8.86 (Pre-monsoon 2003) and 0.28 – 21.62 (Post-monsoon 2003). The trend indicates that the ratio is quite high during post-monsoon period. Further, (Na + K) Vs Total cation also indicates the contribution of cation due to silicate weathering (Fig-4.36).

The Ca+Mg vs. Total Cation plot indicates that data points lie below the equiline which is indicative of silicate weathering (Fig-4.35 a-d)

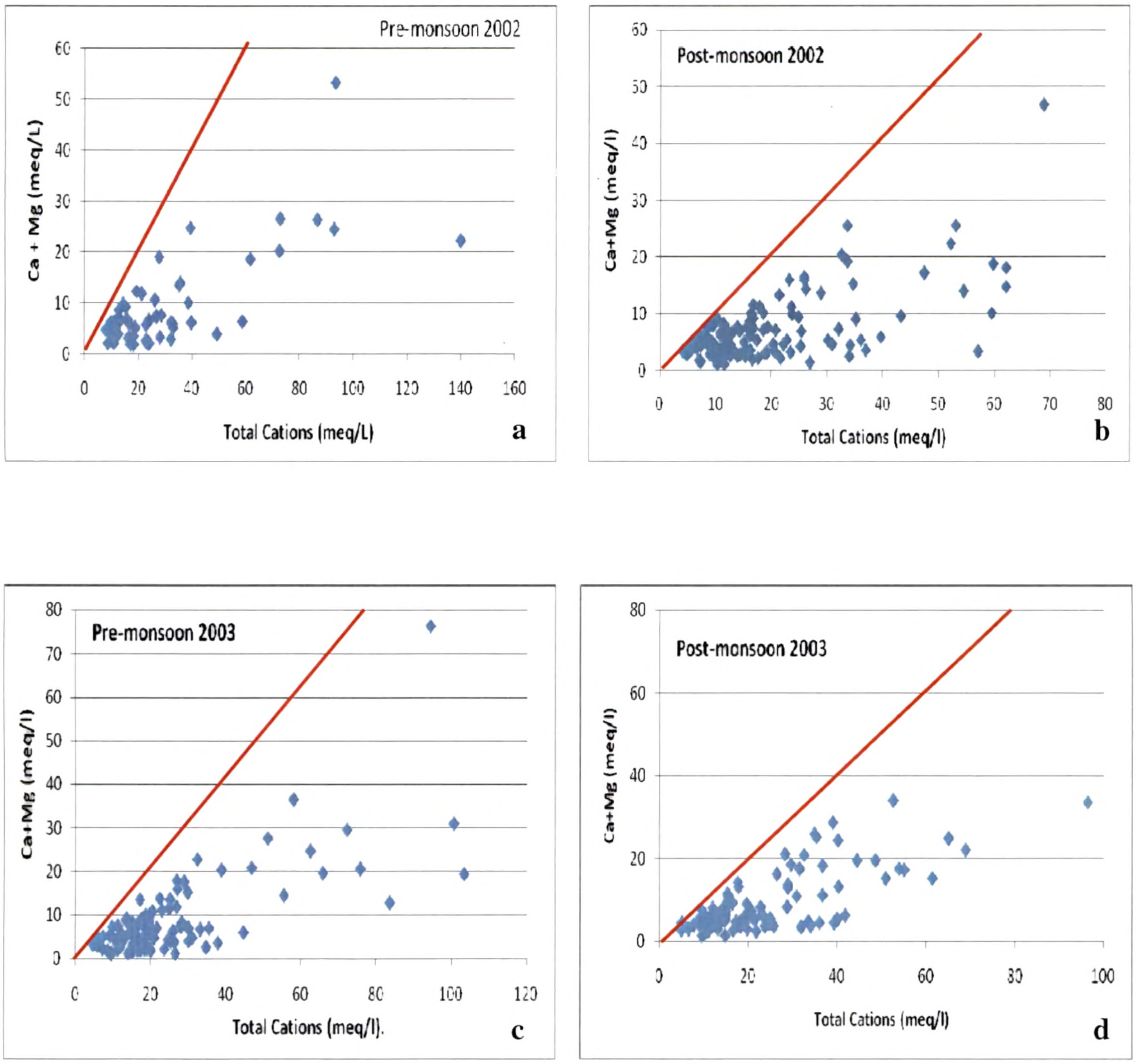


Fig-4.35(a-d) Relation between Ca+Mg and Total Cation

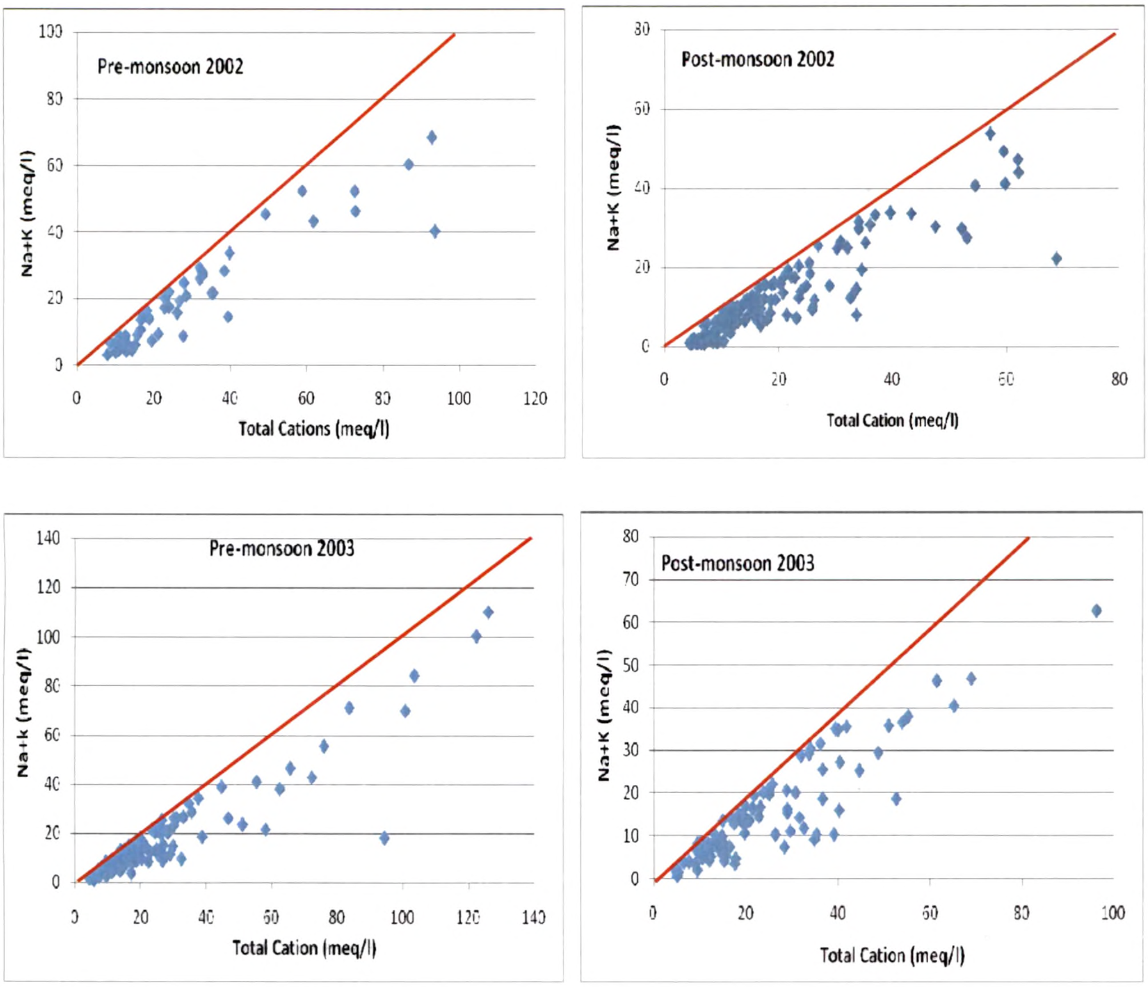


Fig-4.36 Relation between Na+K and Total Cation indicating Silicate Weathering

High ratio, estimated by the index (Na+K) vs. Total cation, indicates that the cation contribution is due to silicate weathering (Mohan et al, 2000).

4.5.4 Gibbs Plot

Gibbs plots are useful for the understanding the relation between different chemical components. The Gibbs ratio-I Cl / (Cl+HCO$_3$) for anions and ratio-II Na+K / (Na+Ca+K) are plotted against total dissolved solids.

The pre-monsoon 2002 samples show that the ratio-I ranges between 0.28 to 0.98, while ratio-II ranges between 0.72 to 0.97. The samples of pre-monsoon groundwater plotted on the diagram suggest strong evaporation controlling the water chemistry (Fig-4.36).

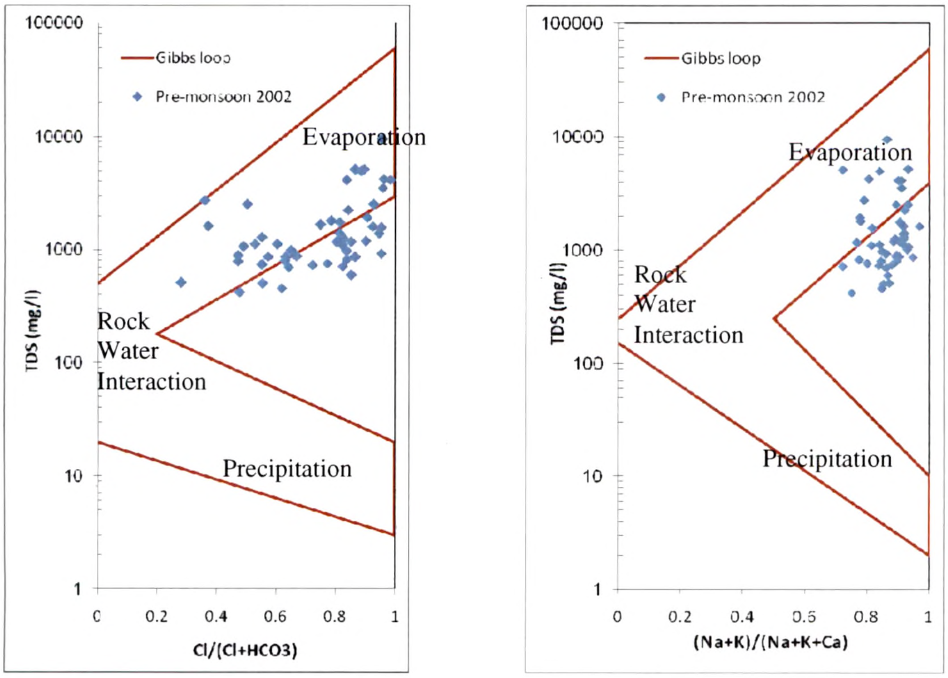


Fig-4.37 Gibbs Plot for Pre-monsoon 2002

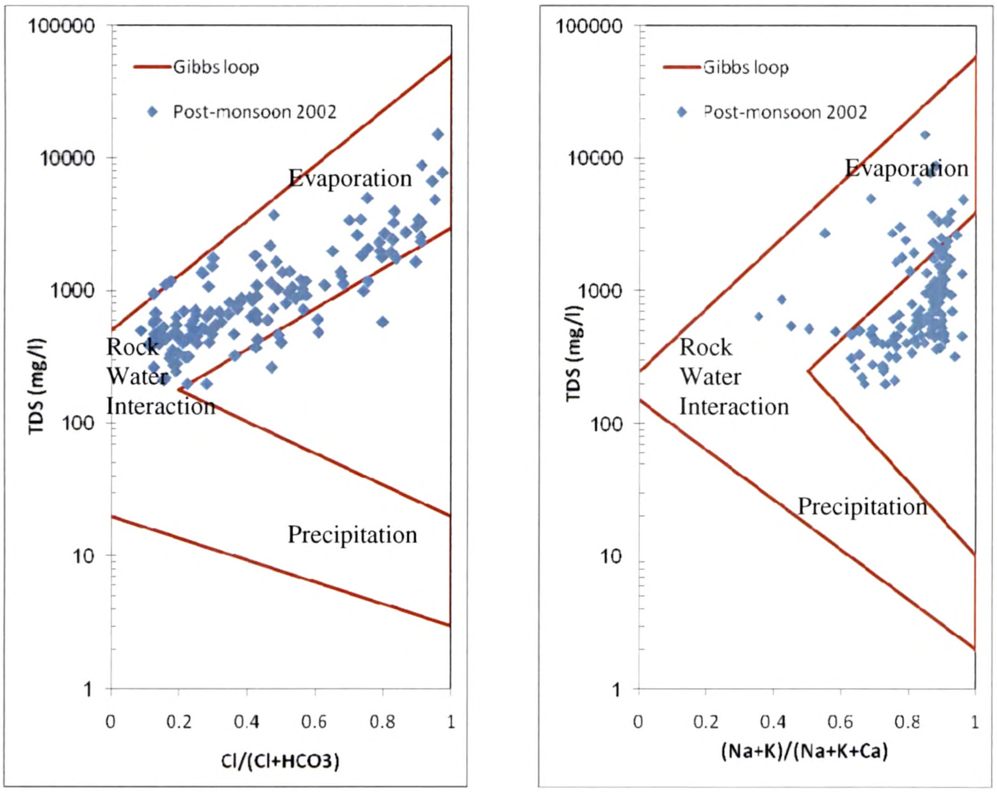


Fig-4.38 Gibbs Plot for Post-monsoon 2002

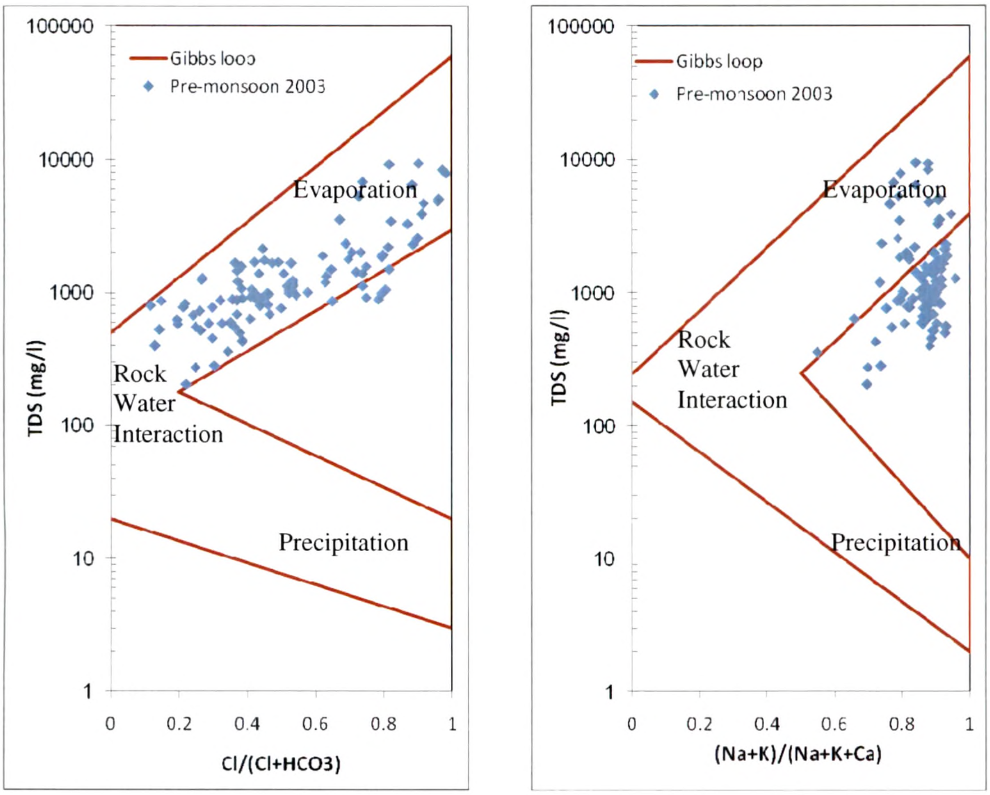


Fig-4.39 Gibbs Plot for Pre-monsoon 2003

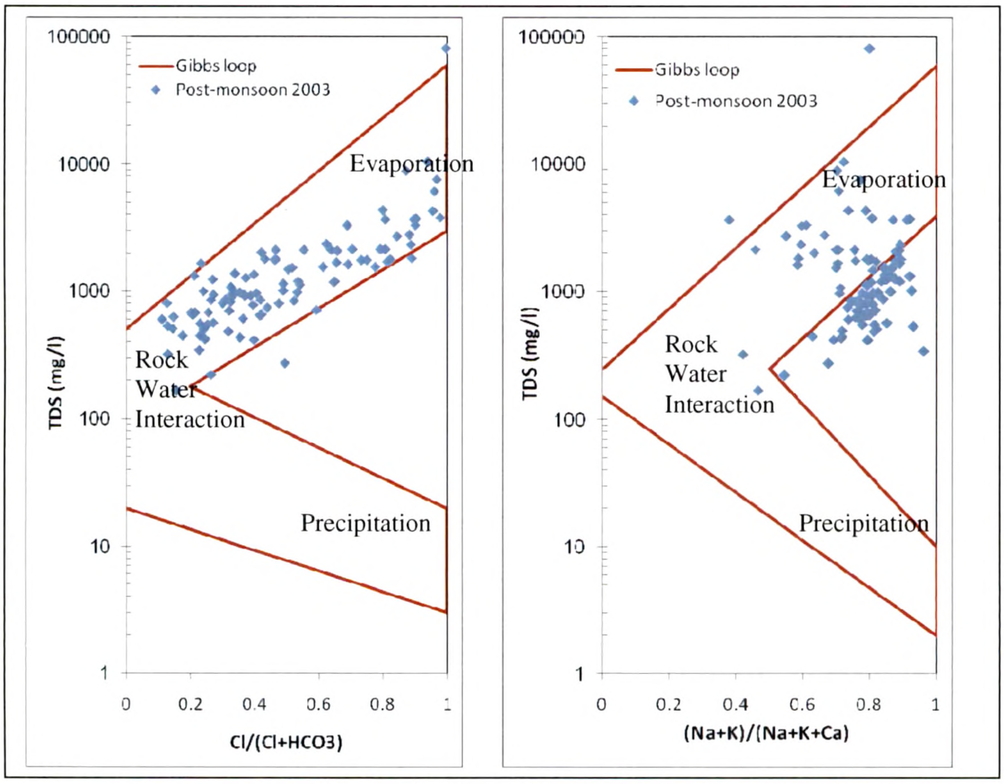


Fig-4.40 Gibbs Plot for Post-monsoon 2003

This is because the samples of pre-monsoon 2002 are mainly from coastal and alluvial plains which are nearer to the coast and especially in coastal area the groundwater is shallow. The post-monsoon 2002 samples indicate that the ratio-I ranges from 0.09 to 0.97 while ratio-II ranges from 0.35 to 0.96. Similarly for pre-monsoon 2003 the ratio-I ranges from 0.12 to 0.98 while ratio-II ranges from 0.55 to 0.96. The post-monsoon 2003 the ratio-I ranges from 0.11 to 0.99 while ratio-II ranges from 0.38 to 0.96

4.6 Oxygen Isotope Behaviour in Groundwater of the Study Area

$\delta\ ^{18}O$ measurements were carried out on 55 samples well spread over the study area, to have understanding on status and mechanism of recharge, evapotranspiration and salinity ingress in the area. The $\delta\ ^{18}O$‰ measurements were done at PRL, Ahmedabad using a Stable Isotope Ratio Mass Spectrometer (GEO 2020, PDZ Europa U.K.) with automatic water equilibration system. The $\delta\ ^{18}O$‰ values are with respect to the V-SMOW and NRM (Narmada water, $\delta^{18}O = -4.5$ ‰) was used as a laboratory water standard.

Observations:

The samples were selected to ensure the spatial representation. The data on $\delta\ ^{18}O$‰ in groundwater is presented in Table-4.15 and shown in Fig-4.40. The $\delta\ ^{18}O$‰ values from study area have helped in the following inferences:

- ✓ The frequency distribution histogram of $\delta\ ^{18}O$‰ have clearly shown that the 80% of the samples are in the range of -2.5‰ to -1.5‰.

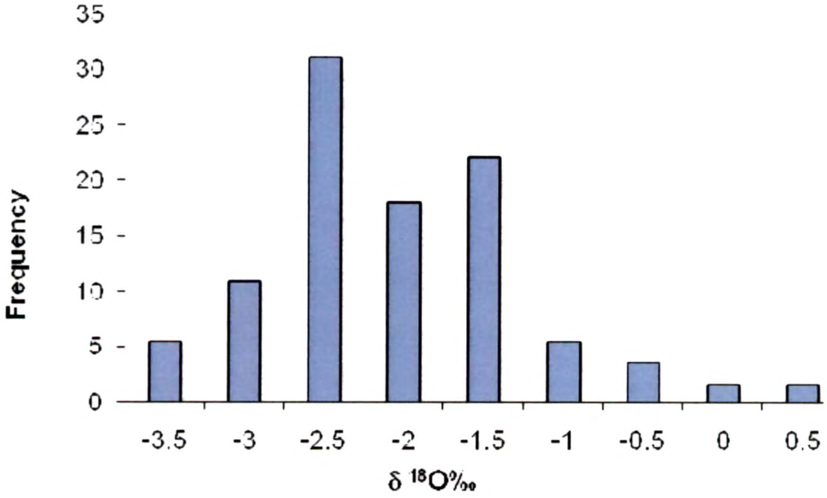


Fig-4.41 Frequency Distribution Diagram of $\delta\ ^{18}O$‰ in Groundwater

Table -4.15 Results of δ ^{18}O‰ from Selected Wells within the Study Area.

Sr. No.	Village	Well type	$\delta^{18}O$	δD
1	Kaliari	HP	-3.16	-15.28
2	Kora	BW	0.27	12.16
3	Nadiad	BW	-3.16	-15.28
4	Dabha	BW	-1.10	1.2
5	Jambusar city	BW	-2.21	-7.68
6	Machhhcsara	BW	-1.30	-0.4
7	Dadapor	BW	-1.34	-0.72
8	Dora	BW	-2.70	-11.6
9	Keshwan	BW	-0.90	2.8
10	Janiadara	HP	1.06	18.48
11	Kakam	BW	-0.48	6.16
12	Manad	HP	-2.03	-6.24
13	Sarnar	BW	-0.51	5.92
14	Vasdada	BW	-3.15	-15.2
15	Uparali	BW	-2.18	-7.44
16	Kavitha	BW	-2.03	-6.24
17	Masar	BW	-1.11	1.12
18	Dhobikuva	BW	-2.48	-9.84
19	Darapura	BW	-2.79	-12.32
20	Chorbhuj	BW	-2.58	-10.64
21	Kiya	BW	-1.54	-2.32
22	Kanthariya	BW	-1.76	-4.08
23	Shankarda	BW	-2.50	-10
24	Sewasi	BW	-2.46	-9.68
25	City	BW	-2.14	-7.12
26	Ankhi	BW	-2.07	-6.56
27	Amarapura	BW	-2.70	-11.6
28	Gothada	BW	-0.93	2.56
29	Manjusar	BW	-2.05	-6.4
30	Manjusar	BW	-1.06	1.52
31	Khakharia	BW	-1.29	-0.32
32	Kamrol	HP	-1.24	0.08
33	Nava Rampura	HP	-1.26	-0.08
34	Falod	BW	-1.27	-0.16
35	Nariya	BW	-1.83	-4.64
36	Dholar	BW	-1.76	-4.08
37	Tarsana	BW	-2.20	-7.6
38	Bhimpura	BW	-1.57	-2.56
39	Asodara	BW	-2.30	-8.4
40	Anandpura	BW	-0.47	6.24
41	Wandarda	HP	-2.00	-6
42	Khunvad	BW	-1.73	-3.84
43	Ladhod	BW	-2.14	-7.12
44	Sardarpura	HP	-1.60	-2.8
45	Uchad	BW	-1.32	-0.56
46	Tarsal	BW	-1.74	-3.92
47	Nanahabipura	BW	-2.01	-6.08
48	Vaniad	BW	-1.96	-5.68
49	Mota Fofaliya	BW	-2.29	-8.32
50	Ambada	BW	-2.06	-6.48
51	Gulvani	HP	-2.77	-12.16
52	Nani Takri	BW	-2.12	-6.96
53	Bediya	BW	-1.96	-5.68
54	Hanf	HP	-2.78	-12.24
55	Nanivant	HP	-1.50	-2

- ✓ The depleted values of $\delta^{18}O$ ‰ indicates that area is being recharged from surface water, while enriched values $\delta^{18}O$‰ from coastal area are in conformity with the coastal salinity ingress process.

- ✓ The highlands and the alluvial plains showing depleted $\delta^{18}O$‰ values (-3.5‰ to -1.5‰). This is in conformity with the fact that highlands and alluvial plains are the main zones of recharge to groundwater mainly through rainfall infiltration.

- ✓ The samples form coastal area along the Gulf of Cambay representing Keshwan, Kalam and Sarnar villages has shown enriched $\delta^{18}O$‰ values relatively. In case of Kora and Janiadara area have shown very high relative enriched values of $\delta^{18}O$‰ (+ve values) have been observed suggesting that these areas have strong influence of salinity ingress.

- ✓ The enriched $\delta^{18}O$‰ value observed for some locations in the high rocky areas and alluvial plains is attributable to the factors like poor recharge, high evaporation or isolated older water mass etc. some locations of Waghodia, Pavi-Jetpur taluka have shown relatively enriched $\delta^{18}O$‰ values.

- ✓ Based on the $\delta^{18}O$‰ values it is imperative to assume that over ±60% of the study area serve as good recharge surface.

- ✓ There is a good correlation between Cl and $\delta^{18}O$, this is very obvious in the area along the Gulf of Cambay, where salinity ingress has contributed to the high Cl concentration and the $\delta^{18}O$ value will be enriched. The high Cl for the location away from the Gulf and not associated with the enriched $\delta^{18}O$ the situation is clearly implying surface contamination and pockets of groundwater having high Cl concentration and enriched $\delta^{18}O$ value, it is imperative to assume that the recharge is poor and hence high evaporation leads to enriched value for both Cl and $\delta^{18}O$.

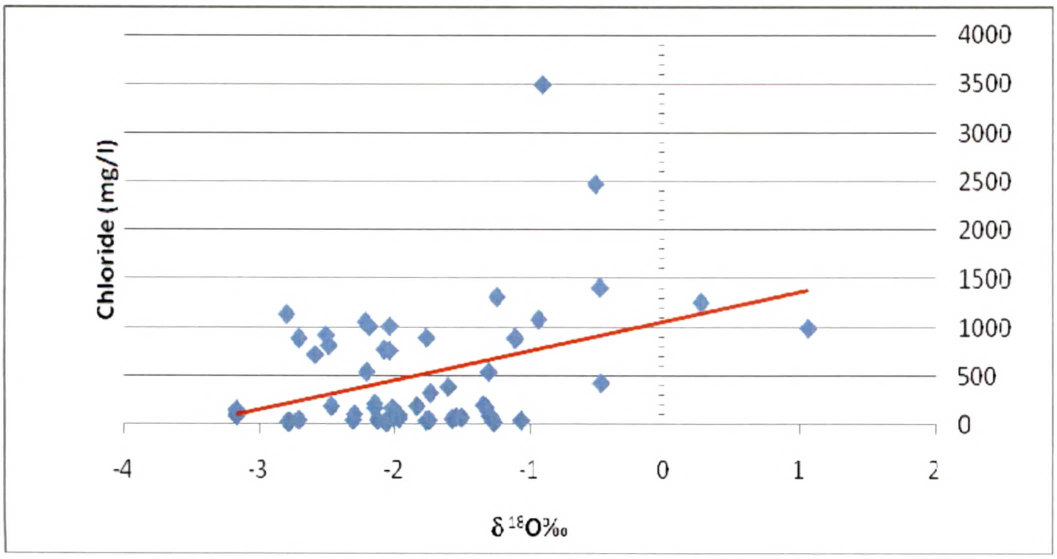


Fig-4.42 Relation Between δ ^{18}O‰ and Chloride

- ✓ Similarly the scattered plot of NO_3 vs. δ ^{18}O‰ shows that at depleted δ ^{18}O‰ value the nitrate concentration is also low and it increases as the δ ^{18}O shift to positive value, linking to salinity ingress.

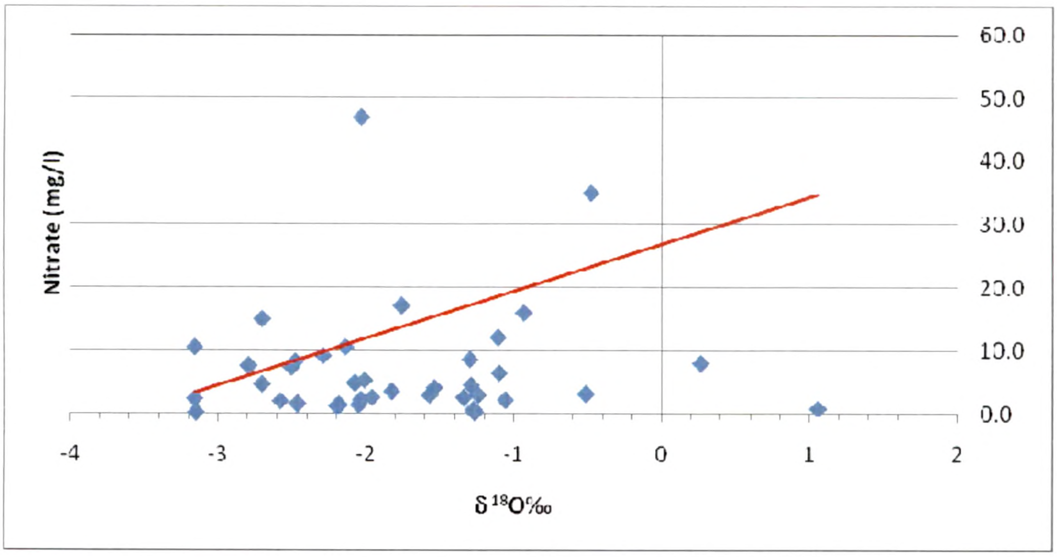


Fig-4.43 Scatter Plot of Nitrate and Oxygen Isotope

4.7 GROUNDWATER QUALITY CHARACTERIZATION

The quality aspect of groundwater is equally important as the quantity. The suitability of groundwater for drinking/domestic, irrigation and industrial uses are assessed depending upon its physical, chemical and biological characteristics causing adverse effects to human beings and plants. In this part the author has dealt with quality characterization for drinking/domestic and irrigation water requirement.

4.7.1 Drinking Water Quality Assessment of Groundwater samples.

Water quality is multivariate in composition as it is composed of different constituents with varying concentration depending upon the geological history of groundwater. Groundwater is hosted either in consolidated or unconsolidated materials consisting of minerals and because of the occurrence and reoccurrence of related mineral species in its flow path, water chemistry invariably changes. Water being one of the basic amenities for living hence there are standards available in terms of physical, chemical and biological quality.

As it has already been enumerated that the study area comprises two important urban centres Vadodara and Bharuch. The vast stretch of study area sprawling over 11,187.89 km^2 area encompasses 37,74,256 population which depends mainly upon groundwater for drinking purpose. Though in Vadodara urban area partly water is utilized from Sayaji Sarovar and partly from Panam reservoir through number of French wells sunked in Mahi river. But the rural area population entirely subsists its drinking water demand solely from groundwater system. Similarly in Bharuch partly water is supplied through pipe line for which surface water is being utilized. As a result it becomes necessary to evaluate groundwater from its potability point of view. In urban areas the water is supplied through Municipal Corporation which is initially being treated before supply. But in rural areas groundwater is directly consumed without knowing its potability characteristics. The major draft structures for drinking purpose mainly in rural areas are hand pumps and tube wells/bore well.

Various institutes/organization has recommended the quality standard for drinking water among them some of the important ones are World Health Organization (WHO), the Indian Council of Medical Research (ICMR) and the Bharat (Indian) Standard Institution (ISI). These standards included minimum desirable value and maximum permissible limit. The suggested drinking water standards by various institutions are given in Table-4.15 along with obtained range of parameters for the groundwater samples from the study area for five different seasons, to observe changes in groundwater condition with time and the effect of rainfall i.e. pre and post-monsoon scenario.

Table-4.16 Comparison of Groundwater Samples from Study Area with Drinking Water Quality Standards

Sr. No.	Parameters	ICMR (1975)	ISI (1983)	WHO (1993)	Study Area Samples			
					Pre Mon 2002	Post Mon 2002	Pre Mon. 2003	Post Mon 2003
1	PHYSICAL PROPERTIES							
2	Colour (Hazen)	5 (25)	10	5 (50)	NA	NA	NA	NA
3	Odour	Not Desirable	Unobjectionable	Not Desirable	NA	NA	NA	NA
4	Taste (JTU)	“	Agreeable	“	NA	NA	NA	NA
5	Turbidity	5 (25)	10	5 (25)	NA	NA	NA	NA
6	CHEMICAL PROPERTIES							
7	pH	7.0-8.5 (6.5-9.2)	6.5-8.5	7-8 (6.5-9.2)	7.61-8.87	7.06-8.6	7.06-8.71	6.65-8.48
8	TDS (mg/l)	500 (1500)	2000	500 (1500)	420-9542	200-15094	205-9450	168-81000
9	TH (mg/l)	300 (600)	300	300 (600)	92.4-2667	58-3500	58-3850	70-16100
10	Calcium (mg/l)	75 (200)	75	75 (200)	18.5-370.6	5-589.5	12.8-384.2	10.1-6115
11	Magnesium (mg/l)	50 (150)	30	50 (150)	0.55-459.6	0.0-492.8	0-863.4	0-260.9
12	Chloride (mg/l)	200 (1000)	250	200 (600)	49.9-3798.8	20-6240	27-4099	60-50000
13	Sulfate (mg/l)	200 (400)	150	200 (400)	50-7800	30-10770	40-7300	19-59189
14	Fluoride (mg/l)	1.0 (1.5)	0.6 (1.2)	--(1.5)	NA	NA	0.11-6.65	0.1-13
15	Nitrate (mg/l)	20 (50)	45	--(50)	NA	NA	0.2-265	0.2-325
16	Copper (mg/l)	0.05 (1.5)	0.05	1.0 (1.5)	NA	NA	0.001-0.018	NA
17	Iron (mg/l)	0.3 (1.0)	0.3	0.3 (1.0)	NA	NA	0.3-1.7	NA
18	Manganese (mg/l)	0.1 (0.5)	0.1	0.1 (0.5)	NA	NA	0.004-0.04	0-2.9
19	Zinc (mg/l)	5.0	5.0	5.0	NA	NA	0.002-0.06	NA

NA- Not Analyzed

4.7.2 Groundwater Classification for Irrigation Purpose

The quality aspect of groundwater for irrigation purpose has been extensively worked by various authors some of the noteworthy contribution to this aspect have come from viz. Dalip and Chawla (1946), Wilcox (1948), Mc Kee and Beacon (1953) U.S Salinity Laboratory Staff (1954), Doneen (1964), Puri (1967), Van Hoorn (1971), Bhumbala and Abrol (1972), Rhoades (1972), USEPA (1973), Ayers and Westcot (1976), Christiansen et al (1975, 1977), Westcot (1979), Suarez (1990), Jankowski and Acworth (1997) etc.

There are various indices available to characterized water based on its ionic chemistry for its irrigation suitability. Some important indices frequently used in irrigation classification are :-

1. Kelley's Ratio
2. Residual sodium Carbonate
3. Schoellar Index
4. Sodium Hazards (SAR)
5. Wilcox Irrigation Water Classification

(1) Kelley's Ratio (KR)

This ratio suggests about the level of alkali hazards in the soil attributed to poor groundwater quality. To evaluate alkali hazards of groundwater Kelley et. at (1940) proposed a following equation.

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

Where ionic concentration are in meq/l.

The Kelley's Ratio less than one indicates that the water is good for irrigation and is free from alkali hazards while the ratio more than one indicates alkali hazards.

The KR during pre-monsoon 2002 was found to be on higher side for most of the samples indicating alkali hazard in the area. Samples which were found to be on lower side are viz. Bhadkhodra BW (0.6) and Machhasara BW (0.7) from coastal plains; Dora HP (0.6), Asoj TW (0.7), Makarpura BW (0.6), Gothada TW (0.5) & HP (0.4), Mindhol TW (0.6) and Mota Fofaliya TW (0.8) from Alluvial plains; and Moti Bhadol TW (0.5) & HP (0.6), Nava

Rampura (0.8) from Piedmont zones. About 23% of the total samples have been found free from alkali hazards (Fig-4.44).

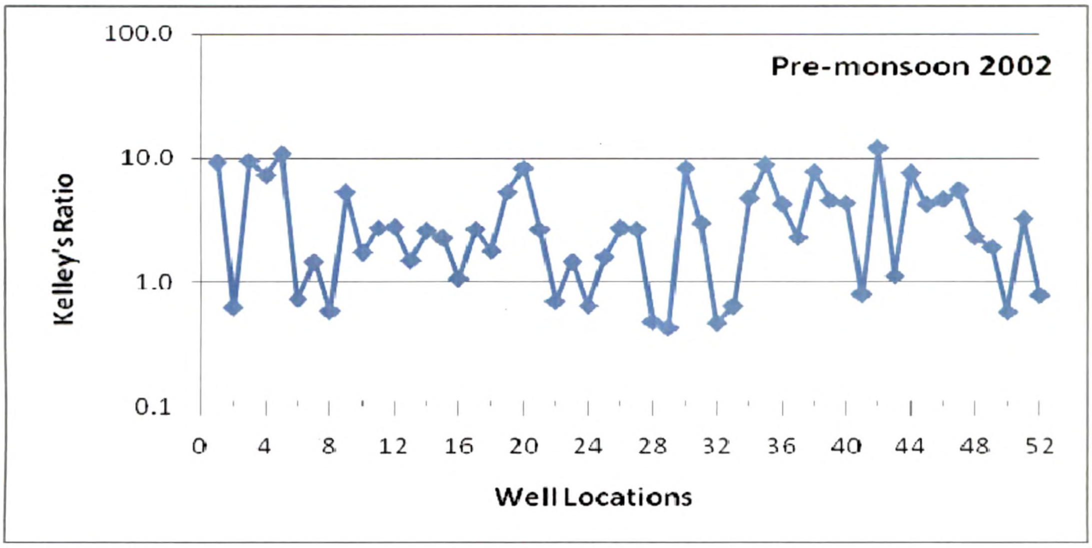


Fig- 4.44 Spatial Distribution Pattern of Kelley's Ratio (Pre-monsoon 2002) in Study Area

Kelley's Ratio for the post-monsoon 2002 season indicates that the eastern highland and piedmont regions is relatively free from alkali hazard except few sporadic samples having KR >1. The piedmont zone and alluvial plains has mix sample with low and high values whereas samples belonging to the coastal plains show pronounced alkali hazard. However, overall about 43% of the samples are found from alkali hazard (Fig-4.45).

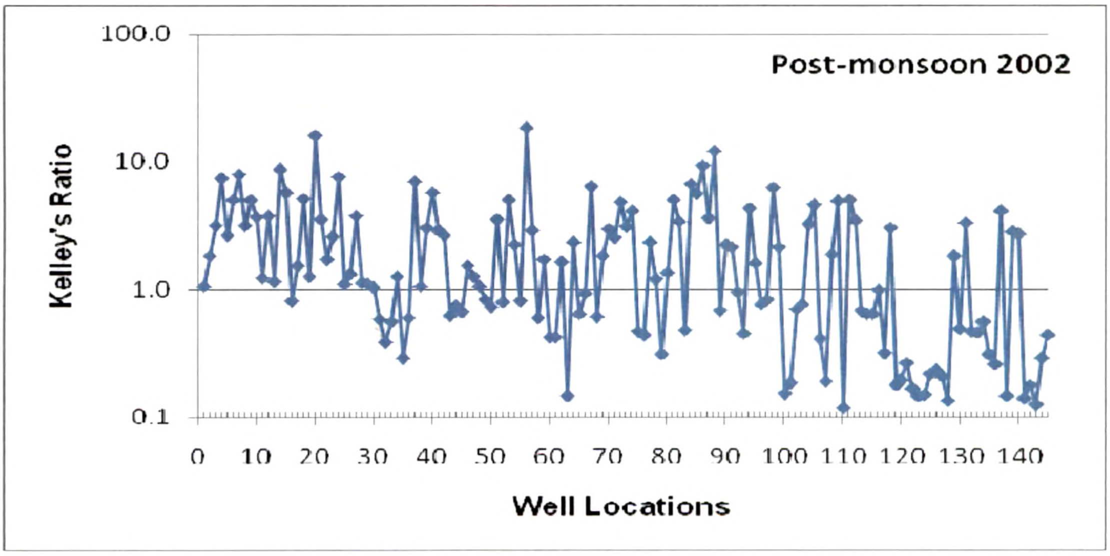


Fig-4.45 Spatial Distribution Pattern of Kelley's Ratio (Post-monsoon 2002) in Study Area.

During pre-monsoon 2003 season about 30 samples i.e. 30% of the samples found free from alkali hazard (Fig-4.46).

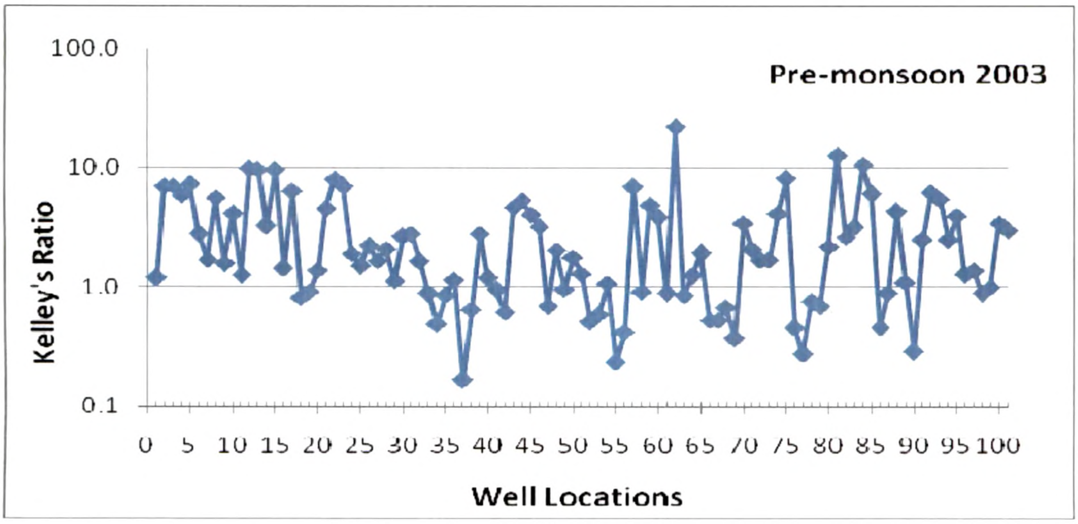


Fig-4.46 Spatial Distribution Pattern of Kelley's Ratio (Pre-monsoon 2003) in Study Area

The groundwater samples of post-monsoon 2003 indicate slight improvement in the level alkali hazards, particularly from the coastal plains. Similar trends from alluvial plains have also been noticed (Fig-4.47). About 32% of the samples are in suitable category. This observed improvement in alkali hazard may be attributed to dilution process due to rainwater recharge.

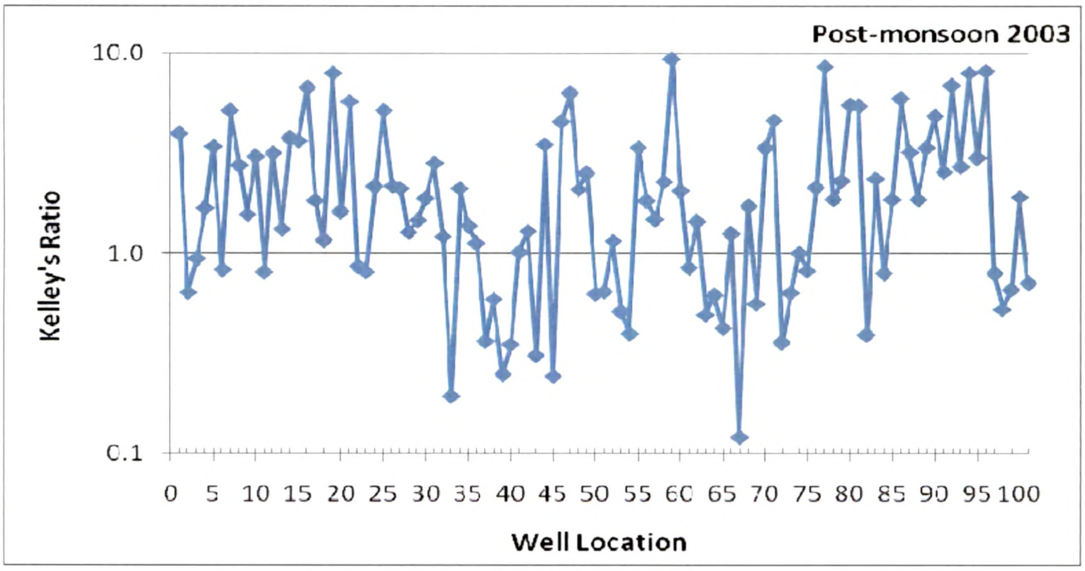


Fig-4.47 Spatial Distribution Pattern of Kelley's Ratio (Post-monsoon 2003) in Study Area

(2) Residual Sodium Carbonate (RSC)

The abundance of carbonate and bicarbonate ions is denoted by Residual Sodium Carbonate. Bicarbonate is present in both surface and subsurface water. Water containing high concentration of bicarbonates have normal tendency to precipitate Ca and Mg as carbonate. It is also obvious that the depletion of bivalent ions in the soil solution leads to the increase in-situ SAR and consequently to ESP. Eaton (1950) has proposed the concept of RSC on the basis that all Ca and Mg precipitate as carbonate. The empirical formula given for the calculation of RSC is

$$RSC = (CO_3 + HCO_3) - (Ca + Mg)$$

A high value of RSC in groundwater leads to increase in the adsorption of sodium on soil (Eaton, 1950). Water quality for irrigation can be assessed based on the RSC values. When RSC >2.5 water is hazardous, 1.25-2.5 is marginal and water with RSC value <1.25 meq/l is safe for irrigation. Irrigation water having RSC > 5 meq/l have been considered harmful to the growth of plants.

The RSC values of pre-monsoon 2002 samples indicate that most of the samples are within the safe to permissible range. Few samples which were found to be unsafe viz. Sindhav TW (3.36 meq/l), Darapore TW from Padra Taluka (5.63 meq/l) and Tarsana TW (3.30) from Vaghodia Taluka in the Alluvial Plains while Kamral from Vaghodia village (Fig-4.34).

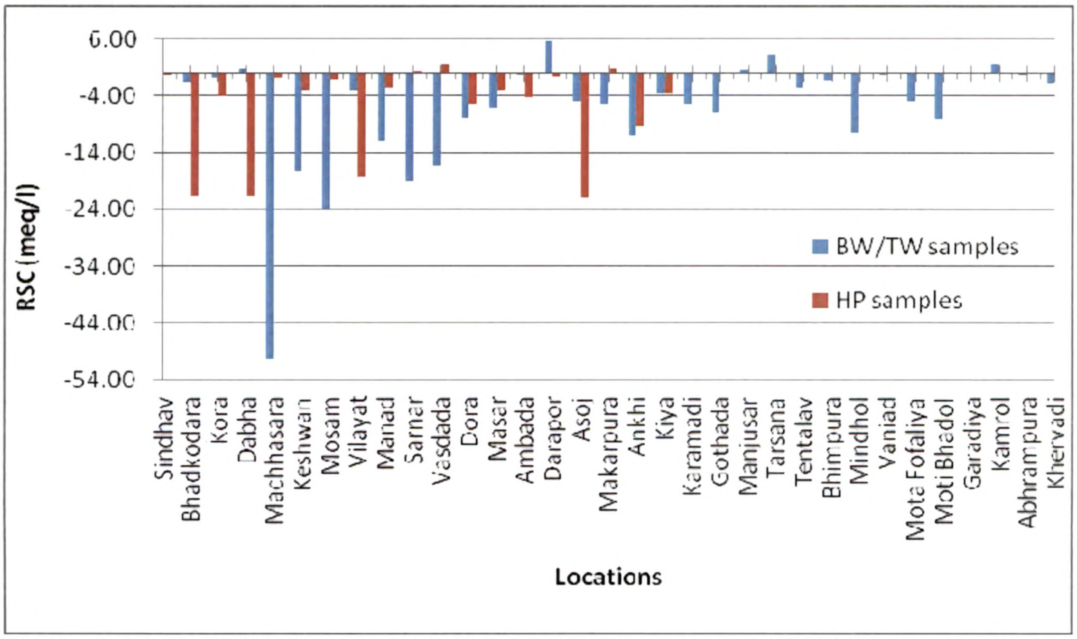


Fig-4.48 Spatial Distribution Pattern of RSC (Pre-monsoon 2002) in the Study Area

The exceptionally high negative values observed during post-monsoon 2002 samples indicate that the concentration of Ca^{2+} and Mg^{2+} ions exceeds far then carbonate and bicarbonate values. Concentration of Ca^{2+} and Mg^{2+} ions is more pronounces in the coastal area as well as in fringe area from the adjacent alluvial plains (Fig 4.49). In alluvial area there is mix concentration wherein some have high concentration of Ca^{2+} and Mg^{2+} while others are rich in carbonates and bicarbonates. The spatial profile across the study area indicates that in alluvial plains the RSC value is more on positive side which means that carbonate and bicarbonate proportion is high therefore, will have a normal tendency to precipitate Ca and Mg as carbonate. Towards highlands the difference between carbonate and bicarbonate and $Ca2^{+}$ and Mg^{2+} tends to decrease thereby indicating balance proportion.

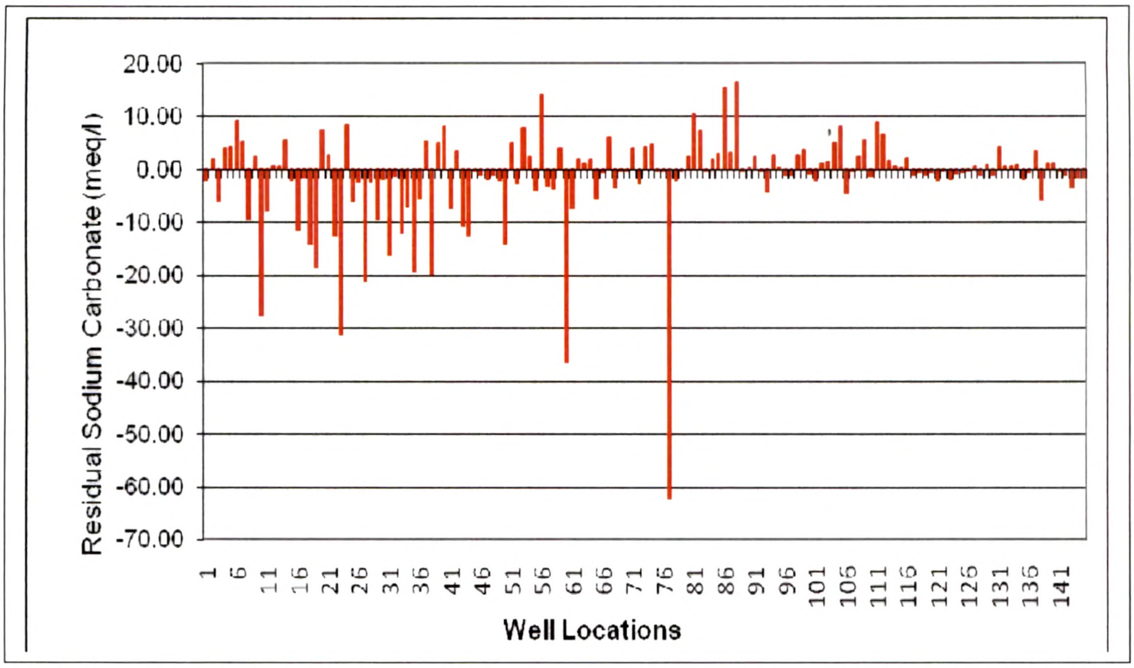


Fig- 4.49 Irrigation Water Classification Based on RSC for Post-monsoon 2002 samples

The pre-monsoon 2003 groundwater samples indicate a bit different trend wherein the proportion of carbonates and bicarbonates is larger than the $Ca2^{+}$ and Mg^{2+} especially in the central parts of the study area. The exceptionally high negative value has been observed in the hand pump sample at Rarod village (Karjan Taluka). RSC shows positive values in Jambusar Taluka whereas other localities from coastal plains viz. Vagra, Amod and Bharuch maximum samples shows negative trend in RSC (Fig-4.50).

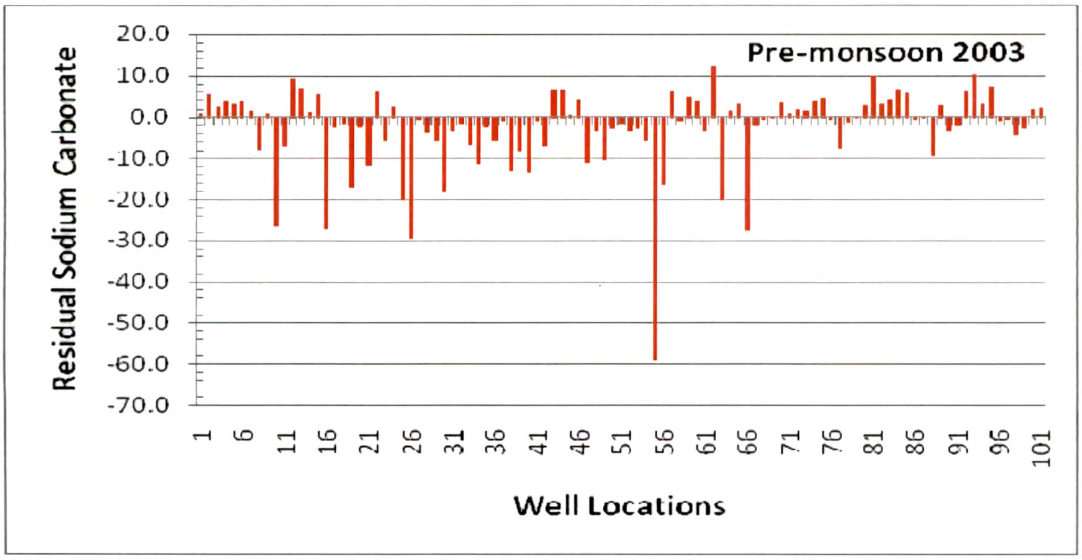


Fig- 4.50 Spatial Distribution Pattern of RSC (Pre-monsoon 2003) in the Study Area

The groundwater samples analyzed for post-monsoon 2003 indicates an overall increase in concentration of Ca2^{+} and Mg^{2+} ions especially along coastal plains and central alluvial plains. The eastern part of alluvial plains has more carbonates and bicarbonates values (Fig-4.51)

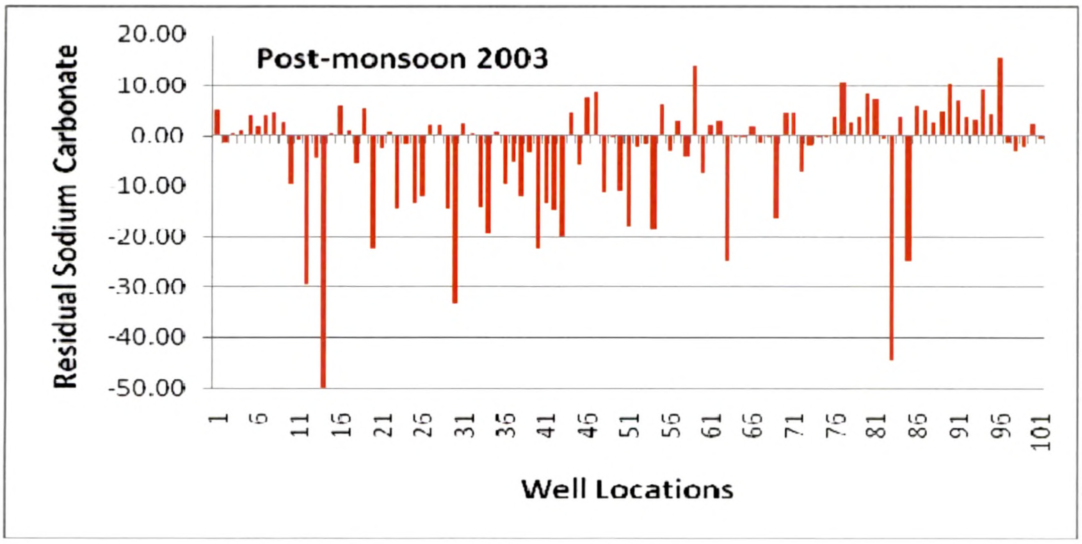


Fig 4.51 Spatial Distribution Pattern of RSC (Post-monsoon 2003) in Study Area

(3) Schoeller Index (SI)

Schoeller (1959) used an index to determine the possibilities of ion exchange reaction taking place in groundwater. This index results due to changes in the chemical composition of groundwater. The Schoeller Index is determined using the following relation:

$$SI = \frac{R \times \{Cl - (Na + K)\}}{Cl}$$

R = total ionic concentration in meq/l

The positive value of the SI is indicative of base exchange reaction i.e. Na + K in water being exchanged with Mg and Ca, whereas, negative value indicate cation-anion exchange i.e. chloro-alkaline disequilibrium (Schoeller, 1962).

The Schoeller Index analysis of pre-monsoon 2002 samples indicate that about 21% tube well (Deep Water) samples (8% from coastal plain, 11% from alluvial plain and 2% from piedmont zone) and 8% samples (2% from alluvial plain and 6% from piedmont zone) from hand pump are indicative of base exchange reaction while 71% samples are indicative of cation-anion exchange reactions (Fig-4.52).

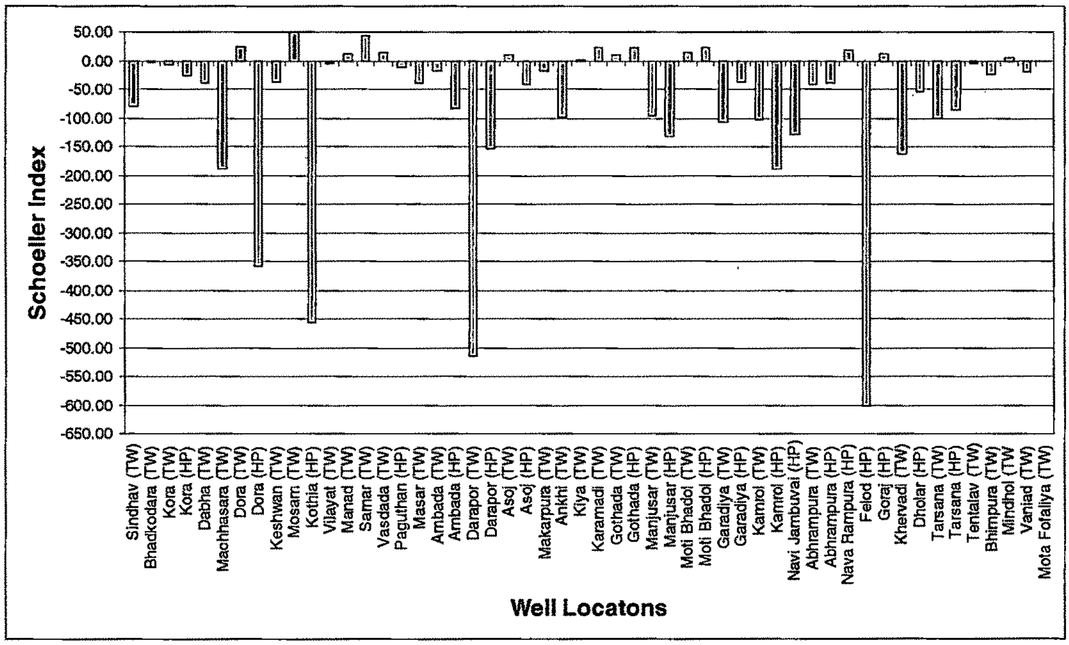


Fig-4.52 Spatial Distribution Pattern of Schoeller Index (Pre-monsoon 2002) in Study Area

The SI index for the post-monsoon 2002 groundwater samples indicate that the cation-anion reaction is more pronounced in the study area (Fig-4.53). While base exchange reactions are more active in the transitional zone of coastal and alluvial plains and to some extent in highlands.

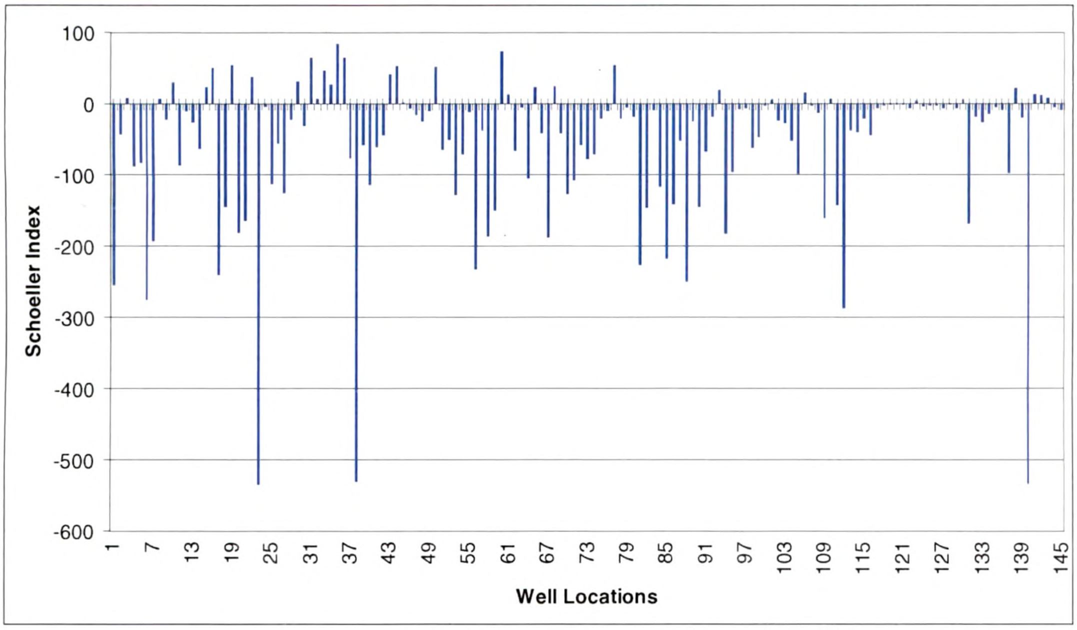


Fig-4.53 Spatial Distribution Pattern of Schoeller Index (Post-monsoon 2002) in Study Area

The SI for pre-monsoon (2003) indicate more pronounced cation-anion exchange i.e. chloro-alkaline disequilibrium. The exceptionally high SI has been observed from Janiadara Village hand pump sample which may be due to high concentration of sodium cation and high value of total ionic concentration (Fig 4.540).

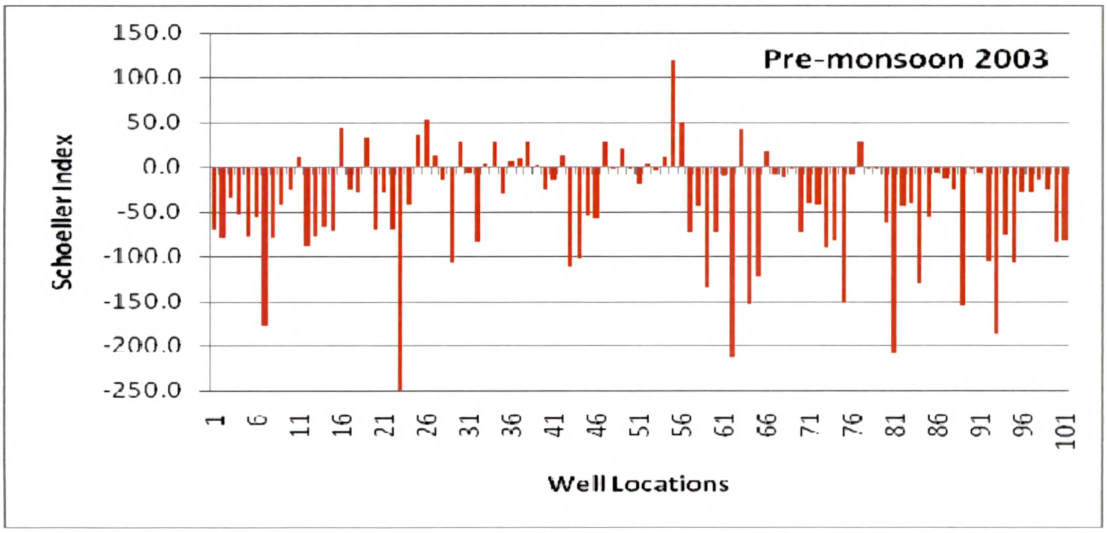


Fig-4.54 Spatial Distribution Pattern of Schoeller Index (Pre-monsoon 2003) in Study Area

Irrigation Water Classification Based on Schoeller Index

Post monsoon 2003 again indicates cation-anion exchange reactions are dominating in the region. Some of the samples shows exceptionally high negative value of SI and they are predominantly from alluvial plains and coastal plains (Fig-4.55). The central alluvium shows some sample with positive SI values indicative of base exchange reaction i.e. Na + K in water being exchanged with Mg and Ca.

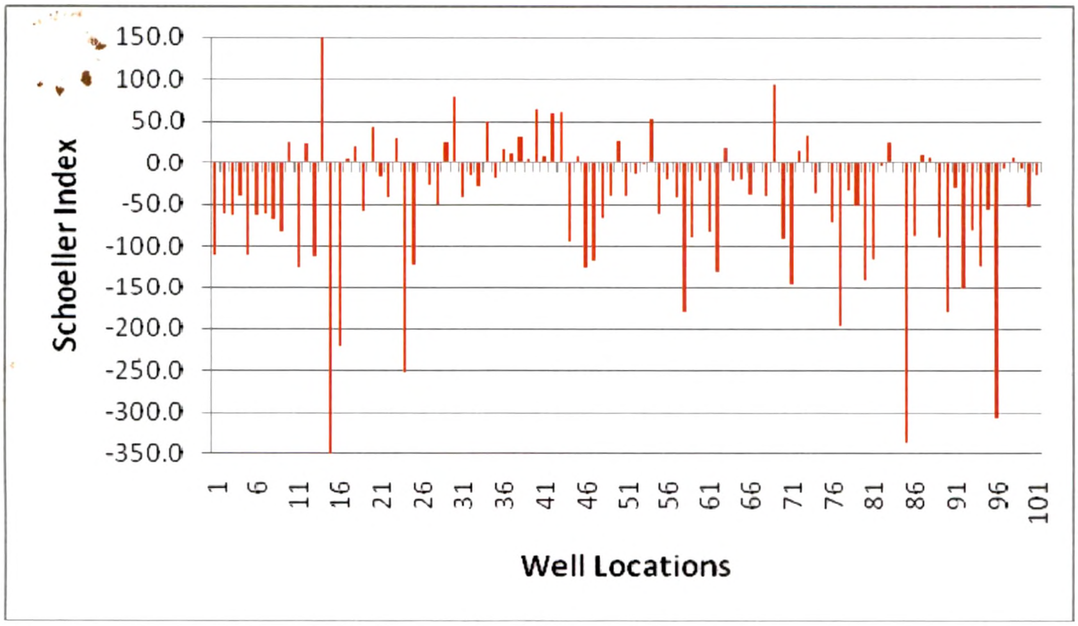


Fig-4.55 Spatial Distribution Pattern of Schoeller Index (Post-monsoon 2003) in the Study Area

(4)Sodium Adsorption Ration (SAR)

SAR has direct relation with the adsorption of sodium by soils (U.S. Salinity Laboratory, 1954). This is measured through the formula:

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

Where Na^{+}, Ca^{2+} and Mg^{2+} are expressed in meq/l

The permissible value of the SAR is a function of salinity. High salinity levels reduce swelling and aggregate breakdown (dispersion), promoting water penetration. However, high proportion of sodium in water reduces water penetration through flocculation of soil crumbs and replacing Ca and Mg. The salinity-SAR plot clearly demarcates the three boundaries where no reduction in rate of infiltration, slight to moderate reduction in rate of infiltration and severe reduction in rate of infiltration (Hoffman, 1997).

The U.S. Salinity diagram is divided into eight different classes viz. C_1, C_2, C_3 and C_4 as Salinity Classes and S_1, S_2, S_3 and S_4 as Sodium Hazard or alkalinity classes. The effect of these Salinity and Sodium hazard classes over soils and their recommended management are given in Table-4.17.

Table-4.17 Classification of Degree of Risk of Using Groundwater for Irrigation (Richards, 1954)

Class	Description
C1	**Low salinity water** (EC <250μS/cm) can be used for most crops on most soils with little likelihood of soil salinity development. Some leaching is required, but this occurs under normal irrigation practices except in soils of extremely low permeability.
C2	**Medium salinity water** (EC 250-750μS/cm) can be used if a moderate amount of leaching occurs. Crops of moderate salt tolerance can be irrigated with this water without special practice.
C3	**High salinity water** (EC 750-2250μS/cm) cannot be used on soils of restricted drainage. Even with adequate drainage special management for salinity control may be required and crops of good salt tolerance can be selected.
C4	**Very high salinity water** (EC>2250μS/cm) is not suitable as irrigation water under ordinary circumstances. It can be used only on crops that are very salt tolerant and only if special practices are followed, including provision of high degree of adverse effects.
S1	**Low sodium water** (SAR<6) can be used for irrigation on most of soils, with little danger of development of the harmful levels of exchangeable sodium.
S2	**Medium sodium water** (SAR 6-12) will present an appreciable sodium hazard in fine textured soil, especially poorly leached soils. Such water may be safely used on coarse textured or organic soils with good permeability.
S3	**High sodium water** (SAR 12-18) may produce harmful levels of exchangeable sodium in most soils and will require special soil management such as good drainage, leaching and addition of organic matter.
S4	**Very high sodium water** (SAR >18) is generally unsatisfactory for irrigation unless special action is taken, such as addition of gypsum to soils.

The inferences derived through the plotted contents on U.S. Salinity diagram from pre-monsoon 2002 to post monsoon 2003 is given in Fig-4.56-4.59. Groundwater samples suggest that majority of groundwater fall within C_4 - S_4 classes indicating bad quality of water. These samples of exceptionally higher values may create alkalinity or sodium salinity hazards to the soil. A comprehensive detail on SAR water samples for the study area is given in Table-4.18.

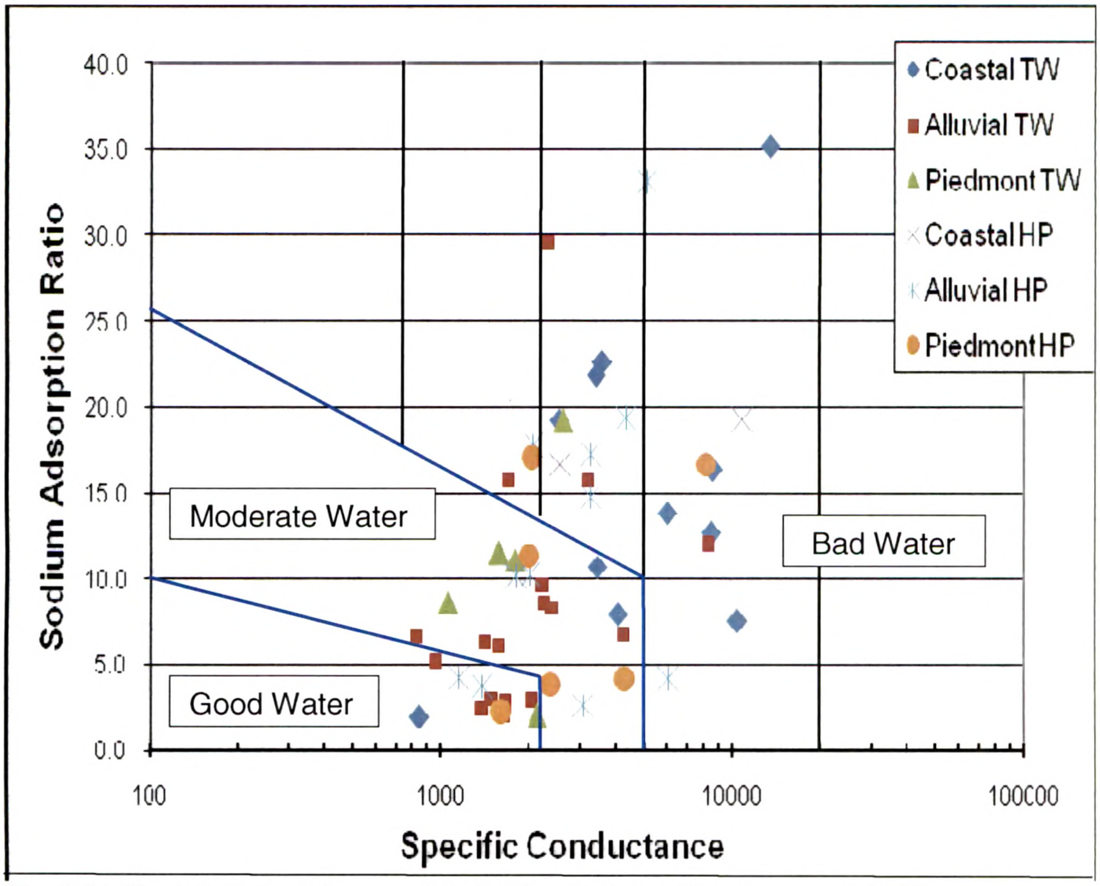


Fig-4.56 U. S. Salinity Diagram for the Study Area (Pre-monsoon 2002)

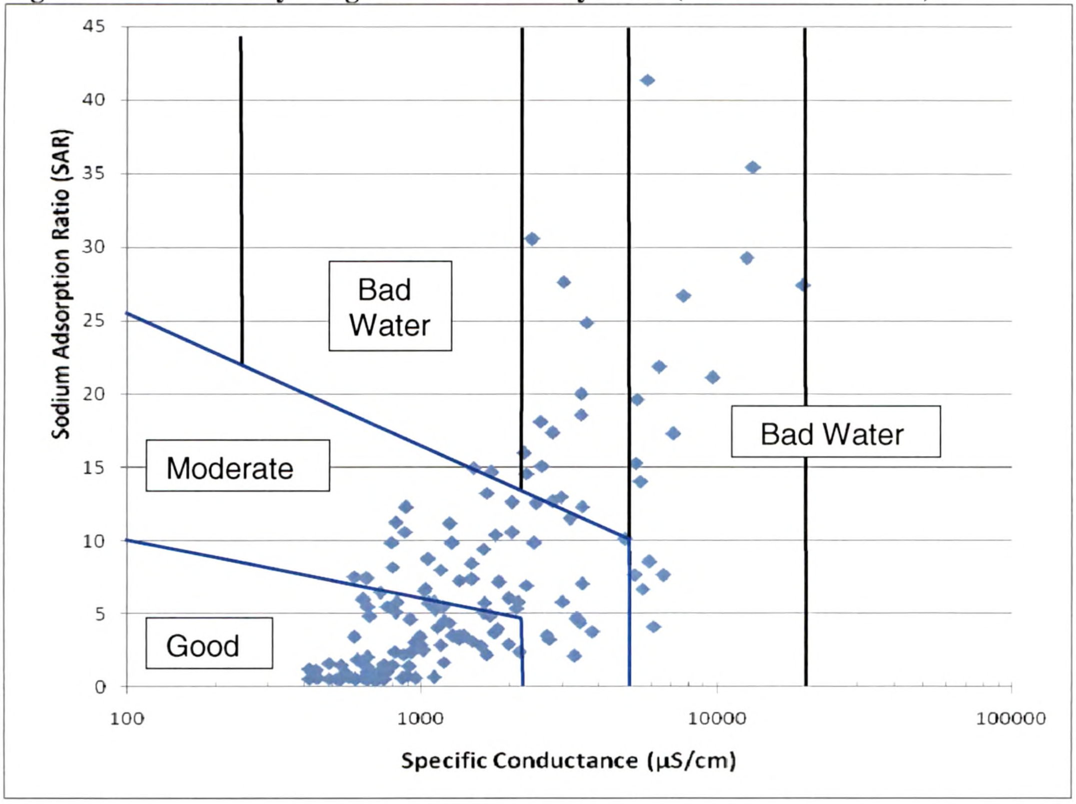


Fig-4.57 U. S. Salinity Diagram for the Study Area (Post-monsoon 2002)

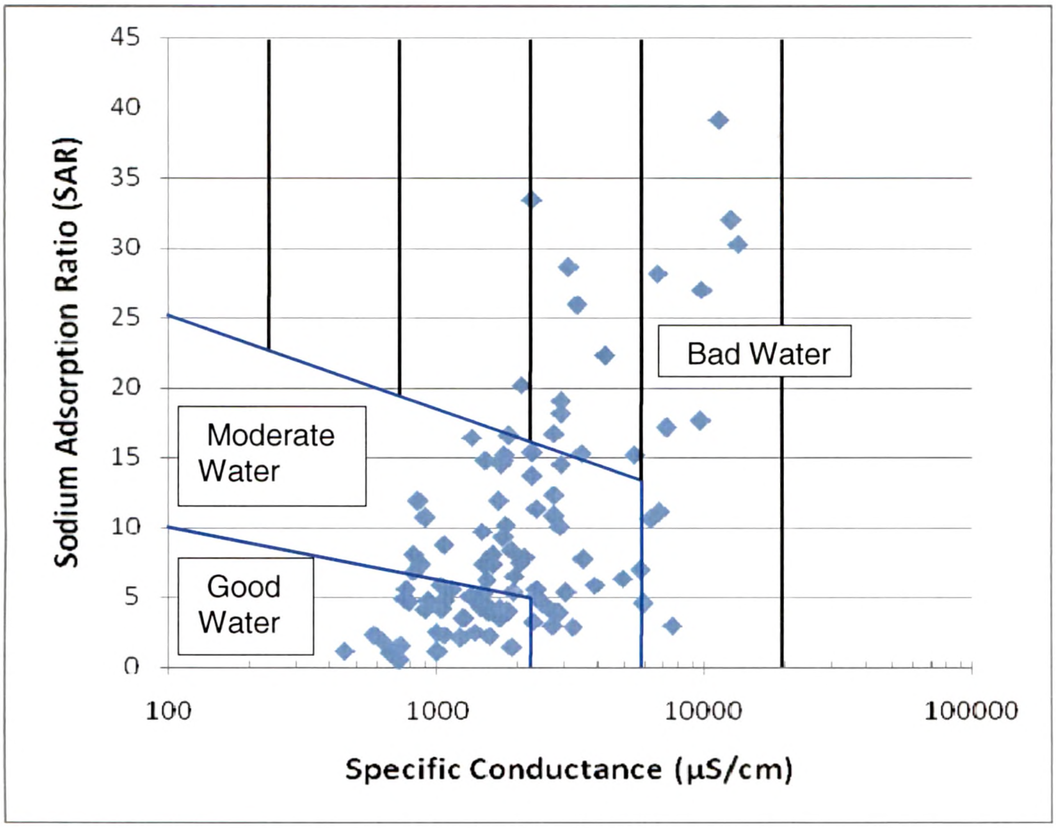


Fig-4.58 U. S. Salinity Diagram for the Study Area (Pre-monsoon 2003)

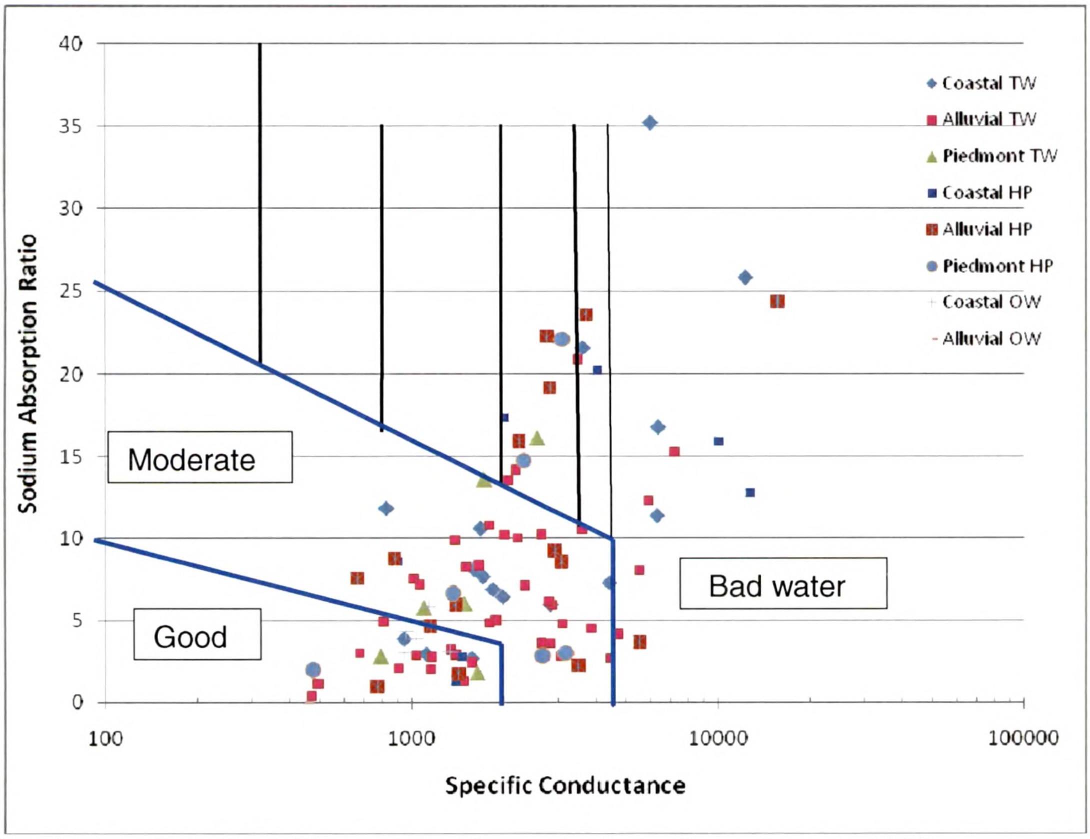


Fig-4.59 U. S. Salinity Diagram for the Study Area (Post-monsoon 2003)

Table-4.18 Details of Groundwater samples belonging to different Class of U.S. Salinity Diagram in Mahi-Narmada inter-stream area

Class	No. of Groundwater samples				Remarks
	Pre Monsoon 2002 (N=52)	Post Monsoon 2002 (N=145)	Pre Monsoon 2003 (N=101)	Post Monsoon 2003 (N=101)	Shallow wells which are near to ponds falls in good class otherwise inland wells are mostly in moderate to bad category.
Good	12	73	36	33	
Moderate	7	40	41	39	
Bad	33	32	24	29	

Above data clearly indicate that there is significant improvement in the overall quality (EC & SAR) of groundwater from pre-monsoon to post-monsoon season. This may be attributed to rainwater recharge causing dilution.

(5) Wilcox Irrigation Water Classification

The quality of groundwater in terms of irrigation potential can be assessed using Wilcox Irrigation Water Classification. Here percent sodium is plotted against total concentration (epm) as electrical conductivity (mmhos/cm). The plot gives five different classes classifying water into excellent to unsuitable category.

The pre-monsoon 2002 water samples as shown in above figure indicate that majority of the samples fall in unsuitable category. Only two tube well samples from alluvial area viz. Bhimpura (Taluka Dabhoi) and Vaniad (Sinor Taluka) villages fall in Class-III category. From pre to post monsoon seasons the categorization of the groundwater samples in given in Fig-4.60-4.62.

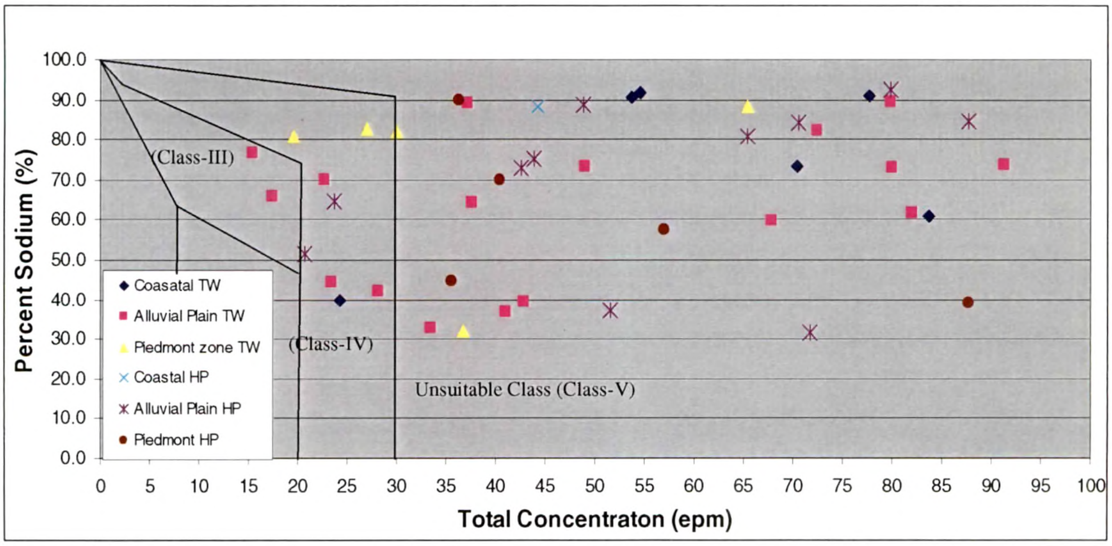


Fig-4.60 Irrigation Water Classification of Pre-monsoon 2002 Groundwater Samples based on Wilcox (1955)

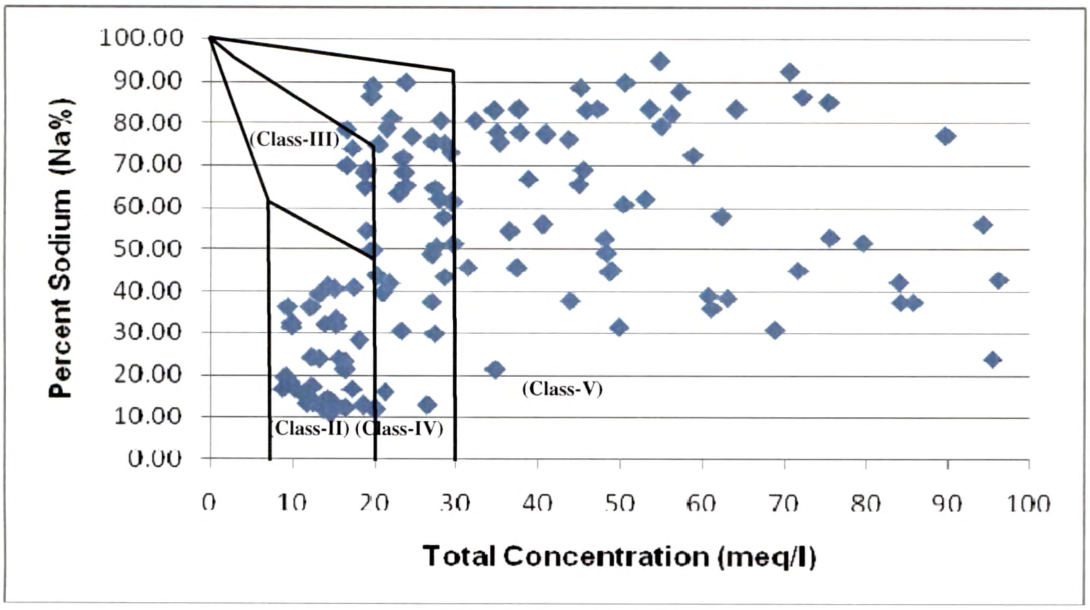


Fig-4.61 Irrigation Water Classification of Post-monsoon 2002 Groundwater Samples based on Wilcox (1955)

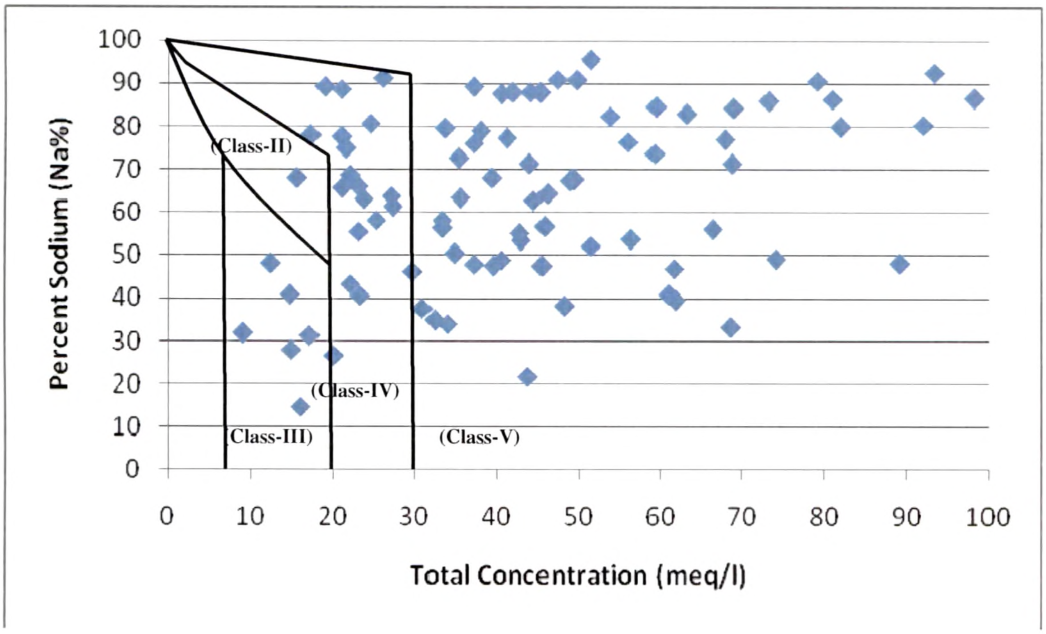


Fig-4.62 Irrigation Water Classification of Pre-monsoon 2003 Groundwater Samples based on Wilcox (1955)

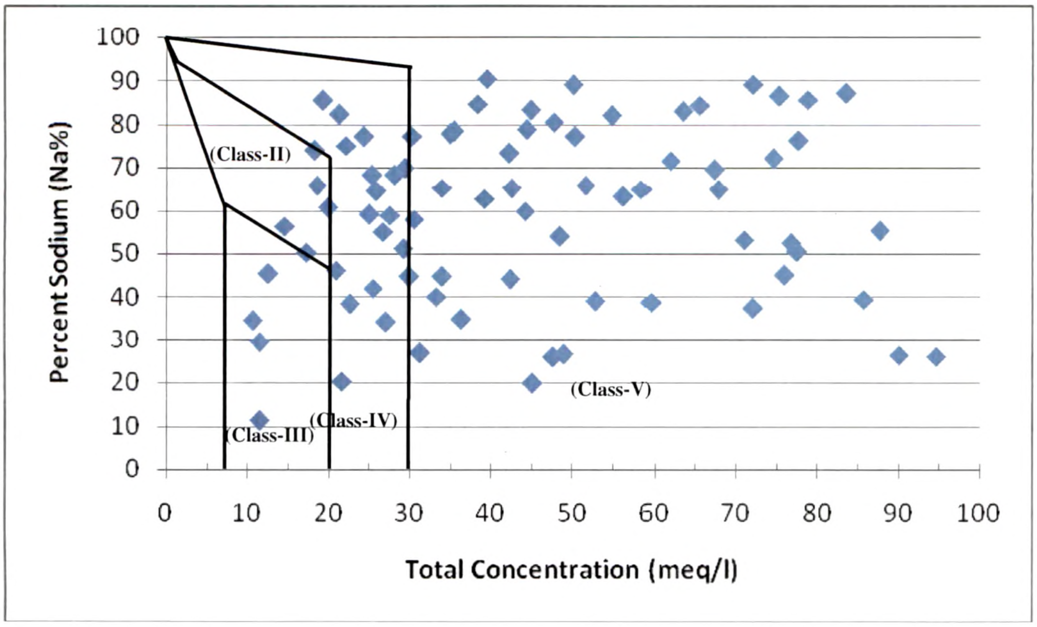


Fig-4.63 Irrigation Water Classification of Post-monsoon 2003 Groundwater Samples based on Wilcox (1955)

(6) Genetic Classification of Groundwater

Piper in 1953 proposed a Trilinear Diagram for representing genetic classification of groundwater. The plots are divided into nine fields depending upon the geochemical characteristic of water as given below.

- Field I: Alkaline earth exceeds alkalies.
- Field II: Alkalies exceed alkaline earth.
- Field III: Weak acid exceed strong acids.
- Field IV: Strong acids exceed weak acids.
- Field V: Carbonate hardness exceeds 50%, i.e. chemical properties of groundwater are by alkaline earths and weak acids.
- Field VI: Non-carbonate hardness exceeds 50%.
- Field VII: Non-carbonate alkali exceeds 50% i.e. chemical properties of groundwater are alkalies and strong acids.
- Field VIII: Carbonate alkali exceeds 50% - very soft water with low TDS content.
- Field IX: No one cation anion pair exceeds 50%.

The Piper Trilinear plot for pre-monsoon 2002 show dominance of cation as Na + K > Mg while anions are SO_4 > Cl type. Majority of samples fall in Field VII indicating NaCl category i.e. alkalies and strong acid dominates the groundwater regime. Some of the samples also fall in Field VII i.e. CaCl type. The groundwater samples (phreatic aquifers) fall mainly in Field VII with four samples (two from piedmont and two from alluvial plain) in Field VI. The deeper groundwater also falls mainly in field VII with eight samples falling in Field VI category. In mixed type water field IX samples from coastal plains are practically absent (Fig-4.64).

The post monsoon 2002 samples indicate that samples from highland area are mainly Mg > Na + K type and HCO_3>SO_4. The samples from piedmont zone, alluvial and coastal plains are Na + K dominating. Similarly anions for highland represents HCO_3>SO_4 type water with few samples falling in Cl domain. The groundwater is generally of NaCl and Ca-Mg HCO_3, while few samples from alluvial plains and highland is CaCl type. Ca- HCO_3 type water is having low Ec values and caused by rainfall recharge process (Fig-4.65). Field IX no dominating type groundwater samples are mainly from alluvial plains and few from highlands and piedmont regions.

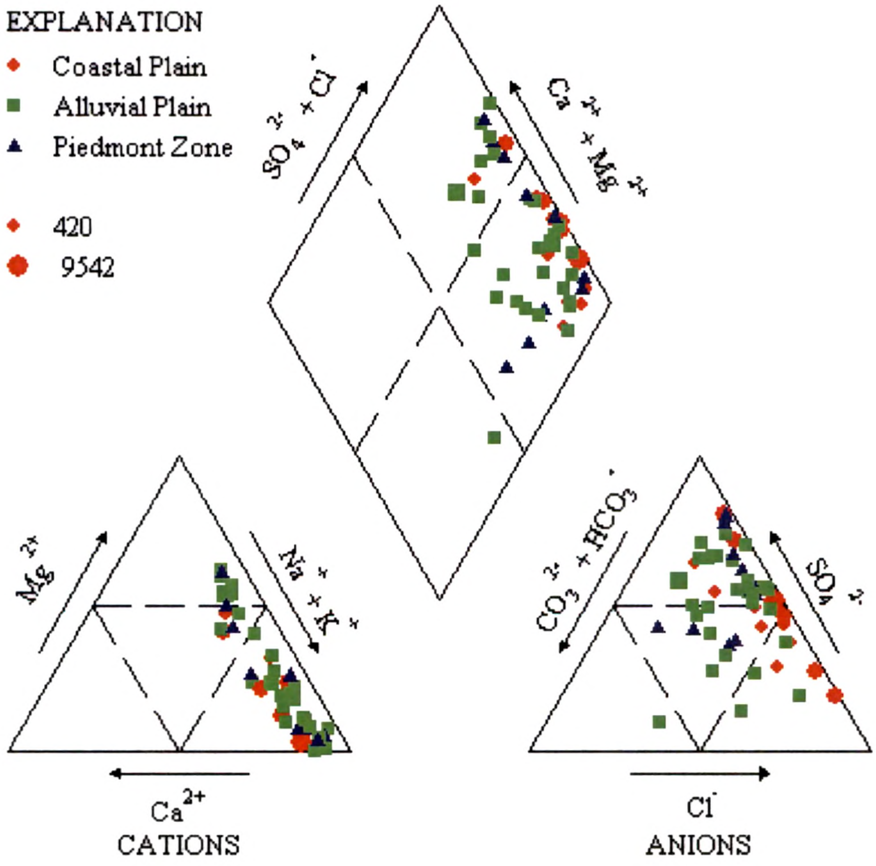


Fig-4.64 Piper Trilinear Plots of Groundwater Samples in Study Area (Pre-monsoon 2002)

The Piper plot of post-monsoon 2003 samples indicate Na + K and SO_4 >HcO_3>Cl type fields. Most of the coastal samples fall in NaCl domain while few in CaCl and Ca-Mg HCO_3 domain. Samples from shallow aquifers (including open well) of coastal plain falls in NaCl > CaCl > Na-HCO_3 domain. Few samples fall in mixed type of water field (Field IX) (Fig-4.66).

The pre-monsoon 2003 samples in Piper plot indicates dominance of Na + K > Mg and SO_4 > Cl > HCO_3 type. However, in diamond plot majority of the samples falls in NaCl > CaCl field. Two samples of piedmont zone show Ca-Mg HCO_3 field and one in Na-HCO_3 field. Majority of the groundwater samples fall in NaCl type field (Fig-4.67).

Therefore the groundwater facies may be characterized as:

Na > Mg >K> Ca : SO_4 >Cl >HCO_3

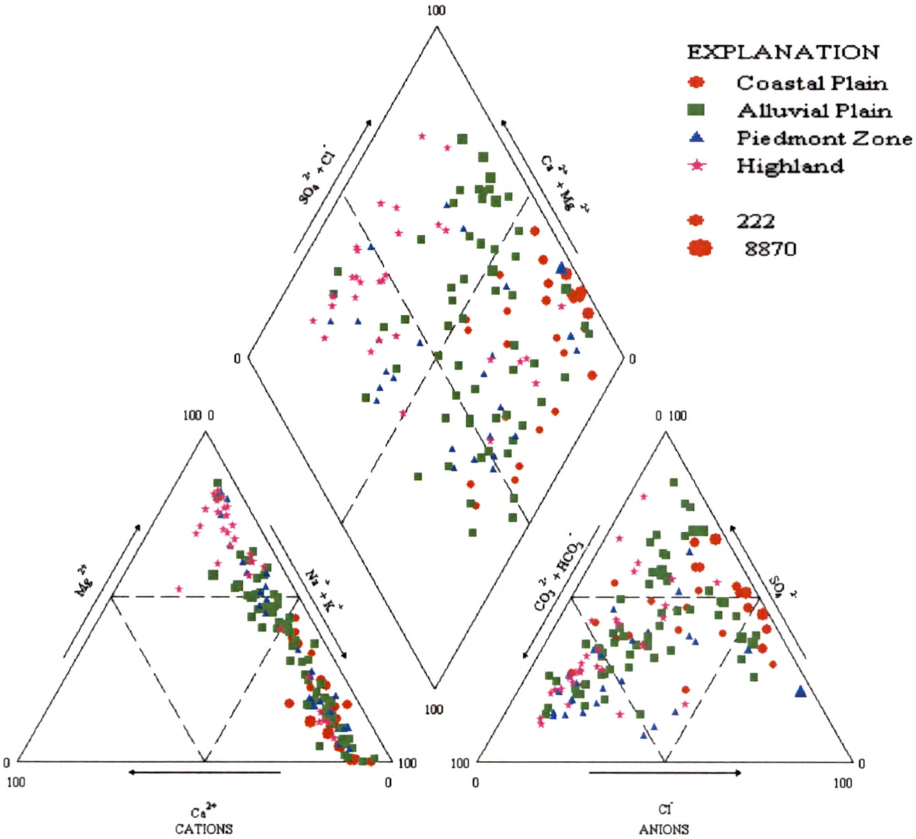


Fig-4.65 Piper Trilinear Diagram Plots of Groundwater Samples in Study Area (Post-monsoon 2002)

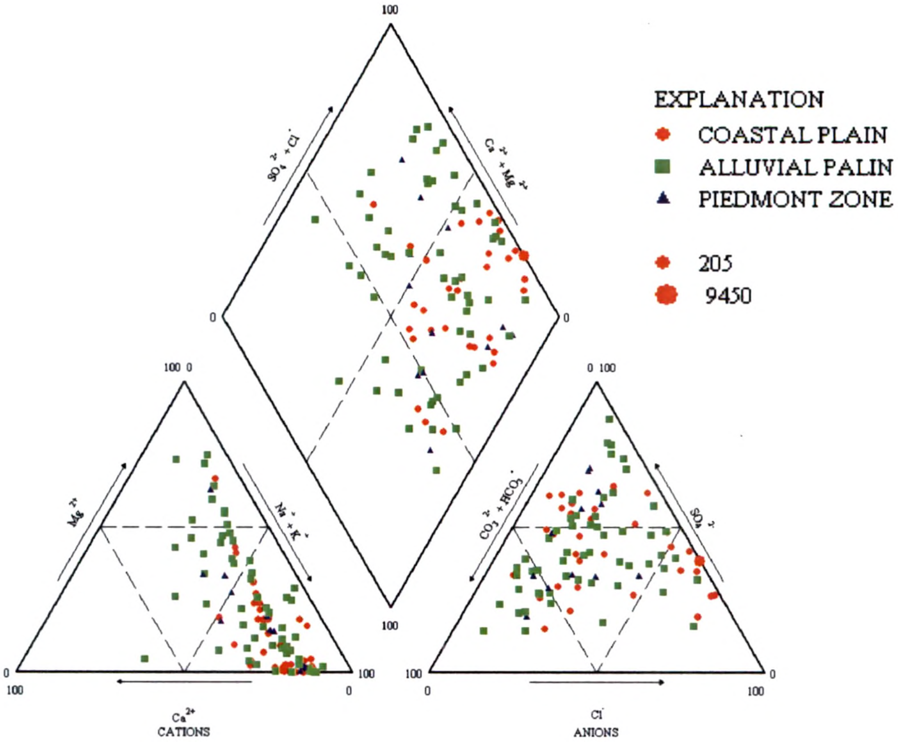


Fig-4.66 Piper Trilinear Plots of Groundwater Samples in Study Area (Pre-monsoon 2003)

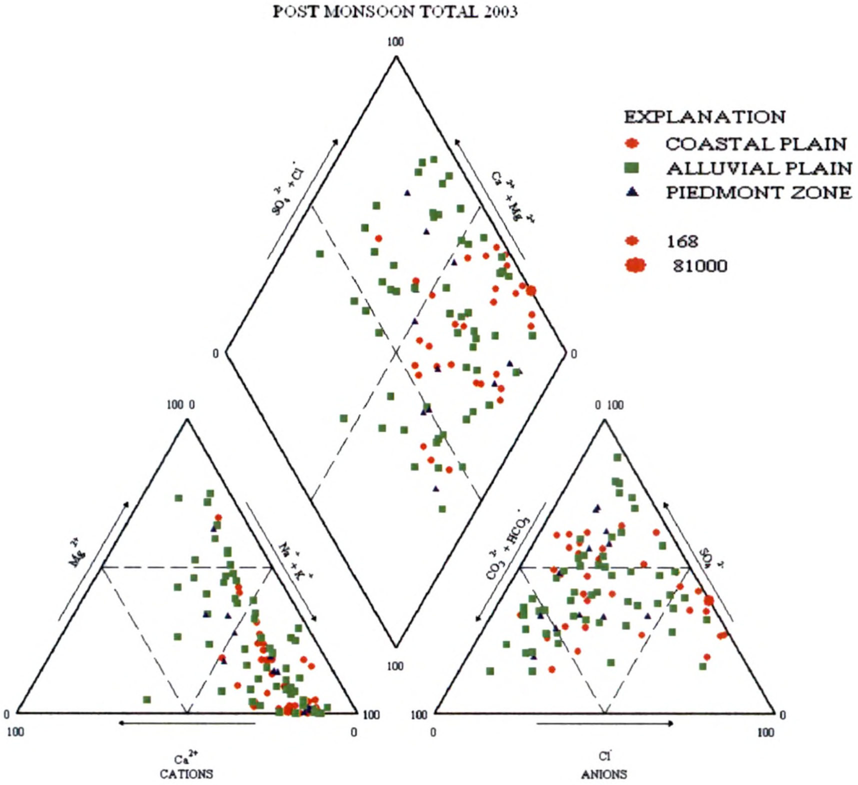


Fig-4.67 Piper Trilinear Plot of Groundwater Samples in Study Area (Post-monsoon 2003)

Table-4.19 Genetic Classification of Groundwater Samples based of Piper Trilinear Diagram

Field No.	Description based on piper fields	Total No. of Samples			
		Pre-monsoon 2002	Post-monsoon 2002	Pre-monsoon 2003	Post-monsoon 2003
I	Alkaline earth exceeds alkalies	12	35	28	27
II	Alkalies exceed alkaline earth	40	110	73	74
III	Weak acid exceed strong acids	1	61	13	21
IV	Strong acids exceed weak acids	51	84	88	80
V	Carbonate hardness exceeds 50%	--	27	2	5
VI	Non-carbonate hardness exceeds 50%	6	8	5	7
VII	Non-carbonate alkali exceeds 50%	39	75	60	55
VIII	Carbonate alkali exceeds 50%	--	1	1	1
IX	No one cation anion pair exceeds 50%.	7	34	33	32

4.7.3 Trace Element Analysis for Assessment of Toxicity

In the study area there are no available data regarding groundwater trace elements. Thus the aim of this study was to determine the background level of trace element in the groundwater with a view to evaluate its toxicity to human health.

Groundwater samples were collected from both shallow and deeper aquifers. The groundwater samples were collected in 100 ml polyethylene bottles which were rinsed several times with water to be sampled prior to filling the bottles with the samples. The samples were then preserved with 0.5 ml concentrated NHO_3 to bring down the pH to ~2. During pre-monsoon 2003 in all 18 trace elements were analyzed. The detail on obtained trace element concentration is given in Annexure-5.6 and summary in Table No. 4.20 .

Table 4.20 Dissolved Concentration of Trace Element in the Study Area

Sr No	Element	*Limit for drinking water (mg/l)	Mean (ppb)	Min. (ppb)	Max. (ppb)	SD
1	Aluminum (Al)	0.03-0.2	47.21	5.5	596.9	79.2
2	Arsenic (As)	0.01	4.22	0.9	16.72	3.29
3	Barium (Ba)	1	19.7	0.3	302.26	43.759
4	Beryllium (Be)	--	0.10	0.0	0.60	0.11
5	Cadmium (Cd)	0.01	0.11	0	1	0.15
6	Cobalt (Co)	--	0.11	0	0.5	0.08
7	Chromium (Cr)	0.05	10.43	4.6	41	7.6
8	Copper (Cu)	0.05-1.5	6.9	1.1	18.82	3.8
9	Iron (Fe)	--	556.37	306.9	1724.8	313.8
10	Manganese (Mn)	0.1-0.3	10.7	4	41.4	8.1
11	Molybdenum (Mo)	--	5.03	0.1	105.68	13.02
12	Nickel (Ni)	--	3.07	0.1	14.2	2.72
13	Lead (Pb)	0.05	18.17	0.4	68.54	17.34
14	Antimony (Sb)	--	0.3	0	4.76	0.59
15	Strontium (Sr)	--	301.89	11.4	5743.48	730.27
16	Uranium (U)	--	1.5	0	24.58	3.42
17	Vanadium (V)	--	25.94	2.6	91.62	19.15
18	Zinc (Zn)	5	20.4	2.4	62.4	14.88

*BIS 10500

Similarly, for post-monsoon 2003 groundwater samples were analyzed mainly for four elements viz. boron, silica, strontium and manganese. The range of minimum and maximum concentrations of B is 0.18-2.32 mg/l; Si 2.37-15.27 mg/l; Sr 0.039-14.79 mg/l and Mn 0.012-2.9 mg/l. Boron shows a negative correlation with Si while +ve with Sr and Mn. Strontium and manganese are +ve corelatable with other trace elements.

From the concentration levels of trace elements in groundwater it is clear that their concentration is within the permissible limit of drinking except for iron and strontium.

4.8 Application of Correlation Analysis for Evaluation of Hydro-Geochemical Parameters

Multivariate analysis is used to evaluate the relative importance of chemical variables in groundwater especially when large geochemical database is available. Moreover, correlation also provides information about the specific hydro-geological processes responsible for presence of certain ions in relation to others. The analysis provides insight into various factors which can explain a large amount of variance in the analytical data (Raju, 2006)

In order to explain the degree of correlatablity between different variables following categories have been used frequently in the text.

Sr. No.	Correlation Coefficient	Category
1	±0.00 to ±0.33	Slightly
2	±0.33 to ±0.66	Moderately
3	±0.66 to ±0.99	Significantly

Pre and Post Monsoon 2002

The mean dominant cations in the pre and monsoon 2002 groundwater samples are in the order of $Na^+ > Mg^{++} > Ca^{++} > K^+$, while anions shows $SO_4^{2-} > Cl^- > HCO_3^-$ dominance respectively. The correlation coefficient between the parameters has indicated various chemical variables in the groundwater samples. pH except alkalinity shows –ve correlation with most of the parameters. The correlation between the Ec and other parameters is significantly positive except K and $Ca^{2+} + Mg^{2+} / Na^+ + K^+$. TDS, Na, Ca is strongly co-relatable with most of the variables except alkalinity and $Ca^{2+} + Mg^{2+} / Na^+ + K^+$. Alkalinity is slightly negative correlatable with Mg, K, and total hardness, whereas significant with Ec and slightly correlatable with other parameters. Chloride is significant with Ec, TDS, Na and Ca while slightly negative with pH, alkalinity and ratio of $Ca^{2+} + Mg^{2+}$ & $Ca^{2+} + Mg^{2+} / Na^+ + K^+$. Sulfate is significant with Ec, TDS, Na, Ca and $Na^+ + K^+$ while negative with pH, and $Ca^{2+} + Mg^{2+} / Na^+ + K^+$ ratio. Ratio of $Ca^{2+} + Mg^{2+} / Na^+ + K^+$ shows negative correlation with most of the parameters except Mg and $Ca^{2+} + Mg^{2+}$.

Pre and Post-Monsoon 2003

The degree of linear association by adopting correlation coefficient method between any two geochemical variables in groundwater is given by correlation matrix for both pre and post-monsoon period of 2002-2003.

The pre and post-monsoon 2003 samples indicate that pH shows –ve correlation with other variables except HCO_3. Similarly Ec and TDS and total hardness are +ve corelatable except with HCO_3. Na is strongly corelatable with Ca, Cl, SO_4 and K while it is moderately corelatable with HCO_3. K shows –ve correlation with bicarbonate and +ve with all other ions. Ca has –ve relation with Si and HCO_3 while shows +ve correlation with others.

Statistical analysis of the major ionic contents with trace element has divulged Na showing +ve correlation with all ions except silica and bicarbonates. Bicarbonate has –ve correlation with all ions except boron. Boron has –ve correlation with Si and Mg while +ve correlation with all other ions. Silica has +ve correlation with NO_3, K and Mg while –ve with all other ions. F shows –ve correlation with Mg, Si and NO_3 and +ve with other ions. Nitrate is –ve with F, Mg, Mn and HCO_3 while +ve with other ions. Sulphate shows –ve correlation with Si and HCO_3 while +ve with others. Chloride is –ve with Si and HCO_3 and +ve with all other ions.

The mean dominant cations in the pre-monsoon 2003 groundwater samples are in the order of $Na^+ > Mg^{++} > Ca^{++} > K^+$, while anions shows $SO_4^{2-} > Cl^- > HCO_3^-$ dominance. Similarly in post-monsoon 2003 samples are in the order of $Na^+ > Ca^{++} > Mg^{++} > K^+$, while anions shows $SO_4^{2-} > Cl^- > HCO_3^-$ dominance respectively

Correlation matrix has also been used to study the possible relationship between the fluoride concentration and other physic-chemical parameters. TDS, EC, Nitrate, Total Hardness, Chloride and Sulfate showed good correlation with fluoride concentration in a decreasing order. Fluoride shows +ve correlation with Na and alkalinity wherein it is strong correlation with alkalinity. However, it shows –ve correlation with Ca, Mg, K and total hardness wherein with Ca and Mg negative correlation is expected due to low solubility of these ions (Hem, 1971 & Das, 2003). Pre and post monsoon correlation of fluoride with different ions is shown in Fig-4.68 and 4.69.

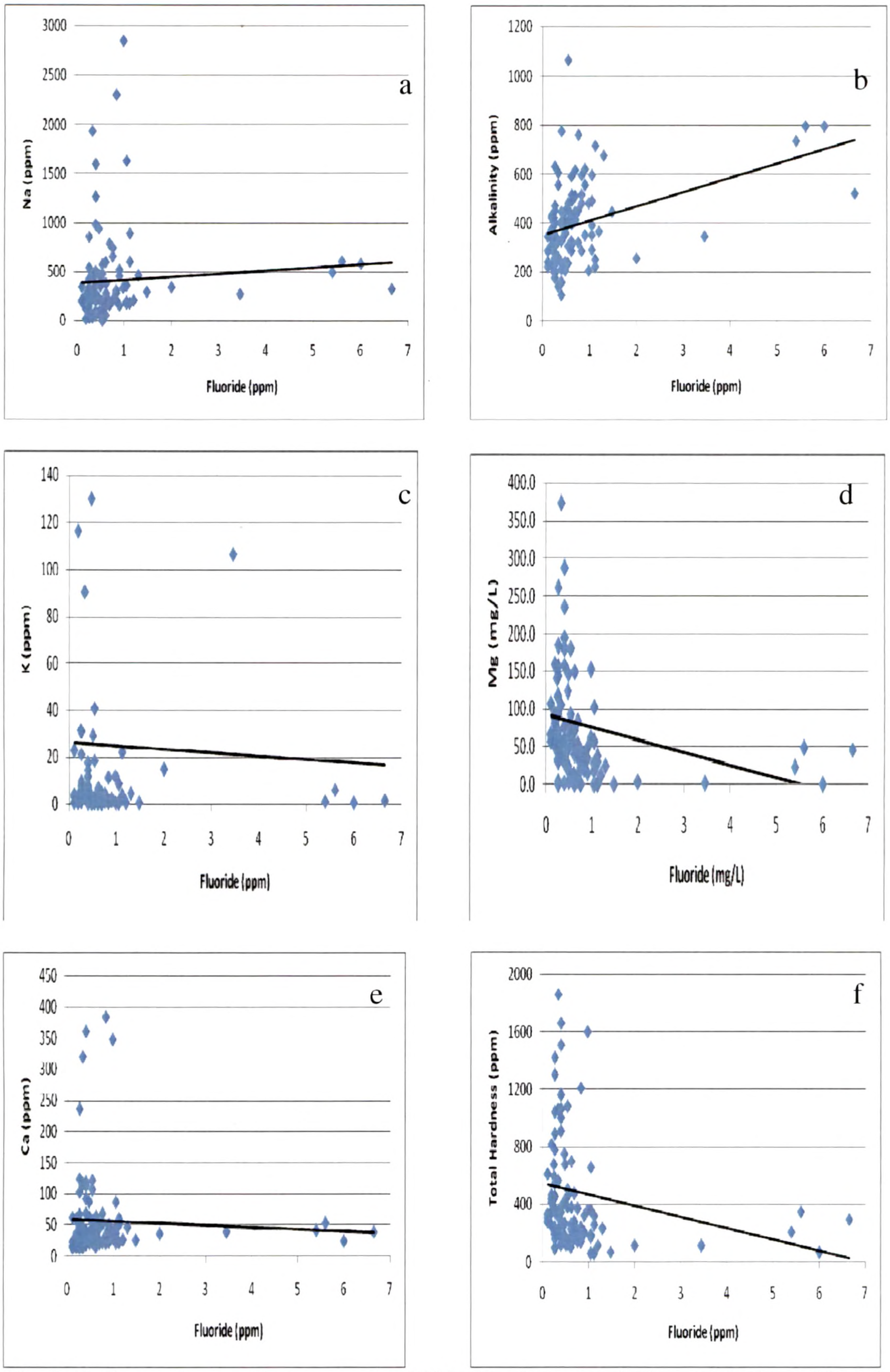


Fig-4.68 Groundwater Pre-monsoon 2003 showing correlation variation of fluoride with different ions (a) Na^+ vs F^-, (b) Total Alkalinity vs F^-, (c) K^+ Vs F^-, (d) Mg^{++} Vs F^-, (e) Ca^{++} vs F^- and (f) Hardness vs F^-. The solid lines indicate trends.

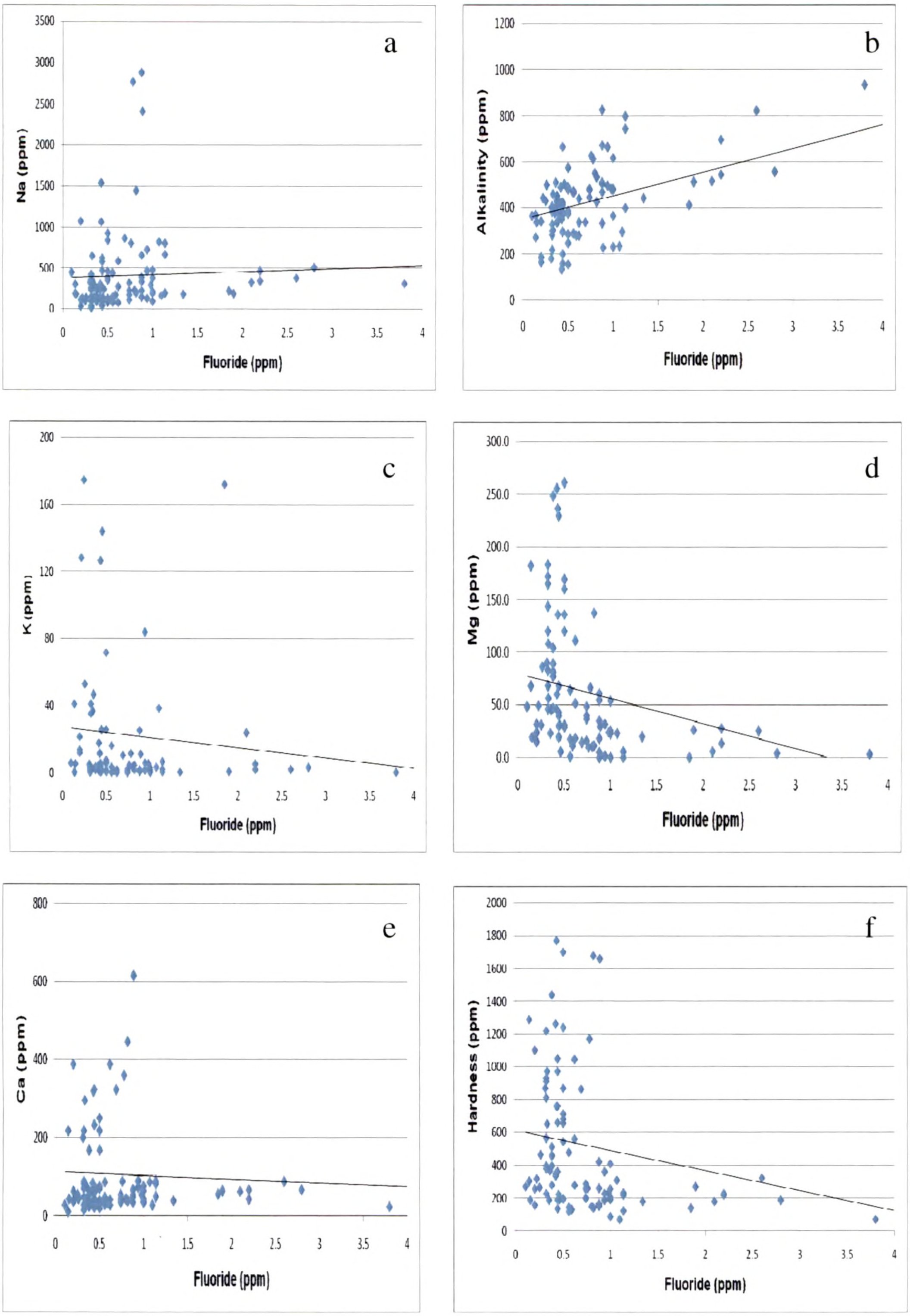


Fig-4.69Groundwater Post-monsoon 2003 showing Variation Correlation of fluoride with different ions (a) Na^+ vs F^-, (b) Total Alkalinity vs F^-, (c) K^+ Vs F^-, (d) Mg^{++} Vs F^-,(e) Ca^{++} vs F^- and (f) Hardness vs F^-. The solid lines indicate trends.

Table -4.21 Correlation Matrix for Water Quality Parameters (Pre-monsoon 2002) (N=52)

Variables	pH	EC	TDS	Na	Ca	Mg	K	TH	Alkalinity	Chloride	Sulphate	$Na^+ + K^+$	$Ca^{++} + Mg^{++}$	$Ca^{2+} + Mg^{2+} / Na^+ + K^+$
pH	1	-0.34	-0.31	-0.17	-0.35	-0.52	-0.16	-0.52	0.15	-0.17	-0.26	-0.18	-0.51	-0.44
EC		1	0.97	0.84	0.89	0.56	0.41	0.76	0.77	0.77	0.74	0.85	0.82	-0.10
TDS			1	0.89	0.89	0.50	0.35	0.72	0.14	0.83	0.78	0.90	0.78	-0.11
Na				1	0.79	0.24	0.20	0.49	0.34	0.79	0.73	0.999	0.57	-0.39
Ca					1	0.51	0.32	0.76	0.07	0.73	0.65	0.80	0.84	-0.05
Mg						1	0.22	0.94	-0.10	0.28	0.44	0.25	0.89	0.48
K							1	0.29	-0.06	0.23	0.22	0.24	0.31	-0.09
TH								1	-0.05	0.49	0.58	0.49	0.99	0.34
Alkalinity									1	-0.02	0.07	0.33	-0.03	-0.32
Chloride										1	0.57	0.79	0.56	-0.16
Sulphate											1	0.74	0.62	-0.08
$Na^+ + K^+$												1	0.58	-0.39
$Ca^{++} + Mg^{++}$													1	0.27
$Ca^{2+} + Mg^{2+} / Na^+ + K^+$														1

Table -4.22 Correlation matrix for water quality parameters (Post-monsoon 2002) (N=145)

Variables	**pH**	**EC**	**TDS**	**Na**	**Ca**	**Mg**	**K**	**TH**	**Alkalinity**	**Chloride**	**Sulphate**	**$Na^+ + K^+$**	**$Ca^{++} + Mg^{++}$**	**$Ca^{2+} + Mg^{2+} / Na^+ + K^+$**
pH	1	-0.02	-0.09	-0.07	-0.07	-0.29	-0.06	-0.23	-0.002	-0.08	-0.08	0.03	-0.25	-0.25
EC		1	0.98	0.95	0.92	0.63	0.21	0.82	0.18	0.63	0.02	0.18	0.06	0.18
TDS			1	0.93	0.95	0.69	0.17	0.87	0.16	0.95	0.66	0.94	0.91	-0.25
Na				1	0.89	0.45	0.06	0.68	0.19	0.92	0.66	0.983	0.75	-0.35
Ca					1	0.60	0.09	0.83	0.09	0.89	0.59	0.88	0.89	-0.21
Mg						1	0.21	0.94	-0.02	0.62	0.35	0.48	0.90	0.07
K							1	0.18	0.22	0.12	0.24	0.24	0.17	-0.11
TH								1	0.02	0.80	0.48	0.70	0.99	0.99
HCO3									1	0.80	0.20	0.23	0.04	-0.35
Chloride										1	0.64	0.91	0.84	-0.23
Sulphate											1	0.69	0.52	-0.25
$Na^+ + K^+$												1	0.76	-0.36
$Ca^{++} + Mg^{++}$													1	-0.08
$Ca^{2+} + Mg^{2+} / Na^+ + K^+$														1

Table-4.23 Correlation Matrix for Water Quality Parameters (Pre-monsoon 2003) (N=101)

Variables	pH	EC	TDS	Na	Ca	Mg	K	Alkalinity	TH	SO4	Cl	NO3	F	Na^+ + K^+	Ca^{++} + Mg^{++}	Ca^{++} + Mg^{++}/ Na^+ + K^+
pH	1.00	-0.29	-0.29	-0.12	-0.24	-0.46	-0.08	-0.23	-0.48	-0.21	-0.27	-0.30	0.19	-0.13	-0.46	-0.27
EC		1.00	0.99	0.93	0.93	0.38	0.12	0.18	0.69	0.77	0.95	0.52	-0.02	0.93	0.77	-0.11
TDS			1.00	0.89	0.93	0.44	0.10	0.19	0.74	0.77	0.92	0.53	-0.03	0.89	0.81	-0.06
Na				1.00	0.89	0.08	0.00	0.12	0.42	0.72	0.88	0.37	0.08	0.98	0.52	-0.31
Ca					1.00	0.23	0.05	0.06	0.59	0.71	0.91	0.49	-0.05	0.88	0.69	-0.13
Mg						1.00	0.08	0.19	0.92	0.19	0.39	0.40	-0.18	0.09	0.86	0.49
K							1.00	0.25	0.09	0.18	0.04	0.08	-0.01	0.22	0.09	-0.11
Alkalinity								1.00	0.18	0.25	-0.02	0.41	0.40	0.17	0.17	-0.13
TH									1.00	0.44	0.69	0.53	-0.17	0.43	0.99	0.36
SO4										1.00	0.69	0.40	0.00	0.74	0.51	-0.08
Cl											1.00	0.47	-0.08	0.87	0.77	-0.08
NO3												1.00	-0.01	0.38	0.56	0.13
F													1.00	0.07	-0.16	-0.26
Na^+ + K^+														1	0.53	-0.33
Ca^{++} + Mg^{++}															1	0.30
Ca^{++} + Mg^{++}/ Na^+ + K^+																1

Table-4. 24 Correlation Matrix for Trace Element with Other Ions in the Groundwater (Post-monsoon 2003) (N=101)

Variables	Na	Ca	Mg	K	B	Si	Sr	Mn	Cl	So_4	Alkalinity	$N0_4$	F
Na	1	0.991	0.175	0.621	0.548	-0.100	0.811	0.977	0.994	0.961	-0.014	0.085	0.201
Ca		1	0.166	0.627	0.555	-0.085	0.844	0.974	0.990	0.964	-0.031	0.148	0.174
Mg			1	0.102	-0.025	0.378	0.267	0.401	0.200	0.164	-0.121	-0.098	-0.188
K				1	0.293	0.003	0.495	0.956	0.630	0.621	-0.015	0.047	0.088
B					1	-0.104	0.541	0.548	0.525	0.599	0.195	0.144	0.317
Si						1	-0.080	-0.095	-0.096	-0.099	-0.127	0.055	-0.282
Sr							1	0.785	0.805	0.779	-0.054	0.328	0.104
Mn								1	0.983	0.979	-0.077	-0.078	0.181
Cl									1	0.952	-0.035	0.055	0.205
SO_4										1	-0.026	0.084	0.171
Alkalinity											1	-0.018	0.834
NO_4												1	-0.018
F													1