ISOTOPIC AND WATER QUALITY CHARACTERIZATION OF RIVER GANGA

A DISSERTATION

Submitted in partial fulfillment of the
requirements for the award of the degree
of

MASTER OF TECHNOLOGY

in

HYDROLOGY

By

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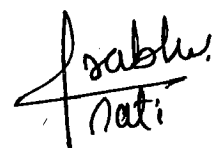ROORKEE - 247 667 (INDIA)
JUNE, 2006

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the dissertation entitled **"ISOTOPIC AND WATER QUALITY CHARACTERIZATION OF RIVER GANGA"**, in partial fulfillment of the requirement for the award of the degree of **Master of Technology** in **Hydrology** submitted in the **Department of Hydrology, IIT-Roorkee**, is an authentic record of my own work carried out for a period of about 11 months from August 2005 to June 2006 under the supervision of **Dr. Himanshu Joshi**, Associate Professor, Department of Hydrology, Indian Institute of Technology Roorkee, Roorkee, India and **Dr. Bhishm Kumar**, Scientist 'F' & Head, H.I. Division, National Institute of Hydrology, Roorkee.

The matter embodied in this dissertation has not been submitted by me for the award of any other degree or diploma.
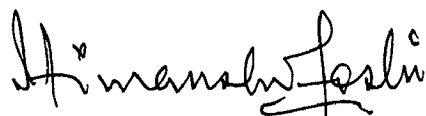
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This is to certify that the above statement made by the candidate is true to the best of my knowledge.

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ABSTRACT

Stable isotopes and geochemical studies have been applied in the investigation of surface water resources in Ganga river of Uttaranchal State in Northern India. A combination of the chemical and isotope data are investigated along the river Ganga and its tributaries. Of all the methods used to understand hydrologic processes in small catchments, applications of tracers in particular stable isotope tracers have been the most useful in terms of providing new insights into hydrologic processes and providing information related to the contribution of different components of snowmelt runoff, ground water and precipitation data. Seasonal and temporal variability of these parameters reveals many complex phenomena taking place in the catchment. This is because they integrate small-scale variability to give an effective indication of catchment-scale processes. In particular, ^{18}O, ^{2}H, are integral parts of natural water molecules that fall as rain or snow (meteoric water) each year over a watershed and, consequently, are ideal tracers of water. Water quality parameters along with isotopes are investigated in order to know geochemical features of the catchment and to find suitable correlation between water quality and isotopic parameters.

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CHAPTER ONE

INTRODUCTION

1.1 General Status and Rationale

Ganga River, located in Uttaranchal state of India (figure 1.1), plays a vital role in the hydrology and ecology of the country because it drains runoff from the Himalaya Mountains and downstream urban areas. India is located in the tropical belt under the influence of Asian Monsoon and receives intense seasonal precipitation in the form of rain in the plains and snow in the upper Himalayan region. Ganga River basin constitutes major captures of the regional precipitation in both the forms snow and rainfall; and flow through this major river transfers this water collection to the Bay of Bengal, completing an important sector in the global hydrological cycle. The rivers and tributaries of Ganga basin supply a major part of the required water for agriculture and household needs. However, increase in population, rapid urbanization and industrialization have caused surface water and ground water quality to deteriorate (Pandey and Hasnain et. al.). Therefore, it is important to characterize the anthropogenic influences along with the resulting change in water quality and quantity. In this context, a study has been carried out aiming at isotopic and Water quality characterization Ganga River from Gangotri upto Haridwar.

1.2 Objectives of Study

This research study has been envisaged with the following objectives:
- Study of the variations in isotopic composition and isotopic characterization of river water
- Study of the temporal and spatial variations in water quality.
- Study of characterization river water quality and explore association between isotopic and water quality parameters.

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1.3 Study Area

The study area (Figure 1) covers Ganga River from near its origin in the Himalayan Mountains until Haridwar. The main stream of the Ganga is formed at Devprayag after the confluence of Bhagirathi River, one of the largest and most important tributary and Alakananda River. Both the rivers originate in the Higher Himalayas (Alaknanda originating from Satopanth and Bhagirathi from Kharak glacier) and form the mountainous catchment of the river Ganga, flowing through the deep gorges of the Garhwal Himalayas. The total length of the river is about 2,510 km (1,557 mi). It forms a large and fertile basin stretching across north India and Bangladesh, and supports one of the highest densities of human population in the world.

The river Ganga (Called Bhagirathhi at Present Place) originates at an elevation of 3812 m from the Gangotri glacier (30 km long and 20 km wide) at Gomukh on the western slope of Chaukhamba in Uttarkashi district. The Ganga traverses around 225 km across the Himalayas before its confluence with the Alaknanda at Devprayag, to form the river Ganga (Figure 1). The study area is from Gangotri until Haridwar. Geographically the catchment is bounded by 30° 59' 40.4" to 29° 51' 25.9" N latitude and 78° 56' 29.9to 78° 10' 33.3" E longitude.

The upper part of Bhagirathhi river basin lying between Gomukh (3812 m) to Harsil (2620 m) has a very steep gradient of 1192 m in a zone of 42 km. This zone is located in a narrow glaciated valley and dominated by rapid waterfall and cascade. The lower part of the Ganga basin extends from Harsil (2620 m) to Devprayag (618 m) with a moderate difference of gradient of 2002 m in a zone of 183 km. This zone is characterized by rapids, cascade and lower gradient relief at many places. The Bhagirathi possesses depositional terraces with Quartnary sediments between Harsil and Gangnani around Uttarkashi and again at Dunda.

Figure 1.1: Ganga River Catchment
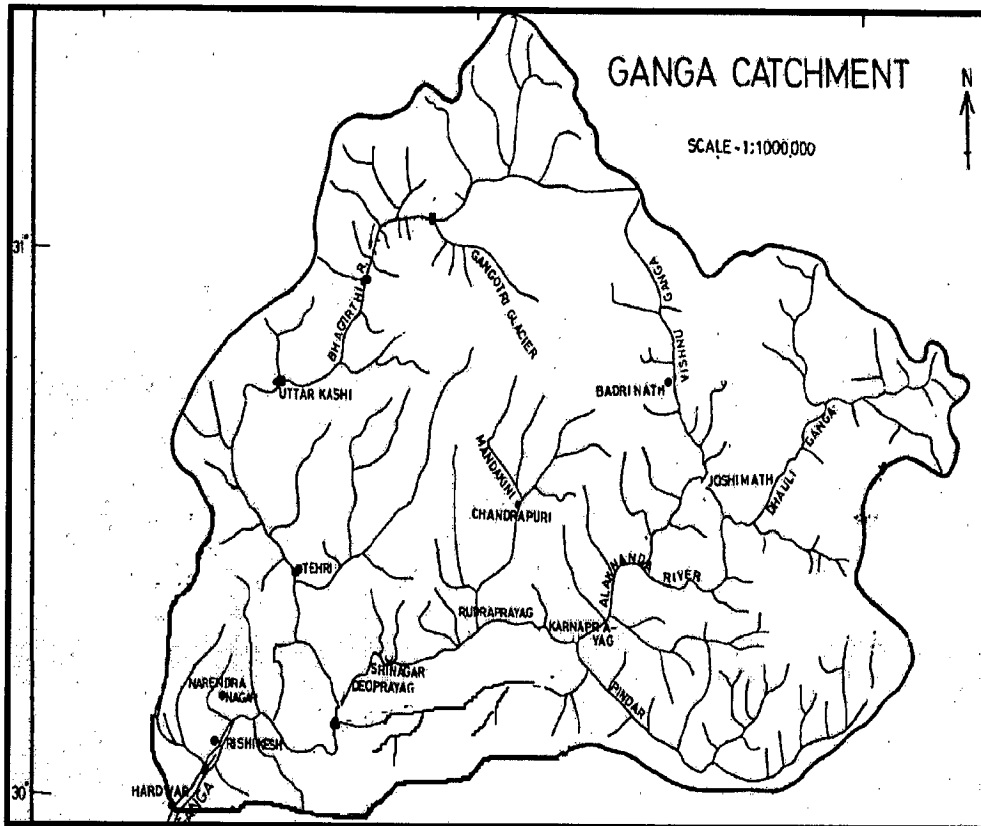
The river Bhagirathi and its tributaries drain largely through the rocks of lesser and Central crystalline (Figure 1.2). The Main Crystalline Thrust (MCT) passes through and beyond Bhatwari, about 20 km downstream, where it has almost an east-west course and separates granite gneisses and garnetiferous schists of the Central Crystalline and cream colored quartzites. The upper catchment of the Bhagirathi is mainly composed of rocks of Central Crystalline rocks primarily consisting of schists, micaceous quartzites, calc-silicates, amphibolites, gneisses, granites, slates and phyllites. The occurrence of several sulphide minerals like pyrite, chalcopyrite and arsenopyrites at the contact of quartz veinlets which traverses the country rocks are reported near the source area (Bhatt, 1963). In the middle and lower reaches, the Bhagirathi flows through limestone and dolomite bearing Uttarkashi Formation and before confluence with Alaknanda, it passes through phyllites and micaceous graywack bearing Chandpur Formation (Chakrapani and Veizer et. al.).

Figure 1.2: Geological Map of Study Area
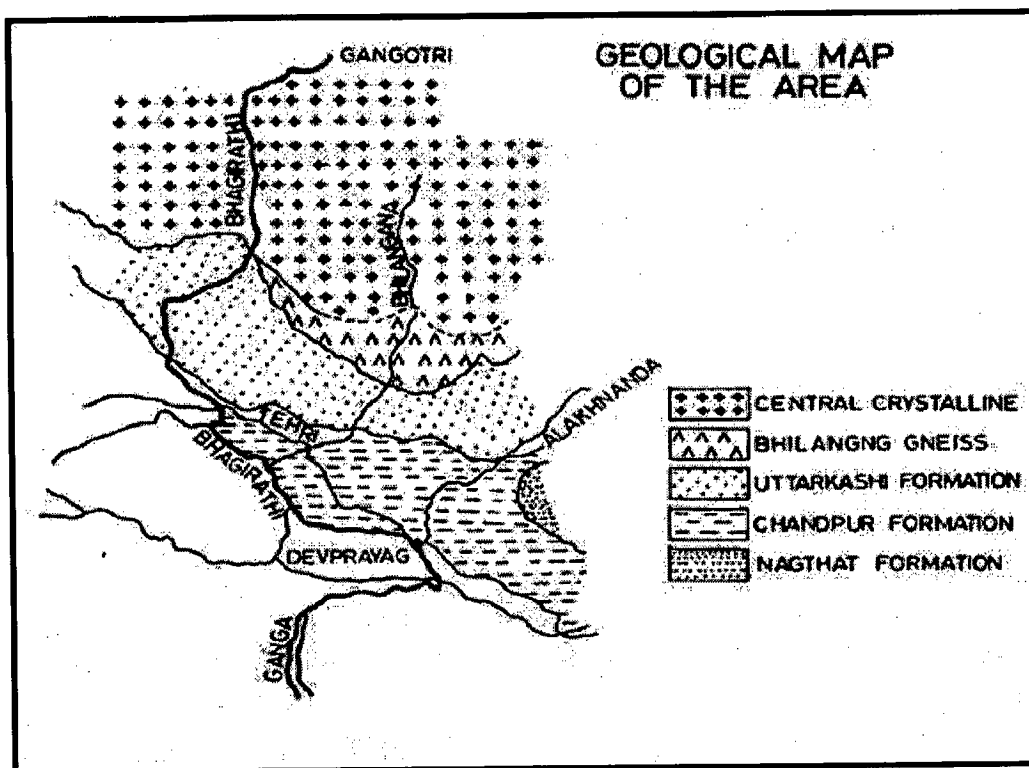
The Ganga River and its tributaries are dependent predominantly on glacier and snow melt and precipitation. The average rainfall for the Garhwal Himalayas varies between 1000 to 2500 mm of which 50—80% falls during the monsoon period between June and September. The Ganga river basin experiences strong climatic seasonal variations, which is also clearly reflected in the monthly variation in stream flows. Maximum flow takes place during June-September, when both rainfall and rate of snow melt are at maximum. Most of the Garhwal Himalayan streams carry 69—83% of their annual flow during the summer monsoonal months. At Haridwar, the total runoff is of the order of 21,400 million m³/year of which 75% flows during monsoon period (June to September) and 25% of runoff is distributed during the remaining part of the year. The average discharge of the river at Haridwar is over 1500 m³/sec during the monsoon period, which decreases to 200 m³/ sec in winter (Dasgupta, 1984).

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1.4 Thesis Organization

The organization of this thesis is as follows:

Chapter two presents the information about the available literature on the different aspects of the study, which has been used to understand various principles and theoretical background of different techniques employed in this work.

Chapter Three describes the analytical and field procedures and different methods used in this study.

Chapter Four aims on discussion on results obtained from various isotopic and water quality investigations

Chapter five discusses conclusions of the results of the study the area and finally ends up with summarizing the outcome of the present work along with scope of future studies.

CHAPTER TWO

BACKGROUND AND LITERATURE REVIEW

2.1   Isotopic Characterization

2.1.1 Introduction to Isotopes

Isotopes (from the Greek *iso-,* equal, and *topos,* place; in reference to isotopes of an element having the same position in the periodical table of elements) are forms of a given chemical element that have different atomic masses. The nuclei of isotopes of an element contain identical numbers of protons, and so the isotopes have the same atomic number. Each isotope has a different number of neurons and thus has a different atomic mass.

2.1.2 Types of Isotopes

- **Radioactive Isotopes**

Radioactive isotopes are nuclides (isotope-specific atoms) that have unstable nuclei that decay, emitting alpha, beta, and sometimes gamma rays. Such isotopes eventually reach stability in the form of non-radioactive isotopes of other chemical elements, their "radiogenic daughters." Decay of a radionuclide to a stable radiogenic daughter is a function of time measured in units of half-lives.

- **Stable Isotopes**

Stable isotopes are those isotopes that do not undergo radioactive decay; thus, their nuclei are stable and their masses remain the same. However, they may themselves be the product of the decay of radioactive isotopes. The isotopic composition of stable isotopes is, however, subject to natural variation due to mass dependent fractionation. That is to say, mass differences between isotopes result in isotopic fractionation during

chemical processes. In hydrological studies, the stable isotopes of interest are generally H, C, N, O, S, B, and Li.

- **Environmental Isotopes**

Payne (1983) defined environmental isotopes as "those isotopes, both stable and radioactive, which occur in the environment in varying concentrations with respect to place and time, over which the investigator has no direct control". The most commonly used environmental stable isotopes are Deuterium (D), Oxygen -18 (^{18}O), Carbon-13 (^{13}C), Nitrogen-15 (^{15}N), Sulpher-34 and radioisotopes tritium (^{3}H), carbon-14 (^{14}C), Chlorine-36, Caesium-137 (^{137}Cs) and Lead-210 (^{210}Pb). People now days using Environmental isotopes very prominently as they are having much advantage over artificial isotopes and however much sophisticated instruments are also available.

- **Water Isotope Hydrology**

It includes those isotopes which from water molecules: the oxygen isotopes (O-16, O-17 and O-18) and the hydrogen isotopes (protium, deuterium and tritium). These are ideal tracers of water sources and movement because they are constituents of water molecules, not something that is dissolved in the water like other tracers that are commonly used in hydrology (e.g. dissolved species such as chloride).

In most low-temperature environments, stable hydrogen and oxygen isotopes behave conservatively in the sense that as they move through a catchment, any interactions with oxygen and hydrogen in the organic and geologic materials in the catchment will have a negligible effect on the ratios of isotopes in the water molecules.

2.1.3 Representation of Stable isotopes

Stable isotope compositions of low-mass (light) elements such as oxygen, hydrogen, carbon, nitrogen, and sulfur are normally reported as δ values. The term "δ " is spelled and pronounced **delta** not **Del**. The word 'Del' describes either of two mathematical terms: an operator (δ) or a partial derivative (δ). δ values are reported in units of parts per thousand

(denoted as ‰ or permil, or per mil, or per mille -- or even recently, per mill) relative to a standard of known composition.

δ Values are calculated by:

$$\delta \text{ (in ‰)} = (R_x / R_s - 1) \cdot 1000$$

Where R denotes the ratio of the heavy to light isotope (e.g., $^{34}S/^{32}S$), and R_x and R_s are the ratios in the sample and standard, respectively. For sulfur, carbon, nitrogen, and oxygen, the average terrestrial abundance ratio of the heavy to the light isotope ranges from 1:22 (sulfur) to 1:500 (oxygen); the ratio ^2H:^1H is much lower at 1:6410. A positive δ value means that the isotopic ratio of the sample is higher than that of the standard; a negative δ value means that the isotopic ratio of the sample is lower than that of the standard. For example, a $\delta^{15}N$ value of +30‰ means that the $^{15}N/^{14}N$ of the sample is 30 parts-per-thousand or 3% higher than the $^{15}N/^{14}N$ of the standard.

Various isotope standards are used for reporting isotopic compositions; the compositions of each of the standards have been defined as 0‰. Stable oxygen and hydrogen isotopic ratios are normally reported relative to the SMOW standard ("Standard Mean Ocean Water" (Craig, 1961b)) or the virtually equivalent VSMOW (Vienna-SMOW) standard. Commonly used isotope and their abundance ratios with reference standards are shown in Table 2.1.

Table 2.1 Abundance ratios and reference standards for some isotopes.

Isotope	Ratio measured	Reference Standard	Abundance ratio of standard
^2H	$^2H/^1H$	VSMOW	$1.5575 \cdot 10^{-4}$
^3He	$^3He/^4He$	atmospheric He	$1.3 \cdot 10^{-6}$
^6Li	$^6Li/^7Li$	L-SVEC	$8.32 \cdot 10^{-2}$
^{11}B	$^{11}B/^{10}B$	NBS 951	4.04362
^{13}C	$^{13}C/^{12}C$	VPDB	$1.1237 \cdot 10^{-2}$
^{15}N	$^{15}N/^{14}N$	atmospheric N_2	$3.677 \cdot 10^{-3}$
^{18}O	$^{18}O/^{16}O$	VSMOW, or VPDB	$2.0052 \cdot 10^{-3}$ $2.0672 \cdot 10^{-3}$

2.1.4 Processes:

The main processes that dictate the oxygen and hydrogen isotopic compositions of water in a catchment are:

a)   Phase changes that affect the water near the ground surface (evaporation, condensation melting) and

b)   Simple mixing at or below the ground surface.

2.1.5 Isotopic fractionation

During isotopic fractionation, heavy and light isotopes partition differently between two compounds or phases. Isotope fractionation occurs because the bond energy of each isotope is slightly different, with heavier isotopes having stronger bonds and slower reaction rates. The differences in bonding energy and reaction rates are proportional to the mass difference between isotopes. Thus, light elements are more likely to exhibit isotopic fractionation than heavy isotopes. For example, the relatively light ^{12}C and ^{13}C isotopes have an 8% mass difference and undergo stable isotope fractionation. In contrast, the heavy isotopes ^{87}Sr and ^{86}Sr have a 1.1% mass difference and do not exhibit detectable mass fractionation. Isotopes especially susceptible to fractionation are of the elements that are among the most abundant on earth: H, C, N, O, and S.

- **Equilibrium fractionation**

Equilibrium fractionation describes isotopic exchange reactions that occur between two different phases of a compound at a rate that maintains equilibrium, as with the transformation of water vapor to liquid precipitation. Although the process is in equilibrium, the rate of these exchanges is different so that the result is an enrichment of one of the isotopes.

- **Kinetic fractionation**

Kinetic fractionation is fractionation that is unidirectional, where equilibrium is not attained. This type of fractionation applies to

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evaporation of surface waters and to most isogeochemical reactions, where the lighter isotope is faster reacting and becomes concentrated in the products.

• Precipitation and equilibrium fractionation

The δD and $\delta^{18}O$ values for precipitation worldwide behave predictably, falling along the global meteoric water line (GMWL) as defined by Craig (1961b), who expresses the relationship between ^{18}O and ^2H in meteoric waters as follows:

$$\delta^2H = 8\ \delta^{18}O + 10‰$$

This relationship for ^{18}O and ^2H isotopes is primarily a reflection of differences in their equilibrium fractionation factors. The slope of the GMWL expresses this ratio, which is eight times greater for oxygen than hydrogen. All surface water bodies undergo evaporation from their surfaces at humidities less than 100% (Gat, 1970). Evaporation is a non equilibrium fractionation process that causes the heavy isotopes of oxygen and hydrogen to be concentrated in the denser phase (residual liquid phase). Such water typically plot along an evaporation line diverges from LMWL (Craig and Gordon, 1965), making them distinguishable from precipitation and ground water. In moderate climates, evaporation of river water is not significant. Therefore, stable isotope values of river water often reflect the source waters. In environments where surface runoff is the dominant source of water to a river, the isotopic values of river water will resemble those of precipitation, displaying seasonal extremes. In environments where ground water baseflow into rivers is significant, the values of river water will have a less seasonally variable signature.

The GMWL indicates the source of water and processes going on. The standard GMWL is shown in figure 2.1, while the GMWL developed by Rozanski et al. (1992) is shown in figure 2.2.

Figure 2.1 Standard Global Meteoric Water Line
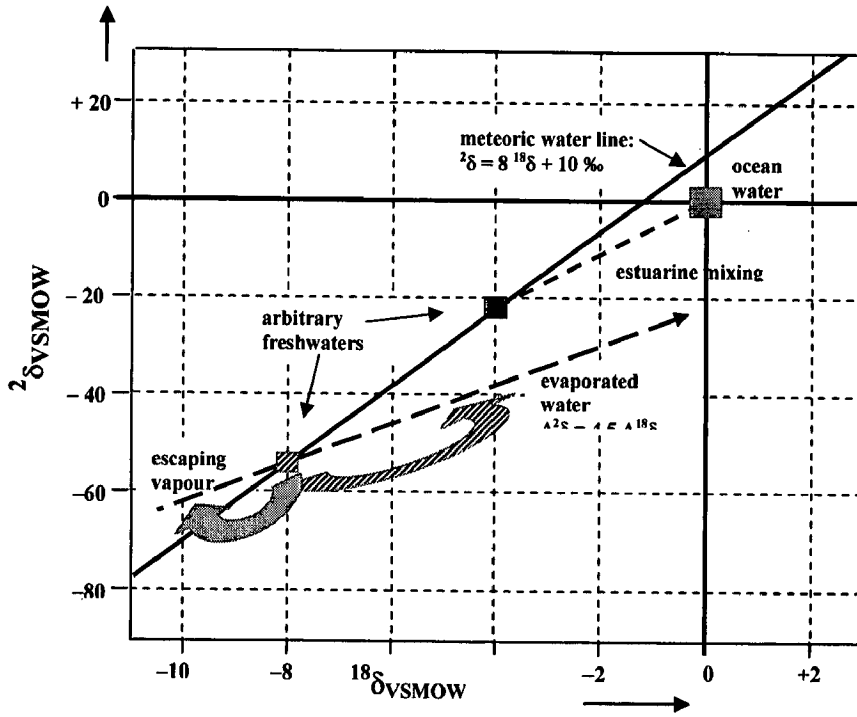
Although Local Meteoric Water Line (RMWL) and Regional Water Lines (RMWL) gives more insight about the hydrological and geological features of the study area and shows little deviations form GMWL.

Fig. 2.2 GMWL prepared by Rozanski et al. (1992).
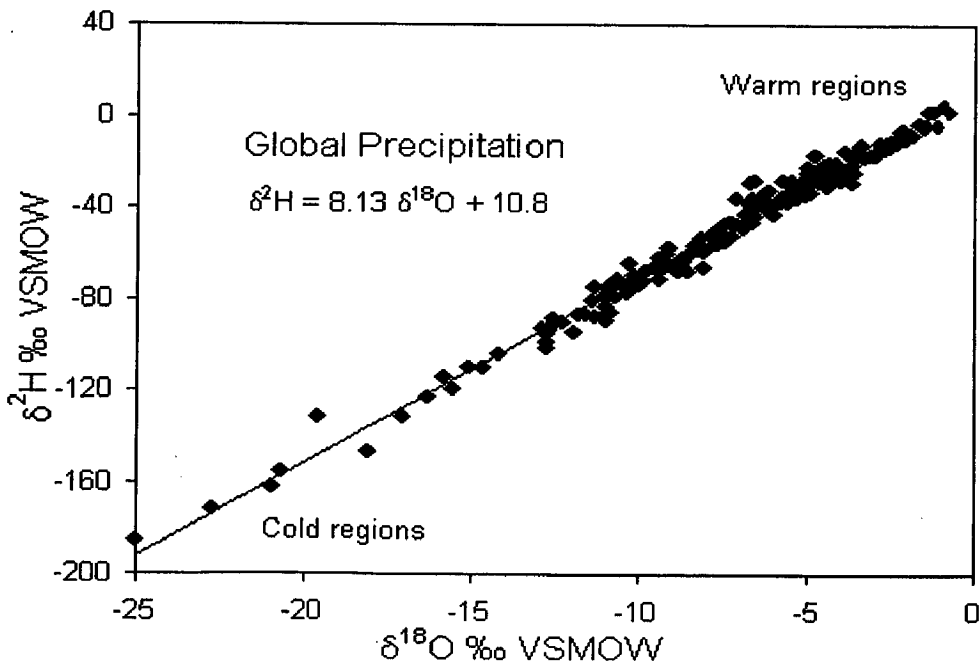
Local Meteoric Water Lines in arid environments will exhibit the same slope, but plot higher in relation to δ^2H because of increased evaporation. Likewise, LMWLs of humid environments maintain the slope of 8, but the line shifts toward increased $\delta^{18}O$ because the phase change tends toward liquid precipitation.

2.1.6 Isotopic Effects

- **Latitude Effect**

Latitude effect is a gradual decrease of heavy isotopic conc. when going from lower to higher latitudes. The latitude effect over the North American Continent is about -0.5% per degree or latitude for $\delta^{18}O$.

- **Continental Effect:**

Continental effect is a decrease in δD and $\delta^{18}O$ when going from coast to a continent inland. As a vapour mass moves from its source region across a continent its isotopic composition continuously depleted due to topographic effects and the temperature extremes.

- **Altitude Effect**

Altitude effect is a decrease in δD, $\delta^{18}O$ with increasing altitude. This effect is most useful in regimes having orographic precipitation. For ^{18}O, the depletion varies between about -0.15 and 0.5% per 100-m rise in altitude, with a corresponding decrease of about -1 to -4% for ^4H. (Ion Clark, Peter Fritz, 1997)

- **Seasonal Effects**

Seasonal variation of δD, $\delta^{18}O$ is related to seasonal variation in temperature. This effect is more prominent in places away from coastal stations, where greater seasonal extremes in temperature are observed. Winter precipitations are depleted in ^{18}O and D relative to the summer precipitations.

2.1.7   Isotopic characterization and its importance

Isotopic characterization of surface water gives generally a graphical and quantitative description of variations of isotopic parameters of the river water and describes distinctive characteristics that are obtained for these parameters at different locations and at different seasons.

The Ganga River is perennial in nature as it receives all the three types of water inputs i.e., snowmelt runoff, rainfall runoff and groundwater. However, the three components vary in space and time. Therefore, the understanding of different components of water input to the River Ganga may reveal its behavior at different locations that may be of great use to manage the groundwater as well as the river in a better way. Keeping this in view, a study of isotopic characterization of Ganga River has been initiated. It is important to characterize the surface water as it can provide information about new hydrologic connections.

2.2 Water Quality Characterization:

Water quality is determined by assessing three classes of attributes: biological, chemical, and physical. There are standards of water quality set for each of these three classes of attributes.

2.2.1. Physical

Temperature: Temperature impacts both the chemical and biological characteristics of surface water. It affects the dissolved oxygen level in the water, photosynthesis of aquatic plants, metabolic rates of aquatic organisms, and the sensitivity of these organisms to pollution.

Total Solids: Total solids are a measure of the suspended and dissolved solids in water. Suspended solids are those that can be retained on a water filter and are capable of settling out of the water column onto the stream bottom when stream velocities are low. They include silt, clay, plankton, organic wastes, and inorganic precipitates such as those from acid mine drainage. Dissolved solids are those that pass through a water filter.

2.2.2 Chemical

Conductivity: Conductivity is the ability of water to carry an electrical current. It indicates the physical presence of dissolved chemicals in the water.

pH: The most commonly measured chemical attribute of water is its acidity or pH. The pH scale ranges from 1 to 14, with 1 being the most acidic and 14 being the most basic.

Dissolved Oxygen: Oxygen is essential for the survival of nearly every living thing even those living in water. The two main sources of dissolved oxygen in stream water are the atmosphere and aquatic plants.

Alkalinity: The natural buffering capacity of a stream may mask the presence of acidic or basic pollutants

Hardness: Stream water hardness is the total concentration of Cations, specifically calcium (Ca^{2+}), magnesium (Mg^{2+}), iron (Fe^{2+}), and manganese (Mn^{2+}), in the water. Water rich in these Cations is said to be "hard." Stream water hardness reflects the geology of the catchment area.

Nitrates: Nitrogen is an essential nutrient that is required by all plants and animals for the formation of amino acids. Nitrate (NO_3^-) or nitrite (NO_2) of these two forms; nitrate is usually the most important.

Total Organic Carbon: A water sample is likely to consist of a mixture of organic carbon and inorganic carbon(IC & OC).

Heavy Metals: The heavy metal can be released in water by natural sources by various ion-exchange processes, Oxidation- reduction reaction or weather of rocks.

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2.2.3 Water Quality Characterization and its Importance

Water quality characterization of surface water is an evaluation of the spatial and temporal characteristics of variations in water quality of a river the upstream from to downstream. It describes distinctive characteristics that are obtained for different water quality parameters at different locations and at different seasons. The study provides an identification of the sources of solutes and sources of potential pollutants in contaminated system along the river.

2.3 Association between Isotopic and Water Quality Parameters

Dissolved oxygen, Bicarbonate, Nitrate, sulphate were measured as a water quality parameter and ^{18}O of the river water as isotopic parameter was also measured. As all of these parameters composed of oxygen as a constituent, so it was believed that their must be some correlation between these parameters. Some graphical and statistical approaches have been applied in order to obtain suitable correlation between isotopic and water quality parameters. Similarly some correlation was also developed between EC and ^{18}O as EC retains some indirect relation with DO.

2.4 Review of Previous Studies

Several previous studies have been carried out by many researchers and hydrologists with different objectives.

Metzger (1997) outlined qualitative information on streamflow gains and losses along San Fanscisquito Creek to determine the chemical quality and isotopic composition of surface and ground water to help to characterize surface and ground water quality of the study area.

Jain and Singhal (1999) have examined water quality and pollution aspects of river Hindon with respect to different heavy metals and mass balance approach was used to differentiate between point and non-point sources of pollution. The river was reported highly influenced due to heavy metals by direct discharges of municipal and industrial effluent.

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Pandey et al. (1999) have carried out weathering and geochemical study of Ganga River during the pre monsoon and post monsoon seasons, in order to assess the solute acquisition processes and sediment transfer in a high elevation river basin. According to the study surface water were dominated by HCO3 and SO4 in anionic abundance and Ca in cationic concentrations. Seasonal and spatial variations in ionic concentration were correlated to lithology and discharge.

Pratap Singh (2000) investigated water quality and suspended sediment concentration analysis of Gangotri glacier melt water and reported that suspended sediment changes significantly over the melt period and a significant variation was found in water quality parameter obtained near Gomukh and Haridwar stations. However Chloride was serving as a conserve parameter.

According to Mariusz and Edrysek et al. (2000), oxygen and sulphur isotope in the SO_4^- reveals dynamics of an urban precipitation. In this study Correlation between sulphate concentration and its $\delta^{18}O$ value in acidrain have been carried out to find regional sulphur and oxygen isotope characteristics of acid-rain sulphate.

Bhattacharya and Jani (2002) determined seasonal variation in oxygen isotope ratios of selected Indian rivers aiming to characterize the climatic and anthropogenic influences impacting on river water supply.

Brenot (2003) investigated isotopic composition of dissolved of SO_4^{2-} for determination of change in weathering condition and water sources in the Moselle River watershed in France.

Tasneem and Aggrawal (2003) presented an interesting relation between dissolved oxygen and $\delta^{18}O$ of dissolved oxygen. The relation between these two parameters was used to determine ratio of community respiration to gross respiration.

Yde (2003) master thesis was focused on the solute composition and stable oxygen isotope ratio in order to understand the consequences of the configuration of meltwater routing within glaciers, and the application of hydrological conceptual modeling of drainage systems.

A similar study is going on in the Wilmot River watershed in Canada by Liao and Savard (2005) targeting water-isotope characterization of ground water, surface water, and precipitation.

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B. Kumar et al. (2005) undergoing isotopic characterization of different sources in a river basin for its better management. A case study was done on Yamuna River. The study reveals Yamuna River has different isotopic characteristics than the Indian precipitation and indicates the contribution of different sources. The variations of isotopic and chemical characteristics with distance and altitude were studied in order to estimate contribution of relative water inputs at different locations.

Chakrapani and Veizer (2005), studied source of dissolved inorganic carbon isotopic compositions in the Upstream Ganga River intended to understand the source of DIC in the Alaknanda and Bhagirathi rivers in the Himalayas by measurement of $\delta^{13}C_{DIC}$ in water samples. Results show that the Ganga River is characterized by dominance of carbonate rock weathering. Relation between HCO_3^- and $\delta^{13}C_{DIC}$ corroborated evidence of carbonate weathering and negated silicate weathering in the study area.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Monitoring and Analysis Protocol for Water Quality

Surface water and ground water samples were collected in different seasons during study period. Details about monitoring protocol are given below.

3.1.1 Monitoring Network

Water samples form River, Spring and Hand-pumps were collected for the analysis of water quality, deuterium (δD) and oxygen-18 (δ O-18) during the period of July 2005 to May 2006 by field observations and site selection. Selection of sites for water sample collection was carried out after a detailed investigation of the Study Area and giving due care to the factor like accessibility, mixing and representability. List of sample locations and sample types are presented in table 3.1

Table 3.1: Sample Location and Sample Type

Location	Sampling type	Source
Gangotri	Surface, Ground Water	River, Hand Pump
Dabrani	Surface Water	River
Uttarkashi	Surface, Ground Water	River, Hand Pump
Tehri	Ground Water	Spring
Devprayag (Alaknanda)	Surface Water	River
Devprayag(Bhagirathhi)	Surface Water	River
Devprayag (Ganga)	Surface Water	River
Rishikesh	Surface, Ground Water	River, Hand Pump
Haridwar	Surface, Ground Water	River, Hand Pump

3.1.2 Monitoring Frequency

River Ganga was sampled for Water Quality analysis during-monsoon (September 05), Post-monsoon (November 05) and Pre-monsoon (May 06) seasons from Gangotri upto Haridwar for the present study. In addition, from Devprayag upto Haridwar monthly sampling was conducted from July to December 2005 for water quality analysis. For Isotopic parameters sampling was done on monthly interval from Gangotri to Haridwar from July 2005 to February 2006 for surface Water only.

3.1.3 Selection of parameters

Following parameters have been studied during the evaluation of study.

a. Water Quality

i.   Temperature (^{0}C)

ii. Hydrogen ion concentration (pH)

iii. Electrical Conductivity (ms/cm)

iv. Dissolved Oxygen (mg/l)

v.   Solids in mg/l

      a. Total Solids

      b. Total Dissolved Solids

      c. Total Suspended Solids

vi. Chloride (mg/l)

vii. Sulphates (mg/l)

viii. Hardness as $CaCO_3$ (mg/l)

      a. Total

      b. Calcium

      c. Magnesium

ix. Total Organic Carbon (mg/l)

x.   Nitrate-NO_3^- (mg/l)

xi. Heavy Metals (Fe, Mg, Zn, Cd, Cr) (mg/l)

b. Isotopic Parameters

i. δD in $^0/_{00}$ (per mill)

ii. δ^{18}O in $^0/_{00}$ (per mill)

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3.1.4 Modality of Sample Collection

The water sampling can be done either from shallow or deeper depths or from both. Depending upon the nature of analysis the water samples were collected from the water surface within 30 cm from the top of the water surface, while collecting samples from the hand pumps, due care was taken to see that effective pumping was done and the samples were collected the reading of electrical conductivity and temperature got stabilized the water samples were collected and into a glass or plastic container and refrigerated. These refrigerated samples were analyzed as soon as possible.

Temperature, EC, and pH were measured at the site location whereas the remaining parameters were measured in the Water Quality Laboratory, Department of Hydrology, and IIT Roorkee. For the estimation of dissolved oxygen, however, the DO fixation and acidification were performed at the site itself after collection of water samples. Heavy metal were analyzed ay Institute Instrumentation Centre, IIT Roorkee, δD and $\delta^{18}O$ analyzed at Nuclear Hydrology Laboratory "National Institute of Hydrology" Roorkee.

3.2 Analytical Methods for Water Quality

Procedure followed for analysis of Water Quality Samples have been in accordance with the "Standard Methods for Examination of Water and Waste Water," 20th edition APHA, AWWA, WER (1998). The parameters and methods used are briefly given in Table 3.2:

Table 3.2: Analytical Methods for Water Quality

Parameter	Method	Reference
Temperature	Thermal Sensor	Method 2550 B
pH	pH meter (Electrometric)	Method 4500 H
Electrical Conductivity	EC meter (Electrometric)	Method 2510 B
Dissolve Oxygen	Volumetric Analysis	Method 4500-O B
TS, TDS, TSS	Gravimetric analysis	Method 2540 B, C, D
Chloride	Volumetric analysis	Method 4500-C B

Alkalinity	Volumetric analysis	Method 2320 Cl
Sulphate	Gravimetric analysis	Method 4500-SO_4 C
Total Hardness	Volumetric analysis	Method 2340 C
Ca Hardness	Volumetric analysis	Method 3500 B
Mg- Hardness	Volumetric analysis	Method 3500-Mg B
Total Organic Carbon	TOC Analyzer	5310 A
Nitrate	Ion Selective method	4500-NO_3 D

For Heavy Metal analysis, Atomic Absorption Spectrophotometer (AAS) was used with following specifications as presented in Table 3.3:

Table 3.3: Atomic Absorption Spectrometer Details

Element	Working Range (ppm)	Sensitivity	Wavelength (nm)	Mode of Analysis
Zn	0.4 – 15	0.008	213.9	Air-acetylene
Cr	2 – 15	0.050	240.7	Air-acetylene
Fe	2 – 9	0.050	248.3	Air-acetylene
Mn	1 – 3.6	0.020	279.5	Air-acetylene
Cd	0.2 – 1.8	0.009	228.8	Air-acetylene
Ni	1.8 – 8	0.040	232.0	Air-acetylene
Na	0.18 - 0.70	0.004	589.0	Air-acetylene
K	0.4 – 1.5	0.008	766.5	N_2O-acetylene

3.3   Monitoring and Analysis Protocol for Isotopes

3.3.1 Sampling of Surface Water

Water samples were collected from rivers in the present study. The water sampling can be done either from shallow or deeper depths or from both. The water samples were collected desired location about 35-45 cm below the water surface to avoid the effect of evaporation, directly by dipping the sample bottle into the water body. In case of sampling from greater depths, a special device called depth water sampler was used. Once the water sample was collected, it can be poured into a plastic container called HDPB (High Density Plastic Bottles) of appropriate size as desired,

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10 ml bottle for D and ^{18}O analysis. Filtration of samples was required in most cases.

3.3.2 Measurement Techniques

To measure stable isotopic composition for hydrogen and oxygen in natural water, isotope ratio mass spectrometer (IRMS) is usually used. In 1947, Alfred Nier developed the first dual-inlet, double-collector gas-source mass spectrometer with sector-type magnetic field (Nier, 1947). Dual inlet isotope ratio mass spectrometer was used in present study to analyze D and ^{18}O of river water. The basic principle of dual inlet IRMS is a comparison between sample and reference gases. Dual inlet consists of two identical halves: one for the sample gas and one for the reference. An automated dual inlet equalizes sample and reference gas pressures, and hence their major ion beam currents, by adjusting the volumes of two storage reservoirs. This ensures that sample and reference gases both flow from their respective reservoirs at the same rate and isotope ratios are measured.

A. Determination of Hydrogen Isotope

The measurement of hydrogen isotope ratios in water requires that the water be reduced to hydrogen gas before analysis in the isotope ratio mass spectrometer. Historically, preparation of the hydrogen gas used uranium as the reducing agent.

$$2H_2O + U \rightarrow UO_2 + 2H_2$$
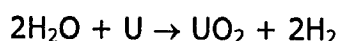
The water sample is cycled through a hot uranium furnace (800^0 C) using a Toepler pump with product hydrogen gas collected on a charcoal substrate. This method, although very precise, presents many technical problems, not the least of which is the disposal of the spent uranium. The system also does not lend itself to running many samples and is very time consuming. Recently, zinc compounds have become the reducing agent of choice.

$$H_2O + Zn \rightarrow ZnO + H_2$$
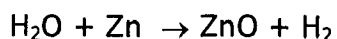
Advantage of using zinc as the reducing agent is that one is able to prepare and analyze batches of samples without the use of very specialized vacuum lines and equipment. To prepare samples using zinc

compounds, a simple vacuum line is used to evacuate a 6 mm pyrex tube which contains 100 mg of zinc alloy. After evacuation, the pyrex/zink tube is back filled with dry nitrogen and removed from the vacuum line. A 2 µl glass capillary is filled with the water sample and dropped into the pyrex tube. The sample tube is returned to the vacuum line; the water is frozen with liquid nitrogen and re-evacuated. The tube is then flame sealed and placed into a 500^0 C muffle furnace for one hour. The product hydrogen gas is ready for immediate analysis on the mass spectrometer.

Most recently, equilibrium method is usually used for automated analysis. In this method, water equilibrated with H_2 gas using Pt catalyst.

$$^2D^1HO + {}^1H^1H \Leftrightarrow H^1HO + {}^2D^1H$$
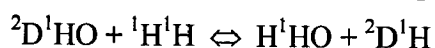
The equipment used in this course for equilibration can set twenty-four sample bottles at the single run. Usually, six working standards and three running standards, for estimating the error at each run, are measured with sample waters. Therefore, fifteen samples at single run can be measured. Isotopic compositions of working standards were determined by international standards (e.g. SMOW) prior to routine analysis for samples. The running standard was used for checking whether all measurements at single run got successfully completed and also for comparing with previous runs.

B. Determination of Oxygen Isotope

To determine oxygen isotope composition of water, the equilibrium method is usually used. In this method, CO_2 that is isotopically equilibrated to sample water is measured instead of water itselves. Between CO_2 and water, there is an isotope exchange reaction as written below, which achieves equilibration easily.

$$H_2{}^{18}O + \tfrac{1}{2} C^{16}O_2 \Leftrightarrow H_2{}^{16}O + \tfrac{1}{2}C^{18}O^{16}O$$

The oxygen isotope distribution between water and CO_2 in above reaction is controlled by temperature. Therefore, reaction temperature must be held constant through each of runs including sample and working standards. The equipment for oxygen isotope analysis was identical to hydrogen analysis, except for Pt catalyst.

CHAPTER FOUR

Results and Discussion

4.1 Isotopic Variations in Ganga River

River basins constitute major captures of the regional precipitation and the flow through a major river, transfers this water collection to the ocean completing an important sector in the global hydrological cycle. Consequently, time variation of isotopic ratios in river waters may be useful in tracing the magnitude of recent climate change induced by increase in greenhouse effect. In addition, study of isotopic characterization of river water from strategic regions may reveal hydrological modifications introduced into the basin by human activities.

4.2.1 Oxygen-18 and Deuterium

Oxygen and deuterium isotope ratios were measured in water samples collected once in a month at sites i.e. Gangotri, Dabrani, Uttarkashi, Tehri, Devprayag (Alaknanda, Bhagirathi, and Ganga) and Haridwar. It is to be mentioned here that the National Institute of Hydrology, Roorkee is carrying out flow study modeling of river Bhagirathhi using isotopic approaches. Therefore keeping in view the constraints in the measurement of $\delta^{18}O$ and δD in the water sample and cost involved, some of the data have been used of samples that were collected by the institute, with the consent, for better understanding and interpretation of the isotopic data generated during this study.

The time variation plots show many interesting features displaying effects of snow melt contribution to integrated rain water capture and evaporation during transport. High altitude area of Ganga River contributes melt waters, which are highly depleted.

4.2.2 Regional Meteoric Water Line and River Water

Figure 4.1(A) shows RMWL for Bhagirathhi River catchment of precipitation having equation $\delta D = 8.23\ \delta^{18}O + 13$ and for river water it is found to be $\delta D = 7.8\ \delta^{18}O + 8.3$. Difference in slope of these two lines indicates the contribution of ground water with slight evaporation effect during infiltration process because evaporated waters plot farther to the right along a line referred to as the evaporative trend line (Gat, 1981).

Bhagirathhi RMWL for PPT & RW

del O-18

Bhagirathhi Catchment ppt
y = 8.23x + 13

Bhagirathii RW
y = 7.7779x + 8.267

del D
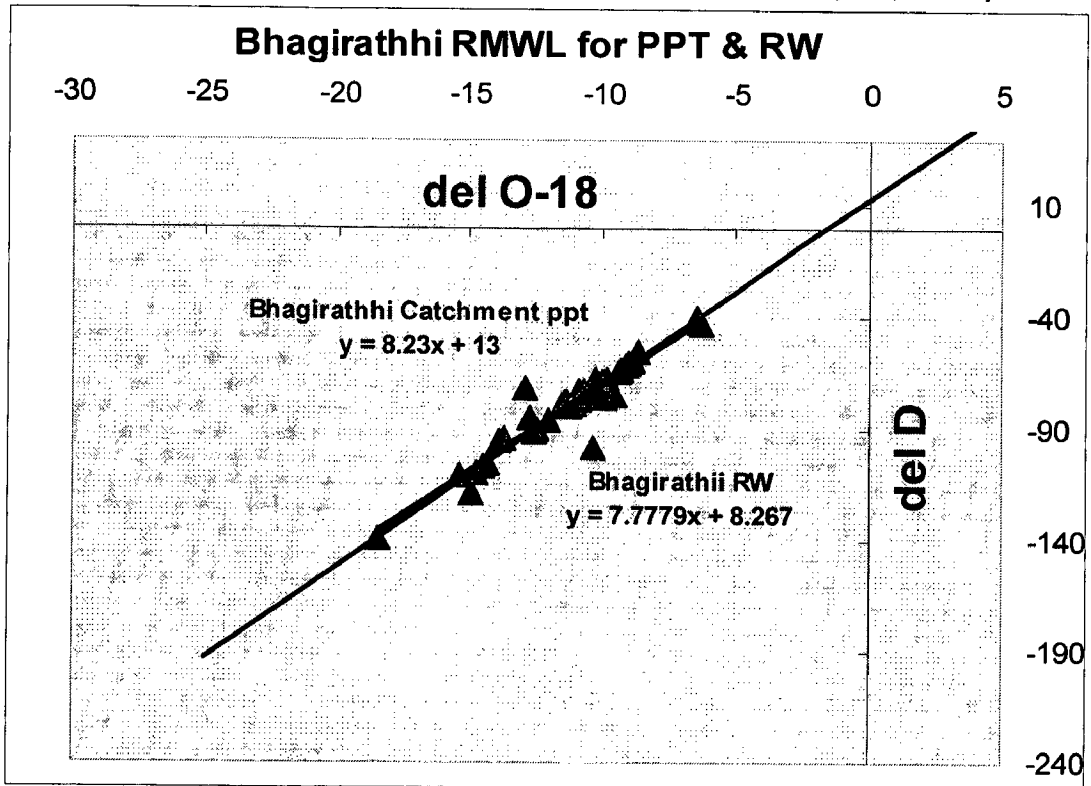
Figure 4.1(A) RMWL of Bhagirathhi Catchment Precipitation and δD vs. $\delta^{18}O$ of river water. Regional Meteoric Water Line (RMWL) of Bhagirathhi River catchment precipitation is developed by the National Institute of Hydrology, Roorkee.

The relationship between the isotopic composition of precipitation (input) and newly formed groundwater and surface runoff (output) is build upon processes that differentiate between rain events on a meteorological or seasonal basis, and processes that fractionate between the different isotopic water species, primarily evaporation. These processes having the collective name of catchment isotope effect may encompass a wide range of temporal and spatial scales. Some occur during or immediately after the rain event on or above the ground surface. Others involve soil moisture or shallow water reservoirs. It is worth to note that the

catchment effect for any given area may vary in time due to both natural (climate) and man-induced changes.

Figure 4.1(B) shows altitude effect in Ganga River water. At Gangotri mainly river contribution is from snow melt hence highly depleted in δD and $\delta^{18}O$, they fall at bottom of the curve at higher altitude side whereas at station Haridwar receives input from ground water, precipitation runoff and snowmelt components and hence have enriched values for δD and $\delta^{18}O$ and fall at extreme upside of the curve. Intermediate regions Dabrani, Uttarkashi, Tehri and Devprayag falls between these two stations. As in colder regions δD and $\delta^{18}O$ values depletes and at warm region δD and $\delta^{18}O$ enriches, figure 4.2 clearly discriminates between these two regions just by knowing δD and $\delta^{18}O$ values.
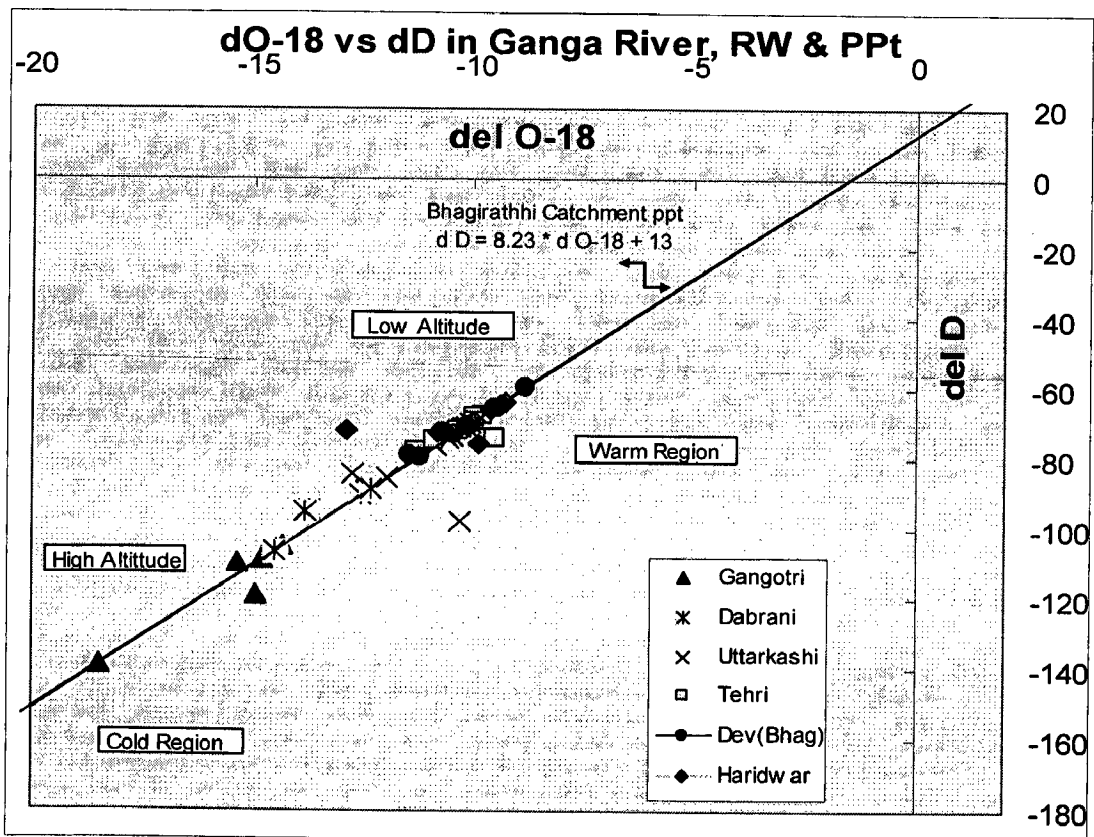
Figure 4.1(B) Relation between δD vs. $\delta^{18}O$ of Ganga River for all stations.

4.2.3 Temporal Variations in Isotopic Composition of Ganga River

The observed spatial and temporal variability of the isotopic composition of precipitation stems from physical processes operating on both micro- and macro-scales. Whereas the equilibrium and kinetic isotope fractionation effects play a decisive role during phase transitions and diffusion-controlled transport, respectively, the Rayleigh mechanism contributes to the observed isotope variability during transport in macroscale.
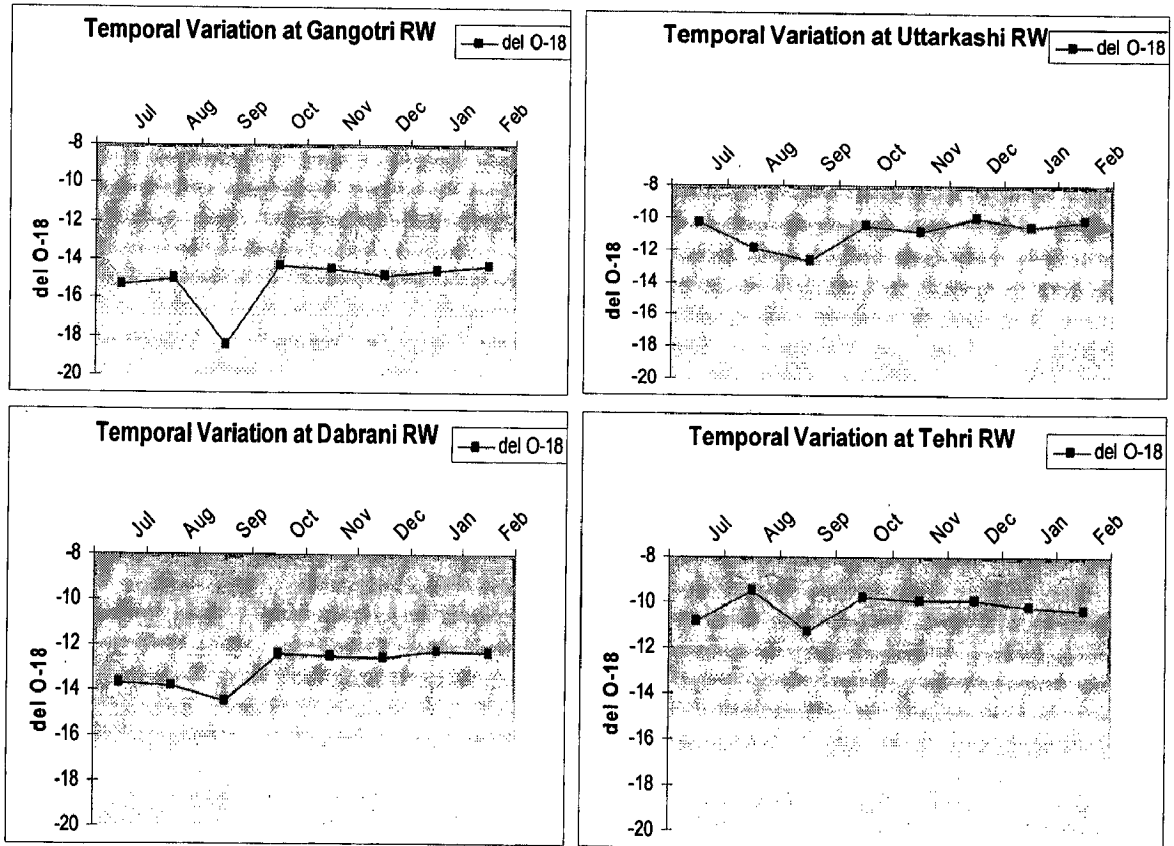
Figure 4.1(C) Temporal variations in Ganga River Water at station (i) Gangotri (ii) Dabrani(iii) Uttarkashi (iv) Tehri.

Figure 4.1(C) shows temporal variations in Ganga River from July to February months of study period (2005-2006) at Gangotri, Dabrani, Uttarkashi and Tehri stations. It is clearly depicted by these graphs that $\delta^{18}O$ values are minimum during the rainy season, particularly in the month of August and September. It reveals that maximum snowmelt runoff and high intensity rainfall runoff contribute to the river during this period. However, the minimum depleted $\delta^{18}O$ that appears and Gangotri (i.e. -19 $^0/_{oo}$) diminishes or gets enriched as we move down stream. This

may be due to altitude effect i.e. the isotopic composition of precipitation depletes at higher altitude and enriches at lower altitude; therefore the rainfall runoff at lower altitude will have enriched values. Further, the contribution of rainfall runoff increases along with ground water contribution as we move downwards, therefore the effect of snowmelt runoff diminishes. At site Tehri, the pattern of variation in $\delta^{18}O$ value is some what different than the sites located at upstream, which may be because the water spread area at Tehri is more, therefore the effect of evaporation increases. Also river Bhilangana joins river Bhagirathhi that has little different isotopic characteristics and mixing of water of different origin and different isotopic composition attributed to this difference in isotopic characteristic.
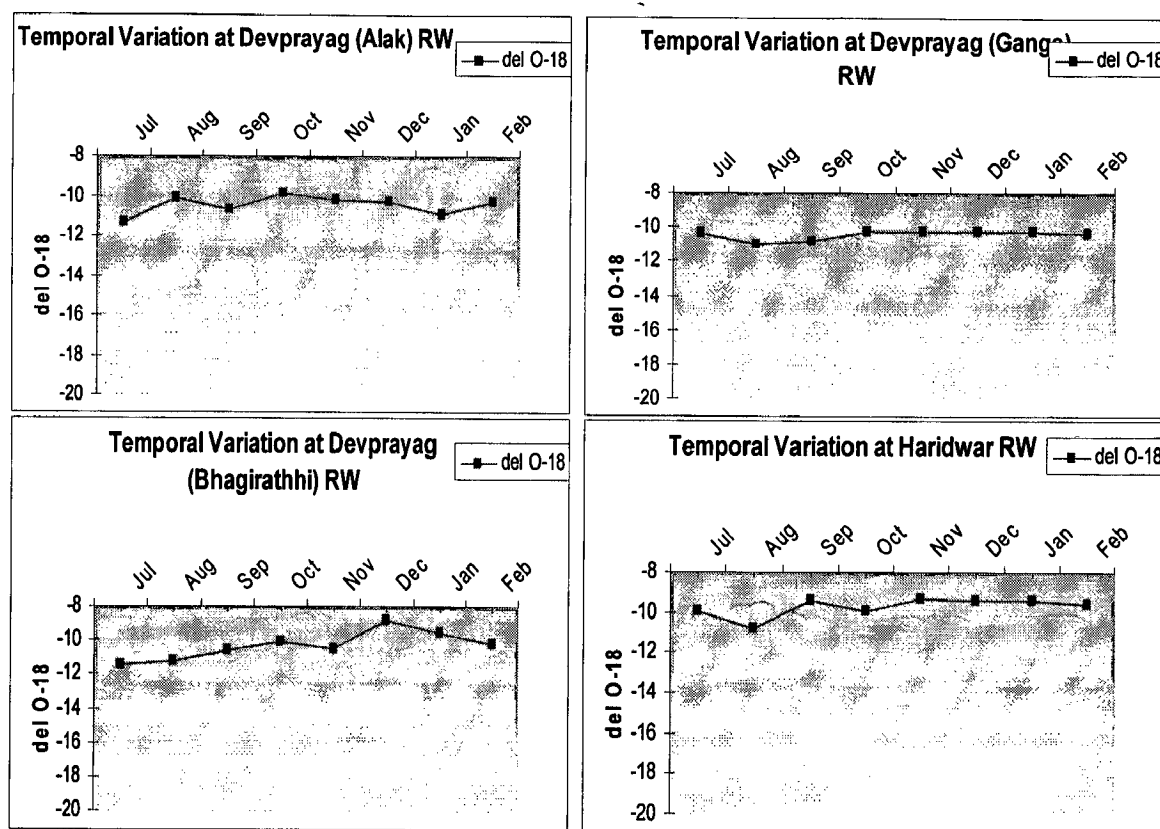
Figure 4.1(D) Temporal variations in Ganga River Water at station (i) Devprayag (Alaknanda) (ii) Devprayag (Bhagirathi) iii) Devprayag (Ganga) (iv) Haridwar

Similarly, figure 4.1(D) shows temporal variations in Ganga River from July to February months at Devprayag (Alaknanda, Bhagirathhi and Ganga) and Haridwar stations. As we reach Devprayag the depletion effect in $\delta^{18}O$ values almost disappears, that is clearly seen in 4.1(D) (i), (ii) and

(iii) in case of river Bhagirathhi, in the case of Alaknanda that joins Bhagirathhi at Devprayag and also in the case of river Ganga (Alaknanda + Bhagirathhi). This may be due to increased contribution of surface runoff and ground water along with altitude effect. Similar variations which are found at sites Devprayag (Bhagirathhi and Ganga) are also visible at Haridwar, located downstream and at lower altitude. Therefore, this aspect required to be studied further.

4.1.4 Seasonal Variation in Isotopic composition of Ganga River

Three representative months are shown in the figure 4.1(E), to show the seasonal variation in the river. The origin of the seasonal variation is attributed to the seasonal variations in precipitation. Thus, Ganga River contains not only old groundwater with a virtually constant isotopic composition, but also a relatively fast component, to be ascribed to surface runoff.

The $\delta^{18}O$ values are depleted in the month of September as the contribution of snowmelt runoff may be more during the month, while, the $\delta^{18}O$ values are enriched in the month of December as snowmelt runoff becomes negligible and ground water contribution dominates. Further, small deviations are seen in $\delta^{18}O$ values in the month of February, which may be due to contribution of winter rains at that time, are always depleted than the monsoon rains.

For September month when snowmelt contribution in the river in maximum, more depleted values are shown and in the month of December enriched $\delta^{18}O$ value are recorded as snowmelt contribution is less in this period and only ground water in dominates. However, in February month again depletion in observed due to the fact that snowmelt contribution again starts increasing in the river with increase in temperature. Similarly trends or variations have been seen in case of δD although not represented here.
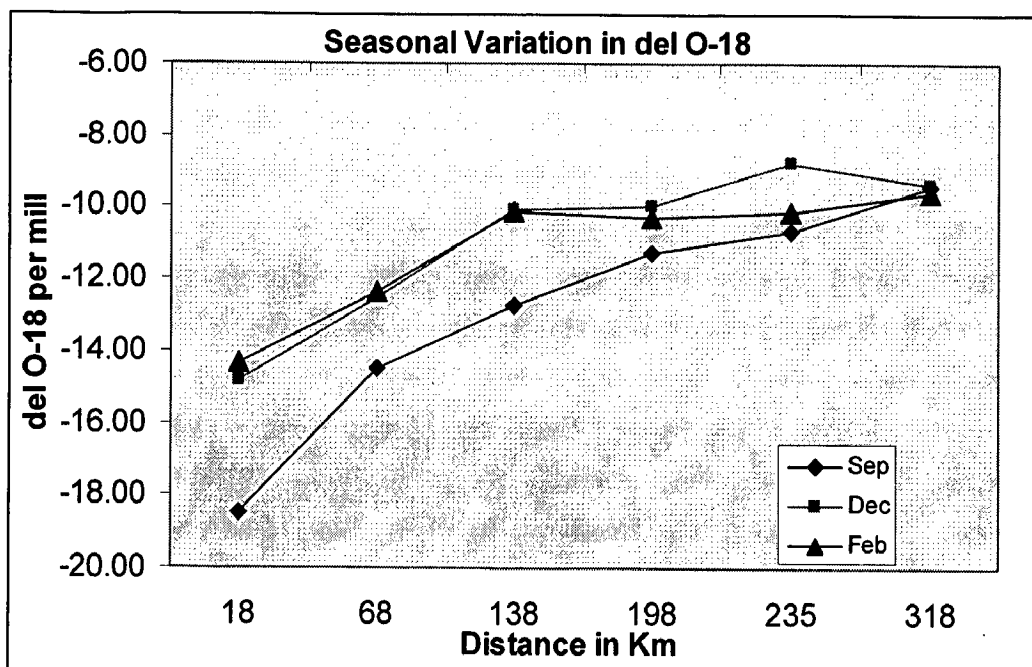
Figure 4.1(E) Seasonal Variations in $\delta^{18}O$ Values with distance

4.1.5 Isotopic Characterization of Ganga River

The isotope data of the Ganga River shows wide variations at different sites as depicted by figure 4.1(F). At site Gangotri (R_g) $\delta^{18}O$ varies from -18.52 $^0/_{00}$ to -14.32 $^0/_{00}$, at Dabrani (R_d) from -14.52 $^0/_{00}$ to -12.33 $^0/_{00}$, at site Uttarkashi (R_u) from -12.74 $^0/_{00}$ to -10.06 $^0/_{00}$, at Tehri site (R_t) from -11.30 $^0/_{00}$ to -10.06 $^0/_{00}$, at site Devprayag-Bhagirathhi (R_b) from -11.44 $^0/_{00}$ to -8.80 $^0/_{00}$ and -9.45 to -9.30 $^0/_{00}$ at site Haridwar (R_h). Similarly, $\delta^{18}O$ values at site Devprayag (Alaknanda) varies from -11.38 $^0/_{00}$ to -10.1 $^0/_{00}$ and at Devprayag (Ganga) varies from -10.66 $^0/_{00}$ to -9.87 $^0/_{00}$. However, these two sites are not depicted in the figure 4.1(F), because Alaknanda river caries almost similar isotopic characteristic as Bhagirathhi and as well Ganga at Devprayag, so the significant change after mixing is not seen at this particular site. These variations clearly indicate the contribution of water from different sources like precipitations runoff, meltwater runoff and ground water.

However, the seasonal variations are also responsible at a particular location, but the depletion in $\delta^{18}O$ values as we move from lower altitude to higher altitude i.e. Haridwar to Gangotri is because of altitude effect in precipitation responsible in addition to the different sources contributing

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water to the river. For example the minimum $\delta^{18}O$ values are during the rainy season (Aug, Sep.) indicates the maximum contribution of snowmelt and rainfall runoff is during this period. On the other hand maximum values during winter (Nov, Dec, Jan) indicate ground water contribution.
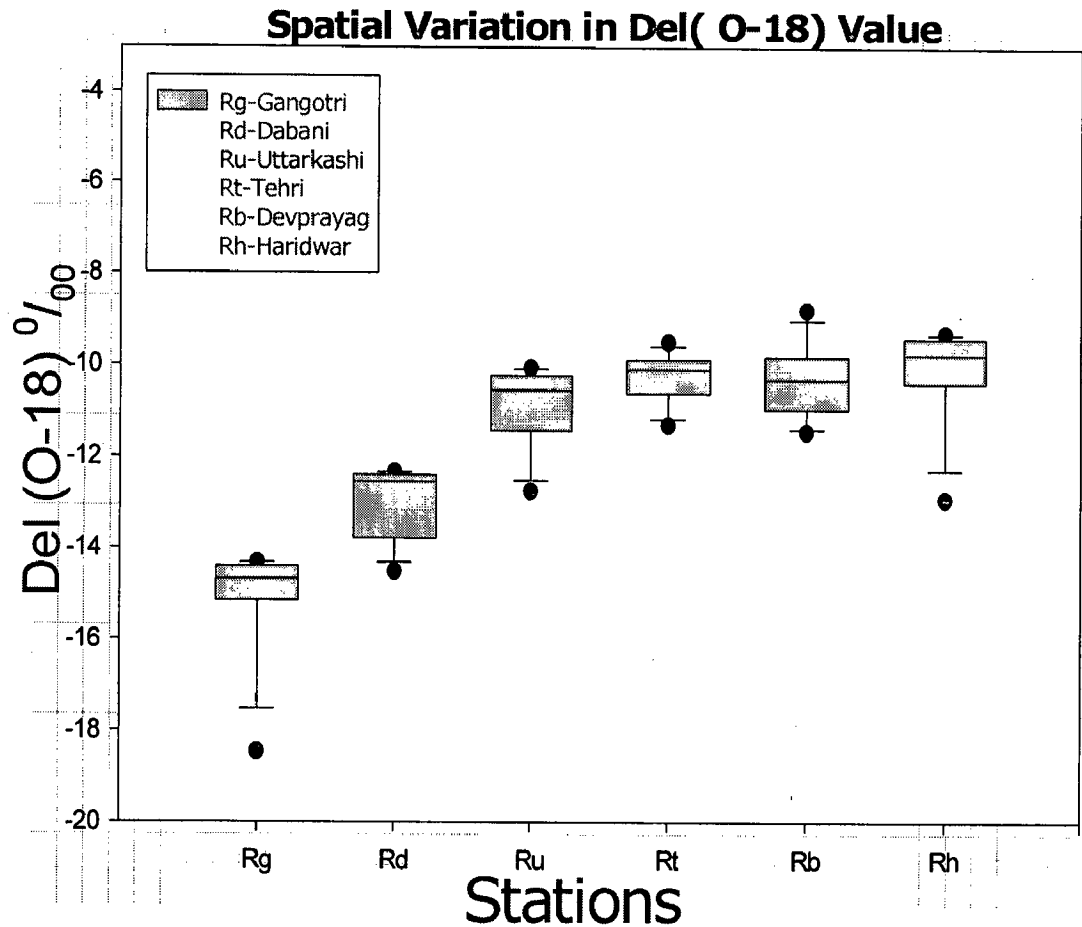
Figure 4.1(F) Spatial variations in $\delta^{18}O$ for different months.

Statistical analysis by "Two way ANOVA without replication" is shown in Table 4.1(F), indicates spatial and temporal variations are highly significant.

Table 4.1: ANOVA test for $\delta^{18}O$

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	166.1426	5	33.22852	84.00186	1.75E-18	2.485143
Columns	29.00611	7	4.14373	10.47537	5.09E-07	2.285235
Error	13.84491	35	0.395569			
Total	208.9936	47				

Figure 4.1 (G) shows variation in δD for different months at different sites. At site Gangotri (R_g) δD varies from -138.93 $^0/_{00}$ to -104.88 $^0/_{00}$, at Dabrani (R_d) from -106.50 $^0/_{00}$ to -88.48 $^0/_{00}$, at site Uttarkashi (R_u) from

-97.77 °/_{00} to -69.79 °/_{00}, at Tehri site (R_t) from -77.98 °/_{00} to -67.57 °/_{00}, at site Devprayag-Bhagirathhi (R_b) from -78.71 °/_{00} to -65.79 °/_{00} and -75.60 °/_{00} to -63.54 °/_{00} at site Haridwar (R_h). Similarly, δD values at site Devprayag (Alaknanda) varies from -77.73 °/_{00} to -68.23 °/_{00} and at Devprayag (Ganga) varies from -75.6 °/_{00} to -63.54 °/_{00}. Again Stations Alaknanda and Bhagirathhi at Devprayag site are not depicted in figure 4.1(G).
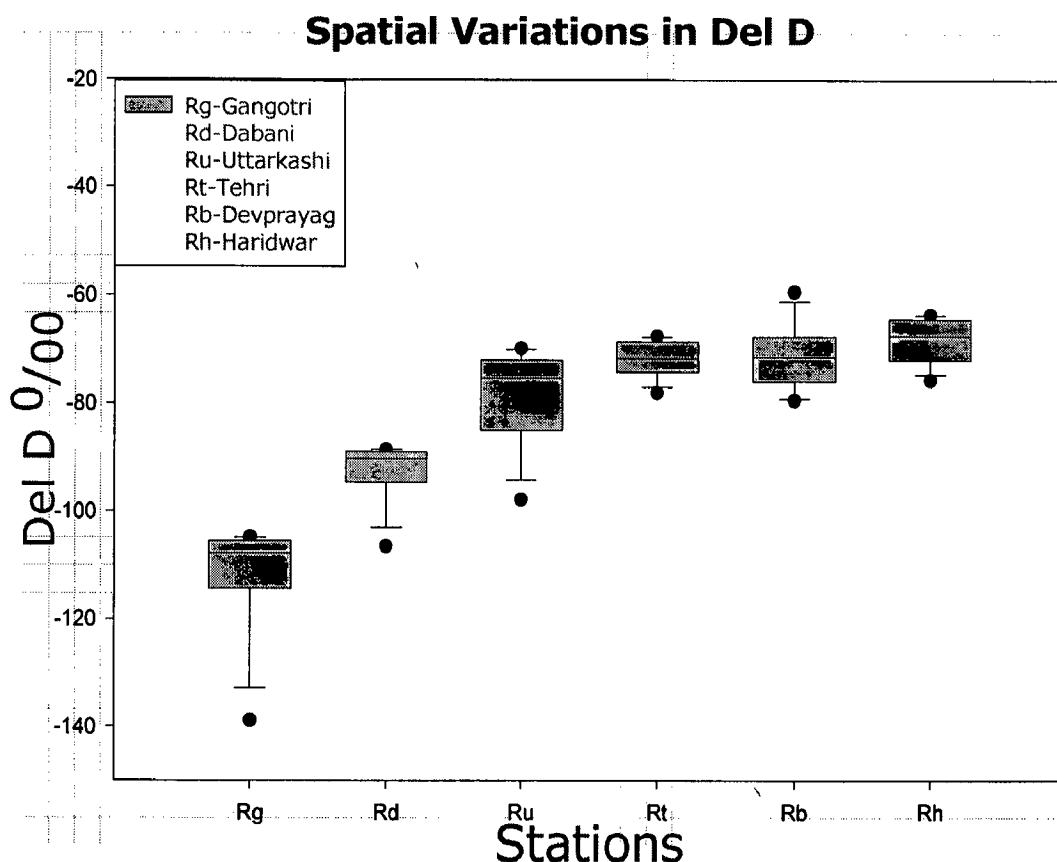
Figure 4.1 (G) Spatial variations in δD for different months.

Monthly means of $\delta^{18}O$ for each station is plotted against altitude of respective stations in figure 4.1(H) shows that altitude effect is -0.21 °/_{00} per 100 m which is well with in the values -0.10 to -0.40 °/_{00} per 100 m observed in other parts of the world (McMurtry et al.). However, this requires further investigations and comparison with the altitude effect to be estimated from precipitation data.

Monthly Mean of del O-18 vs Altitude
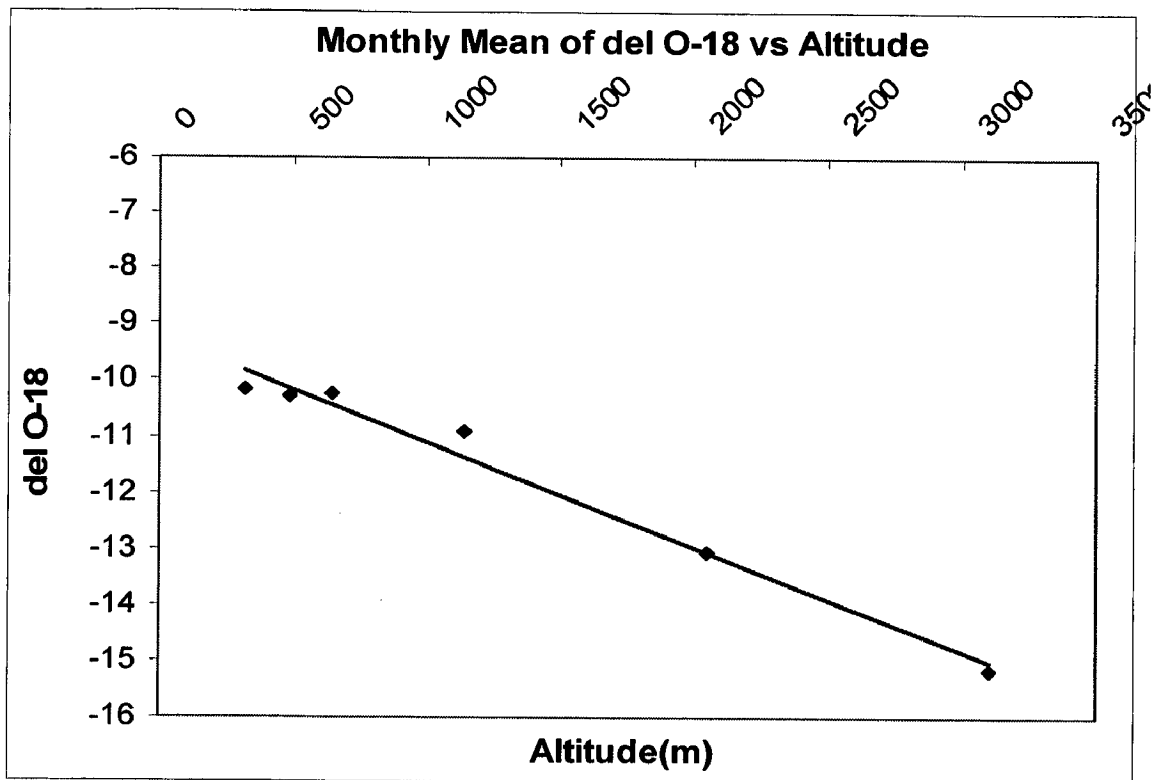
Figure 4.1(H) Monthly mean of $\delta^{18}O$ variations with Altitude.

4.2. Water Quality status in and Around Ganga River

The discussion on the above is presented in respect of the studied parameters for both the network viz. macro network (Gangotri to Haridwar) and macro network (Devprayag to Haridwar). Monthly variations are analyzed using Box Plot approach and variation in monthly data is analyzed using Two WAY ANOVA statistical test.

4.2.1 Electrical Conductivity

The conductivity depends on the amount of dissolved constituents in water and it indicates the suitability of water for irrigation and drinking etc (Rajamohan et.al., 2004). The leaching of pollutants from landfill may increase the conductivity of water due to increase in metal ion concentration.

Electric conductance generally varies inversely with streamflow. During low streamflow conditions, streamflow primarily constitutes of baseflow therefore, contains more dissolved solids (that is, large specific conductance values).

Figure 4.2(I) Seasonal Variation in EC
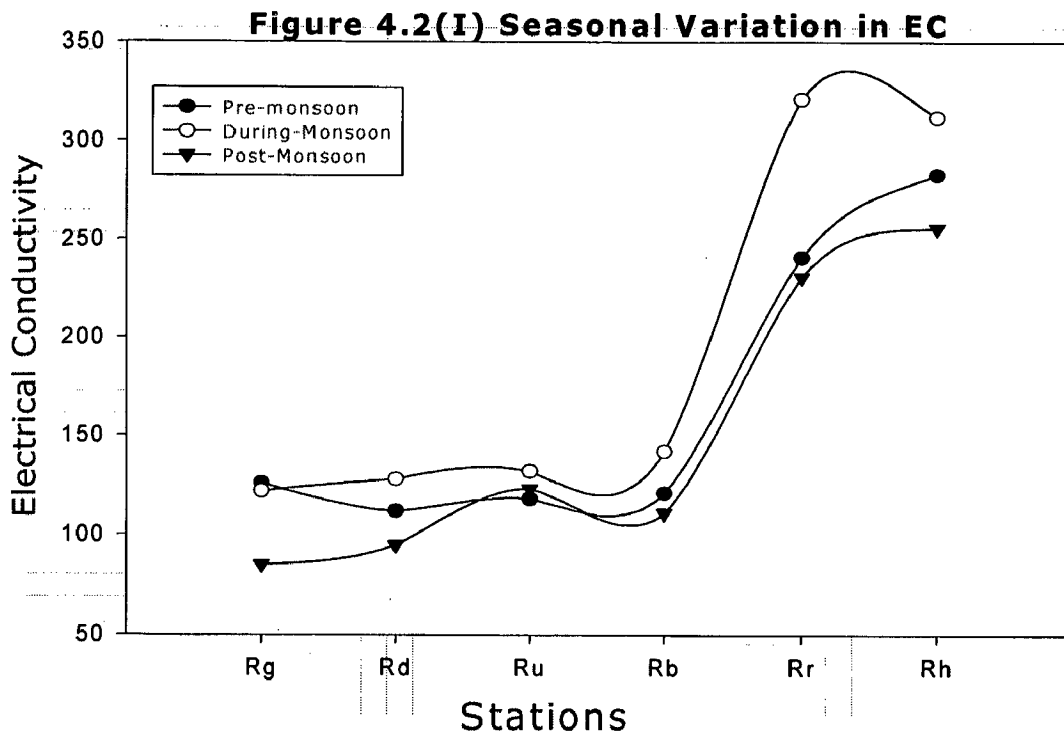
For Pre-Monsoon season high value of EC is due to increase in total dissolved solids and gathering of dust particles around wetlands. EC value ranges from 122 to 182 µS/cm (Pre-Monsoon), from 99 to 182 µS/cm (During-Monsoon) and from 85 to 195 µS/cm (Post-Monsoon) as shown in Figure 4.2(I).

EC of river water near Haridwar and Rishikesh show high conductivity due to influence of land use and external inputs, such as agriculture (irrigation), urban development (removal of vegetation, sewage and effluent discharges), industrial development (industrial discharges).

ANOVA table 4.2(I) verifies significant seasonal and spatial variations in EC.

Table 4.2(I): ANOVA table for EC

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	7027	2	3513.5	7.915411	0.005015	3.738892
Columns	16199.29	7	2314.185	5.213525	0.004267	2.764199
Error	6214.333	14	443.881			
Total	29440.63	23				

Figure 4.2(II)Monthly Variations In EC

Legend:
Ra-->Devprayag(Alaknanda)
Rb-->Devprayag(Bhagirathhi)
Rm-->Devprayag(Ganga)
Rr-->Rishikesh(Ganga)
Rh-->Haridwar(Ganga)

Y-axis: Electrical Conductivity µS/cm
X-axis: Stations (Ra, Rb, Rm, Rr, Rh)
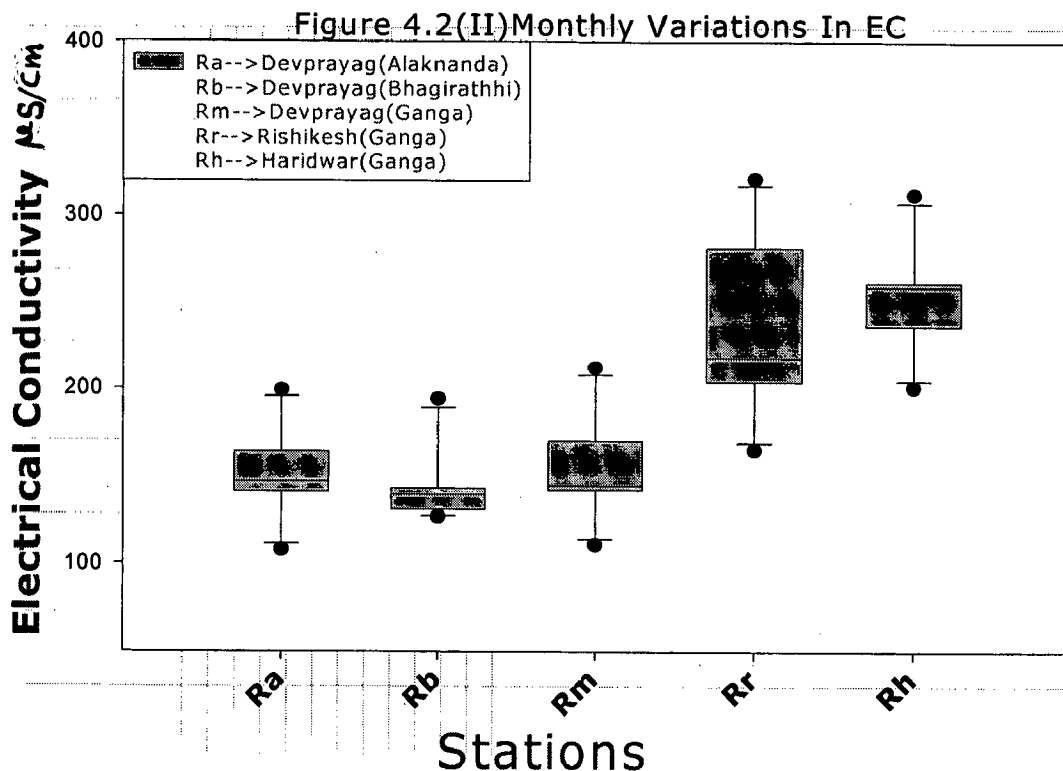
For micro-network monthly variations are shown in figure 4.2 (II).Mean values for stations R_a, R_b, R_m, R_r and R_h are 151.00, 145.6, 154.0, 233.3 and 254.5 µS/cm respectively. Variations in EC in Alaknanda River are more compared to Bhagirathhi and after mixing similar variations are also reflected in Ganga River. At Haridwar, EC values are very high due to above stated reasons.

EC values of ground water samples are shown in table 4.2 (II). Maximum values are apparently visible during pre monsoon season. A trend of general increase in the EC values with downstream distance has been displayed understandable because of increasing industrial development in the area.

Table 4.2 (II): EC in Ground Water

	Gangotri	Uttarkashi	Rishikesh	Haridwar
Pre-Monsoon	253	294	526	690
During Monsoon	222	260	356	412
Post- Monsoon	293	260	373	423

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4.2.2 pH

The value of pH decides the fate of various geochemical reactions in water body because most of the chemical reactions are dependent on pH of solution (Drever, 1997). It also controls the reactions involving trace metals and other organic metals compounds.

Figure 4.2(III) Seasonal Variations in pH
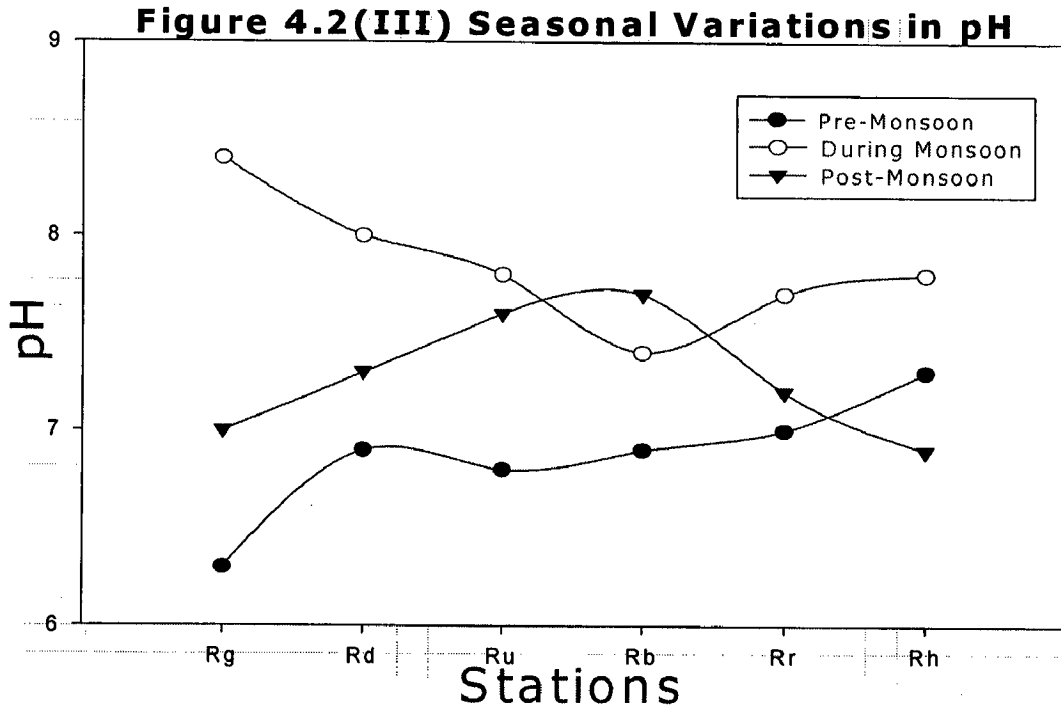
The pH of River is slightly acidic in pre-monsoon and during monsoon and slightly alkaline in Post-monsoon. pH of river water is ranges from 6.8 to 8.4 (During Monsoon), from 6.3 to 7.3 (Pre-Monsoon) and 5.9 to 7.7 (Post-Monsoon) as shown in figure 4.2(III). The seasonal variation of pH occurs due to thermal variation, rock-water interaction and mixing of different water component (Ground Water, Precipitation, Snow melt etc). All values of pH and temperature of river water are within the normal range. Also leaching of pollutants in the downstream part (Rishikesh, Haridwar) is an important factor for high pH value, which is 6.5 to 8.5.

ANOVA Table 4.2(III) shows that seasonal variation is significant whereas spatial variation is not significant.

Table 4.2(III) ANOVA table for pH

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	2.723508	2	1.361754	**4.554044**	0.02996	**3.738892**
Columns	0.540896	7	0.077271	**0.258413**	0.960501	**2.764199**
Error	4.186292	14	0.299021			
Total	7.450696	23				

For the stretch from Devprayag to Haridwar, monthly mean values are more or less constant around 7.8 shown by figure 4.2(IV). Maximum variations were reported for Haridwar site. Monthly pH values have been found lower in the downstream (R_r and R_h), apparently due to increase in temperature of water body. Values at stations R_a, R_b, R_m, R_r and R_h lie between 6.8 to 9.4, 5.9 to 9.1, 7.2 to 9.2 , 7.4 to 9.0 , 7.0 to 9.1 respectively.

Figure 4.2(IV) Monthly Variations In pH

Ra-->Devprayag(Alaknanda)
Rb-->Devprayag(Bhagirathhi)
Rm-->Devprayag(Ganga)
Rr-->Rishikesh(Ganga)
Rh-->Haridwar(Ganga)

pH
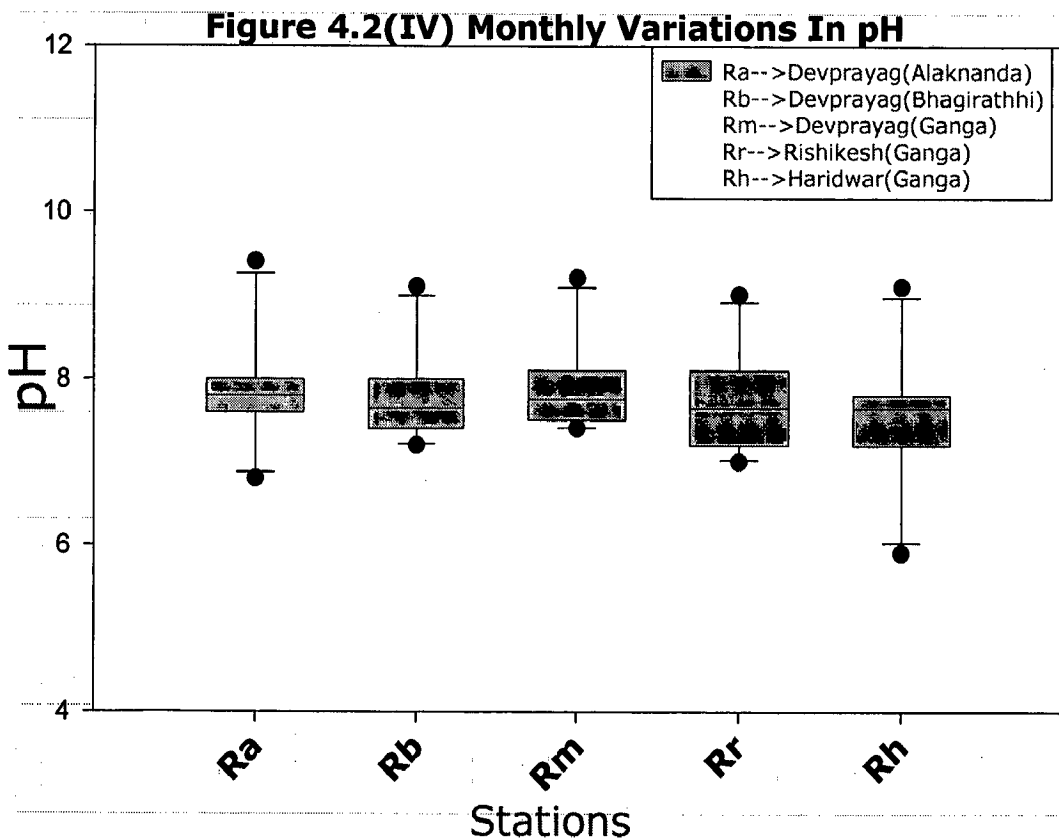
Stations

pH of groundwater in the study area also does not display significant variations other than the fact that it has generally higher values than the surface water, which is as expected.

Table 4.2 (IV): pH of Ground Water

	Gangotri	Uttarkashi	Rishikesh	Haridwar
Pre-Monsoon	6.5	7.1	7	8.2
During Monsoon	6	6	6	6
Post- Monsoon	8.2	7.3	7.6	8.3

4.2.3 Dissolved Oxygen

Dissolved-oxygen concentrations are used extensively to evaluate the ability of a stream to support higher forms of aquatic life that require oxygen for survival (Hem, 1992). The amount of oxygen that can be held by the water depends on the water temperature, salinity, and pressure. Both the partial pressure and the degree of saturation of oxygen change with altitude. The amount of oxygen absorbed in water decreases as altitude increases because of the decrease in relative pressure.

Figure 4(V) Seasonal Variations in DO
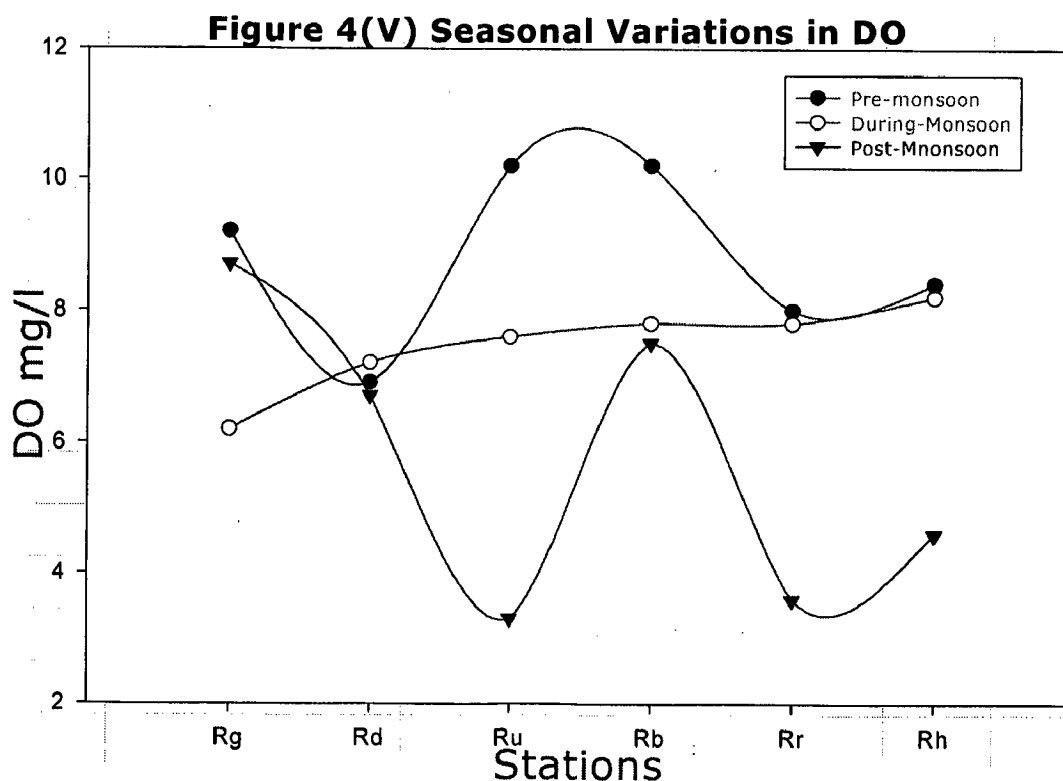
A seasonal DO cycle in which concentrations are lower in the winter months and greater in the summer months (Pre-Monsoon) was observed. This can be attributed to higher stream flow during the summer that

greatly affects reaeration which in turn affects DO values. Moreover, DO concentrations are reduced when an increase in temperature occurs as oxygen saturation levels are temperature dependent. The concentration of DO generally decreased along the Ganga River (downstream) with slight fluctuations near agricultural and urban zones. However, during monsoon period DO almost constant. Seasonal variations are shown by figure 4.2(V).

DO values ranged from 6.9 to 10.2 mg/l (Pre-Monsoon), 6.2 to 8.2 mg/l (During –Monsoon) and 3.3 to 8.7 mg/l (winter). Seasonal dependence of DO was mainly attributed to volume and velocity of water flowing in the river. The organic pollution in the river seemed to be insignificant as evidenced by high values of DO throughout.

Seasonal variation has been displayed significant in accordance with ANOVA table 4.2(VI); spatial variation however, in DO is not significant.

Table 4.2(V) ANOVA table for DO

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	31.37333	2	15.68667	7.585079	0.005866	3.738892
Columns	12.39292	7	1.770417	0.856061	0.561898	2.764199
Error	28.95333	14	2.068095			
Total	72.71958	23				

Monthly variations in DO values for micro- network are shown in figure 4.2(VI) below. DO values lies in the range 7.0 to 10.9 mg/l, 7.3 to 10.7 mg/l, 7.7 to 11.1 mg/l, 3.6 to 8.0 mg/l, 4.6 to 11.6 mg/l for stations R_a, R_b, R_m, R_r and R_h respectively. Variation is observed to increase as one move downstream, with Haridwar station showing maximum variation.

Figure 4.2(VI) Monthly Variations In DO
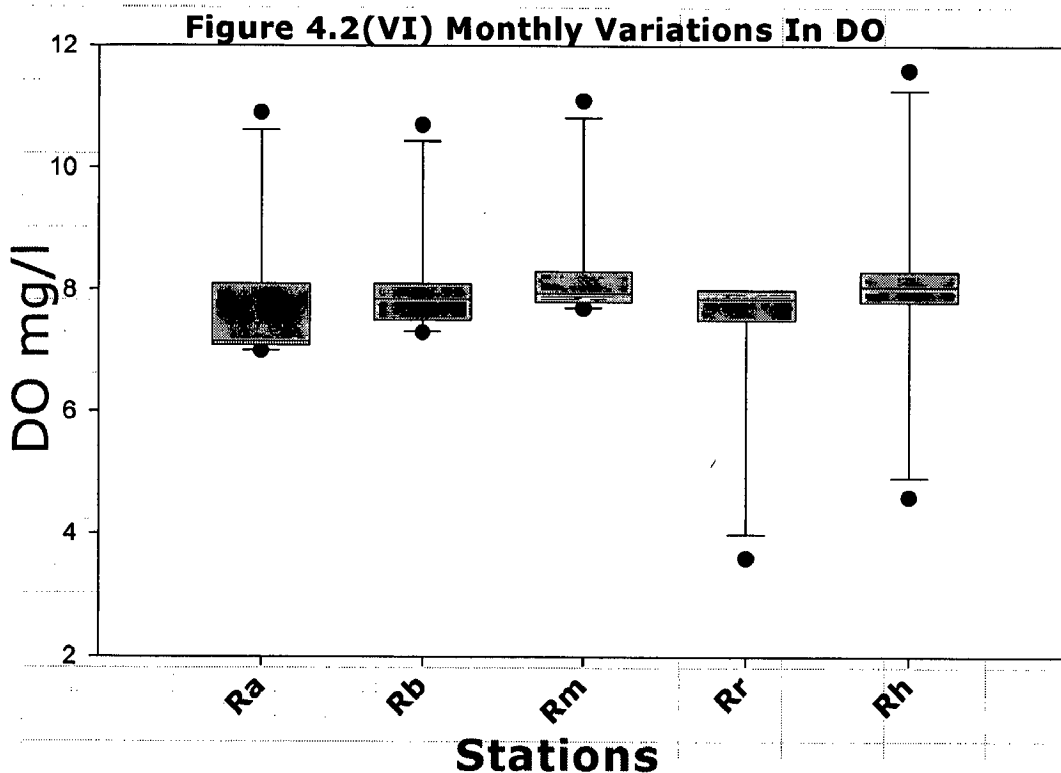
DO values groundwater is shown in Table 4.2 (VI).

Table 4.2 (VI): DO in Ground Water

	Gangotri	Uttarkashi	Rishikesh	Haridwar
Pre-Monsoon	3.2	2.7	10.6	9.4
During Monsoon	3.9	ND	6.6	5.6
Post- Monsoon	3.5	3.3	2.4	4.8

4.2.4 Total Dissolved Solids

Dissolved salts in groundwater can originate from various physical, chemical and biological processes in an aquifer system. The parameter total dissolved solids is an indicator of mineralization of water.

River Water samples show TDS/EC relation ranging in between 0.6 to 0.8 indicates the conductivity increases with dissolution/oxidation-reduction reaction of ion (Drever, 1997).The EC and TDS show very good correlation in all seasons.

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Figure 4.1(VII) Seasonal Variations in TDS
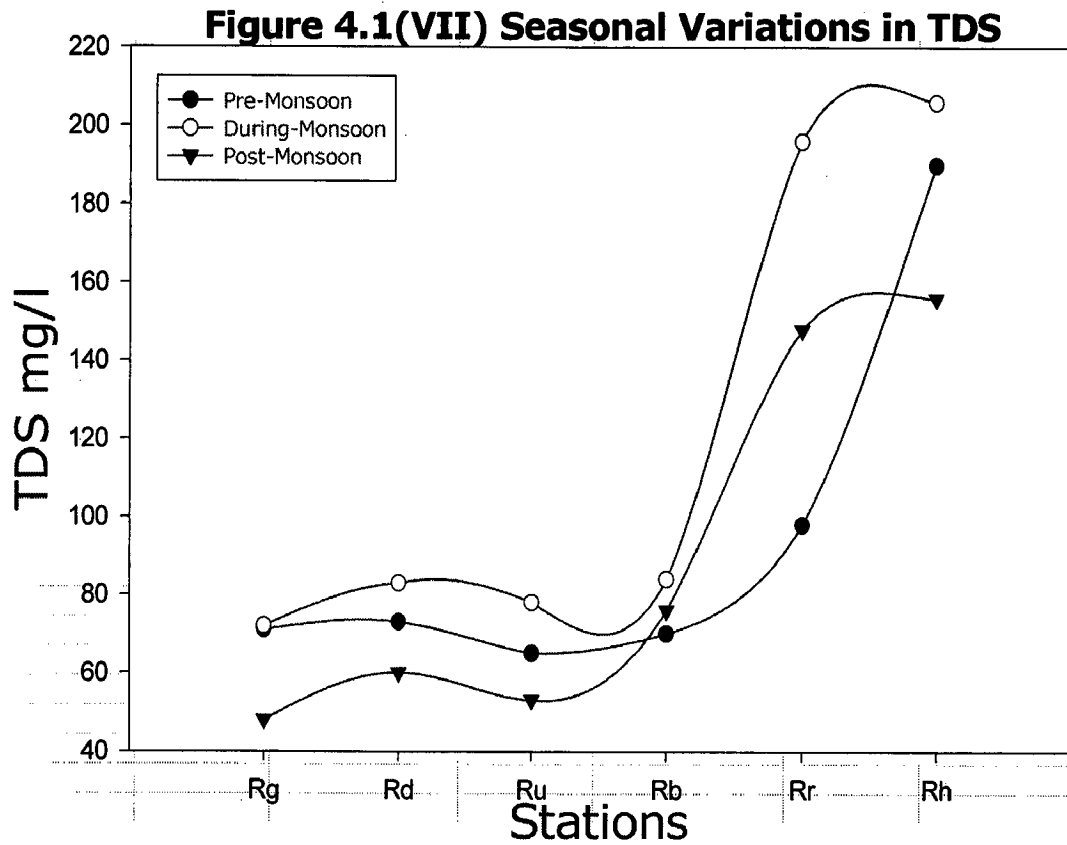
The data indicate an increasing trend in total dissolved solids at the downstream stations. High TDS summer values may be due to flushing of forest litter and soils as snow begins to melt. Trends in spatial and temporal variation are almost same as these of electrical conductivity.

Seasonal variations in TDS values have been observed to be significant in comparison to spatial variations as shown by table 4.2(VII).

Table 4.2(VII) ANOVA table for TDS

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	14435.83	2	7217.914	**6.23432**	0.011582	**3.738892**
Columns	19444.7	7	2777.814	**2.399278**	0.077436	**2.764199**
Error	16208.79	14	1157.771			
Total	50089.32	23				

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Figure 4.2(VIII) Monthly Variations in TDS
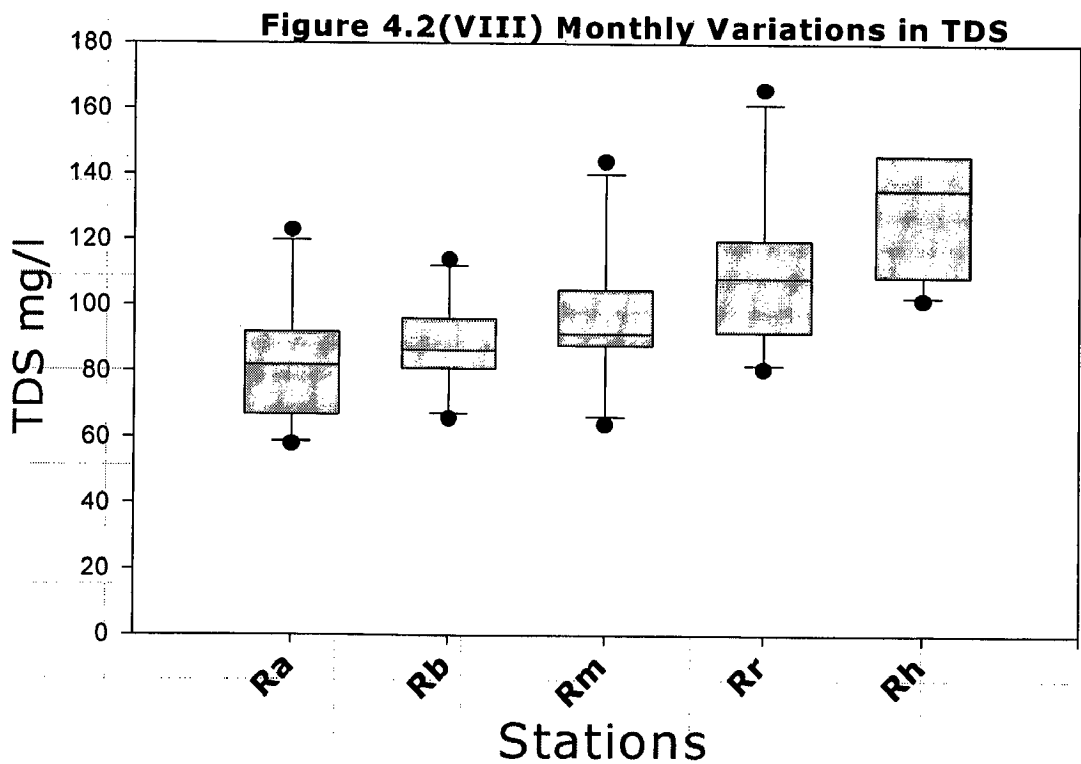
The data exhibit the highest monthly variation in TDS was found at Rishikesh station. However, monthly mean of the data also suggests that an gradual increasing trend was present in the TDS from upstream to downstream. Variation in TDS value of Alaknanda River was high in comparison to Bhagirathhi River at Devprayag and after confluence in Ganga River high TDS values were recoded.

A gradual increase in TDS value of ground water is also observed, as one travels downstream.

Table 4.2 (VIII): TDS in Ground Water

	Gangotri	Uttarkashi	Rishikesh	Haridwar
Pre-Monsoon	170	200	295	428
During Monsoon	149	177	239	243
Post- Monsoon	196	177	209	262

4.2.5 Total Organic Carbon

Total organic carbon (TOC) provides a speedy and convenient way of determining the degree of organic contamination. Two other test methods that offer on organic contamination possible are biochemical oxygen demand (BOD) and chemical oxygen demand (COD). However, TOC provides a more direct expression of the organic chemical content of water than BOD or COD.

Higher value of TOC is recorded in river water during Pre-Monsoon period associated with low flows (dilution) at high temperature and lowest during monsoon period. At station R_g, R_d, R_u and R_b high TOC values recorded during pre-monsoon period indicates flushing of forest litter and soils as snow begins to melt which adds organic materials into river.

Figure 4.2(IX) Seasonal Variations in TOC
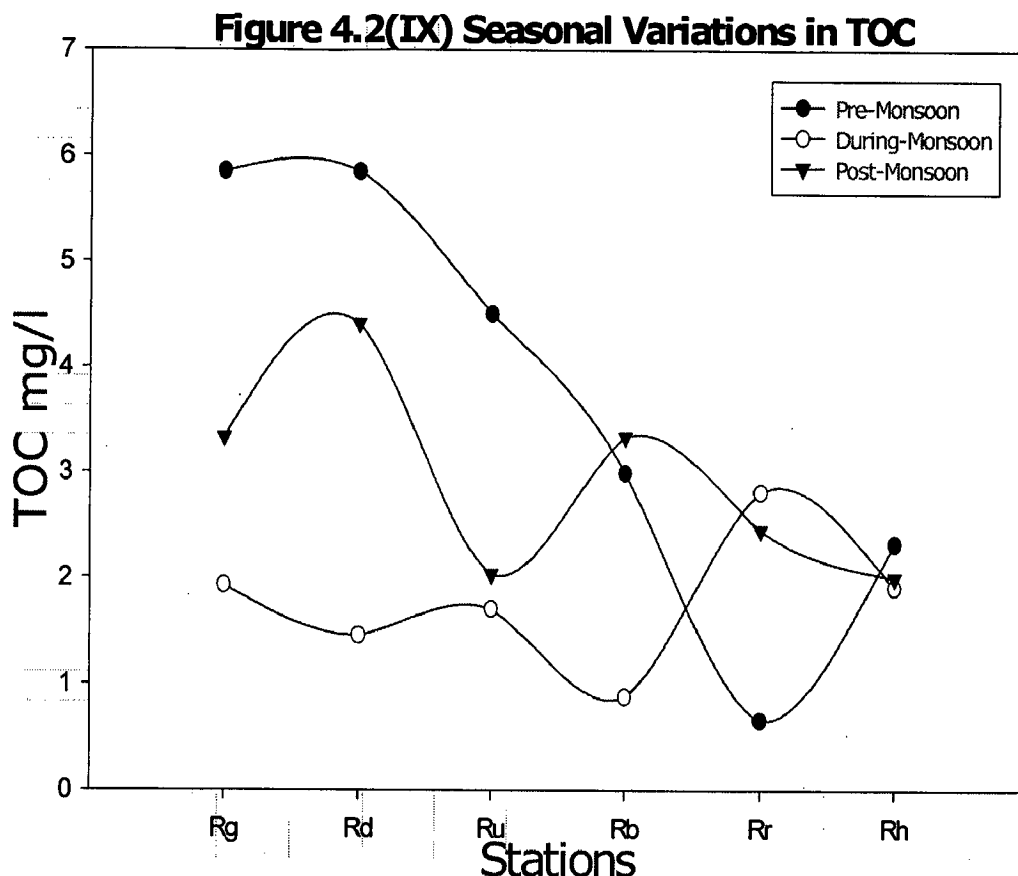
No significant spatial variations were found in the data although good seasonal variations are depicted by the ANOVA table 4.2(IX).

Table 4.2 (IX): ANOVA table for TOC.

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	17.1118	2	8.5559	6.296617	0.011207	3.738892
Columns	10.84946	7	1.549923	1.140648	0.39315	2.764199
Error	19.02333	14	1.358809			
Total	46.98459	23				

For stretch from Devprayag to Haridwar, monthly mean values were observed to be more or less constant around 7.8 as shown by figure 4.2(IV). Maximum variations were reported for Rishikesh site. Monthly TOC values have been found lower in the downstream stations (R_r and

R_h). Values at stations R_a, R_b, R_m, R_r and R_h were recorded between 1.3 to 18.64, 0.88 to 22.69, 1.77 to 23.26, 2.06 to 19.74, 1.91 to 5.07 mg/l respectively. Maximum variations were found near Devprayag.

Figure 4.2(X) Monthly Variations in TOC
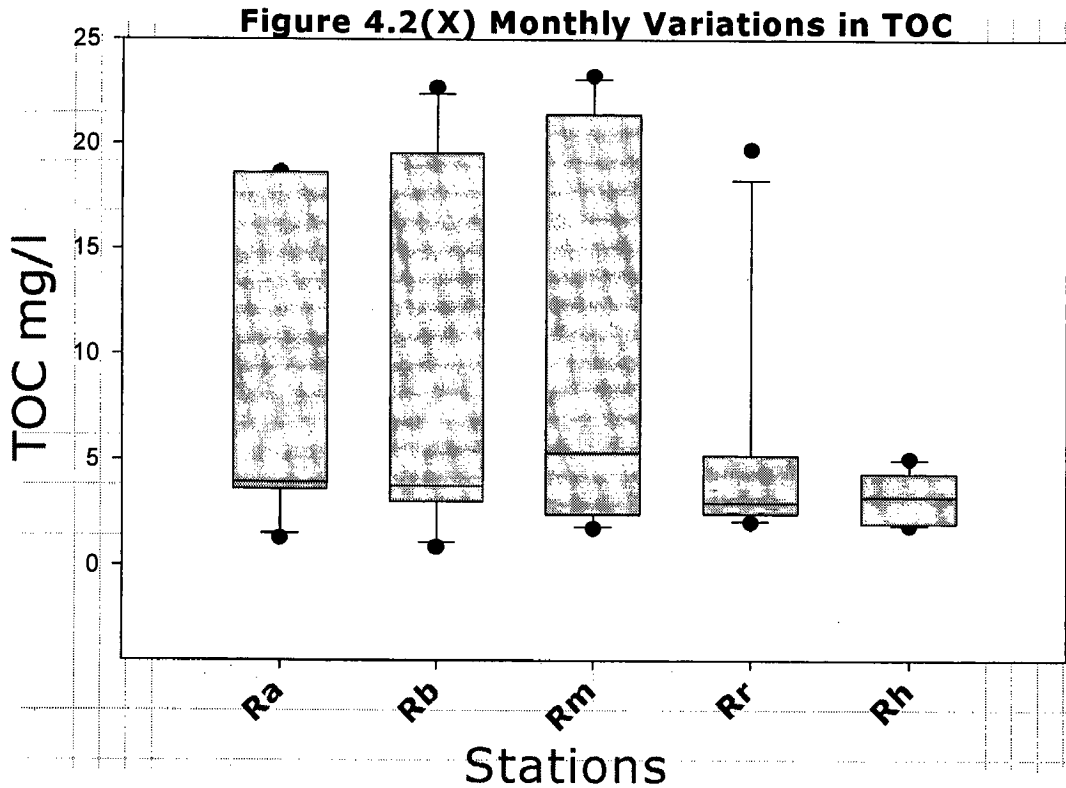
TOC measured in ground water in vicinity of Ganga River were quite low as shown in Table 4.2(X). Few high values however, displayed localized influences.

Table 4.2 (X): TOC in Ground Water

	Gangotri	Uttarkashi	Rishikesh	Haridwar
Pre-Monsoon	2.444	3.02	0.77	2.33
During Monsoon	1.766	5.28	1.29	1.27
Post- Monsoon	4.893	2.15	1.13	1.14

4.2.6 Major Anions
A. Sulphate

Naturally occurring Sulphate are often the result of the breakdown of leaves that fall into a stream, of water passing through rock or soil containing gypsum and other common minerals, or of atmospheric deposition. Point sources include sewage treatment plants and industrial discharges such as tanneries, pulp mills, and textile mills. Runoff from fertilized agricultural lands also contributes sulfates to water bodies.

Figure 4.2(XI) Seasonal Variation in Sulphate
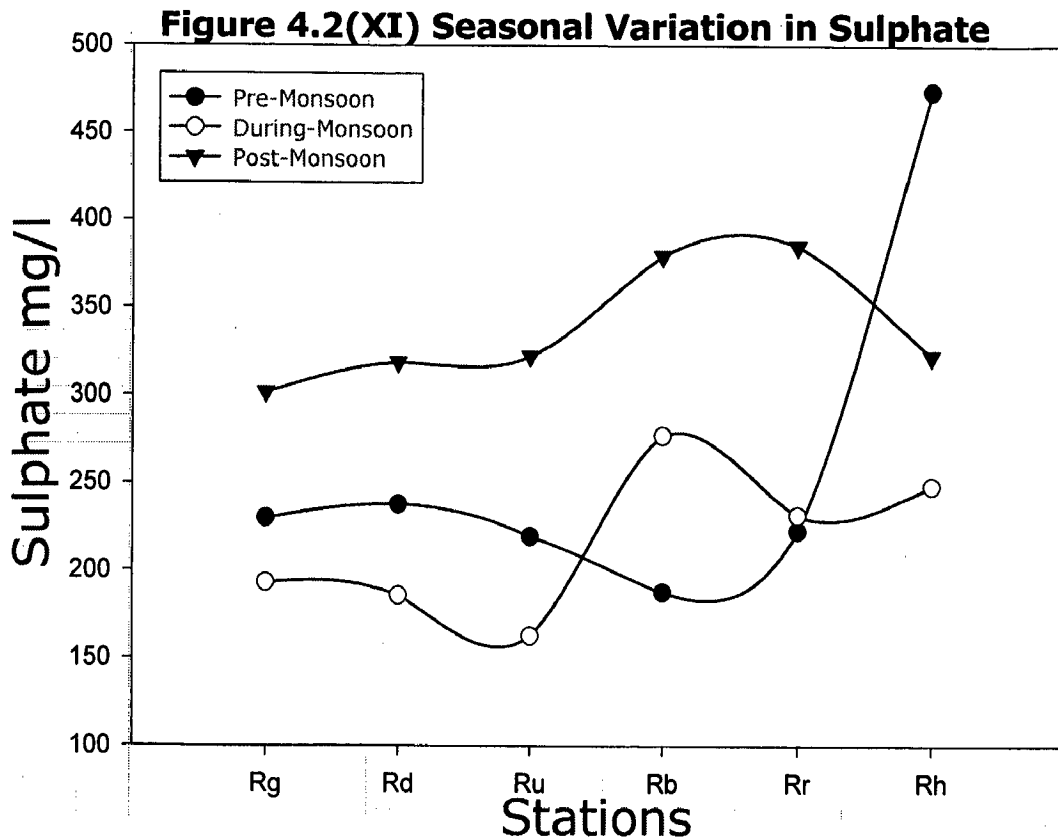
The sulphate concentration in River water ranges from 187.87 mg/l to 473.98 mg/1 (Pre-Monsoon), 166.62 mg/l to 281.26 mg/l (Post-Monsoon) and 485.10 mg/l to 579.33 mg/l (winter). The seasonal variation is occurring due to dilution of River water in various proportions with rainwater (Rajamohan et.al. 2004). The geology of region is other source responsible for high concentration of sulphate in post-monsoon in comparison to winter and pre-monsoon in River water due to leaching with rainwater.

Highly significant Variation is observed in seasonal sulphate values; however, spatial variations are not very significant in accordance to ANOVA table 4.2(XI).

Table 4.2(XI) ANOVA table for sulphate

ANOVA						
Source of Variation	SS	df	MS	F	P-value	F crit
Rows	64111.56	2	32055.78	15.84744	0.000253	3.738892
Columns	15961.48	7	2280.212	1.12727	0.400013	2.764199
Error	28318.83	14	2022.773			
Total	108391.9	23				

Figure 4.2(XII) Monthly Variations in Sulphate
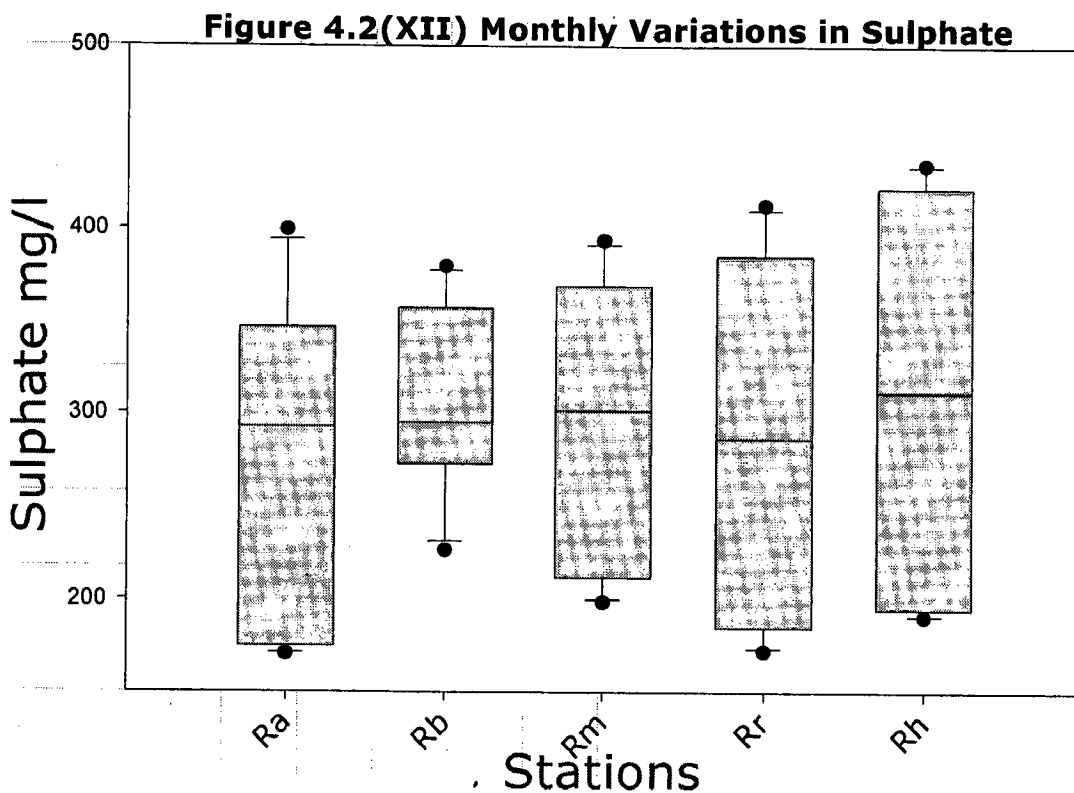
Groundwater shows relatively high sulphate values than river water due to reason that in groundwater, the sulphate concentration increases by ion exchange or oxidation-reduction processes taking place in groundwater aquifer system shown in table 4.2(XII). Sulphate was the predominant anion in Ganga River.

Table 4.2 (XII): Sulphate in Ground Water

	Gangotri	Uttarkashi	Rishikesh	Haridwar
Pre-Monsoon	239.12	231.85	258.61	198.9
During Monsoon	140.01	192.84	187.78	233.56
Post- Monsoon	389.35	331.22	392.17	363.69

B. Chloride

Chloride is an indicator of sewage, animal wastes, and road salt. It is present in all potable water supplies and in sewage, usually as a metallic salt. Chloride ion almost constant throughout the river stretch for a particular season, works as an ideal tracer. The high chloride concentrations were observed during monsoon season because of dissolution of chloride salt present in the rocks (Shivaliks series). The chloride concentration ranges from 5 to 10 mg/l (Pre-monsoon), 17 to 25 mg/l (During monsoon) and 9 to 39 mg/l (Post-monsoon).

Figure 4.2(XIII) Seasonal Variation in Chloride
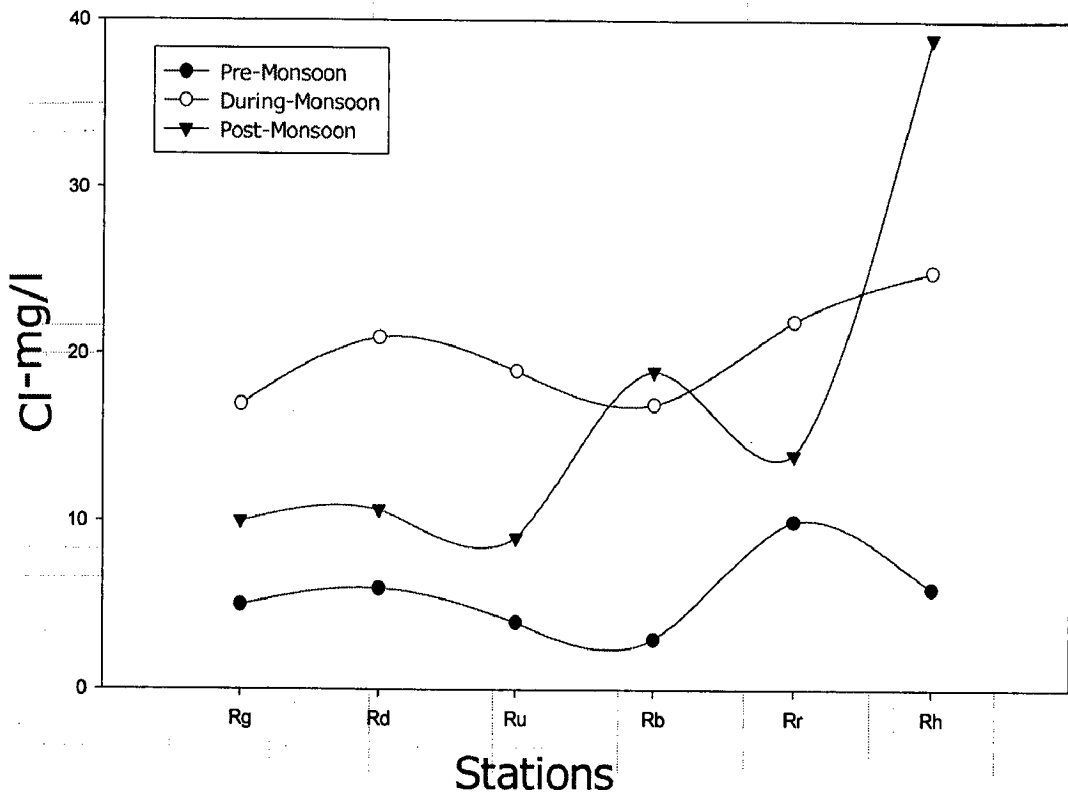
ANOVA table 4.2(XIII) shows significant seasonal variations.

Table 4.2(XIII) ANOVA table for chloride

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	1044.56	2	522.2801	17.64897	0.000149	3.738892
Columns	345.1237	7	49.30339	1.666067	0.197049	2.764199
Error	414.2975	14	29.59268			
Total	1803.981	23				

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Figure 4.2(XIV) Monthly Variations In Chloride
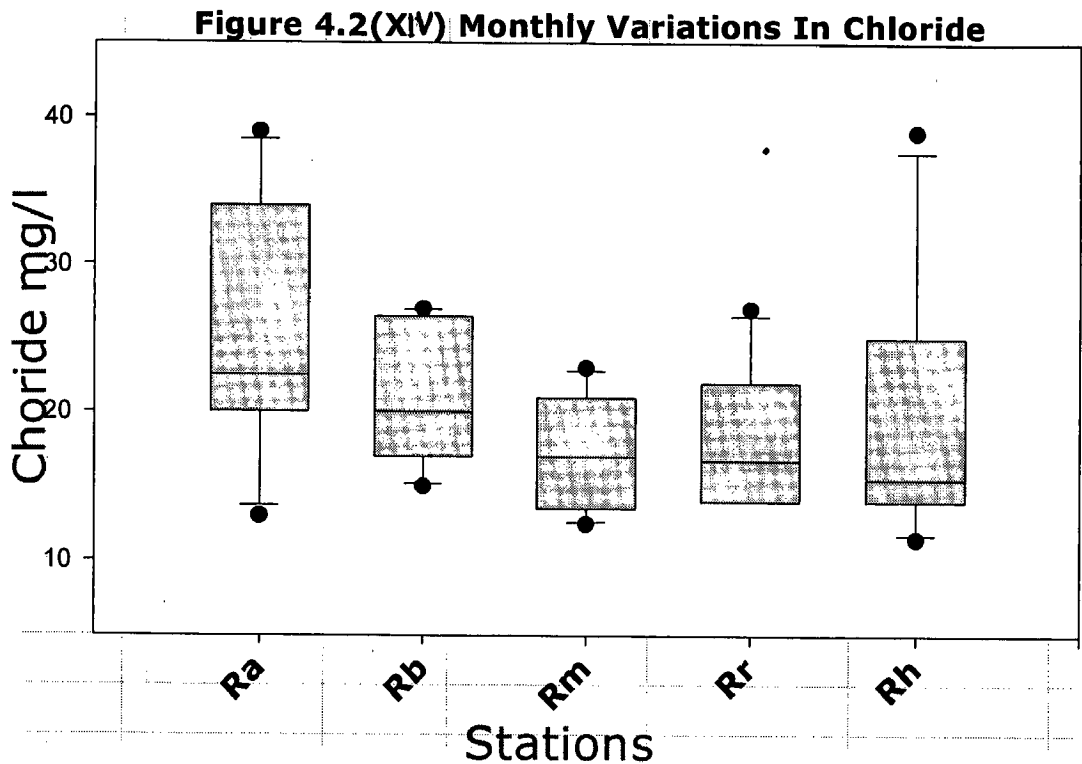
Figure 4.2(XIV) shows monthly variations in chloride. Monthly mean of chloride was calculated 25.2, 20.92, 17.33, 18.42, 20.10 mg/l for stations R_a, R_b, R_m, R_r and R_h respectively. Monthly variations in Chloride concentration have been observed to be significant, which may be due to variation in discharge of river is different for different months

There are very less known natural sources of chloride, hence it is one of the good indicator of anthropogenic inputs like agricultural waste and domestic sewage in the downstream stations like R_r (Rishikesh) and R_h (Haridwar), where slightly high values of chloride concentration were observed. Groundwater chloride concentration is shown in table 4.2(XIV). In the mountainous stretch, low chloride values mainly reflected the presence of evaporites. In the stretch through the plains, however, point and non-point discharge served as their main source.

Table 4.2 (XIV): Chloride in Ground Water

	Gangotri	Uttarkashi	Rishikesh	Haridwar
Pre-Monsoon	8.5	8	3	7.5
During Monsoon	28.0	27	23	28
Post- Monsoon	20.0	22	12	18

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C. Nitrate

The major source of nitrate in surface water is nitrification of organic matter, run off from the agricultural field, animal wastage and industrial discharge.

High nitrate concentrations have been observed in Pre-monsoon and Post Monsoon periods as shown in Figure 4.2(xv). This is most likely the result of runoff after fertilizer application during the fall season. Likewise, nitrate concentrations increase from upstream to downstream due to industrial discharge and runoff from agricultural fields to the river in downstream stations.

Figure 4.2(XV) Seasonal Variations in Nitrate
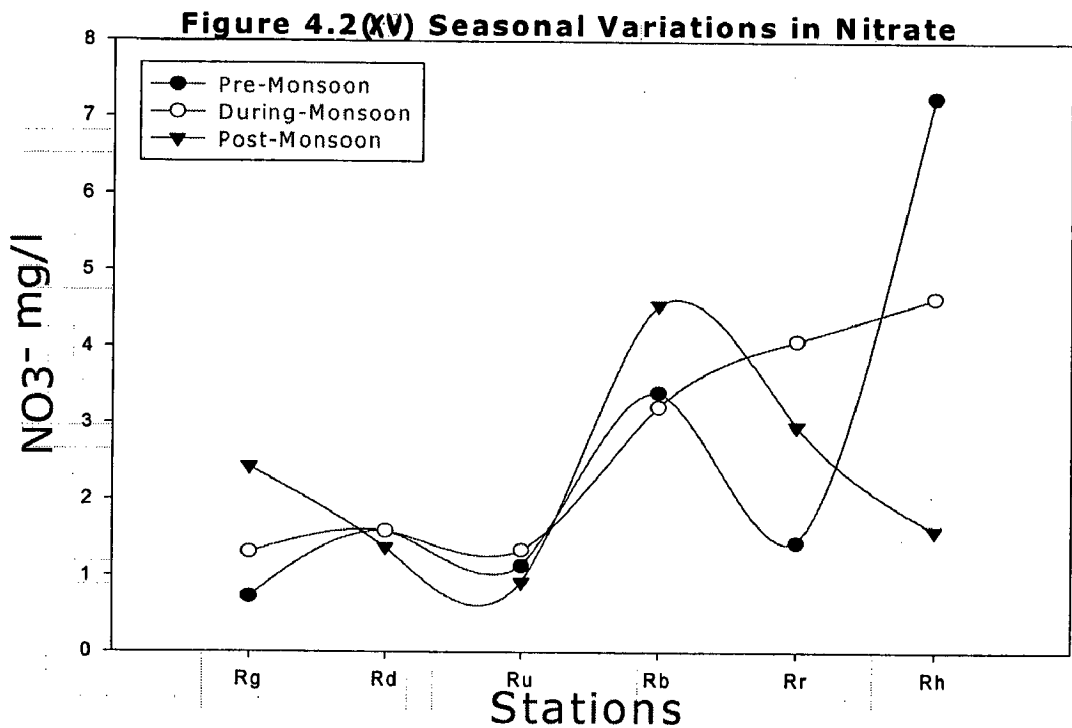
There are no apparent seasonal variations in nitrate. However spatial variations in nitrate are significant.

Table 4.2(xv) ANOVA table for Nitrate

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	0.248192	2	0.124096	**0.0677**	0.9349	**3.7389**
Columns	31.64534	7	4.520764	**2.4657**	0.0714	**2.7642**
Error	25.66896	14	1.833497			
Total	57.56249	23				

Monthly Variation in Nitrate values are shown in Figure 4.2(xv) shows that variations near Haridwar and Devprayag (Bhagirathhi) are much more than compared to other stations. Values range from 1.36 to 3.80 mg/l,

1.06 to 4.56 mg/l, 1.25 to 2.98 mg/l, 0.995 to 4.09 mg/l and 1.60 to 4.66 mg/l from Devprayag to Haridwar stations shown by figure 4.2(XVI).

Figure 4.2(XVI) Monthly Variations In Nitrate
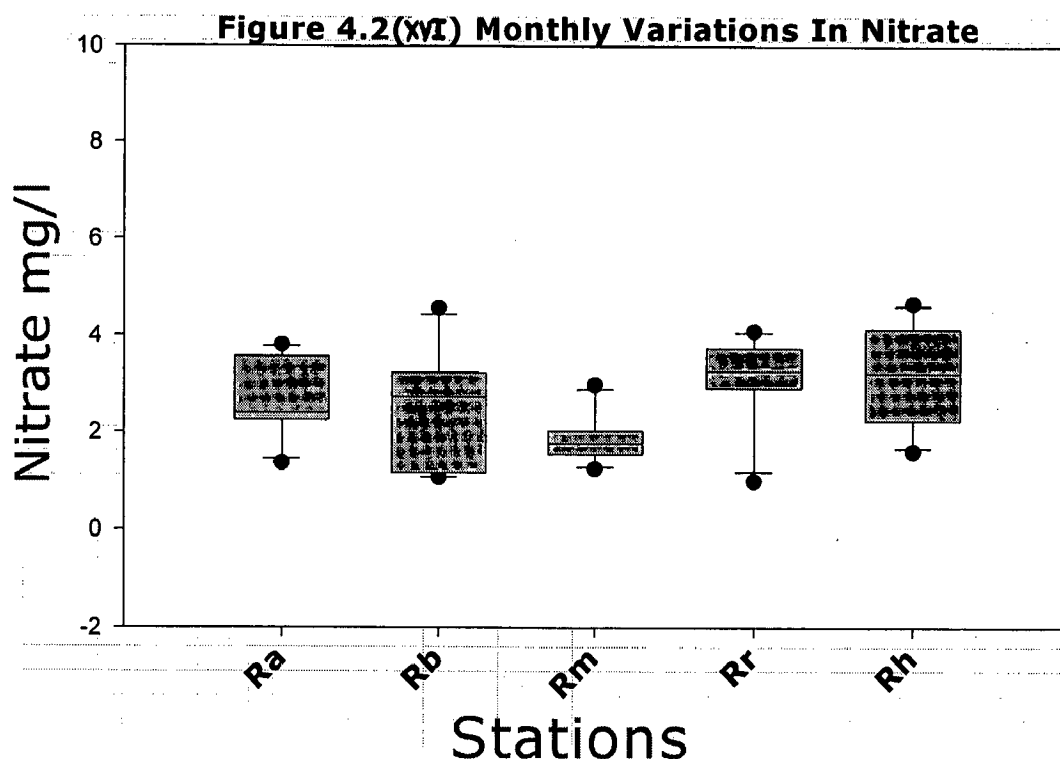
Table 4.2(XVI) shows nitrate concentration in groundwater which is high at stations Rishikesh and Haridwar during monsoon season, indicating the influences of leachates from damped organic waste.

Table 4.2 (xvi): Nitrate in Groundwater

	Gangotri	Uttarkashi	Rishikesh	Haridwar
Pre-Monsoon	4.91	1.19	4.36	2.63
During Monsoon	11.2	12.1	13.8	9.2
Post- Monsoon	4.61	2	3.03	6

D. Bicarbonate

Alkalinity/ Bicarbonates are a measure of water's capacity to neutralize an acid. It is an important property because it can reverse natural and human caused changes in pH. The bicarbonate ion showed a relatively strong seasonal and spatial effect, as well as increasing trend from Gangotri to Haridwar stations. Bicarbonate ion concentration changes with increase in

50
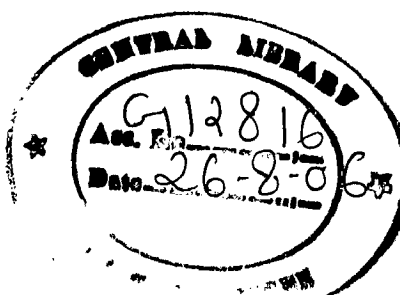
distance from the source, due to continuous chemical weathering of limestone and sedimentary rocks in the Ganga River catchment.

Figure 4.2(XVII) Seasonal Variations in Bicarbonate
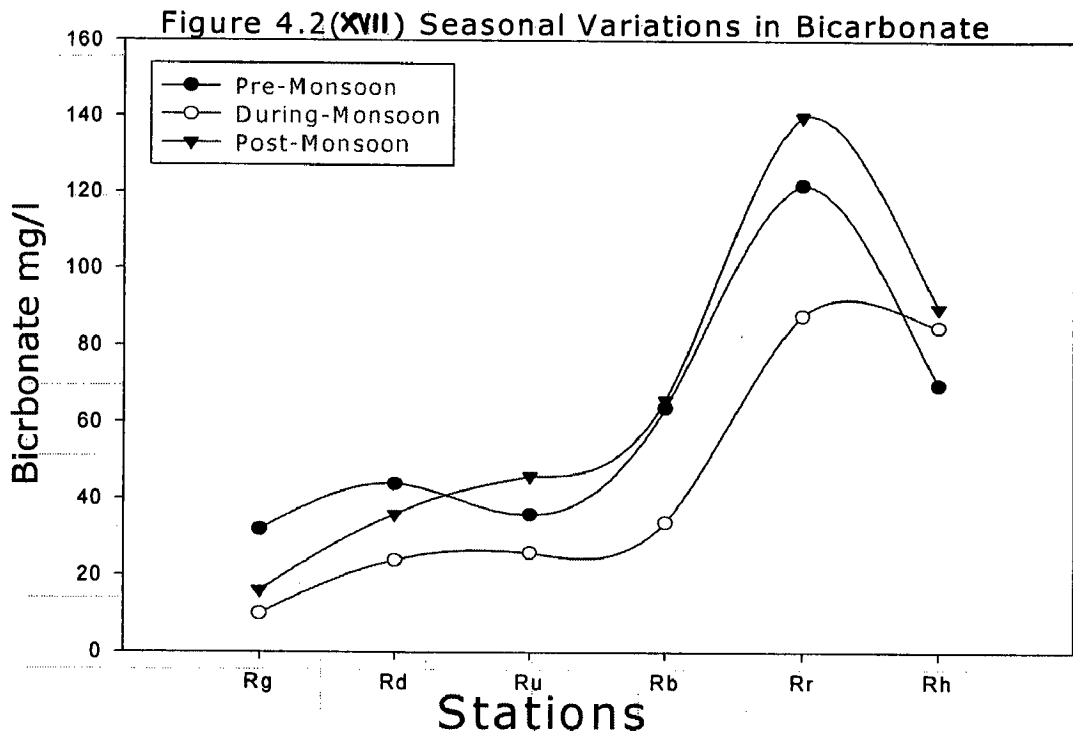
The concentration of bicarbonate varies from 32 to 122 mg/l (Pre-monsoon), 10 to 88 mg/l (During monsoon) and 16 to 140mg/l (post-monsoon). An appreciable increase in bicarbonates between Devprayag and Rishikesh during the pre and post-monsoon season indicated possible recharge through carbonaceous shales present in the Shivaliks encountered only in this stretch. Figure 4.2(XVII) shows that very high values recorded for station R_r (Rishikesh), probably due to mixing of a tributary (Chandrabhaga) before sampling location, having high bicarbonate concentration.

ANOVA table 4.2(xvii) also verifies strong seasonal and spatial variation in River water.

Table 4.2(xvii) ANOVA table for Bicarbonate

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	2057.583	2	1028.792	**9.971557**	0.002031	**3.738892**
Columns	19598.96	7	2799.851	**27.13754**	4.16E-07	**2.764199**
Error	1444.417	14	103.1726			
Total	23100.96	23				

Wide ranges of monthly variations were seen in bicarbonate at all stations. At sites Rishikesh and Haridwar bicarbonate values were high due to geology of the area, since the major source of bicarbonate is natural processes.

Figure 4.2(XVIII) Monthly Variations in Bicarbonate
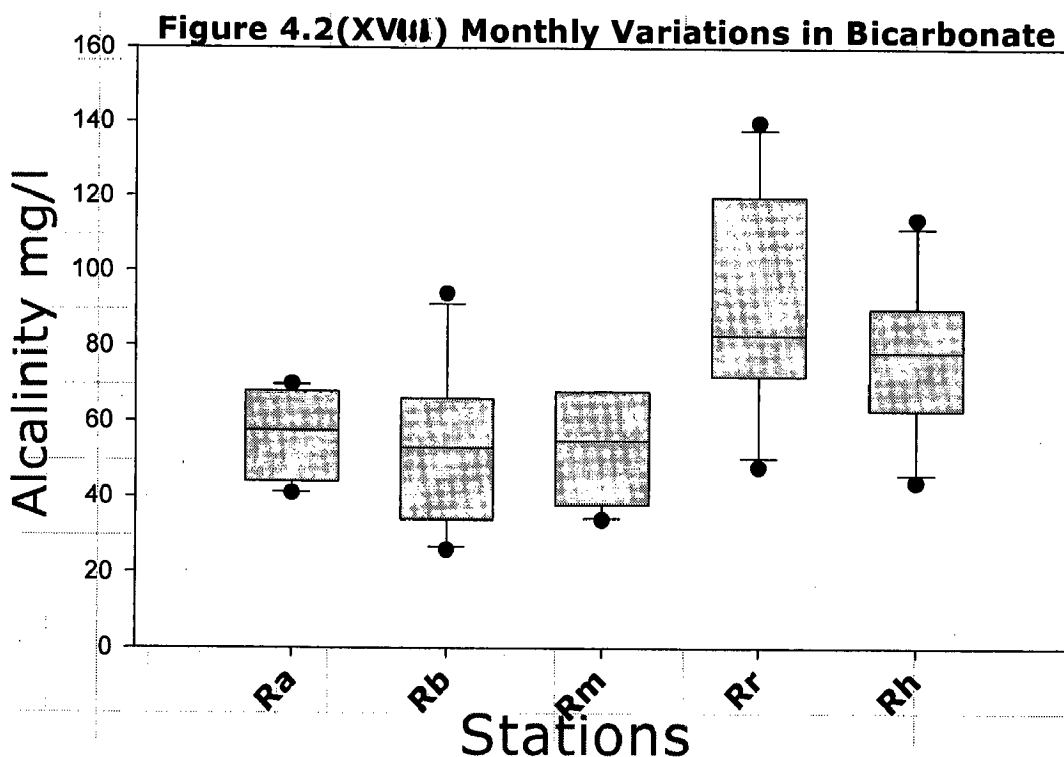
Groundwater in the vicinity of Ganga River had high bicarbonate concentration, indicates geological formation of Ganga catchment as limestone and calcite.

Table 4.2 (XVIII): Bicarbonates in Groundwater

	Gangotri	Uttarkashi	Rishikesh	Haridwar
Pre-Monsoon	42	116	170	102
During Monsoon	34	94	BDL	10
Post- Monsoon	38	118	158	134

4.2.7 Major Cations
A. Calcium
Calcium salts and calcium ions are among the most commonly occurring in nature. They may result from the leaching of soil and other natural sources or may come from man-made sources such as sewage and some industrial wastes. Calcium is usually one of the most important contributors to hardness.

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The river water is moderately hard with calcium 9 to 33 mg/l (Pre-Monsoon), 12 to 32 mg/l (During Monsoon) and 9 to 39 mg/l respectively. Increase in the value of Ca^{++} on the temporal scale may be due to concentration-dilution effect related to climate. Calcium was predominant anion in Ganga River.

Figure 4.2(XIX) Seasonal Variations in Ca^{++}
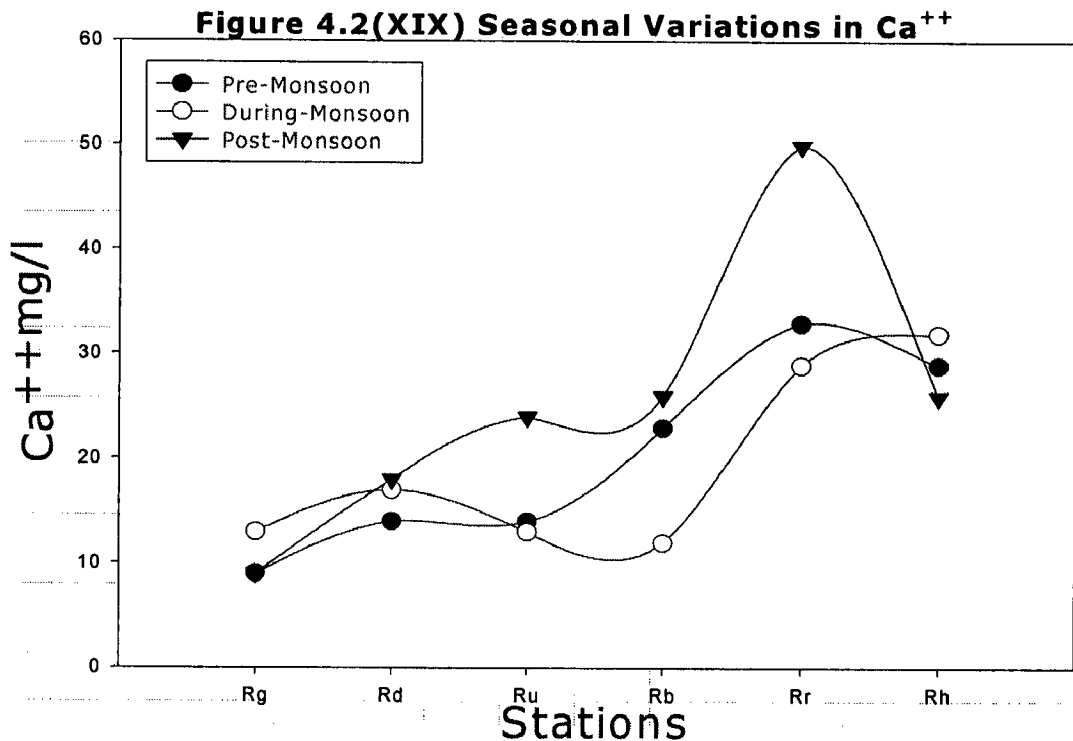
ANOVA table 4.2(XIX) shows significant spatial variations in bicarbonate concentration.

Table 4.2(XIX) ANOVA table for Calcium

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	100.334	2	50.167	0.952993	0.409234	3.738892
Columns	1609.186	7	229.8838	4.366968	0.009182	2.764199
Error	736.981	14	52.6415			
Total	2446.501	23				

Figure 4.2(XX) Monthly Variations in Ca^{++}
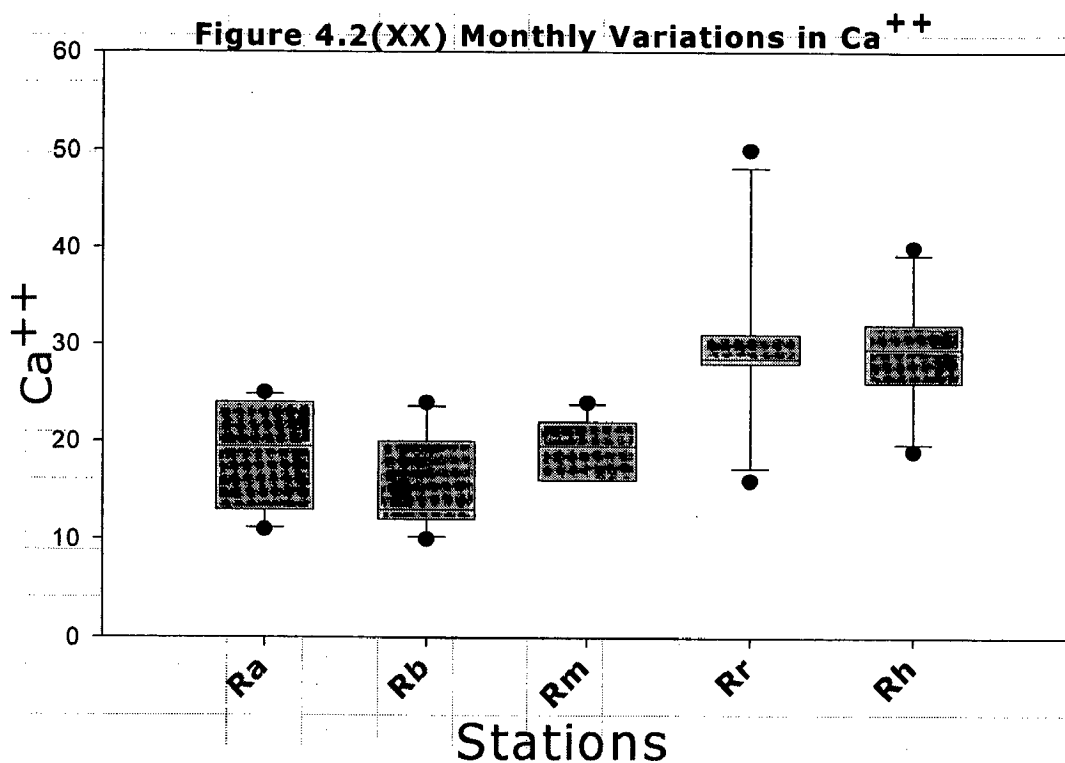
According to table 4.2(XX) and figure 4.2(XIX) calcium was the predominant cation in surface-water and in the ground-water samples indicates the geology of study area is limestone.

Table 4.2 (XX): Calcium in Ground Water

	Gangotri	Uttarkashi	Rishikesh	Haridwar
Pre-Monsoon	23	26	49	39
During Monsoon	16	31	31	33
Post- Monsoon	18	24	46	61

B. Magnesium

Magnesium is widely distributed in ores and minerals. Magnesium ions contribute to water hardness. The Mg^{++} ion concentration shows similar as calcium ion because of same natural origin, but spatial distribution of magnesium shows anthropogenic inputs. High magnesium values are recorded for monsoon.

Figure 4.2(XXI) Seasonal Variations in Mg^{++}

S
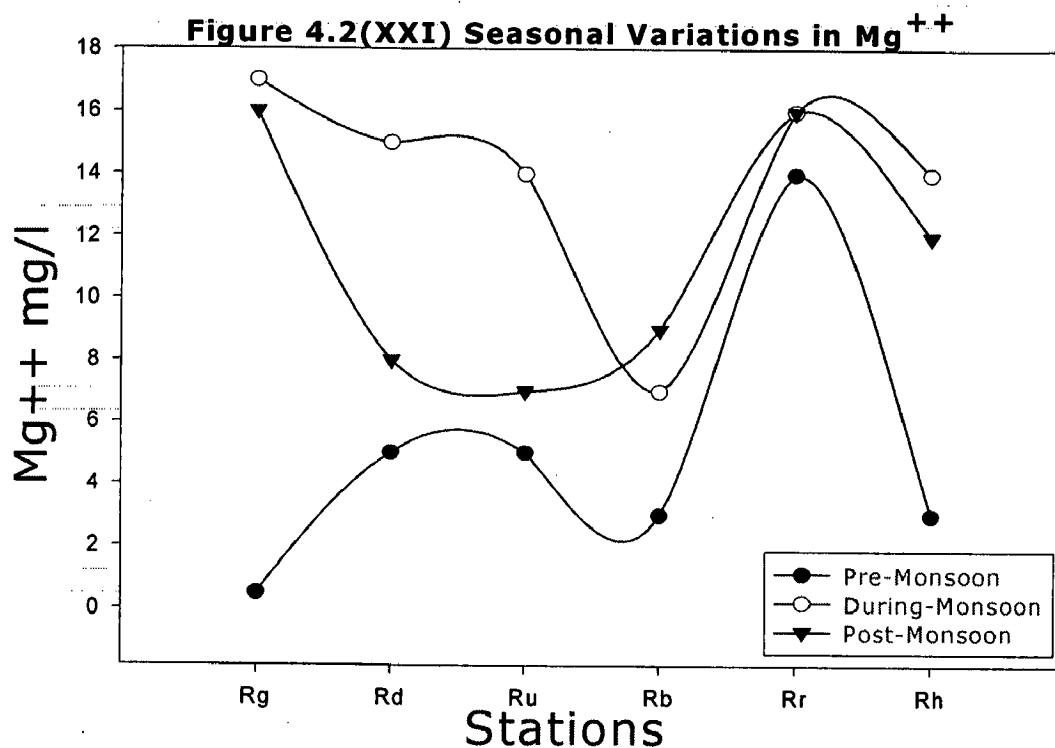
patial variations are significant according to the ANOVA table 4.2(XXI).

Table 4.2(XXI) ANOVA table for Magnesium

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	313.0044	2	156.5022	16.12537	0.000233	3.738892
Columns	132.3947	7	18.91352	1.948775	0.136422	2.764199
Error	135.8748	14	9.705342			
Total	581.2738	23				

Wide ranges of monthly variations were shown by figure 4.2(XXII) for each stations of Magnesium ion. Monthly mean are 8.33 mg/l, 6.33 mg/l, 6.83mg/l, 9.8333 mg/l and 10.8333 mg/l respectively at each station shown above from Devprayag to Haridwar.

Figure 4.2(XXII) Monthly Variation in Mg++

Figure 4.2(XXII) Monthly Variation in Mg++
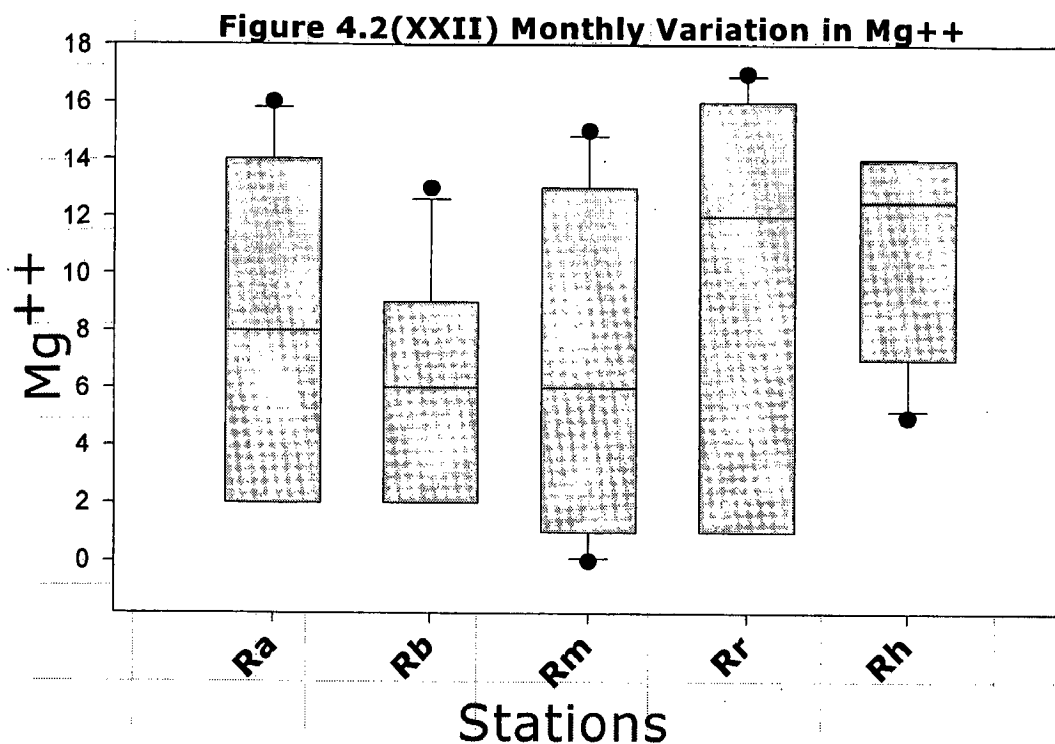
Magnesium ion concentration also varies seasonally in ground water which may be attributed to dilution of ground water in various proportions with rainwater (Rajamohan et. al. 2004).

Table 4.2 (XXII): Magnesium of Ground Water

	Gangotri	Uttarkashi	Rishikesh	Haridwar
Pre-Monsoon	2	3	18	4
During Monsoon	19	21	19	16
Post- Monsoon	3	2	13	13

C. Sodium

The higher concentration of Na during the high discharge period near the glacial portal source region like at Gangotri and Dabrani may also be explained on the basis of greater availability of freshly derived suspended sediments. High concentration of Na in River may be due to quick dissolution of suspended bound ions, which may increase the ionic concentration during the monsoon period.

Figure 4.2(XXIII) Seasonal Variations in Na⁺
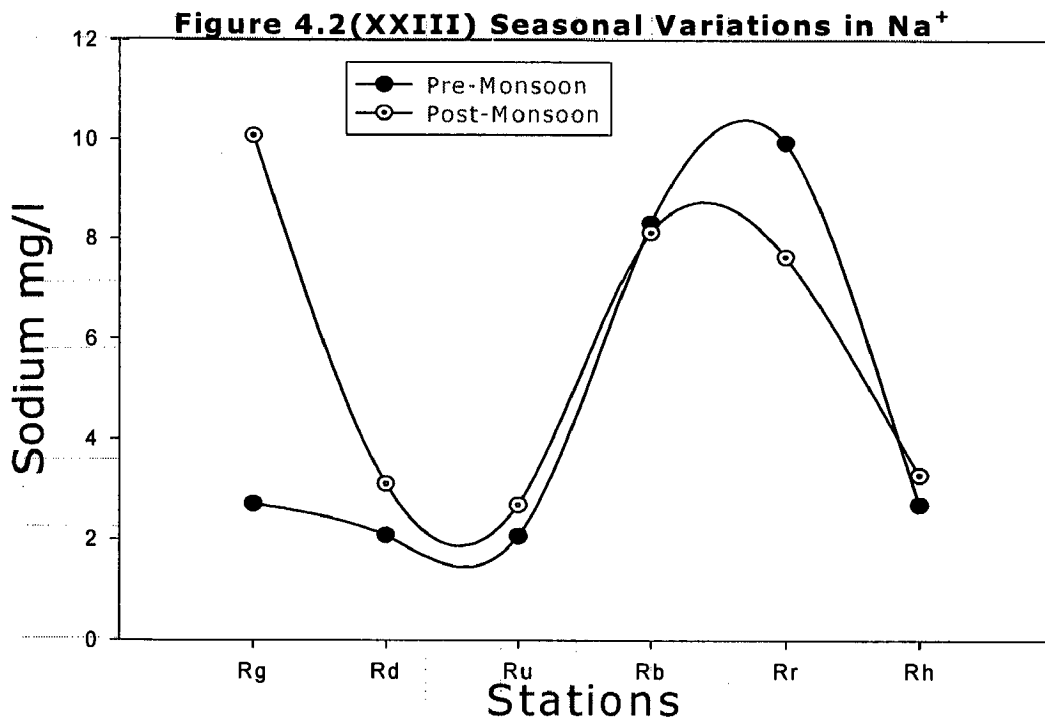
According to ANOVA table spatial variations are significant.

Table 4.2(XXIII): ANOVA table for Sodium

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	7.95381	1	7.95381	2.020167	0.198205	5.591448
Columns	115.348	7	16.47828	4.185275	0.0392	3.787044
Error	27.56043	7	3.937204			
Total	150.8622	15				

High concentration of Na ion was reported near Uttarkashi Ground-water shown in the figure, which is reflected in the Ganga river water near this station. However, variations in ground water inputs of sodium salt by anthropogenic source like leaching of pollutant from landfill (Table 4.2(XXIV).

Table 4.2 (XXIV): Sodium in Ground Water

	Gangotri	Uttarkashi	Rishikesh	Haridwar
Pre-Monsoon	1.235	10.295	7.96	3.443
Post- Monsoon	4.835	10.82	8.425	2.888

D. Potassium

The concentration of K registered a higher concentration during the higher discharge period (Pre-Monsoon).Potassium is commonly fixed in specific clay minerals, after being released during primary weathering reactions and therefore does not behave in the same way as other weathering derived ions (Stott and Burt, 1997). Availability of fresh abraded and fine suspended sediments resulting from glacial erosion and mass movement during high flow may play an important role in acquisition of K ion.

Figure 4.2(XXIV) Seasonal Variations in K^+
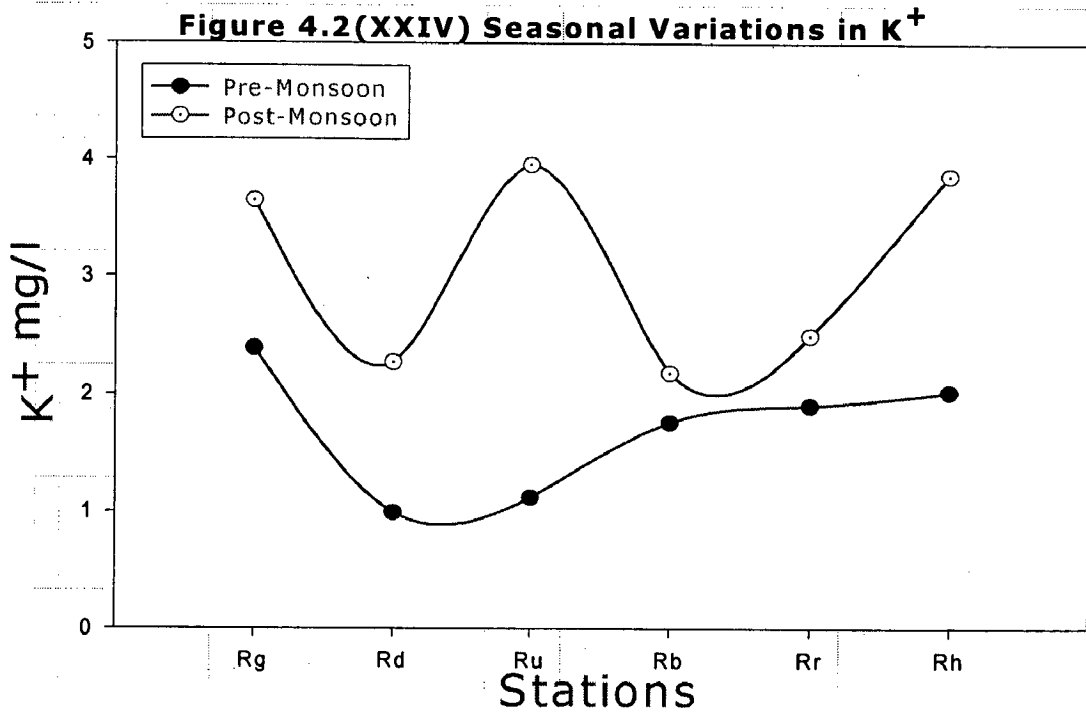
Seasonal variations in is verified by ANOVA table 4.2(XXV).

Table 4.2(XXV) ANOVA table for Potassium

Source of Variation	SS	df	MS	F	P-value	F crit
Rows	4.557158	1	4.557158	10.5272	0.014163	5.591448
Columns	3.042869	7	0.434696	1.004163	0.497884	3.787044
Error	3.030256	7	0.432894			
Total	10.63028	15				

Seasonal variation in potassium ion concentration may be attributed to dilution of ground water in various proportions with rainwater.

Table 4.2 (XXVI): Potassium in Ground Water

	Gangotri	Uttarkashi	Rishikesh	Haridwar
Pre-Monsoon	1.997	2.66	1.9	0.815
Post- Monsoon	2.365	3.025	2.265	1.87

4.2.3 Heavy Metals

Table 4.2(XXVII): Heavy Metal Concentration

Metal	Conc. Range (mg/l)
Iron	0.034 – 1.088
Magnesium	0.01- 0.06
Cadmium	0.001- 0.008
Chromium	BDL
Nickel	0.02- 0.15
Zinc	0.01- 0.9

Six heavy metals investigated, Zn, Fe, Cd, Mn, Ni and Cr, were found to be present in the river water. The concentration of dissolved metals was found within WHO permissible limits. No anthropogenic heavy metal pollution source could be identified in the entire region. The main reason appeared to be the geochemical cycling of rocks and soils. In the mountainous stretch, the river flows through complex rock assemblages so these metals still present in the Ganga River Water. In the lower stretch, an additional source could be agricultural runoff containing trace metals from fertilizers applied to the soil. However, little is known about it presently due to lack of geological information and experimental measurement.

4.3 Association between Isotopic and Water Quality Parameters

Dissolved oxygen, Bicarbonate, Nitrate, sulphate were measured as a water quality parameter and ^{18}O of the river water as isotopic parameter was also measured. As all of these parameters composed of oxygen as a constituent, so it was believed that their must be some correlation between these parameters.

Correlation matrix is shown in table 4.3(I) for pre-monsoon and table 4.3(II) for during monsoon period. In post monsoon period $\delta^{18}O$ values exhibit good correlation with EC, Total hardness and bicarbonates, that clearly indicates the good contribution of ground water in the river. The bicarbonate of the river water also increases during the post monsoon period in comparison to the monsoon period and it has also good correlation with $\delta^{18}O$ during post monsoon that again confirm the contribution of mineralized ground water to the river during post monsoon period.

Table 4.3(I) Correlation coefficient of measured parameter in post monsoon samples

	EC	pH	DO	Total Hardness	Chloride	Sulphate	Nitrate	Bicarbonate	TOC	TDS	Ca++	Mg++	O-18
EC	1.00												
pH	-0.19	1.00											
DO	-0.28	0.17	1.00										
Total Hardness	0.29	-0.42	-0.82	1.00									
Chloride	0.82	-0.27	-0.08	-0.08	1.00								
Sulphate	0.51	0.09	-0.28	0.39	0.04	1.00							
Nitrate	0.35	0.27	0.48	-0.28	0.11	0.66	1.00						
Bicarbonate	0.84	-0.13	-0.57	0.67	0.40	0.73	0.27	1.00					
TOC	-0.39	0.15	0.59	-0.56	-0.35	-0.02	0.25	-0.43	1.00				
TDS	0.98	-0.22	-0.35	0.34	0.79	0.54	0.31	0.86	-0.35	1.00			
Ca++	0.25	-0.18	-0.92	0.94	-0.10	0.39	-0.35	0.66	-0.60	0.30	1.00		
Mg++	0.18	-0.73	-0.06	0.53	0.01	0.12	0.08	0.28	-0.11	0.23	0.19	1.00	
O-18	0.80	0.02	-0.65	0.65	0.38	0.73	0.23	0.98	-0.49	0.82	0.70	0.10	1.00

Table 4.3(II) Correlation coefficient of measured parameters in during monsoon samples

	EC	pH	DO	Total Hardness	Chloride	Sulphate	Nitrate	Bicarbonate	TOC	TDS	Ca++	Mg++	O-18
EC	1.00												
pH	0.46	1.00											
DO	0.26	-0.44	1.00										
Total Hardness	0.56	0.43	0.20	1.00									
Chloride	0.52	0.01	0.61	0.80	1.00								
Sulphate	-0.28	-0.24	0.62	0.04	0.19	1.00							
Nitrate	0.29	-0.20	0.57	0.49	0.60	0.47	1.00						
Bicarbonate	0.34	-0.23	0.69	0.70	0.80	0.42	0.87	1.00					
TOC	0.41	0.44	0.07	0.85	0.46	-0.02	0.30	0.56	1.00				
TDS	0.97	0.37	0.38	0.55	0.62	-0.19	0.27	0.36	0.33	1.00			
Ca++	0.54	0.18	0.53	0.89	0.87	0.32	0.80	0.90	0.68	0.55	1.00		
Mg++	0.31	0.60	-0.42	0.68	0.29	-0.44	-0.25	0.03	0.70	0.28	0.27	1.00	
O-18	-0.11	-0.63	0.68	0.13	0.33	0.37	0.54	0.70	0.27	-0.10	0.39	-0.33	1.00

CHAPTER FIVE

CONCLUSIONS AND SCOPE OF FUTURE WORK

Present study, isotopic and water quality characterization of Ganga River, reveals many unanswered questions about the river catchment and gives suitable understanding about the river behavior during different seasons and at different locations. Following conclusions were noted from this study.

5.1 Conclusions

- $\delta^{18}O$ and δD values have been different at different locations. The variations observed due to (i) altitude effect in precipitation (ii) snowmelt contribution at upper reaches.

- The temporal variations also been observed at different time at each location, due to contribution from different sources like snowmelt runoff, precipitation runoff and ground water. Temporal variation may be due to reason of amount effect in precipitation.

- $\delta^{18}O$ and δD value reveals that snowmelt contribution is maximum in the month of September i.e. while ground water contribution is maximum in winter month particularly in the month of December.

- The altitude effect in precipitation is -.21 $^o/_{oo}$ per meter, which is well within the expectable limits (-0.10 to -0.40 $^o/_{oo}$ per meter). However, this requires further investigations and comparison with the altitude effect to be estimated from precipitation data.

- The minimum $\delta^{18}O$ value (-15.35 $^o/_{oo}$) is obtained at Gangotri while progressively enrichment while moving downstream, indicating the increase in contribution of ground water.

- There is considerable contribution of snowmelt runoff in Bhagirathhi that appears at site Devprayag in Ganga River however, its effect diminishes considerably as we move more downwards.

- Most of the ions show increasing trends with decreasing elevation and increasing basin area. However the concentrations of K and SO4 show

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maximum concentrations near the source region. The values of conductivity, dissolved oxygen, alkalinity, and sulphate increased at downstream sites, i.e. Rishikesh and Haridwar in comparison to the values obtained near Gangotri, which indicates the Pollution inputs and rapid urbanization in the downstream of the study area i.e. at Rishikesh and Haridwar.

- The increasing trend of ionic concentration with decreasing elevation may be related to lithology, anthropogenic inputs, soil thickness, and temperature. Sulphate is found dominant anion while Ca^{++} is dominant cation. NO considerable change in Chloride is obtained during a particular season except post-monsoon season.

- Change in lithology and increasing temperature downstream is also responsible for the increasing trends of solute concentration downstream. Such changes in water quality is related to the anthropogenic inputs and meeting of several other streams to the Ganga River at different locations and due to mixing of ground water to the river.

- The $\delta^{18}O$ value exhibits good correlation with EC and bicarbonates during post monsoon period and with DO and bicarbonate during monsoon period.

The quantitative estimation and further confirmation of results require more data with representative cycles including isotopic and chemical characteristics.

5.2 Scope for future work:

- The isotopic indices of ground water at different altitudes, snowmelt and glacier melt runoff and precipitation are required to estimate the contribution of different components to the river at different location and different time. Once quantitative estimation of ground water, snowmelt runoff and precipitation runoff are available, the flow modeling of the river can be carried out for future predictions. This will help in managing water availability in Tehri dam and canals etc. at downstream.

- Sources of pollutants in the river are brought into account in present study, can be further explored in order to manage water resources.

- Hydrograph separation studies can be done after getting the information about the variation in isotopic composition of river water.

- New hydrological connections can be predicted.

REFERENCES CITED

APHA. AWWA and WPCF (1998) Standard Methods for Examination of Water and Waste Water," 20th edition-1998. Washington, DC: APHA.

Bhatt, B. K. (1963) Preliminary study of the Bhagirathhi basin between Uttarkashi and Gomukh. In *Proc. Nat. Symp. On Himalayan Geology, Calcutta*. Geol. Soc. Ind. Miscl. Publ. No.15, 1–8.

Brenot A., Carignan J. L. (2003) C.F. isotopic characterization of sulphate sources in the Moselle River watershed, France, Geophysical Research, Vol. 5, 04325.

Chakrapani, G.J. and Veizer J. (2005) Dissolved inorganic carbon isotopic compositions in the Upstream Ganga River in the Himalayas. CURRENT SCIENCE, VOL. 89, NO. 3, 10

Drever, J. I. (1997) *The Geochemistry of Natural Waters: Surface and Groundwater Environments*, Prentice-Hall, Upper Saddle River, N. J., 1997.

Druecker, M. and Fan, P. (1976) Hydrology and chemistry of ground water in Puna, Hawaii: Ground Water, v. 14,no. 5, p. 328-338.

EDRYSEK, M. O.J. (2000) Oxygen and Sulphur isotope dynamics in the SO_4^- of an urban precipitation, *Water, Air, and Soil Pollution* 117

Fritz, P. and Fontes, J. Ch., eds., Handbook of Environmental Isotope Geochemistry, Vol. 1, The Terrestrial Environment: Elsevier, Amsterdam, p. 74-134.

Huth, A.K. Leydecker, A. Bales, R.C.A. (2004) Two-component hydrograph separation for three high-elevation catchments in the Sierra Nevada, California, Hydrological Processes. 18, 1721–1733

Jain C.K., Singhal D.C. and Sharma M.K., (1999) Water quality and pollution aspects of Hindon river system, Proceedings of the 11th National symposium on Hydrology with focal theme on water quality, India

Liao, S.L. Savard, M.M. and Somers, G.H. (2005) Preliminary results from water-isotope characterization of ground water, surface water, and precipitation in the Wilmot River watershed. Current Research. 2005-D4.

McMurtry, G.M. Fan, P.F. and Coplen, T.B. (1977) Chemical and isotopic investigations of groundwater in potential geothermal areas in Hawaii. American Journal of Science, v. 277, p. 438-458.

Metzger, L.F. (1997), Streamflow Gains and Losses along San Fanscisquito Creek and characterization of surface water and ground water quality, Southern San Mateo and Northern Clara Countries, California, 1996-97, USGS. Water Resource Investigation Report 02-4078.

Michael, P.A. and Chamberlain, C. P. (2001) Empirical relation between elevation and the stable isotope composition of precipitation and surface waters: Considerations for studies of Paleoelevation change, American Journal of Science, Vol. 301, January, 2001, P 1–15.

Pandey, S.K. SINGH, A.K. and Hasnain, S. I. (1999) Weathering and Geochemical Processes Controlling Solute Acquisition in Ganga Headwater–Bhagirathi River, Garhwal Himalaya, India. Aquatic Geochemistry 5: 357-379

Tasneem, M.A. and Aggrawal, P.K., (2003) Stable isotope of dissoloved oxygen an innovative tool for water quality parameter estimation, National symposium on isotope Hydrology and integrated water resource management. Viana, IAEA-CN-104

Wasson R. J., A sediment budget for the Ganga–Brahmaputra catchment Centre for Resource and Environmental Studies, CURRENT SCIENCE, VOL. 84, NO. 8, 25 APRIL 2003.