#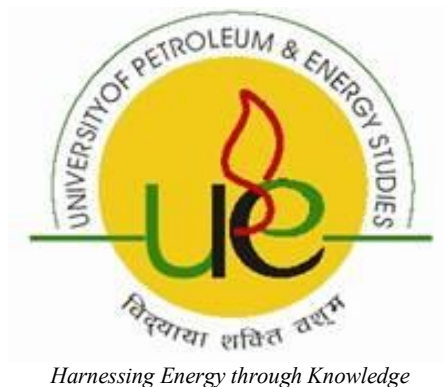 A STUDY ON SURFACE AND GROUNDWATER QUALITY OF DEHRADUN AND HARIDWAR DISTRICTS OF UTTARAKHAND: IMPACT ASSESSMENT OF URBANIZATION AND INDUSTRIALIZATION

A Thesis carried out at Wadia Institute of Himalayan Geology Dehradun

By

KANCHAN DEOLI BAHUKHANDI
COLLEGE OF ENGINEERING

Submitted

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IN PARTIAL FULFILLMENT OF THE REQUIREMENT OF THE DEGREE OF

DOCTOR OF PHILOSOPHY

To

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DEDICATED TO MY

BELOVED

GRANDFATHER

LATE GANGA PARASAD DEOLI

ACKNOWLEDGEMENTS

DECLARATION

I hereby declare that this submission is my own work and that to the best of my knowledge and belief, it contain no material previously published or written by another person nor material which has been accepted for the award of any other degree or diploma of the university or other institute of higher learning , except where due acknowledgement has been made in the text.

Kanchan Deoli Bahukhandi

University of Petroleum and Energy Studies

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THESIS COMPLETION CERTIFICATE

This is to certify that the thesis entitled **"A Study of Surface and Groundwater Quality of Dehradun and Haridwar districts of Uttarakhand: Impact Assessment of Urbanization and Industrialization"** by **Kanchan Deoli Bahukhandi** in partial completion of the requirements for the award of the Degree of Doctor of Philosophy (Science) is an original work carried out by her under our joint supervision and guidance. It is certified that the work has not been submitted anywhere else for the award of any other diploma or degree of this or any other University.

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Abstract:

A study of surface and groundwater was undertaken in Dehradun and Haridwar district with the following objectives:

1. Understanding the regional surface and groundwater quality for better knowledge of surface and groundwater regime for optimum management of water resources.
2. To evaluate the major ion chemistry of surface and groundwater in terms of chemical weathering and to understand factors controlling water chemistry of the region.
3. Impact assessment of urbanization and industrialization on the water chemistry.

Surface and groundwater samples from Dehradun and Haridwar districts were collected during January, May and October representing the winter season, summer and post monsoon season in the year 2008. The groundwater samples from tubewells and handpumps were collected from three broad land use categories i.e. industrial, agricultural and urban. Accordingly the samples have been broadly classified as groundwater of industrial area, groundwater of urban area, groundwater of agricultural area of Dehradun district, surface water of Dehradun (Bindal, Suswa, Rispana, Nun, Asan and Yamuna river), ground water of urban area of Haridwar, groundwater of industrial area of Haridwar and groundwater of agricultural area of Haridwar district , Surface water (Ganga river) of Haridwar and Risikesh. These samples were analyzed for dissolve major ions (HCO_3^-, SO_4^{--}, Cl^-, NO_3^-, PO_4^{---}, F^- , Na^+, K^+, Mg^{2+}, Ca^{2+} and SiO_2 and for heavy metals As, Cd, Mn, Co, Cu, Cr, Ni, Fe, Zn, Pb, Ba, and Sr in selected samples.

The abundance of major ions and their ratios have been used to evaluate the major ions chemistry of surface and groundwater of Dehradun and Haridwar district to identify ionic sources and to understand factor controlling water cehmsitry of the region in terms of chemical weathering of rocks.

Among the anions, bicarbonate is the most dominant(65%) with minor contribution from sulphate (23.3%), chloride (6.4%), nitrate 4.9%, fluoride 0.4 %, and phosphate 0.3 % in winter season.

Calcium and magnesium are the major cations accounting for 87% of the total cations. Among cations, calcium (63%) is most dominant ion in study area followed by Mg (24%), Na(11%) and K (2%) in winter season, during summer season the percentage of various ions are Ca(58%) , Mg(32%), Na(8%) and K(2%) and during post monsoon season the contribution of calcium is (61%) followed by Mg(30%), Na(7%) and K (2%). The order of abundance of major cations in the study area in winter season, summer and post monsoon season is Ca>Mg> Na>K. The average concentration of silica is 130 μmole/l, 74 μmole/l and 129 μmole/l respectively in winter season, summer and post monsoon season.

Majority of the samples belongs to Ca-Mg-HCO_3-SO_4 hydrochemical facies during winter, summer and postmonsoon season. In the study area, the marine contribution of cyclic salts is insignificant relative to chemical weathering thus rock weathering is the most important mechanism controlling the water chemistry.

The average (Ca+Mg)/HCO_3 equivalent ratio of 1.4, HCO_3/TZ- ratio of 0.6, relatively high contribution of calcium and magnesium to the total cations TZ + and high 9.1 ratio of (Ca+Mg)/(Na+K) indicate that the carbonate weathering is primary source of major ions to these surface and groundwater, an observation consistent with regional lithologies. Further, the relatively low silica (129μmole/l) and Na^+ and K^+ in these waters and high (Ca+Mg): (Na+K) equivalent ratio 1.2 to 43.9 with an average of 9.1) lead to the conclusion that the silicate weathering in these drainage basin is of minor importance. Influence of carbonate lithology on water chemistry is further evident from the high (Ca^{2+}+ Mg^{2+})/HCO_3 ratio (1.4) and good of correlation of HCO_3 with both Ca and Mg which improve further (0.95) sulphate is taken into account. A rough estimate of the contribution from silicates is obtained using the (Na *+K): TZ ratios is 0.13 (Na* signifies sodium corrected for chloride) as a index of silicate weathering which indicate the contribution of

the sodium and potassium derived from silicate weathering is accounting for less than 13% in study area.

In surface water of Haridwar that is Ganga river the (Ca+Mg) account for more than 90% in the cation balance and HCO_3 account for about 73% of the anions. These observation seems to favor the carbonate weathering as a major source of dissolved constituent and contribution of soil salts is relatively moderate in pre monsoon season.

In surface water of Dehradun the abundance of major ions is influenced by weathering of carbonate rocks. The relative proportion varies seasonally thereby providing an unique opportunity to study the weathering process regulating the abundance of major ions in these river waters in different season. During summer season the contribution of cations and anions (alkaline soils) is more pronounced. The seasonal data shows minimum concentration of the ions in post monsoon, and maximum concentration during winter season. Most of the ions in surface water of Dehradun and Haridwar districts are high in summer season as compared to post monsoon period reflecting the concentration effect due to elevated temperature and increased evaporation during the low water level period of the season. The decrease of most of the ions in post monsoon season can be attributed to increased recharged during monsoon season. The relatively high groundwater flow velocity during post monsoon reduces residence time of water to interact with rocks in order to appreciably dissolved them.

In Dehradun, groundwater the TDS concentration is found maximum 565.8mg/l in post monsoon season, minimum 307mg/l in winter season and moderate 369 in summer season. The ions i.e Cl, NO_3, SO_4, Mg, Ca, SiO_2 and hardness tend to decrease in groundwater during summer season while ions K, Na tend to increase in summer season with respect to post monsoon season. The increase of ions in groundwater during post monsoon season is possibly due to additional dissolution of ions attached with clay minerals of the soil due to recharge during monsoon thereby increasing the ion concentration in postmonsoon season in comparison to summer season.

In microbiological analysis for water quality two test - Total coliform and E coli were carried out. During winter season out of 94 samples of surface and groundwater, in 46 samples or about 49% samples showed positive result with respect to total coliform while 23 samples (28%) showed positive result with respect to feacal coliform.

The percentage of positive result of Total coliform and E.coli has increased to 73% and 36% during summer season and 70% to 47% respectively during postmonsoon indicating higher bacteriological pollution during summer and postmonsoon season. The increase in bacteriological count in summer season is because of the flow of river is predominantly maintained by domestic and sewage waste. The absence of adequate natural surface runoff, river losses its self purification capacity and the ecology of the river is adversely affected which is evident by growth of hyacinth along the bank of Asan river. The bacteria counts in shallow groundwater (handpumps and tubewell) also shows seasonal variation. Although number of infected handpumps are more (34% of the analyze sample) in winter season in comparison to summer (28%) and 17 % in post monsoon, the concentrations of TC and EC are high in summer season indicating increased effect of faulty municipal waste disposal system. The result also demostrate adverse impact of urbanization on water quality.

The concentration of F, Cl, PO_4, Na, K, Mg and Ca are found to increases in handpump water in comparison to tubewell water of Roshnabad industrial area of Haridwar disttrict. The possible source could be contamination of shallow aquifer due to leaching of industrial effluents which are directly generated from and discharged into open drainage and in soil without any treatment. Another reason could be contamination of shallow aquifers from sewage and domestic waste.

The parameter such as HCO_3, Cl, PO_4, Ca, Mg, Na, are under permissible limit of BIS and WHO standards for drinking water quality. However the ions,viz; F, K, NO_3 and SO_4 crossed permissible limit of BIS and WHO standards for drinking water quality at few locations of Dehradun district besides the concentration of Cl, NO_3, PO_4 and K has been found very high at few sampling locations of surface and groundwater of Dehradun and Haridwar

district. The TDS concentration appear to first hand indicator of anthropogenic contamination and in groundwater of Dehradun it generally increased in three landuse category in following order; industrial area >village area> urban area. This indicate that, although, no noticeable impact of industrialization has been observed till date but the urban area indicate the contamination of groundwater quality from the anthropogenic sources.

In Haridwar industrial area the concentration of TDS was 408mg/l, agricultural area 481mg/l, urban area 318mg/l and in surface water 103mg/l which indicate that groundwater quality of industrial and agricultural and village area of Haridwar has been deteriorated due to urbanization and partly due to industrialization. It has been observed that the effluent from Sidcul Industrial area are directly discharged in unslope of the village area without any treatment and at the same time the waste from household including sewage is deteriorating the quality of groundwater of industrial, urban and agricultural area of Haridwar district. Further major ions (Cl, NO_3, PO_4, K and Na) are tend to increase in surface and groundwater of industrial and agricultural area of Haridwar in comparison to urban area. The reason could be that in village area is taken from handpump while in urban area samples were taken from tubewell which also indicate the deterioration of the water quality of shallow aquifers.

The trace metals Fe, Pb, Cd, Hg, Pb, Cr, Co, Sr, As, Cu, Ni,B, Fe and Mn were analyzed in selected samples and they were found to be under permissible limit of BIS and WHO standards of Drinking Water Quality except the Cu which has crossed the desirable limit 50ppb of BIS standard at few sampling location of urban area of Haridwar in all three seasons viz. winter, summer and post monsoon season but remained under maximum permissible limit of 1500ppb.

The major physic-chemical parameters, which decide the suitability of river water for irrigation are pH, EC, TDS, hardness, chloride, sulphate, carbonate , bicarbonate, nitrate, sodium, potassium, calcium magnesium and SAR, PI etc. The water in the study area found to moderate to no problem category for irrigation use.

An assessment of temporal changes in water quality , carried out by the comparing the present data of Jain (1998, 2002) revealed that the EC and TDS has been drastically increased in year 2008. The other parameter i.e HCO_3, NO_3, PO_4, Cl in Haridwar and Dehradun district. This indicate that over the decade the phenomenal growth of urban and industrial centers after the formation of Uttarakhand had deteriorated the quality of surface and groundwater.

Scope of Research and Study

Variation in surface and groundwater quality in an area is a function of physical and chemical parameters that are greatly influenced by geological formation and anthropogenic activities. The measurements of water chemistry parameter have been used for assessing the chemical quality of water for drinking, domestic, irrigation industrial and other uses. The data generated are used to assess impact assessment of industrialization and urbanization on surface and groundwater quality. The data generated are useful for better understanding of surface and groundwater regime and management of water resources of the region.

The thesis has been compiled in eight chapters.

Chapter I **:** This include an introduction to the research problem and area with respect to location, climate, topography, soil, geology and previous work.

Chapter II **:** It include literature survey and previous work done at national and international level.

Chapter III **:** This describe surface and groundwater resources of the region and geohydrological frame work of the Dehradun and Haridwar district has been discussed.

Chapter IV **:** It include the description of various parameter of water quality and their health effect and permissible limit as per WHO and BIS standards.

Chapter V **:** It describe methodology for the sampling and analytical techniques used for water quality analysis.

Chapter VI **:** This discuss the result of water analysis in the study area and their interpretation with respect to the factor controlling the water chemistry . The compositional variability of major ions in surface and groundwater has been evaluated in terms of chemical weathering of rocks and soil of the drainage basin. The seasonal variation of dissolved major ions have been discussed in water of study area.

Chapter VII **:** The chapter gives an account of impact of industrialization and urbanization on water quality parameters in the study area. It also includes identification of the sources of pollutants.

Chapter VIII **:** The chapter gives summary and significant conclusions drawn from the study.

Chapter IX **:** The chapter gives of references of the research material used in the study.

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CERTIFICATE

Certified that Ms Kanchan Deoli Bahukhandi has carried out the study for the award of Ph.D degree on the topic **"A Study on Surface and Groundwater Quality of Dehradun and Haridwar Districts of Uttarakhand: Impact Assessment of Urbanization and Industrialization"** under my supervision at Wadia Institute of Himalayan Geology, Dehradun.

The thesis embodies the original work of the candidate.

(S. K. Bartarya)
Scientist 'E'

CHAPTER-I

INTRODUCTION

1.1   INTRODUCTION

Water is the elixir of life. It is an essential component of all animal and plant life. Water is a very precious natural resource present on earth. Ocean contains about 97% of earth's water resource which is unfit for human consumption and other uses because of high salt content. Of the 3% fresh water, about 2% lies in polar region and only about 1% is available for human consumption (Fig. 1.1).
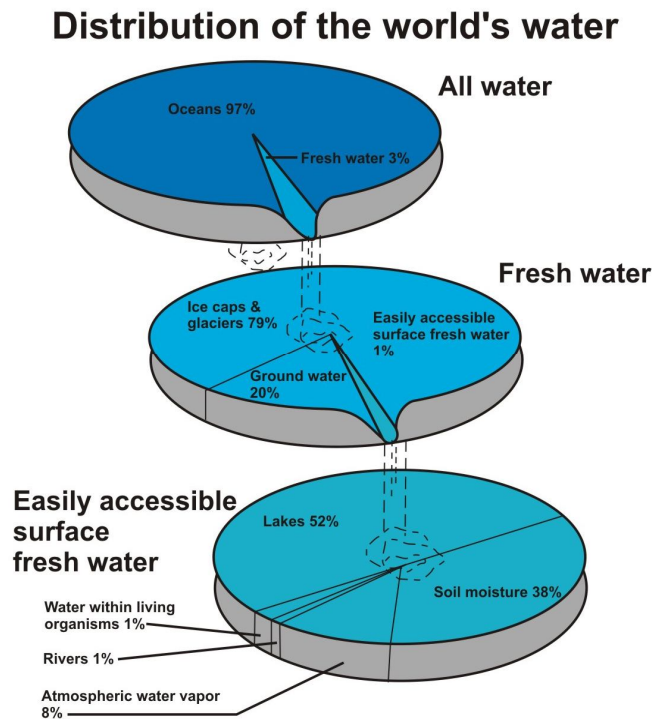
Fig. 1.1: Distribution of worlds water

The rapid industrialization and urbanization has led to the over exploitation of the natural resources. Industrial, domestic and agricultural activities sometime uses large quantities of water a part of which returns to the environment via discharges into the atmosphere and the water bodies. And these anthropogenic activities are the main causes for the different kind of pollutions we are facing today.

Safe drinking water is the demand of the world to lead a healthy life. It has become imperative to protect and conserve the water of the world not only as a resource for their present use but also for their prospective uses. Protection of water quality is not only urgently required in the area which are heavily polluted but is also necessary as precautionary measure for the conservation of undamaged area. Water quality analysis is an important issue in the surface and groundwater studies. Water resource need to be conserved, managed and developed in an integrated and environmentally sound basis. A water quality management programme require information on the existing water quality and criteria for present and future use. The evaluation of the impact of industrialization and urbanization on water resources is an integral part of development and management strategy of water resources development programme. Quality of surface and groundwater is equally important to its quantity owing to the suitability of water for various uses.

After the formation of Uttarakhand state, pace of urbanization, growth of population centers, introduction of industries and employment of auxiliary means of agriculture have increased manifold in Uttarakhand region in general and in Dehradun and Haridwar districts in particular. This is deteriorating the natural quality of surface and `groundwater. Pollutants are increasingly added to the surface and groundwater system through various human activities and the natural degradation processes. Application of fertilizer and pesticides to enhance crop production has become a common practice. Untreated disposal of wastes are adding pollutants to the surface and groundwater system and continuous addition accelerate their movement towards production well. Industrial wastes that includes heavy metals and toxic compounds are deteriorating groundwater quality. Keeping in view the problems being faced

by the newly created Uttarakhand state it is proposed to undertake "A study of surface and groundwater quality in Dehradun and Haridwar districts of Uttarakhand : Impact assessment of urbanization and industrialization" with under mentioned objectives".

1.2   OBJECTIVES

a) Understanding the regional surface and groundwater quality for better knowledge of surface and groundwater regime for optimum management of water resources.

b) To evaluate the major ion chemistry of surface and groundwater in terms of chemical weathering and to identify ionic sources.

c) To understand factors controlling the water chemistry of the region.

d) Impact assessment of urbanization and industrialization on the chemistry of surface and groundwater.

This chapter includes a brief introduction to the study area describing its location, climate, drainage, topography, socioeconomic condition, soil, geology, groundwater and natural vegetation.

1.3   STUDY AREA

The study area of the research lies in Dehradun and Haridwar districts of Uttarkhand in Outer Himalaya and Tarai region (Fig. 1.2).
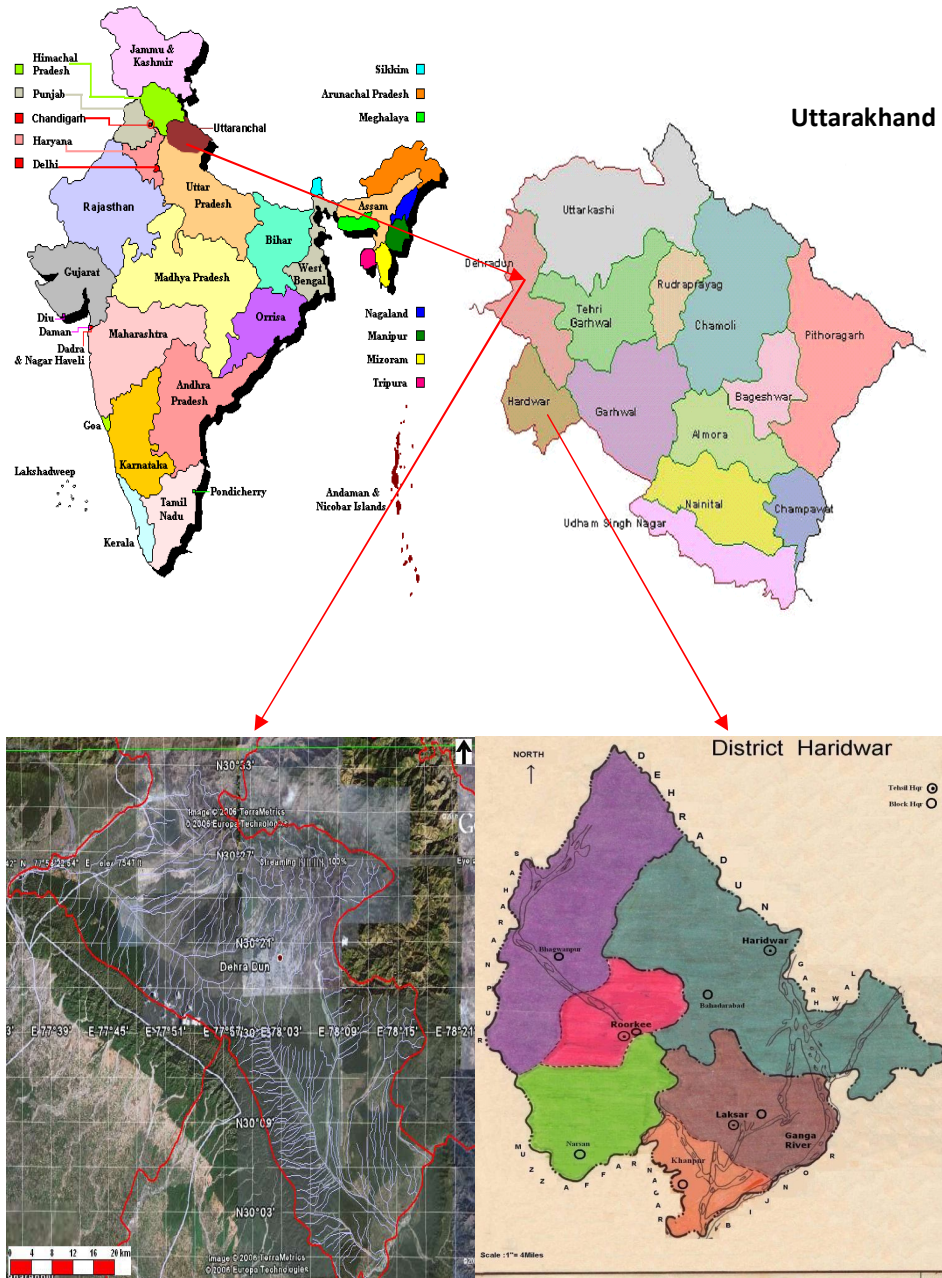
Fig. 1.2: Location Map of the Study Area

1.3.1 Location of the Dehradun District

Dehradun, is the capital city of the Uttarakhand state, lies between latitudes 29° 55' and 30° 30' and longitudes 77° 35' and 78° 24'. It comprises townships of Vikasnagar, industrial area of Selaqui and townships of Rishikesh. The district head quarter lies in an intermontane Doon valley surrounded by the lesser Himalayan ranges in the north and Siwalik hills in the south, the river Ganga in the east, and the river Yamuna in the west. The water divide of Ganga and Yamuna passes through the city. The study area has humid subtropical to tropical climate with heavy precipitation during July to September, moderate to high sunshine, humidity and evaporation. The average annual precipitation is about 205 cm in Dehradun district and about 150cm in Haridwar district.

1.3.2 Location of Haridwar District

Haridwar district, covering an area of about 2360 km², is in the southwestern part of Uttarakhand state of India. Haridwar is situated at an altitude of about 250 metres above the sea level, between Siwalik Hills in the North and Northeast and Ganga River in the South.

The city is situated between longitude range 39^0 ' to 30^0 '15 N and latitude range 77° 45' to 78^0 10' E. The district has 6 administrative block namely, Bhagwanpur, Roorkee, Narsan, Bahadarabad, Laksar and Khanpur. The study area is drained by upper Ganga canal, which originate near Har- ki- Pairi in the city of Haridwar and drain over its total channel network length of ~ 300 km. Among the natural stream the region encompasses entire solani river basin which is extended over an area of 655 km^2 and other small rivulets like Ranipur Rao and Pathi Rao originating in the Siwaliks, Pir Khala and Sila khala originating in the plains and river Banganga and Begam Nadi the older channels of the river Ganga.

1.4 PHYSIOGRAPHY

1.4.1 Physiography of Dehradun District

In the Shiwalik range of outer Himalaya, there are number of logititudinal valleys called Duns. The Doon valley is a synclinal depression between the

Lesser Himalayan Mountains in the north and Sub Himalayan Siwalik hills in the south. Aligned parallel to the general trend of Himalaya, it is veritable intermontane valley, bottom of which is filled up with thick detritus shed from overlooking hill slopes. Broadly the Doon valley can be divided into three different slopes: Northeastern slope of Siwalik, Doon Valley proper and southwestern slope of outer Himalaya range. The northeastern slope of Siwaliks are quite steep in higher reaches and have less gradient lower down. These are cut by a large number of short, shallow and boulder stream which carry discharge into Asan, Suswa and Song rivers. The southern slope are very steep and are covered with poor vegetation.

1.4.2 Physiography of Haridwar District

The area of Haridwar is comes under Tarai region except the presence of Shiwalik mountain in north (Hardwar city itself). There is no void features except that the presence of rivers and nallas. The district is bound by Siwalik ranges and river Ganga at north and east respectively.

1.5 CLIMATE AND VEGETATION

1.5.1 Climate and Vegetation of Dehradun District

The Climate of the Dehradun district is generally subtropical. It varies greatly from tropical to severe cold depending upon the altitude of the area. The district being hilly, temperature variations due to difference in elevation are considerable. In the hilly regions, the summer is pleasant, but in the Doon, the heat is often intense, although not to such degree as in the plains of the adjoining district. The temperature drops below freezing point not only at high altitude but even at places like Dehradun during the winters, when the higher peaks remain under snow. The area receives an average annual rainfall of ~205cm. Most of the annual rainfall (~90%) in the district is received during the months from June to September.

During the summers, the temperature ranges between 17°C to 36°C and in winters, the temperature varies in between 5.2°C and 23.4°C (Table 1.1).

Table 1.1. Climate Data of Doon Valley for all the months is as under on the basis of mean of last 25 years. (NIC – National Informatics Centre, Dehradun)

Month	Rainfall (mm)	Relative Humidity (%)	Maximum Temperature	Minimum Temperature	Average Temperature
January	46.9	91	19.3	3.6	10.9
February	54.9	83	22.4	5.6	13.3
March	52.4	69	26.2	9.1	17.5
April	21.2	53	32	13.3	22.7
May	54.2	49	35.3	16.8	25.4
June	230.2	65	34.4	29.4	27.1
July	630.7	86	30.5	22.6	25.1
August	627.4	89	29.7	22.3	25.3
September	261.4	83	29.8	19.7	24.2
October	32.0	74	28.5	13.3	20.5
November	10.9	82	24.8	7.6	15.7
December	2.8	89	21.9	4.0	12.0
Annual Average	2051.4	76	27.8	13.3	20.0

The farming system in the Dehradun district comprises agriculture, horticulture, herb culture, tea garden practices and nurseries fruit plantation and reforestation. The farming of crops is mostly traditional. Owing to the diversity in climates from the low-lying river valleys and foothill plains such as Tarai, Bhabar and Doon to highly elevated snow clad areas, the cropping seasons, cropping pattern, land use pattern, production and productivity of crops and ecological zones and sub zones are varied accordingly. The main crop seasons are Rabi and Kharif. Rabi season generally occurs from November to April. The main crops during the Rabi season are, wheat, barley, ray, sarson (mustered), pea, gram, and masur. wheat, gram and pea are grown extensively. The period of the Kharif season is from June to October. The main crop of the season is rice. During the same season, varieties of other

crops such as pulses and vegetables are also grown. Among them the main crops are millets including mandua, jwar, bajra, ramdana, maize, etc.

1.5.2 Climate and Vegetation of Haridwar District

There are four distinct season viz. winter, autumn, spring and summer in Haridwar district of Uttarakhand. The climate of the Haridwar District is relatively hot and humid with an average annual rainfall of about 1127.2 mm. The highest average temperature in the district is 40.9° C in summer and the lowest average temperature is $16.6\ ^{\circ}$C in winter season.

The area is characterized by evergreen forest with some deciduous species of tropical and subtropical origin. The pattern of vegetation is controlled by altitude zonation and topography. The peak of Siwalik hills have a different type of vegetation from that of damp sheltered area of Raiwala and that of Pathri forest in south. The peaks of Siwalik are characterized by the presence of *Anogeissus, Latifolia, Centratherum anthelminticum, Drypetes roxburghii, Embelica officinalis* and to some extent by *Terminailia chebula* and *Terminalia bellrica*. Raiwala possesses characteristics vegetation comprising *piper longum, Centella asiatica, Helictres isora, Bacopa monniri* and *Tamarix dioecia* in addition to trees like *Shorea robusta, Salix trasperma, Limonia elephantum* and *Ficus hispida*. The vegetation in the souhtern side in pathri forest comprises of *Plumbago zylanica, Piper longum, Centella asiatica, Alangium salvifolium sp, Lanna coromandlica and Terminalia arjuna*.

The flora found in the area is diverse with distinct vegetation zones that include broadleaved deciduous forests, riverine vegetation and grasslands along with picturesque forests of pine trees that lend a unique charm to the environment.

1.6 GEOLOGY

1.6.1 Geology of Dehradun district

Geological structure of Doon valley is characterized by two major faults, crustal and fractures along with rock slabs of mountain mass have been

uplifted and moved southward. The Doon valley and Siwalik range is principally composed of the rocks classified into the Lower, the Middle and the Upper Siwaliks. The southern limb of the Doon valley and Siwalik range are made up of the Middle and Upper Siwalik. The Middle Siwalik area composed of 1500 -1800 m thick fluviatile sediments. They consist of sandstone –mudstone couplets in the lower part and a multistory sandstone complex in the upper part with few pebbly horizons to the top. This sequence of the Middle Siwalik passes transitionally upwards into thickly bedded conglomerate of the Upper Siwalik. The conglomerates are composed predominant of pebbles and boulders of sandstone, limestone and quartzite derived from the lower Himalaya – similar to that of Mussoorie range. The lower Siwalik is exposed on limited outcrops on the northern limb of the Doon valley. It is made of purple clay and sandstone. The rock of Siwalik Group overlain by the Doon gravel, sand and boulders with clay bands, filled up the large part of the Doon valley. The thickness of Doon gravel is variable from 52 to > 500 meters in the central of the valley.

1.6.2 Geology of Haridwar district (Rishikesh, Haridwar-Roshnabad area)

The study area in Haridwar district is a part of Indogangetic plain and Siwalik hills. The Indogangetic plain is composed of Pleistocene to recent alluvium material brought down by river from the Himalayan regions. The alluvium is consist of sand, silt, clay, kankar and gravel. The deposits of sand are the main source of groundwater in the district. As described earlier Siwaliks rocks are made up of sandstone, grits, conglomerate, pseudo conglomerate, clays, and silt having the character of fluviatile deposit of torrential stream and floods in shallow fresh water basins. Towards north the Siwalik formations are separated by hard rock of Lesser Himalaya by main boundary thrust (MBT).

1.7 DRAINAGE PATTERN

1.7.1 Drainage Pattern of Dehradun

An intermontane, Doon valley is characterized by the Asan and Song river. A single valley, apparently, consists of two shallow valleys, the western and the eastern Doon valley respectively. The two rivers are separated by a low water

divide, running from Mohand Pass to Landour at Mussoorie. The river tons are the main tributary of Asan in western part of the valley discharging their water to Yamuna. Rispana, Bindal, Suswa, Jakhan are in the eastern part of the Doon valley and discharge their water to the Song and then to Ganga. The perennial rivers, Ganga and Yamuna, emanating from glaciers are forming the eastern and western limit of Doon Valley. The perennial drainage in the eastern parts of the valley comprises Song and Bandal, Rispana and Suswa River originating from Shiwalik hills while seasonal stream called 'Raos' include - Bindal, Jakhan, Motichur, Kansro, Chandrabhaga and many other tributaries meeting Song which eventually join the Ganga near Raiwala in the western part of the valley. The two perennial streams in the eastern part of the valley are Tons and Asan and their seasonal tributary streams include: Bared, Nimi, Gulata, Darer, Agli Nala, Suarna, Chorkhala, Seetla, Dudhiya etc., joins the Yamuna river near Herbertpur . Other source of water include spring present in Lesser Himalaya and Siwalik ranga and dugwells (though mostly abandoned at present), handpump and tubewell drawing water from shallow and deep aquifers respectively.

1.7.2   Drainage Pattern of Haridwar District

Most of the river of Haridwar district are flowing from west to east. The river are ephemeral in nature. However the water from groundwater storage flow round the year. The most important rivers of Haridwar are Ganga, Solani and Ratmau. Besides these river Ganga Canal at Har ki Pauri receive its water from Ganga itself at Haridwar.

1.8   SOIL

1.8.1   Soil of Doon Valley

Due to wide variations in topography, intensity of erosion, parent material and other factors, the soils of Doon Valley show wide variation in their properties especially texture, depth, stoniness, colour, drainage, moisture status, organic matter content and cation exchange capacity (Sharma 1982). The soil overlying the boulder mass is much variable, both in depth and richness, and is altogether absent in rao beds. It is generally sandy with varying proportions of

locally deposited clay. Because of great thickness of underlying boulders, the permanent level of groundwater is at considerable depth.

The forest soils of the Doon Valley mainly belong to the orders as Inceptisol, Mollisol and Alfisol as could be determined by their diagnostic and other properties (Soil Survey Staff, 1978).

Coarse loamy thermic udic haplustoll

These soils occur mainly on the gentle slopes and were identified in Dharmawala block of Dehradun Forest. These soils are brownish in colour, loam to sand in texture and acidic to near neutral in reaction withour an argillic and calcic or gypsic horizons. Gravels and stones in the lower depth of these soils have adversely affected the fertility status due to reduction in effective soil volume available to roots.

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These soils which occur commonly in the foot hills and lower portions of the gentle slopes are found in the in the Jhajhra and Sahansara blocks of Dehradun Forest. The main characteristics of these soils are their fine loamy to coarse loamy texture, acidic reaction and high percentage base saturation. Calcareous is absent from profile but the argillic horizon is present. The organic matter content and base saturation status indicate high fertility but the presence of gravels and stones, relatively more in Sahansara than Jhajhra block, decreases the effective fertility through reduction in soil volume available to roots and also water holding capacity (Soil Survey Staff, 1978).

Coarse loamy thermic fluventic haplumbrept

These are the freely drained non-calcareous soils developed under very short dry season of Lambirao and Bahera blocks of Dehra Dun Forest. The presence of coarse stratification and lack of clay indicate their recent origin. These soils, which are umbric at the surface, have acidic to near neutral reaction and texture from loam to loamy sand throughout the depth, but unlike the Haplustalfs, gravels and pebbles are found embedded.

Fine laomy thermic mollic haplustalf

These soils occur under miscellaneous vegetation and on gentle slopy terrains of Suswa, Lachhiwala and Bibiwala block of Dehradun Forest.

These soils also have a characteristic argilic horizon and a high base saturation states up to 1.25 m depth or above the lithic contact. The soils are brownish in colour, acidic to near neutral in reaction and clay loam to silty loam in texture.
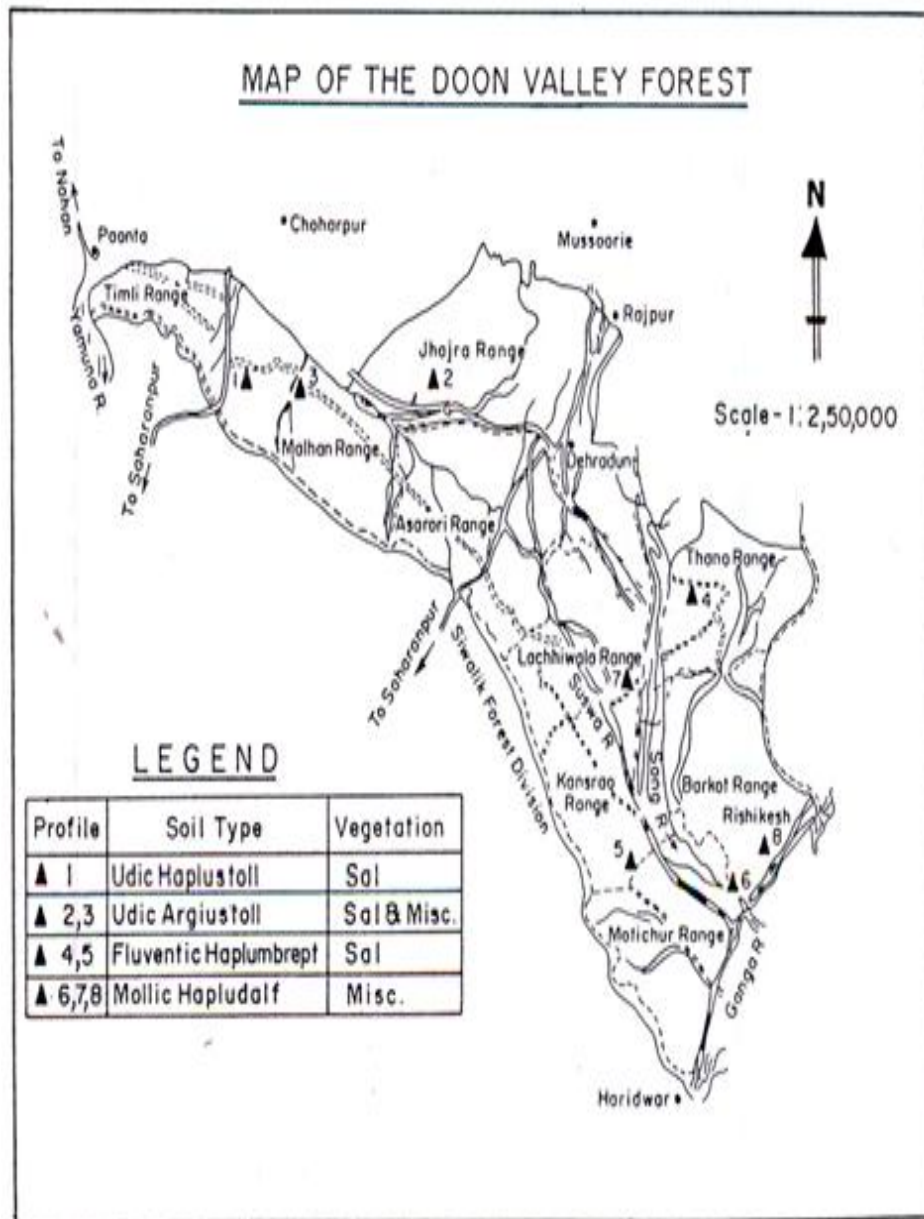
Fig. 1.3: Map of Doon valley forest showing soil profile

1.8.2 Soil pattern of the Haridwar District

The geological structure of the Siwalik is responsible for the type of these hills, whereas the piedmont soil is formed by regular deposition of material from the Siwaliks as well as other genetic factors.

The soils arc classified into various physiographic units and landform as below:

a) *The Siwalik hills:* Lithic udorthents is the dominant soil sub-group on extremely steep slopes of the Siwalik hills whereas Typic udorthents is the major sub-group on hill aspects with relatively lesser slopes ranging from moderately steep to steep. Typic Hapludalfs subgroup is occurring on western and northern hill slopes covered with good forest vegetation as compared to eastern and southern aspects which are more exposed to sun and are found having Typic Dystrochrepts soils compositioil. In the Siwalik hills soil texture varies from loamy skeletal to coarse loamy.

b) *Piedmont Zone:* In the piedmont zone the dominant soil association found is Typic undorthents, Typic Dystrochrcpts, and Typic Hapludalfs where the soil texture ranges from coarse loamy to fine loamy. Other soil associations classified in Ganga system are Typic Ustipsamments, Typic Haplustalfs, and Typic Hapludolls.

c) *Alluvial Plain:* The nearly level to very gently slopingplain, and flood plain and depressional areas having same gradient are supported by soils dominant in fluventic and aquic characters. The Soil types association is like piedmont in the transition zone. The soil classes are Typic Hapludolfs, Typic Haplustalfs, Udic Ustrochrepts, Udic Ustorthents, Typic Ustifluvents, Typic Undorthents, Aquic Udorthents, Typic Ustorthents and Typic Ustipsamments.

The area estimate of soil type reveal that an area of 171.94 sq km (11.58%) has alluvial soils and rest of the area in the revenue villages of the Bhabar tracts is under piedmont soils. The alluvial soil occur in the transitional zone adjoining southern boundary.

1.9   POPULATION

1.9.1   Population and Population Growth of Dehradun District

Dehradun has been a tourist place since long time. More than 80% of drinking water supply in Doon valley comes from groundwater. Excess use of fertilizer and pesticides in agricultural field find way to groundwater through recharge. After the formation of capital of Uttarakhand many people came here from across the state and country.

As per census of 2001, Dehradun district has a total population of 12.80 lakh. Dehradun has seen its overall population growth from a scant 28,100 in 1901 to 12.80 lakh in 2001 (Census of India 2001). The district itself saw a population boom, starting at 180,000 in 1901, reaching about 1,026,000 in 1991 and passing 1,280,000 in 2001. Dehradun average population increased of 44% per decade in the last half century (Ghosh, 1998). From 1991 to 2001, Dehradun population has increased ~52% even outstripped national average of 36% for Urban area.

Between 1981 and 1991 decade, the decadal change in population of Dehradun was 21.33% and 21.85% respectively. The sudden jump to 39.73 % in the next decade (1991-2001) is explained by the fact that in this decade Uttarakhand was made a separate State with Dehradun as its capital. The decade (1991-01), population growth rate of 39.73 %, which was considerably higher than the national average of 21.53 % (Directorate of Economics and Statistics, Government of Uttarakhand, Statistical Diary, Uttarakhand,2004-05).

Table 1.2: Population growth of Dehradun district

Year	Population ('000 persons)	Decadal Growth Rate (%)
1981	211	21.53
1991	270	21.85
2001	448	39.73

Table 1.3: Population of Dehradun district

Year	Population
1817	2,100
1901	180,000
1991	1,026,000
2001	1,280,000

The possibility of its maintaining a relatively high growth rate of population is due to State's initiative to achieve higher rate of growth of the economy and expansion of the industrial base of Dehradun among other areas. Besides, the impact of factors like large investments in industries, the planned infrastructure and institutional improvement and the proposed overall development of the town under the Jawaharlal Nehru National Urban Renewal Mission will widen employment opportunities both in secondary and tertiary sectors. These factors together will lead to the much faster rate of population growth due to large in-migration of workers to this town besides the natural growth of population. As Dehradun urban area started with a low population base of 4.48 lakhs only (2001) its population growth rate in terms of percentage is expected to be faster in the coming decades as a result of its economic factors mentioned above.

Thus population of the city increased from 2.7 lakh in 1991 to 4.48 lakh in 2001. By 2011 the population of the city is expected to grow 4% per annum till 2010, after which the growth rate is expected to drop to 3.5%. Dehradun is also a famous township city and hence the tourist arrival in the city have increased from 4.6 lakh in 2000, 9.3 lakh in 2003. The floating population of the city is estimated at 35,000 person per day.

1.9.2 Population Growth of Haridwar District

Population growth rate of 3% per annum has been taken and airthmatetic increased method has been adopted for projected population. The entire Haridwar town with its permanent and floating population and adjoining rural areas are covered with water supply scheme moreover some rural area adjoining to Haridwar town. Large number of people arrive for religious activities through out the year and the figure increase considerably during the religious festivals and Yatra Season. More over to enter the Garhwal States from most of tourist visiting Garhwal area also visit Haridwar and its near by thus lot of people from hills as well as plains arrive here for their business as well as pilgrimage activities. Haridwar is also a centre of Chaar Dham Yatra of Uttarakhand state. All this permanent and floating population growth has exerted tremendous pressure on the quality and quantity of water resources of Dehradun and Haridwar districts.

Table 1.4: Population of Haridwar district

Permanent Population			EQ. Floating Population			Total Equivalent Population		
2001	2007	2022	2001	2007	2022	2001	2007	2022
177509	209461	303718	160000	181280	273760	337509	390741	577478

The map shows population distribution. The most populous villages are shown in dark tones of brown and the least populous villages in lighter tones of yellow.
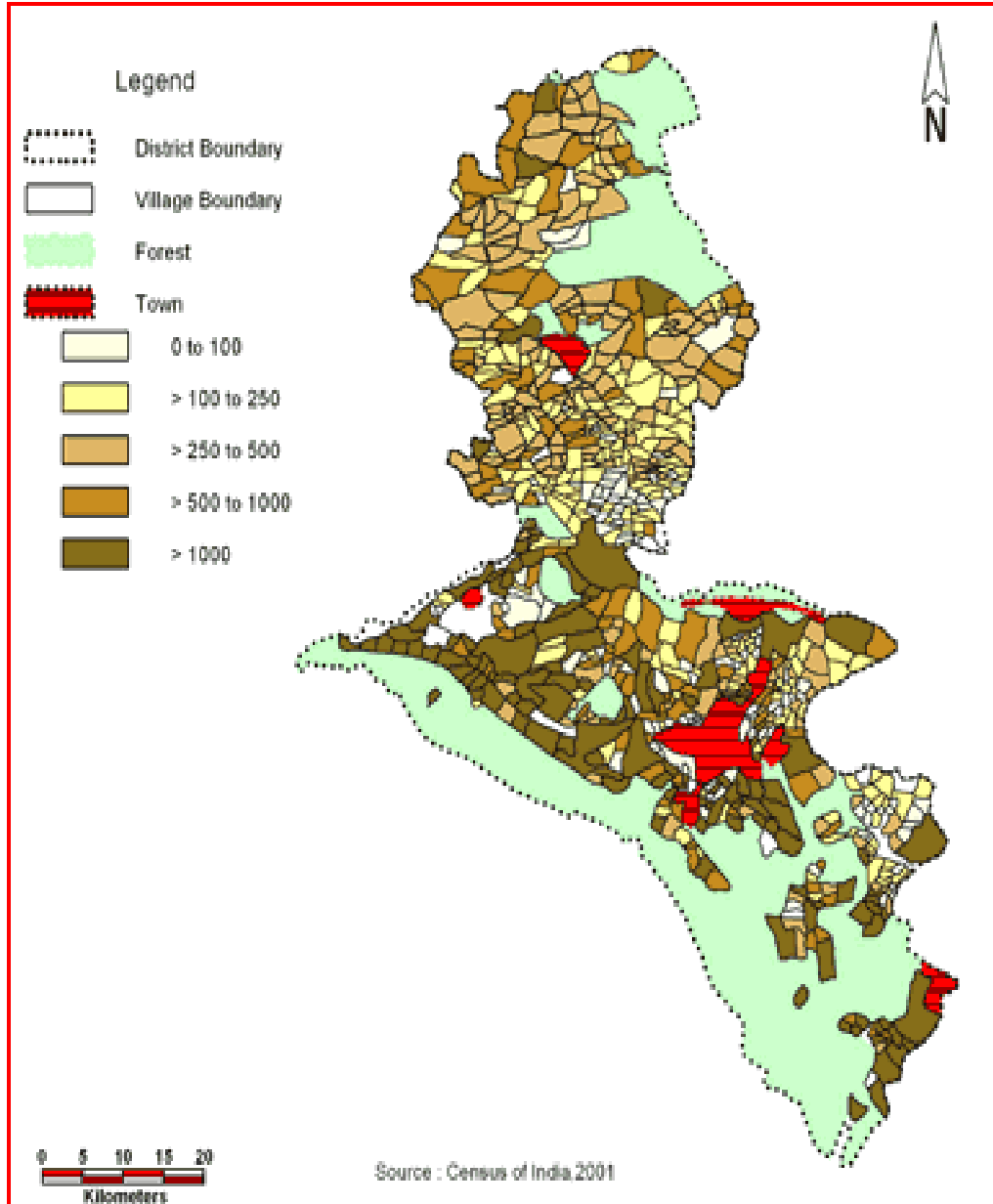
Fig. 1.4: Population Map of Dehradun District based on 2001 Census
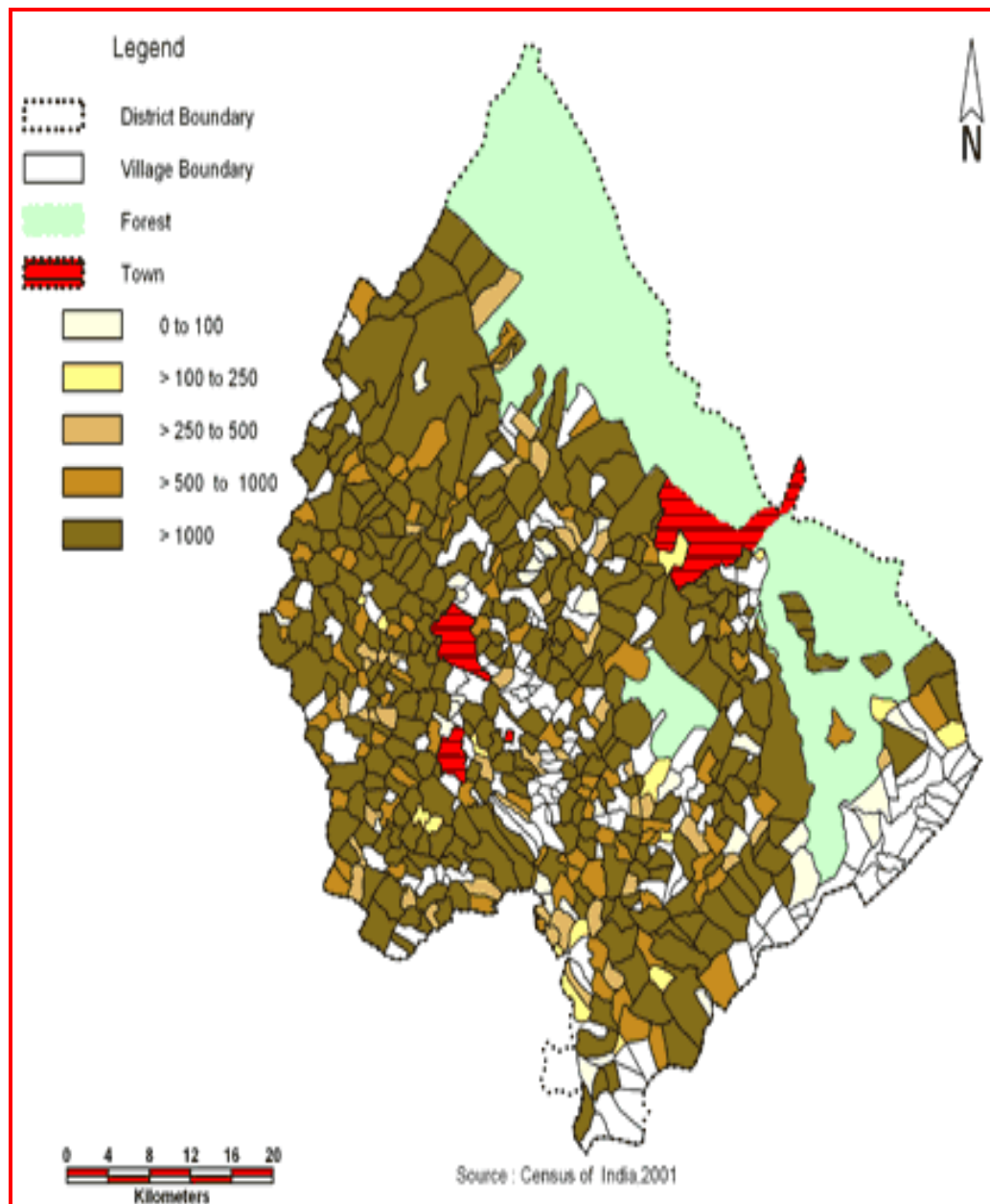
Fig. 1.5: Population Map Haridwar District - 2001 Census
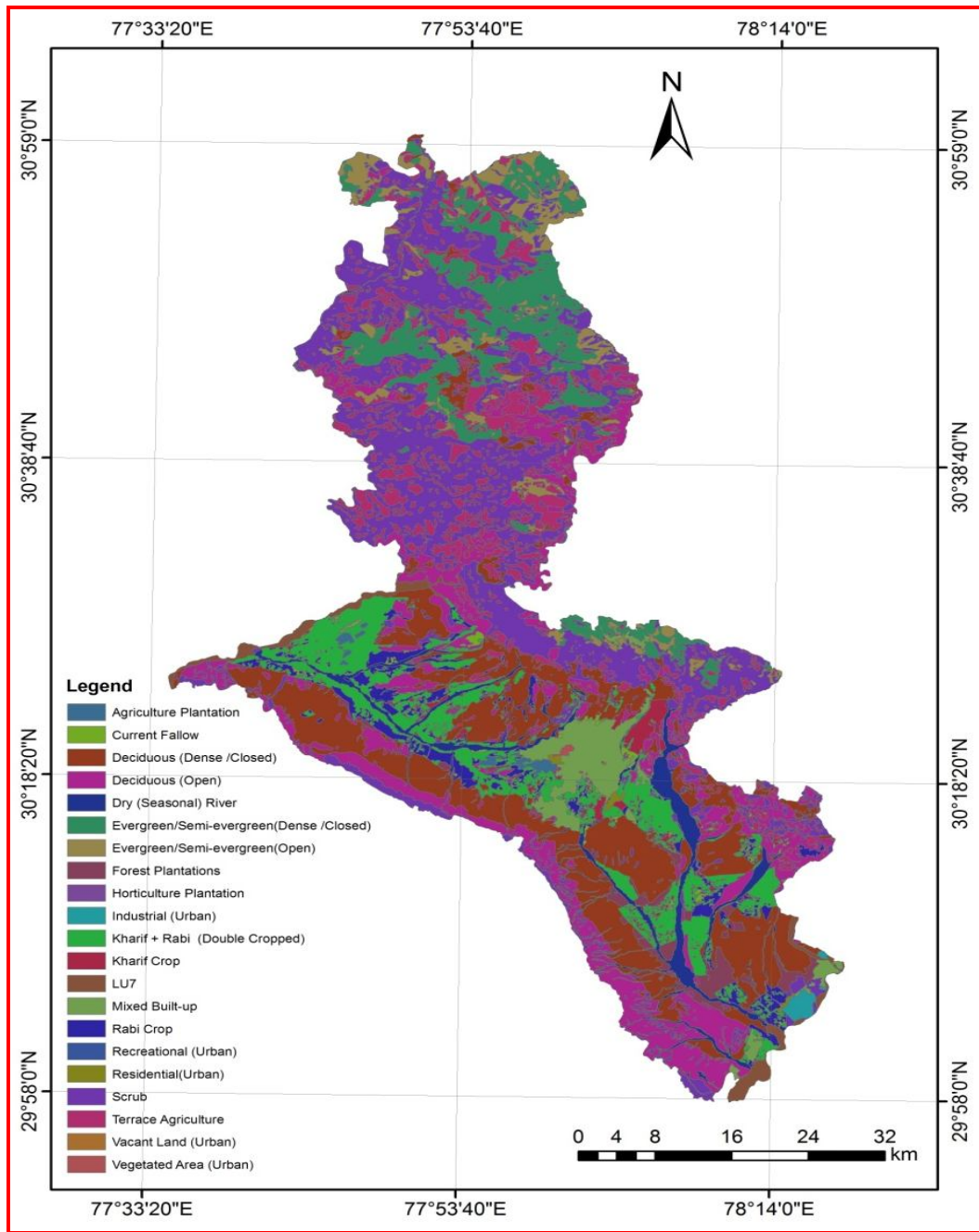
Fig. 1.6: Land use Map of Dehradun District

CHAPTER-II

LITERATURE SURVEY

This chapter reviews the literature relevant to the present study. The literature review is focused on contemporary work being done on water quality analysis, weathering control and factors controlling the water chemistry etc. A summary of the previous work relevant to the hydrochemistry, major ion and trace element chemistry carried out by various researchers at national and international level and in and around the study area are included in this chapter.

Variation of water quality in an area is a function of physical and chemical parameters that are greatly influenced by geological formations and anthropogenic activities. Knowledge on hydrochemistry is more important to assess the quality for understanding its suitability for various needs and also to evaluate the aspect of chemical weathering of rocks. A number of studies have been carried out at national and international level.

Globally, weathering of rocks is the major source of ions in the water bodies. Physical chemical and biological processes are involved in rock weathering. The chemical reactions between rock minerals and soil water produce cations, anions and heavy metals in surface and groundwater. The chemical composition of the world river has been reviewed by Meybeck (1976), Livingstone (1963), Turekian (1969, 1971), Durum and Haffty (1963). This compilation provided a general idea of chemical composition of rivers flowing through different geological terrains and climatic regimes. It can be observed from the data compiled by Livingstone (1963) and Meybeck (1976) that ionic ratios in the water of major river are fairly constant. Among cations Ca were found to be most abundant cation while among anions HCO_3 were found to be most abundant anions in water. This is the case for more than the 90 % of the

rivers which have rock dominant type of the water described by Gibbs (1970). The remaining rivers are Na, Cl, SO$_4$ ion dominant type where water is either rain dominant type or the evaporation-crystallization types (Gibbs, 1970, Feth, 1971). The rock – dominated type of waters reflect the weathering of minerals found in surface rocks, particularly the calcium carbonate minerals in sedimentary rock. He found that that the chemistry of river water is influenced by precipitation, rock interaction and evaporation. Gibbs (1970) plotted TDS verses the Na/Na+Ca, the two end member of sea water and of fresh water and showed the mechanism controlling water chemistry in river. Rivers with Na/Na+Ca between 0.2 to 0.6 and TDS concentration approximately between 90mg/l to 450 mg/l owe most of the chemical composition due to rock weathering.

Weathering of both silicate and non silicate rock contribute ~ 70% of river alkalinity while remaining 30% is caused by river based biological processes due to decomposition of organic matter Probst et al. (1998). The relative weathering contribution in the beginning of monsoon season is likely to be high due to large discharge of various river systems flushing out weathered top soil in the initial stages of rain water when biochemical reactivity is inhibited by rapid flow of water.

The chemistry of some of the large rivers of the Asian region such as the Ganges, Brahmaputra, Changjiang and Huanghe have been studied extensively by a number of workers, Raymahasay, (1970), Hu et al., (1982), Abbas and Subramanium, (1984), Sarin and Krishnaswami, (1984), Sarin et al. (1989), (1990), hang et al. (1990), (1995), Chakrapani et al., (1995), Bhatt and Saklani (1996). The water chemistry of the Indus in Pakistan was studied by Meybeck (1976). In India some of the tributaries of the Indus were studied by Subramanian (1979) and Pande et al.(1994).

Chakrapani 's (2005) studies on major and trace element geochemistry in upper Ganga river, Himalaya found large seasonal variation in major element concentration. The water type was categorized as HCO$_3^-$, SO$_4^{2-}$, Ca^{2+} dominant which constitute >60% of the total water composition. It was observed that

only 5-12% of bicarbonate is derived from silicate lithology indicating strong influence of carbonate lithology on water chemistry in the head waters of Ganga river. More than 80% Na^+ and K^+ are derived from silicate lithology.

Further major south Asians rivers reveals strong seasonal variation in their solute transport reflecting variable export of silica, Ca, Mg and alkalinity in response to seasonal changes in   i.e. precipitation and temperature. The value for alkalinity, Ca and Mg in winter season are generally higher than summer season in downstream region of river Indus in Pakistan, (Karim and Veizer 2000).   Similar variation were also observed for the river Indus from Ladakh Himalaya (Ahmad et al., 1998) as well as for Ganga and Brahmaputra

Ca/Na and Mg/Na observed by Quade et al. (2003) result in seasonal variable fractions of CO_2 consumed by silicate weathering and observed silicate weathering contribution of ~ 15 -19% and 36 % during the rainy and non rainy season, respectively.   These estimates are slightly higher than that reported by Galy and France- Lanord (1999). West et al. (2002) found silicate weathering to be much more intense in huge Ganga basin as compared to higher Himalayan basin.

Water quality has been a major issue throughout the world since long time and a number of studies have been carried at international level. Some of them are discussed here.   Shah et al. (1997) studied the source tracking of fecal pollution from the Bagnallas beach, Australia. The study showed that the urban runoff and birds are the major contributing sources of fecal contamination in all water sample collected from the Bagnalls beach. Feleke et al. (2007) studied fluoride in groundwater in the rift valley region of Ethiopia and reported that dental and skeletal fluorsis is common health problem in the region due to drinking of high fluoride water (up to 33 mg/L fluoride).

Iqbal (2007), has discussed the As variation with respect to depth, season and age of tube wells in Bangladesh and observed that higher As concentration (300 microgram/ liter) was observed for the depth of 140, 150 and 165 ft. Saleh (2007) recorded high concentration of sulphate in deep well due to

presence of rock sulphate salt like gypsum at some places in the groundwater of Nineveh Governorate, in Iraq. Amadi and Amadi (1980) studied salt water intrusion in the coastal aquifer of southern Nigeria using hydrochemical data . Udom et al. (2002) studied fifteen groundwater samples from functional boreholes in Khana and Gokana areas of Rivers State in Nigeria and also recorded salt water intrusion in coastal aquifers. Offiong and Edet (1989) assessed the water quality of cross river basin, south eastern Nigeria.

Mangore1 (2007) evaluated the groundwater quality for industrial, commercial and domestic uses in Bulawayo, Zimbabwe and 27% of the samples are positive with respect to total colifrom and 8% with respect to fecal coliform. The study reveals that leaks from industrial and domestic sewers from the old sewer lines is the cause of this pollution. Further they observed that the groundwater quality is being adversely affected by land-use related activities. Sadek and El-Sami (2001) studied the susceptibility of quaternary aquifers in the vicinity of Cairo and found that the chief pollution hazards are the infiltration of domestic sewage and discharge of untreated industrial wastewater into the subsurface aquifers. Similarly numerous studies (Barrett et al., 1999; Yang et al., 1999 and Cronin et al., 2003) carried out on the aquifers underlying the city of Nottingham in the UK, revealed that sewer leakages have an impact on the groundwater quality. Korfali and Jurdi (2003) investigated the water quality of free flowing river and reservoir in Lebanon and found that the reservoir with catchment area having agricultural and industrial activities had a high pH (8.4) than the free flowing river, which received domestic wastewater (high carbon dioxide content) and observed significant differences in the water quality of the two water bodies. They attributed differential water quality of two water bodies to the nature of the water resources and the exposure to the contaminants. Cronin et al., 2003 has also made an attempt to characterize the spatial and temporal variations in sewage-related microbial and anthropogenic-related inorganic contamination of the aquifer in U.K. Hajalilous et. al (2009) had investigated hydro chemical factors and groundwater quality assessment in Marand Municipality, northwest of Iran and extracted three parameter based on factor analysis.

According to Cluster dendrogram the highest similarity exists between HCO_3^{2-} and Mg^{2+} in the groundwater regime. Changes in spatial distribution of groundwater parameters indicated that the quality and geochemical characteristics of groundwater had a close correlation with topography, geology and hydrology of Marand plain and it was concluded that groundwater quality in southern part (close to recharge centre) are appropriate, but towards the end of plain (discharge centre) ion concentration increased and water quality declines. Some parameters including flow direction, water level rise, development of agricultural activities and increasing industrialization and urbanization had deteriorated the quality of water.

In India, a number of studies on surface and groundwater water quality, impact assessment and chemical weathering processes have been taken up by a number of workers. The rivers draining the Himalaya contribute significantly to the global sediment and water discharge (Milliman et al.,1983). They have recently attracted attention of several workers because of the possible connection between chemical weathering in the Himalaya and global climate (Raymo and Ruddiman, 1992) as silicate weathering is thought to be a global sink for CO_2 on geologic time scales (Walker *et al.,* 1981, Berner, 1995). Such a hypothesis has led to a number of studies on rivers draining the Himalaya (Krishnaswami *et al.,* 1992, Sarin *et al.,* 1992; Pande *et al.,* 1994, Galy and France-Lanord, 1999). These studies are based mainly on isotopic and major ion composition of dissolved load of rivers. The major ion chemistry and chemical weathering in Ganga basin has been carried out by several workers, notably among them are Trevedi et al (1992), Krishnaswami et al (1999), Sarin et al 1992, Abbas and Subramanian (1984) etc. Sarin (1983) and Sarin et al (1984) carried out major ion and isotope chemistry of high land and low land river of Ganga and Brahamputra basin and observed that the chemistry of high land river was dominated by weathering of carbonate rocks present in the basin and silicate weathering in these drainage basin is of minor importance. The seasonal variation in these rivers indicated that during lean flow (premonsoon season) the contribution from alkaline and saline salt effected soil is more pronounced and during peak flow (post monsoon) the

chemical composition of these rivers closely follow that of "rock dominant" type of water. Study on major ion chemistry and weathering control in a high altitude basin at Alaknanda river Garhwal Himalaya was carried out by Singh and Hasnain (1998). They observed that among anions, bicarbonate is the most dominating anion (78%) with minor contribution of sulphate (19%), and chloride (3%). It has been concluded that rock weathering is the most important mechanism controlling the water chemistry and water chemistry of the basin is controlled by carbonate weathering and partly by silicate weathering. The seasonal and spatial variation in TDS was attributed to climatic and lithological control over ionic concentration.

Dalai *et al., (*2002a, b, c and 2003), carried out a part of detailed geochemical and isotopic investigation of the Yamuna River System (YRS) in the Himalaya (i) to characterize chemical weathering in the YRS basin and (ii) to assess relative mobility of elements during weathering and transport. He found that carbonate weathering is contributing to major ion composition of Yamuna water.

However, geochemical studies of sediments in the headwaters of rivers in the Himalaya are limited. Variable geochemical studies of river sediments in the Indian Himalaya include reconnaissance survey of the Ganga and the Yamuna (Subramanian, 1987, Jha *et al.,* 1990; Chakrapani and Subramanian, 1996; Subramanian and Ramanathan, 194, Ramesh *et al.,* 2000) and the Indus (Ahmad *et al.,* 1998).

The sediment loads of Asian rivers are reported to be the highest in the world, delivering approximately 80% of the global sediment input to the oceans (Holeman, 1968). A total of 1.8 Gt year^{-1} of suspended sediments or ~ 9% of the total annual load carried from the continents to the oceans (worldwide) are transported in three river systems, the Ganga, Indus and Brahmaputra, in a combined runoff of 1.19 x 10^3 km^2 (Meybeck, 1976). These large sediment loads are due to the exposure of the geologically young rocks forming the Himalayan mountain chain, which has the world's greatest range of relief and extremes of climate.

High seismicity, steep valleys with frequent avalanching, intense monsoonal rainfall and glacial activities support high erosion rates in the Himalayan catchments (Singh and Hasnain, 1998, Pandey et. al., 1999, Hasnain and Thayyen, 1999). Himalayan glaciers produce a large amount of rock debris and have large lateral moraines compared with glaciers in many other areas. Further, high velocity erosive glaciers driven by high gradients, accumulation, and ablation rates result in high concentrations of sediments in the melt water. Such glaciers are thought to be important active agents of erosion and sediment transport in regional denudation systems (Gardner, 1986).

Silicon oxide is the most abundant component of the Earth's crust. It occur as a silicate minerals associated with igneous, metamorphic and sedimentary rocks. Weathering of silicate rock is also a measures of sources of alkalinity in river water. South Asian river basins are important in transferring silica and alkalinity to rivers and oceans because of geological and anthropogenic factors (Subramanian et. al 2006).

Alkalinity load and dissolved silica is shown to be related with land use pattern and therefore prone to the anthropogenic alteration. Lesser Himalayan studies indicate that steep relief, resulting in abundant supply of eroded material, is not a limiting factor in case of Himalayan rivers, West et al. (2005).

The chemistry of' the sediments, in particular shales and other finer sediments such as loess, have become a very important tool for estimating the composition of the upper crust in a particular area, or on global scale (Taylor and McLennan, I985). This tool is being used in conjunction with other studies to understand crustal evolution. In the Himalayas, this approach has not previously been adopted, although preliminary information are now available on some of' the major Indian rivers including the Ganges and the Brahmaputra (Subramanian et al., 1985).

Among the water quality studies, a regression model between total dissolve solid, silica and specific electric conductivity for well water of upper Gunjanaeru river basin, Cuddapah district, Andhra Pradesh was used by Raju

et al. (1992), to study seasonal variation in groundwater quality. Narayan and Suresh (1989) evaluated the chemical quality of groundwater of Manglore city Karnataka. Ramesh et al. (1995) conducted study on migration and contamination of major and trace element in groundwater in Madras city. Sujatha et al., (2003) have studied groundwater and its suitability for irrigation in the southeastern part of the Ranga Reddy district, Andhra Pradesh, India. Ahmed et al., (2002) have compared the analytical results of groundwater in Rajshahi city of Bangladesh with the recommended limits suggested by World Health Organization (WHO 1971). Anbazhagan et al.,(2004) have used the geographical information system (GIS) to represent and understand the spatial variation of various geochemical elements in Panvel Basin, Maharashtra, India. Saleh et al., (1999) have prepared correlation matrixes for the relationship between physical and chemical parameters of groundwater. They focused on boron concentration in groundwater to classify the irrigation water for various categories.

Rajsekhar et. al., (2007) have studied the chemical composition of well water for its suitability for irrigation and to identify the extent of sea water intrusion into the groundwater in the coastal belt of Ramnathapuram and Kadaladi taluk. Madhnure et. al, (2007) studies on assessment of groundwater pollution in the vicinity of industrial complex, Manad District, Maharashtra and found that the groundwater is of Ca- HCO_3 type and around established industrial complex groundwater is rich in calcium and magnesium chloride.

Sellamuthue et. al., (2007) found the effect of industrial effluent on surface and groundwater quality of Noyal River basin of Tamil Nadu. They observed that the Noyal has been mainly polluted by untreated effluent water discharge from the textile dyeing and processing factories located in and around Tirpur and the summer values of the chemical parameters were higher than the winter values with consistent seasonal trend at all locations.

Dhotre et.al, (2007), studied the impact of sugar factory on groundwater quality. The treated effluent from sugar factory and distillery are poured in the lagoon near the factory and part of effluent is dumped into the nearby drain that meets to river. They observed that after monsoon until the before

monsoon of next year, the movement of pollutant continued to groundwater and hence the ionic concentration were higher before monsoon. The concentration of ions in the soil were reduced after monsoon, due to leaching by rains during monsoon After monsoon, the salt continue to add in the soil due to irrigation from the well water as a result of which the ionic concentration were higher before monsoon. Nagaraju et, al. (2007*)* studied groundwater quality of Lokapavni micro Watershed, Madya District, Karnataka. The groundwater of the granitic terrain has shown an electric conductivity ranging from 296μs/cm to 3500μs/cm.

Maheswari et al., (2007), while assessing Impact of Coffee Processing Waste water on river water quality found that the pH of water is acidic in coffee processing season and neural in off season in Kodwar river and the pollution level of the Kodavanar river water was slightly higher than the prescribed limits during the coffee processing season (September to January) in comparison with the off season.

Das (2001) have studied impact of human interference on coastal groundwater regime in India and found that use of chemical fertilizer has enriched groundwater with high nitrate, sulphate, and phosphate in the coastal region of Mahanadi basin.   The untreated industrial effluents and municipal wastes, caused contamination of groundwater with high cyanide, phosphate, salinity, and heavy metals particularly arsenic in the coastal cities of Kolkata, Puri, Balasore, Visakhapatnam, Chennai.

Jaidev et al.(2007), studied the microbial contamination in dug wells of Thiruvanathapuram and demonstrated that 23% well do not have contamination, while 19% well had 1 to 50 MPN/100 ml of coliforms and 28.6% well have coliform in the rage of 501 – 5000 MPN /100ml. Sellamuthu et al. (2007), studied the groundwater quality parameter for Kodangipalayam watershed in borewells in Coimbatore district and revealed that TDS concentration crossed the limit prescribed by WHO standards for drinking water quality. The comparison of result of open is better and boreholes result were compared indicated that the boreholes were superior in quality with respect to TDS, Ca, Mg, and SO_4.

Sunil et al.(2007), studied the groundwater quality in the vicinity of selected land fill sites in Delhi from may 2004 to June 2006 and observed that the recharge to groundwater at deeper level is mostly through leakage from unconfined aquifer and partly from lateral groundwater flow from north and south and west. Based on ionic constituent they observed water types, hydro chemical facies and factors controlling groundwater quality. Ramchandramoorthy et al. (1997), studied the fluoride level and other water quality parameter of the Holy water sample (Theertham) of Ramanathsamy temple in Rameswaram, Tamil Nadu for premonsoon and post monsoon period. Their study has shown a decrease in concentration of TDS, EC, cation and anions and salinity in post monsoon period. Singh and Ghosh (2007), carried out studies on the sources of heavy metal pollution and its effect on vegetation. Dewangan and Goel (2007) studied seasonal and spatial variation in the As and F in the groundwater of Kaudikasa area in central India.

In India, arsenic pollution in groundwater is a matter of great concern and several studies have shown that As was first reported in early eighties in groundwater, has now affected 1312 villages till 2007. On an approximation 34000 sq.km land area in the West Bengal state is having high concentration of arsenic in drinking water abstracted from tube well. The As pollution is mostly reported from the intermediate water depth of 20-80 meter below ground level and the concentration on level in the most affected district was found between 0.05ppm to 1.28ppm which was high as compared to BIS and WHO standard for drinking water quality. The study of Panda et al. (2007), in Bengal Delta Plain (BDP) aquifer indicated that aquifer of the districts are infested with high As concentration.   Jena and Patel (2007), studied impacts of coal mine on surface and groundwater. The concentration of As were found high in area of open and underground mine.

Hydro chemical study in Krishna Delta by Saxena (2007) indicated that suspended sediments are comparatively more enriched in metallic trace element than bed sediments, and groundwater. He found that B and Sr are the dominating trace elements over other elements and Sr, B, Mn, Fe, Cu, Cr, Fe, Se and Be are more in northern side of delta (right side of Krishna river) in

comparison to southern part (left side of Krishna river). The considerable variation in the concentration of metallic trace element in Krishna delta may be due to variation in the sub basin geology and degree of human activities. Prasad, et al (2007) while carrying out study on fluoride contamination in Kurmapali watershed, Nalgonda district, AP found positive co-relation of fluoride with alkalinity and pH and suggested that the higher alkalinity of groundwater promotes the leaching of fluoride and thus effect the concentration of fluoride in groundwater. They have postulated the consumption of fluoride concentration may increase due to excessive utilization of groundwater.

Several studies have been conducted to assess the impact of industrial development on the quality of water sources. Some of the important studies carried out in recent years and are discussed in following paragraph are by Parekh and Patel, (2007) who conducted geochemical assessment of Meghal Tidal Regulation of Saurashtra region indicated high concentration of TDS and particularly of Ca, Na, Cl, Mg and SO_4 due to industrial development. Dasaram, Satyanarayan, (2007) studied geochemical mass balance of major chemical constituents and aspects of trace element geochemistry in groundwater of Patancheru Industrial Area, Andhra Pradesh. The area around treatment plant is one of the most contaminated area identified by CPCB and frequently referred to as a area of ecological disaster. Groundwater samples collected from open and drilled wells during pre and post- monsoon in and around Patancheru Industrial area indicate more than the desirable level of As, Se, Cr, Cu, Mn, etc. in drinking water.

Ramesh and Elango,(2007), conducted geochemical studies of soil and water of an intensively irrigated region and found that indiscriminate use of agrochemical and irrigation return flow affects the soil structure and groundwater quality in intensive cultivated region. Prasad and Gupta (2007), studied ground water contamination due to leaching of fluoride from fly ash generated from thermal power plant due to combustion of the coal. Higher concentration of fluoride was found in ground water beneath the ash filled mine. Pandey et al. (2007), studied Hexavalent Chromium contamination of

groundwater in Bhilai city and found the presence of Cr (VI) above the Indian Permissible limit 0.05 mg/L in both the ground and surface water samples collected from several location in the industrial estate and from the surrounding colonies. The improper handling and disposal of the chromium products and wastes from industrial area appears to be the reason behind the large scale contamination.

Kumar et al. (2007) have evaluated the hydro-geochemical process in the groundwater of Muktsar District of Punjab and noted the presence of NO_3 and PO_4 clearly showing fertilizer impact on groundwater quality in the area. Dewagan and Patel (2007) studied nitrite and nitrate pollution in groundwater of Chattisgarh and found that in the about 82% of the Chattisgarh area, the nitrite and nitrate content are above the tolerance limits of drinking water quality. Dewangan and Patel (1997) studied phosphate pollution in Chattisgarh and collected 54 ground water samples from different stretches of Chattisgarh and observed that phosphate concentration ranged from 0.1 mg/l to 1.8 mg/l.

Saxena et al. (2007), have estimated the nitrate content quantitavely in the groundwater sample of Krishna delta and observed that about 39% samples have nitrate content exceeding 50 mg/L. In north Krishna delta 49% and in south Krishna Delta 26% water sample were found to exceed the permissible limit of BIS standard of drinking water quality. Nitrate level was found more in dug wells compared to hand pump and bore wells. The possible sources of high nitrate level in ground water have been identified as excessive utilization of nitrogenous fertilizers, insecticides and pesticides for agricultural purpose.

The rapid industrialization and urbanization of Visakhapatnam in Andhra Pradesh led to rise in conductivity from 2500µs/cm to 3500µs/cm and heavy metal exceeded permissible drinking water limit (Subba Rao et al 1993 and 2007).

Kumar et al. (2007) while studying hydro geochemistry in national capital city Delhi found that the EC, SO_4, NO_3 and PO_4 concentration were high in all season and weathering of carbonate, silicate minerals and ion exchange and

surface water interaction seems to be major control on water quality of the region.

Further, Malarkodi and Krishnaswamy (2007) studied the trace metal levels in groundwater of Coimbatore district of Tamil Nadu. The disposal of industrial and urban waste to soil and water bodies has led to high level of Cr in Tirupur ($0.062 \pm$ mg/L) areas mainly due to discharge of Cr rich untreated dyeing and tannery effluents. Although manganese concentration in all samples is found to comply with the WHO limit for drinking water, the concentration of Pb and Cd exceeded the threshold limit in area indicating the possibility of pollution from sewage and electroplating effluent.

Rai et al. (2006) studied sedimentation rate and physico-chemical characteristics of Mansar , Dal and Wooler lake in Jammu & Kashmir and suggested that anthropogenic activities in recent year have greatly affected the hydrological regime of lakes for eg. inflow of eroded material have accelerated eutrophication process.

Singh et al. (2005), conducted study of six reservoirs of Damodar River basin in pre- and post-monsoon, to study the major ion chemistry and the weathering and geochemical processes controlling the water composition. The seasonal data shows a minimum concentration of most of the ions in post-monsoon and a maximum concentration in pre-monsoon seasons, reflecting the impact of elevated temperature and increased evaporation during the low water level period of the pre-monsoon season. Water chemistry of the reservoirs strongly reflects the dominance of continental weathering aided by atmospheric and anthropogenic activities in the catchment area. Higher concentration of SO_4 and TDS in Panchet, Durgapur and Tenughat reservoirs indicate effect of mining and anthropogenic activities on water quality. The high contribution of (Ca+Mg) to the total cations, high concentration of dissolved silica, relatively high (Na+K)/TZ^+ ratio (0.3) and low equivalent ratio of (Ca+Mg)/(Na+K) suggests combined influence of carbonate and silicate weathering. Kaolinite is the possible mineral which is in equilibrium with the water, implying that the chemistry of reservoir water favours kaolinite formation. The calculated

values of SAR, RSC and sodium percentage indicate the 'excellent to good quality' of water for irrigation uses.

Kirch (2003) has conducted study of impact of tourism and urbanization on water supply and water quality in Manali, Himachal Pradesh and revealed that water quality in the Beas River in Manali is generally good, but urbanisation and tourism affect the downstream water quality. They have observed that water borne diseases occur in all areas despite the location of drinking water sources upstream from major contaminants sources. Sharma et al. (2005), reviewed the water quality status at different sources in the Central Himalayan Kingdom of Nepal. The study showed that water of inner and outer Himalaya is vulnerable to fecal pollution. Shallow groundwater in Terai region is at risk due to pathogenic bacteria, pesticides, nitrate and industrial effluent. Deep ground water in Kathmandu and Terai region are largely anaerobic and vulnerable to increased concentration of iron, manganese and ammonium.

Nachiappan et al. (2002), while discussing the hydrochemical characteristics of the groundwater in and around the Nainital lake basin, revealed that the groundwater is geochemically under saturated with respect to calcite and dolomite and has a tendency to dissolve the calcareous rocks more readily than expected in ideal dolomite terrain. The groundwater movements enhance dissolution of carbonate rocks and lead to enlargement of fractures and therefore the quantum of groundwater seepage and their hydrochemical character seem to play a crucial role in the landslide hazards as frequently experienced in the lake basin.

Ravichandran **et al.,** (1996) conducted the regional water quality analysis **from** February to July 2001 in catchment area of Sharawati in Karnataka and observed that biodiversity and cultivation practice using inorganic fertilizer do have impact on water quality parameters. Hosanagar area has impact on water quality parameters.

Jain (2001) undertook hydro chemical study of mountainous watershed of river Ganga and observed increased conductivity (330μS/cm) during low flow

periods and total dissolved solids (2002 mg/L) during monsoon periods due to high sediment concentration. The amount of nitrates and phosphates compounds is slightly high in the samples due to high agricultural activities in the catchment area. Hussain and Ahmed (2002) assigned the variability of physico-chemical parameters of river Pachin, Itanagar during different flow periods to dilution of river water by runoff, runoff, human activities and organic load. Bharathi and Krishnamurthy (1990) studied the effect of industrial effluent on the lotic habitat into river Kali in Dandeli, Karnataka.

Kumar et.al (1988) have studied the variation of plant species in relation to water quality of Doon and concluded that *Pogostemon species a*nd *Rumex nepalensis* are capable of growing in acidic condition associated with very high K, Na and low DO in stream water which receive effluents from distillery. Kumar and Mathur (1989) studied the water quality status of Song and Suswa in Doon Valley Forest. Further, Kumar et al. (1990,1995) studied the physo-chemical and biological characteristics of Song river in eastern Doon Valley forest and highlighted the changes in vegetation and fish at different sites. Jain (1997) has also studied groundwater quality of Doon valley and found that majority of ground water samples falls in the Ca-Mg-HCO_3 hydro-chemical facies and low sodium absorption ratio indicate low sodium hazard. A study on environmental pollution gradient in river Sone near the Rewa city by Srivastava and Mathur (1997) observed adverse effect of industrial effluent discharge on the river which in turn affected the composition of plant species growing on the bank of river. This is manifested in the decrease in the species diversity as polluted water seeps into the soil close to the river banks and as the distance increase in the downstream, diversity index also increase to regain its original species diversity. The impact assessment of community toilet on surface and groundwater quality was studied by Srivastava (2000).

Chakrapani (2002) studied Himalayan lake in Kumaun region namely: Nainital, Bhimtal, Sattal and Naukchiatal and found that water chemistry is dominated by Ca, Mg and HCO_3 indicating carbonate lithology the major

source of ions. Chakrapani (2005) also studied major element geochemistry in upper Ganga river and found large seasonal variation. He observed that the water of the Ganga HCO_3^- SO_4^{2-} and Ca^{2+} are the dominant ions which constitute > 60% of total water composition and about 5 -12 % of HCO_3 and more than 80% Na^+ and K^+ were derived from silicate lithology indicating the predominance of carbonate lithology on the ionic composition of Ganga water. R.K Subdhi et al. (2007) studied temporal variation in dissolve composition of the Ganga river at Rishikesh Uttarakhand.

While carrying out geohydrological studies of the Gaula river basin, District Nainital, Bartarya (1988) has analyzed samples from springs, rivers and lakes and he observed (1993) dominance of $CaHCO_3$ hydrochemical facies over Ca-Mg-SO_4 facies and the chemistry of spring water present in the Lesser Himalayan rocks elucidated influence of rock types of their catchment.

Jain (1999) has carried out physiochemical assessment of surface and groundwater quality of Haridwar and found that quality of groundwater up to 50 feet is not suitable for drinking purposes because of the leaching of organic and inorganic contaminants. The sources of water pollution were found to be from municipal, agricultural, industrial and disposal of solid waste and leakage of petroleum and other oil.

Despite studies of Jain(1996-1997), Jain (2002), Divya (2007), Central Ground Water Board - annual reports of (2001, 2002, 2003, 2004, 2005, Pandey (1999), Haridwar Jal Sansthan (2005, 2006), impact assessment of industrialization and urbanization on water quality has not been carried out in Dehradun and Haridwar district

Further, the factors that control the chemical composition of these waters remain poorly understood. These considerations have led to undertake a detailed water quality investigations of surface and groundwater of Dehradun and Haridwar districts with a view to understand major ion chemistry of surface and groundwater and impact assessment of urbanisation and industrialization.

CHAPTER III

HYDROGEOLOGY OF THE DEHRADUN AND HARIDWAR DISTRICTS

3.1 HYDROGEOLOGY OF DOON VALLEY

Initially by Meijerink (1974); Saxena (1974); Saxena et al. (1979); Kainthola et al. (1988), and Roy, A.K. (1991) has provided the initial geohydrological framework of the Doon Valley. Latter, Bartarya (1995) has given detailed hydrogeology of the Doon valley. Hydrogeologically, the Doon valley has been subdivided (Bartarya 1995) into :

1. Lesser Himalaya Zone
2. Synclinal Central Zone
3. Siwalik Zone

3.1.1 Lesser Himalaya Zone

Steeply sloping northern flank of the valley comprising rocks of the Lesser Himalayan formations, such as quartzite, schist, slates, phyllite, hard sandstone limestone and dolomite of the Chandpur, Nagthat, Blaini, Krol and Tal formation of the lesser Himalaya having secondary porosity and permeability is characterized by spring and seepage. Though sedimentary in nature the rock have very low intergranular porosity and are characterized by fissures, fracture and joints. The zone of lineament, fault and main boundary thrust show pocket of high secondary porosity.
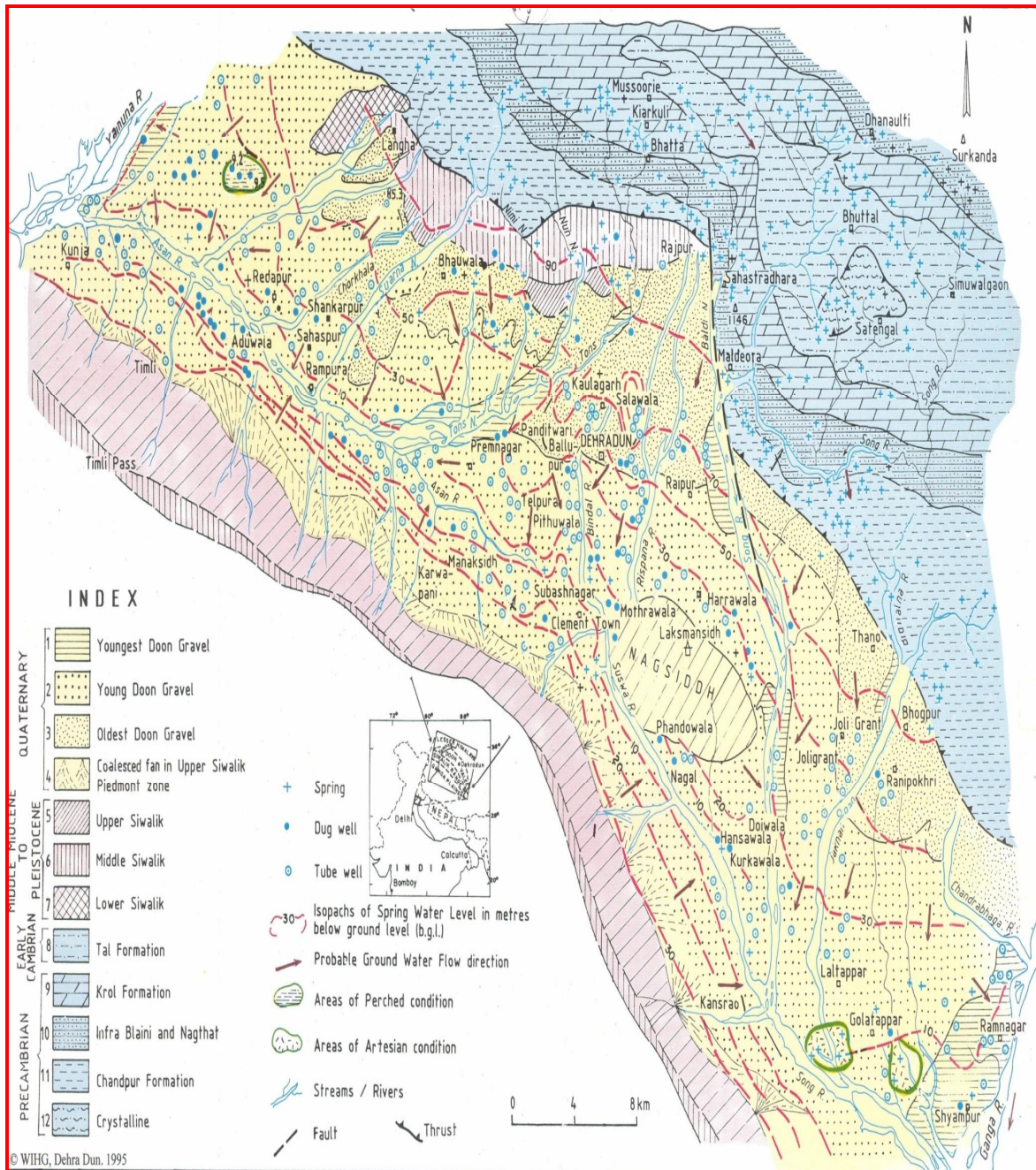
Fig. 3.1: Geohydrological Map of Doon Valley (from Bartarya, 1995)
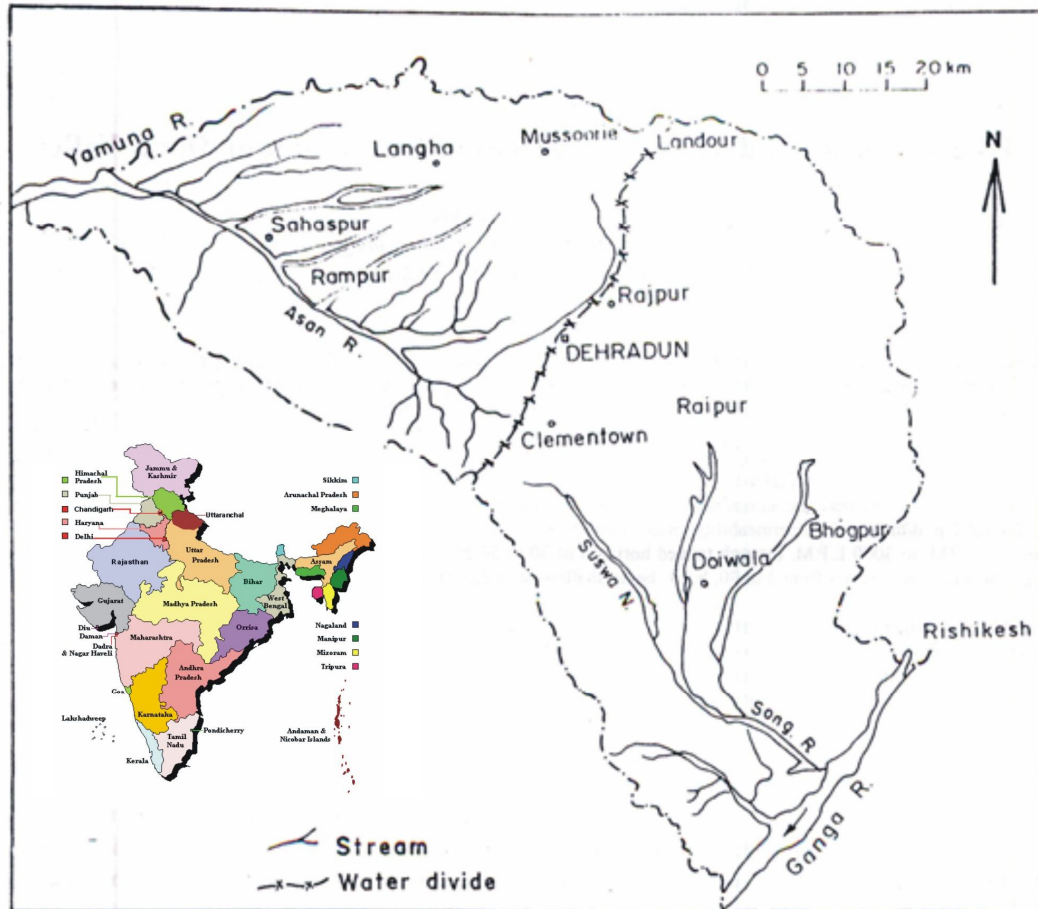
Fig. 3.2: Drainage Map of Doon valley (After Bartarya, 1995)

The sub–surface water in this zone occurs largely as disconnected local bodies in favourably perched aquifer under both confined and unconfined condition and also in zone of jointing fracturing and faulting. Relatively flat areas and gently sloping ground characterized by deep weathering such as hill tops, ridges, saddles, spurs and bulges of old landslide debris, river terraces and fluvial fans from the recharge area while steeper hill slopes first and second order stream at slope breaks and scrap of fans are sites of discharge.

The upper portion of the catchment area are saucer-shape giving rise to large underground bodies of perched water. The spring and seepage issue out from all side of the individual aquifer at different elevation through fractures and joints and from weathered material within short distances.

The limestone and dolomite of Krol formation is characterized by cavities and solution channel oriented along WNW-ESE and NW-SE trending joints. Selective solution along these fracture and joints has created network of underground water courses leading to almost complete lack of first and second order perennial stream over ground. The yield of spring in the karst belt is very high of the order of 173000l/day to 536000 l/day.

The sand–gravel deposit of fluvial and colluvial origin in the Lesser Himalayan Zone lying in the lower reaches of the stream or near the confluence of two stream in the form of fans and terraces are highly porous and permeable and therefore hold sufficient quantities of water. Reliable ground water supply from stream in quantities enough to meet the need of small villages of 150-400 persons are thus available in almost all valley in which traces of sand - gravel deposit are present such as Manjgaon – Pipalsain – Nayar etc. along the Song river. The springs show wide discharge variability from 1400 to 150700l/day.

3.1.2   Synclinal Central Zone

The zone classified under predmont zone occupied by the Doon gravels, having primary porosity and permeability is forming the main aquifer in the area. The ground water is present in multi-tiered aquifers under confined and

unconfined conditions. The coarse and gravel underlain by clay beds is the main water bearing strata. The zone is characterized by high infiltration rate. A number of dug well and tube wells are largely confined in this zone. The depth of water table varies from 3m to 90m below ground level.

A number of water table springs (classifies as springs related to fluvial deposits) are present along the valley floor and along the terrace and fan scarp contributing to the base flow of streams during the lean period of discharge. The discharges of such springs are usually high and vary from 2000 l/day to 2507000 l/day.

3.1.3   The Siwalik Zone

The water is present under confined condition and the water table is relatively deep. Though, the conglomeratic unit of the upper Siwalik is highly porous and permeable but because of steep slopes, due to fans forming piedmont zone along the southern fringe of the valley, and moderate to steep dip of beds the water quickly goes as runoff.

3.2   SUB SURFACE GEOHYDROLOGY

The idea of the subsurface geohydrology of the area can best be had from the available lithologs of the borehole drilled for tube well and from the vertical section exposed in the surrounding areas. The lithologs of the tubewell maintained by CGWB, state irrigation and Jal Nigam department indicate that the horizon comprising boulder and gravel set in coarse sandy matrix are the main water bearing horizons. Such horizon are encountered more than once in the deep drill. These horizon are separated by clay horizon, few are also present in Dharmawala, Raipur and Karanpur. Such horizon do possess water in their pore space but yield from such horizon is rather poor or low. The water yielding horizon occur at about 20m below ground level in western part of the valley. Few horizon of perched nature of limited dimension and yield are also present in northwest, southeast and eastern part of the valley.

Since the Doon gravels are dominantly fan deposit, they generally follow topographic profile where they have been deposited. The various water bearing horizon in the present area tapper towards the foot of the fans, that is towards the Asan and Song River and hence the shallow depth of water table, whereas towards their head region they occur at higher levels.

3.3   TRANSMISSIVITY AND PERMEABILITY

The porosity and permeability of the aquifer varies according to the nature and size of fragment and degree of cementing. Geohydrological data of tubewell drilled by CGWB in Doon valley indicate transmissivity values ranging from 1.648×10^6 to 3.5×10^6 liter per day /m^2 while the filed permeability range from 0.586×10^5 to 1.04×10^5 1.pd/ m^2. The discharge from the tubewell varies from 600 LPM to 3000 LPM through a tapped horizon of 30 to 50 m with a depression of 2 to 7 m.

3.4   TYPES OF SPRING

Based on the genesis, nature of water bearing formation and condition governing the formation of spring can be classified into the following types:

3.4.1   Fault – Lineament Related Spring

Fault planes and lineaments extending deep underground serve as pathway along which the underground water moves and rises upto the surface give rise to such as Kaphlani, Chhansari, near Hathipaon Talai. The discharge of these spring varies form 15800 l/day to 1038,000 l/day.

3.4.2   Fracture –Joint related spring

Spring of this type are formed in fractured and jointed hard sedimentary rock such as in Masrana, Anand Chauk-Kathu-ki-chail, Dibli, Dwara, area. These spring originate either along the hill slope or along stream beds wherever the local water table is intersected by fracture or joint or by the ground surfaces . The average such spring varies form 1300 l/day to 55000 l/day.
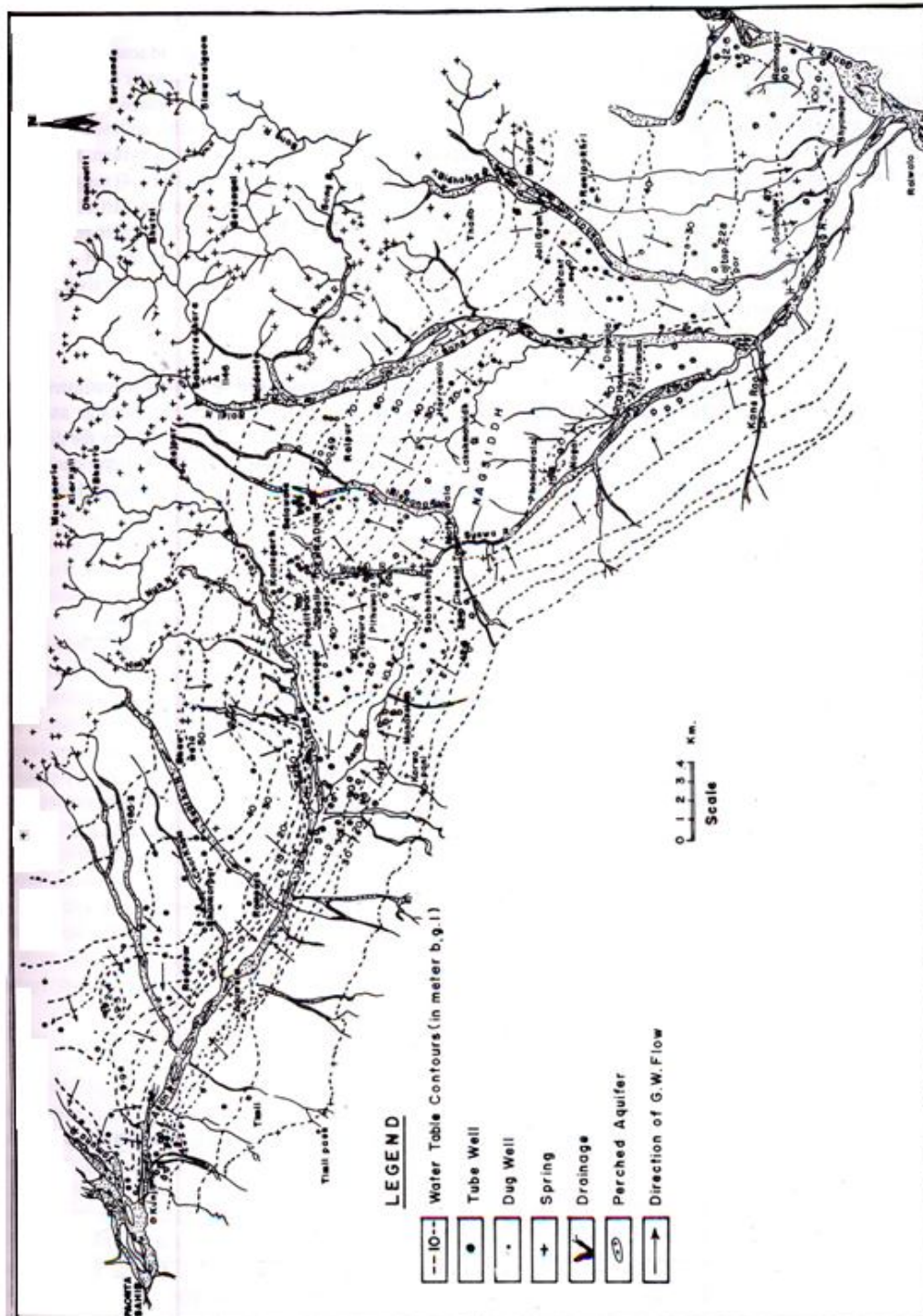
Fig. 3.3: Ground water map of Doon Valley showing direction of ground water flow (After Bartarya, 1995)

3.4.3 Colluvial Spring

The upper slope of the recharge area of the spring are generally low (8-12°) which provide good hydraulic gradient. Such spring occur at Selagaon, Suakholi, Ghaisain etc. The discharge varies from 55 LPM / day.

3.4.4 Fluvial Deposit Related

Because of difference in porosity and permeability of the deposits and underlying bed rock, the groundwater is discharged as spring through the contact of alluvial fans and terraces deposit on terrace and also at the contact of fluvial deposit and the bed rock. Example are galore in the valley of Tal, upper reaches of Song R. Jalikhal, Surna N, Nun N, Baldi and Bindal etc. The discharge of such spring is usually quite high and varies widely from 21500 to 1586,000 l/day.

3.4.5 Karst Spring

Water emanating through cavities and underground channel in dolomites and limestone such as in Sahastradhara and Dharmawala area . The diameter of these cavities and channel when open to the surface varies from 0.2m to 1.5 m . Most of these cavities and channel are joint or fault controlled. Discharge of Karst springs is comparatively higher than other types and varies from 5000 to 536,000l/day during lean - period.

3.5   WATER TABLE

The depth of the water table in Doon valley varies from less then 3 to 90 m below ground level. It is shallowest in the central part of the valley, in subcatchment of the Asan river and deepest close to water divide of Assan and Song river near Kaulagarh, north of Dehradun. Perched condition of shallow water table of local extent are also present in Doon valley, viz, northwest of Redapur and east and west of Doiwala. In general, water table occur at shallow depth towards the distal part of the fans, that is towards the Asan and Song river and at hither levels towards the proximal part of the fan.

3.6   HYDROGEOLOGY OF STUDY AREA (HARIDWAR)

The most common groundwater utilization in the area is through handpump and tubewells. The groundwater condition in the study area are influenced by the varying lithology of the subsurface formation. It has been observed that the strata exhibit great variation both laterally and vertically due to fluvial nature of the deposit of Indogangetic plain. The main source of groundwater recharge is the monsoon rainfall, however replishment of groundwater also take place through infiltration from the rivers, canals and ponds, irrigation etc. Two type of aquifers have been reported from the area (Singh et al 1979). The upper one is the shallow unconfined aquifer which generally extends to the depth of around 25 m. The deeper one is confined to semi confined in nature. The main water yielding horizon is coarse sand separated by clay bed. These water being bearing horizons are present in multitier condition at different depth. Water table contour in the area indicate the south ward trend of groundwater flow both to confined and unconfined aquifers. The Roshnabad industrial area located south of Siwalik foothills. It consist of alluvial material deposited by the stream descending down from the Siwalik range. This predominant unit possesses a series of wide fans, developed into the fancent terrace. Water table is relatively deep and much of the groundwater is recharged through percolation of rainfall to deep aquifers. The Haridwar and Risikesh area are characterized by palaeo- channels, and old terraces. Geologically the area can be divided into four major region these are **Siwalik Range** (the outermost range of Himalayas, extending over a altitude rage of 500 -900 m, **Bhabhar (**foot hill or **Piedmont Alluvial Plain**), **Tarai (**The spring line or seepage zone) and **Indogangetic plain** (the alluvial plain).

3.6.1   Piedmont Alluvial Plain

The piedmont zone is located to the south of the Siwalik foothills of the Himalaya and present several difficulties in groundwater exploration and development due to occurrence of thick deposit of poorly sorted indurated sediments, deep water table and the associated problem during drilling. Due to these problem, the groundwater availability in the area becomes

cost prohibitive and generally unavailable to the rural users for the societal needs. Much of groundwater is recharged by percolation to deep aquifers situated further downstream, because of the southward gradient of the land surface in the Bhabhar zone. The piedmont alluvial plain bordering the Siwalik hill range is a distinct physiographic unit of almost uniform composition and has been formed by accumulation of fluvial debris brought down by the Siwalik streams. The slope being homogeneous, all the streams are of ephemeral type. This zone occurs to the south of the Siwalik foot hills where the streams drain into the open relief less country. It occurs as a flat terrain bordering the southern limit of the Siwaliks. It is composed of the alluvial material deposited by the streams descending down from the windward slopes of the Siwalik range. A major portion of this strata is under forest cover/vegetation and the remaining is under agricultural activity. This piedmont unit possesses a series of wide fans, developed into the fancut terraces. These terrace levels have been cut by few seasonal streams which had once formed It. A small precipitation can cause transportation of huge quartzite boulders. In fact it is a zone of infiltration and drainage is internal. Water can be find after digging these dry beds. These drainage/water channels appear again on the surface across the boundary in the south. The landforms characterizing the piedmont zone are abandoned channels, channel bars, alluvial fans, Braided streams and terraces. Water table is very low and mostly dry farming is practiced.

3.6.2   Upper piedmont zone (Bhabhar)

The Himalaya is skirted by an Upper piedmont zone along its southern margin and is referred differently as "kandi" in the north western India and "Bhabhar" in the northern India. The upper Piedmont zone also known as "Bhabar" bodering the Siwalik, has gentle slope comprise of unconsolidated course material. For the groundwater point of view this belt provides an excellent hydrological set up for recharge and infiltration. The depth of the groundwater varied from 11 to 29 m. (Israil 2006) .

3.6.3 The lower piedmont zone (Tarai)

The lower piedmont zone located further southward is referred as "Tarai" is separated from the upper piedmont by the spring line along their junction line. The zone is composed of coarse-grained sand and clays with gravel (boulders and pebbles). The groundwater level varied in this area from 2 to 7m and the groundwater prospects are very good to excellent.

3.6.4 The Indo-Gangetic Plains (The alluvial plain)

The indo-gangetic plain or Gagnga alluvial plain is located south of the lower piedmont zone, toughtout the length of the Ganga river. The zone is consist of medium garined sand siet and clay beds. The ground water occurs under unconfined conditions and water table varies from 2 m to 25 m b.g.l and ground water prospects are excellent.

CHAPTER IV

SIGNIFICANCE OF WATER QUALITY PARAMETERS
USED IN THE PRESENT STUDY

4.1   WATER QUALITY PARAMETERS

The chapter discusses various measured parameters of water quality, their controlling factor and their environmental effects and importance for the better management of water resources.

4.1.1   Temperature

Measurement of temperature is an important parameter required to get an idea of self purification of rivers, reservoirs and control of treatment plant for fish life and calculating the solubility of the oxygen and carbon dioxide, bicarbonate and carbonate equilibrium. The temperature of surface water is influence by latitude, altitude, season, time of day, air circulation cloud cover, flow and depth of biological process in water bodies. Temperature affects physical, chemical and biological process in water bodies. As water temperature increases the rate of chemical reaction generally increases together with the evaporation and volatilsation of substance from the water. Increase temperature also decrease the solubility of gases in water, such as O_2, CO_2, N_2 and CH_4. Warm water is less capable of holding dissolved oxygen. Ground water usually maintain a fairly constant temperature which for surficial aquifer is normally close to the mean annual air temperature. However deep aquifer have higher temperature due to earth's thermal gradient. Factors affecting temperature may include flow rate, passed surfaces, industrial discharge sewage outflow etc.

4.1.2 Dissolve Oxygen

Dissolved oxygen (DO) refers to the volume of oxygen that is contained in water. Dissolved oxygen (DO) is important in precipitation and dissolution of inorganic substances in water. The solubility of atmospheric oxygen in fresh water ranges from 14.6 mg/L at 0°C to about 7.0 mg/L at 35°C under one atmospheric pressure.

The introduction of excess organic matter may result in a depletion of oxygen from an aquatic system. Prolonged exposure to low dissolved oxygen levels (less than 5 to 6 mg/l oxygen) may not directly kill an organism, but will increase its susceptibility to other environmental stresses. Exposure to less than 30% saturation (less than 2 mg/l oxygen) for one to four days may kill most of the aquatic life in a system.

If all oxygen is depleted, aerobic (oxygen-consuming) decomposition increases and further organic breakdown is accomplished anaerobically. Anaerobic microorganisms obtain energy from oxygen bound to other molecules such as nitrates and sulfates. The oxygen-free conditions result in the mobilization of many insoluble compounds. As sulfate compounds break down, the water may smell like rotten eggs. Low dissolved oxygen levels may occur during warm, stagnant conditions that prevent mixing. In addition, high natural organic levels will often cause a depletion of dissolved oxygen.

The factor which affects the DO concentration in water are volume and velocity of water flowing in the water body, weather, altitude, dissolve and suspended solids, amount of nutrient in water, organic waste, riparian vegetation, groundwater inflow, seasonal stratification, microbes etc.

Very high DO concentrations can also be harmful to aquatic life. Fish in waters containing excessive dissolved gases may suffer a condition in which bubbles of oxygen block the flow of blood through blood vessels, causing death. Abrupt changes in dissolved oxygen induce stress and subsequently make fish more susceptible to disease. Although no criteria is given for DO in BIS and WHO.

The ideal dissolved oxygen concentration for many fish is between 7mg/l and 9mg/l; the optimal DO for adult brown trout is 9mg/l-12 mg/l. Most fish cannot survive at concentrations below 3 mg/l of dissolved oxygen.

4.1.3 pH

The pH is an important variable in water quality assessment as it influences many biological and chemical processes within a water body. Water (H_2O) contains both hydrogen (H^+) and hydroxyl (OH^-) ions. The activity of hydrogen ions can be expressed most conveniently in logarithmic units. pH is defined as the negative logarithm of the activity of H^+ ions:

$$pH = -\log [H^+]$$

Where $[H^+]$ is the concentration of H^+ ions in moles per liter (a mole is a unit of measurement, equal to 6.022×10^{23} atoms). Because H^+ ions associate with water molecules to form hydronium (H_3O^+) ions, pH is often expressed in terms of the concentration of hydronium ions. The pH of water is a measurement of the concentration of H^+ ions, using a scale that ranges from 0 to 14. A pH of 7 is considered "neutral", since concentrations of H^+ and OH^- ions are equal. Liquids or substances with pH 7 are considered "acidic", and contain more H^+ ions than OH^- ions. Those with pH above 7 are considered "basic" or "alkaline," and contain more OH^- ions than H^+ ions. For every one unit change in pH, there is approximately a ten-fold change in acidity or alkalinity. Therefore, a pH of 4 is 10 times more acidic than a pH of 5. Similarly, a pH of 9 is 10 times more alkaline than a pH of 8 and 100 times more alkaline than a pH of 7.

Most streams have a neutral to slightly basic pH of 6.5 to 8.5. If streamwater has a pH less than 5.5, it may be too acidic for fish to survive in, while streamwater with a pH greater than 8.6 may be too basic. Fossil fuel combustion products, especially automobile and coal-fired power plant emissions, contain nitrogen oxides and sulfur dioxide, which are converted to nitric acid and sulfuric acid in the atmosphere. When these acids combine with moisture in the atmosphere, they fall to earth as acid rain or acid snow.

A change in stream water pH can also affect aquatic life indirectly by altering other aspects of water chemistry. For example, low pH levels can increase the solubility of certain heavy metals. This allows the metals to be more easily absorbed by aquatic organisms.

A shift of pH in either direction from neutral may indicate the presence of a pollutant in the stream. However, since some streams are naturally acidic or basic pH may not necessarily indicate pollution. The pH of clean water depends on several factors, including the types of rock and vegetation within the watershed. The water that enters a stream passes through the canopy of the trees, percolates through the soil, and flows through the groundwater system to eventually empty into the stream. During its travels, the water weathers the rocks and soils and picks up acidic and alkaline (high pH) compounds throughout the watershed. For example, streams draining forests and marshes are often slightly acidic due to the presence of humic acids produced by decaying vegetation in the soil. On the other hand, streams in watersheds situated on limestone ($CaCO_3$) contain high concentrations of bicarbonate ions. This results in alkaline waters.

Alkaline water can act as a weak buffer solution, depending on the concentrations of carbonates and bicarbonates. Therefore an acidic pollutant may be present in such water, yet not cause a change in the stream's pH. For this reason, alkalinity should be examined in conjunction with pH. Several factor which affect pH of water include concentration of carbon dioxide in water, drainage for mix sites, geology and soil watershed.

The U.S. Environmental Protection Agency (U.S. EPA) & WHO and BIS sets a secondary standard for pH levels in drinking water between pH 6.5 and 8.5.

4.1.4 Total Dissolved Solid (TDS)

Total Dissolved Solids (TDS) are solids in water that can pass through a filter (usually with a pore size of 0.45 micrometers). TDS is a measure of the amount of material dissolved in water. This material can include carbonate,

bicarbonate, chloride, sulfate, phosphate, nitrate, calcium, magnesium, sodium, organic ions, and other ions. A certain level of these ions in water is necessary for aquatic life. Changes in TDS concentrations can be harmful because the density of the water determines the flow of water into and out of an organism's cells (Mitchell and Stapp, 1992). However, if TDS concentrations are too high or too low, the growth of many aquatic life can be limited, and death may occur.

TDS is used to estimate the quality of drinking water, because it represents the amount of ions in the water. Water with high TDS often has a bad taste and high water hardness and could result in a laxative effects.

The factor affecting TDS water are urban runoff, fertilizer runoff, waste water and septic tank effluent, soil erosion, decaying plants and animals etc.

The U.S. Environmental Protection Agency (U.S. EPA) sets a secondary standard of 500 mg/l TDS in drinking water. Secondary standards are unenforceable, but recommended, guidelines for contaminants that may cause cosmetic or aesthetic effects in drinking water. High TDS concentrations can produce laxative effects and can give an unpleasant mineral taste to water. High TDS concentrations in water is also unsuitable for many industrial applications.

4.1.5 Conductivity

Conductivity or specific conductance is measure of ability of water to conduct an electric current. There are several factors that determine the degree to which water will carry an electrical current. These include: the concentration or number of ions, mobility of the ions, oxidation state (valence) and temperature of the water resistance, which is an electrical measurement expressed in ohms, is the inverse of conductivity. Conductivity is then expressed in reciprocal ohms. A more convenient unit of measurement in the chemical analysis of water is micro omhos. The specific conductance or conductivity measurement is related to ionic strength. It is defined as the "reciprocal (opposite) of the resistance in ohms measured between opposite

faces of a centimeter cube of an aqueous solution at a specified temperature" (Hem, 1985).

That is conductance = 1 / resistance

Specific conductance is measured using a sensor which measures resistance. The unit of conductance was originally ohm spelled backwards – "mho." More recently, however, the name "siemen" has been used to match the term used by the International System of Units. Because SC in natural waters is usually much less than 1 siemen/cm, SC is usually reported in microsiemens (1/1,000,000 siemen) per centimeter, or μS/cm. SC is affected by temperature, so for consistency SC values are converted to what they would be at room temperature (25^0 C). The factors affecting conductivity are geology and soil in the watershed, acid mine drainage, agricultural and road runoff.

Generally, there aren't regulatory levels for conductivity. Instead, the concentration of total dissolved solids (TDS) is often regulated. However, conductivity is an easily-obtained parameter that is a good indicator of the amount of dissolved solids in a water, and thus can be used to detect contaminants in water. Pure water would theoretically have an conductivity value of zero μS/cm at 25^oC, however, this water is very difficult to produce. Distilled or deionized water has an conductivity of at least 1 μS/cm. Sea water has conductivity of approximately 50,000μS/cm, because of the large amount of dissolved salts it contains.

4.1.6   Alkalinity

Alkalinity is a measure of the buffering capacity of water, or the capacity of bases to neutralize acids. Measuring alkalinity is important in determining a stream's ability to neutralize acidic pollution from rainfall or wastewater. Alkalinity does not refer to pH, but instead refers to the ability of water to resist change in pH. The presence of buffering materials help neutralize acids as they are added to the water. These buffering materials are primarily the bases bicarbonate (HCO_3^-), and carbonate (CO_3^{2-}), and occasionally hydroxide

(OH^-), borates, silicates, phosphates, ammonium, sulfides, and organic ligands.

Waters with low alkalinity are very susceptible to changes in pH. Waters with high alkalinity are able to resist major shifts in pH. As increasing amounts of acid are added to a water body, the pH of the water decreases, and the buffering capacity of the water is consumed. Alkalinity not only helps to regulate the pH of a water body, but also the metal content. Bicarbonate and carbonate ions in water can remove toxic metals (such as lead, arsenic, and cadmium) by precipitating the metals out of solution. Alkalinity values of 20-200 ppm are common in freshwater ecosystems. Alkalinity levels below 10 ppm indicate poorly buffered streams. These streams are the least capable of resisting changes in pH, therefore they are most susceptible to problems which occur as a result of acidic pollutants.

Alkalinity results from the dissolution of calcium carbonate ($CaCO_3$) from limestone bedrock which is eroded during the natural processes of weathering. The carbon dioxide (CO_2) released from the calcium carbonate into the streamwater undergoes several equilibrium reactions.

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \longleftrightarrow 2H^+ + CO_3^{2-}$$
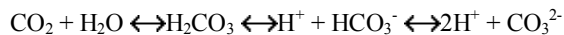
As depicted in the above set of reactions, carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions act as hydrogen ion absorbers.

The factors affecting alkalinity include geology and soils, changes in pH and sewage outflow. This is expressed as mg of $CaCO_3$/L even though actually may be contributed by $MgCO_3$, Na_2CO_3 or K_2CO_3.

Alkalinity is important for fish and aquatic life because it protects or buffers against rapid pH changes. Living organisms, especially aquatic life, function best in a pH range of 6.0 to 9.0. Alkalinity is a measure of how much acid can be added to a liquid without causing a large change in pH. Higher alkalinity levels in surface waters will buffer acid rain and other acid wastes and prevent pH changes that are harmful to aquatic life.

4.1.7 Hardness

Hardness is measure of polyvalent cations (ions with a charge greater than +1) in water. Hardness generally represents the concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions, because these are the most common polyvalent cations. Other ions, such as iron (Fe^{2+}) and manganese (Mn^{2+}), may also contribute to the hardness of water, but are generally present in much lower concentrations. Waters with high hardness values are referred to as "hard," while those with low hardness values are "soft".

Hardness affects the amount of soap that is needed to produce foam or lather. Hard water requires more soap, because the calcium and magnesium ions form complexes with soap, preventing the soap from sudsing. Hard water can also leave a film on hair, fabrics, and glassware. Hardness of the water is very important in industrial uses, because it forms scale in heat exchange equipment, boilers, and pipe lines. Some hardness is needed in plumbing systems to prevent corrosion of pipes. Hardness mitigates metals toxicity, because Ca^{2+} and Mg^{2+} help keep fish from absorbing metals such as lead, arsenic, and cadmium into their bloodstream through their gills. The greater the hardness, the harder it is for toxic metals to be absorbed through the gills.

Hardness is generally measured by titration. A buffer and a color indicator are added to a volume of water. An acid (the titrant) is then added to the water, and it reacts with the Ca^{2+} and Mg^{2+} in the water. The volume of acid required to change the color of the sample reflects the Ca^{2+} and Mg^{2+} concentration of the sample. The more acid needed, the more Ca^{2+} and Mg^{2+} in the sample. Hardness is generally expressed in units of milligrams per liter (mg/l) or parts per million (ppm) of $CaCO_3$ (calcium carbonate).

Hardness can also be calculated from measurements of calcium and magnesium using the following formula:

Hardness, mg equivalent/L $CaCO_3$ = ([Ca, mg/l]*2.497) + ([Mg, mg/l]*4.116)

The factors affecting hardness include geology of the area, mining activities, industrial effluent, sewage outflow. Because hardness varies greatly due to differences in geology, there aren't general standards for hardness. The hardness of water can naturally range from zero to hundreds of milligrams per liter (or parts per million). Waters with a total hardness in the range of 0 to 60mg/L are termed soft; from 60mg/l to 120mg/L moderately hard; from 120mg/l to 180 mg/L hard; and above 180 mg/L very hard.

The desirable limit for total hardness in drinking water is 300mg/L while the permissible limit is 600mg/L as per BIS standards whereas no guideline were given for total hardness by WHO standards for drinking water quality.

4.1.8   Fluorides

Fluorides are compounds containing the element fluorine. Some of the most common of these compounds include the following: sodium fluoride (NaF), sodium silicofluoride (Na_2SiF_6), and calcium fluoride (CaF_2). Fluorine is the most reactive nonmetallic element. It forms compounds with all elements except helium, neon and argon and also form salts in combination with metals.

Fluoride ions may be present either naturally or artificially in drinking water and are absorbed to some degree in the bone structure of the body and tooth enamel. Fluoride at extremely high levels can cause mottling (discoloration) of the teeth. Some fluoride compounds may also cause corrosion of piping and other water treatment equipment. Natural fluorides occur in rocks in some areas. Another source of fluorides in streams and reservoirs is releases from sewage treatment plants, since most public water supplies add fluoride to drinking water to reduce dental decay.

The Kentucky Water Quality Standards maximum for fluoride in streams is a concentration of 1 mg/L or 1 part per million. Higher levels may be harmful to aquatic life. Fluoride concentration in water to be used for domestic water supply should not exceed 1.0 mg/L.

4.1.9 Chloride

Chloride is generally present in natural waters. The presence of chloride in natural waters can be attributed to precipitation dissolution of salt deposits, discharges of effluents from chemical industries, oil well operations, sewage discharges, irrigation drainage, contamination from refuge leachates, and sea water intrusion in coastal areas. Each of these sources may result in local contamination of both surface water and groundwater. The salty taste produced by chloride depends on the chemical composition of the water. A concentration of 250mg/L may be detectable in some waters containing sodium ions. On the other hand, the typical salty taste may be absent in water containing 1000mg/L chloride when calcium and magnesium ions are predominant. A high chloride content also has a deleterious effect on metallic pipes and structures as well as on agricultural plants.

Chlorides are salts resulting from the combination of the gas chlorine with a metal. Some common chlorides include sodium chloride (NaCl) and magnesium chloride ($MgCl_2$). Chlorine alone as Cl_2 is highly toxic and it is often used as a disinfectant. In combination with a metal such as sodium it becomes essential for life. Small amounts of chlorides are required for normal cell functions in plant and animal life.

Chlorides are not usually harmful to people, however, the sodium part of table salt has been linked to heart and kidney disease. Sodium chloride may impart a salty taste at 250 mg/L, however, calcium or magnesium chloride are not usually detected by taste until levels of 1000mg/L are reached. Chlorides may get into surface water from several sources including; rocks containing chlorides, agricultural runoff, wastewater from industries, oil well wastes, effluent wastewater from wastewater treatment plants, and road salting.

Chlorides can corrode metals and affect the taste of food products. Therefore, water that is used in industry or processed for any use has a recommended

maximum chloride level. Chlorides can contaminate fresh water streams and lakes

The permissible limit of chloride is 100mg/L while the required desirable limit is 250mg/L as per BIS for dirking water quality. The most desirable limit for Cl is 200 mg/L and maximum allowable limit is 600mg/L as per WHO guidelines.

4.1.10 Nitrate

Nitrogen is required by all organisms for the basic processes of life to make proteins to grow and to reproduce. Nitrogen is very common and found in many forms in the environment. Inorganic forms include nitrate (NO_3), nitrite (NO_2), ammonia (NH_3), and nitrogen gas (N_2). Organic nitrogen is found in the cells of all living things and is a component of proteins, peptides, and amino acids. Nitrogen is most abundant in Earth's environment as N_2 gas, which makes up about 78 % percent of the air we breathe.

The nitrate ion (NO_3^-) is common form of combined nitrogen found in natural water. It may be biochemically reduced to nitrite (NO_2) by denitrification processes, usually under anaerobic condition. The nitrite ion is rapidly oxidized to nitrate. Igneous rock, land drainage, plant and animal debris are the natural sources of nitrate. The nitrate ion can be increased by municipal and industrial wastewater including lechate from the waste disposal sites and sanitary landfill. In rural area and suburban area the use of inorganic nitrate fertilizer can be significant source. Seasonal fluctuation in nitrate occur with aquatic plant growth and decay.

Common forms of nitrogen in water are nitrate and nitrite. Nitrate is highly soluble (dissolves easily) in water and is stable over a wide range of environmental conditions. It is easily transported in streams and groundwater. Nitrates feed plankton (microscopic plants and animals that live in water), aquatic plants, and algae, which are then eaten by fish. Nitrite (NO_2) is relatively short-lived in water because it is quickly converted to nitrate by

bacteria. Excessive concentrations of nitrate and or nitrite can be harmful to humans and wildlife. Nitrate is of most concern for humans. Nitrate is broken down in our intestines to become nitrite. Nitrite reacts with hemoglobin in human blood to produce methemoglobin, which limits the ability of red blood cells to carry oxygen. This condition is called *methemoglobinemia* or *"blue baby"* syndrome (because the nose and tips of ears can appear blue from lack of oxygen). Wells contaminated by sewage or agricultural runoff are a major concern in some areas.

The factors which affects nitrate and nitrite concentrations include wastewater and septic system effluent, fertilizer runoff, animal waste, fossil fuels and industrial discharge. The most desirable limit of nitrate for drinking water is 45 mg/L as per BIS and WHO standard.

4.1.11 Phosphate

Presence of phosphates in water and waste water analysis has a great significance. Phosphates in small concentration are used in water supplies to reduce scale formation, to increase carrying capacity of mains, to avoid corrosion in water mains, to remove iron and manganese in micro quantities and in coagulation especially in acid conditions. The presence of phosphate in large quantities in fresh waters indicates pollution through sewage and industrial wastes. It promotes growth of nuisance pausing micro organisms. Though phosphate posses problems in surface waters, its presence is necessary for biological degradation of wastewaters.

Phosphorus is also a nutrient required by all organisms for the basic processes of life. Phosphorus is a natural element found in rocks, soils and organic material. Phosphorus clings tightly to soil particles and is used by plants, so its concentrations in clean waters is generally very low. However, phosphorus is used extensively in fertilizer and other chemicals, so it can be found in higher concentrations in areas of human activity. Phosphorus exists in water in either a particulate phase or a dissolved phase. Phosphates can be in inorganic form

(including orthophosphates and polyphosphates), or organic form (organically-bound phosphates).

The various factors which affecting phosphate concentrations in water include: wastewater and septic system effluent, detergents, fertilizers and animal waste and industrial discharge, mining, forest fires and formation of synthetic material.

No national or state criteria have been established for concentrations of phosphorus compounds in water. However, to control eutrophication, the EPA makes the following recommendations: total phosphate should not exceed 0.05mg/L (as phosphorus) in a stream at a point where it enters a lake or reservoir, and should not exceed 0.1 mg/L in streams that do not discharge directly into lakes or reservoirs (Muller and Helsel,1999). Phosphate levels greater than 1.0mg/L may interfere with coagulation in water treatment plants. As a result, organic particles that harbor microorganisms may not be completely removed before distribution.

4.1.12 Sulfate

Sulfate is second to bicarbonate as the major anion in hard water reservoirs. Sulfates can be naturally occurring in waters passing through rock or soil containing gypsum and other common minerals, or of atmospheric deposition or the result of municipal or industrial discharges. 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.

A sulfur cycle exists which includes atmospheric sulfur dioxide (SO_2), sulfate ions and sulfides. Sulfides, especially hydrogen sulfide (H_2S), are quite soluble in water and are toxic to both humans and fish. Sulfates are not considered toxic to plants or animals at normal concentrations. In humans the sulphate concentrations of 500mg/l to 750mg/L cause a temporary laxative

effect. However doses of several thousand mg/L did not cause any long-term ill effects. At very high concentrations sulfates are toxic to cattle. Problems caused by sulfates are most often related to their ability to form strong acids which changes the pH. Sulfate ions also are involved in complexing and precipitation reactions which affect solubility of metals and other substances.

Recommended desirable limits for water used as a Domestic Water Supply are below 200mg/L and permissible limit is 400mg/L as per BIS standard for drinking water quality.

4.1.13 Calcium

Calcium is the fifth most abundant element in the earth's rock and soil and it is readily leached out by rain water particularly as carbonate and sulphates, especially from limestone and gypsum. This present Ca^{2+} in all surface water as at varying concentration. One of the main reasons for the abundance of calcium in water is its natural occurrence in the earth's crust. It occurs naturally as anorthite ($CaAl_2Si_2O_8$), calcite ($CaCO_3$), dolomite ($CaMg(CO_3)$, gypsum occur naturally as ($CaSO_4.2H_2O$), fluoride (CaF_2), fluoroapatite ($Ca_5(PO_4)_3F$ and hydroxyyapatite ($Ca_5(PO_4)OH$).

Calcium compounds are stable in water when carbon dioxide is present, but calcium levels fall when calcium carbonate precipitate due to increased water temperature, photosynthesis activity. Calcium is a dietary requirement for all organisms apart from some insects and bacteria. Calcium carbonate is a building stone of skeletons of most marine organisms, and eye lenses.

Some environmental effects of water hardness include hardening of domestic equipment. Calcium is a dietary mineral that is present in the human body in amounts of about 1.2 kg. Calcium phosphate is a supporting substance, and it causes bone and tooth growth, together with vitamin D. Calcium is also present in muscle tissue and in the blood. It is required for cell membrane development and cell division, and it is partially responsible for muscle contractions and blood clotting. Calcium regulates membrane activity, it

assists nerve impulse transfer and hormone release, stabilizes the pH of the body, and is an essential part of conception. In order to stimulate these body functions a daily intake of about 1000 mg of calcium is recommended for adults. This may be achieved by consuming dairy, grains and green vegetables. Calcium carbonate works as a stomach acid remedy and may be applied to resolve digestive failure.

WHO and BIS has given the most desirable limit for Ca is 75 mg/L while maximum allowable limit is 200 mg/L.

4.1.14 Magnesium

Weathering of rock containing ferromagneisum mineral and from some carbonate rock is the main source of Mg in water. Magnesium occur mainly in organometallic compound. Magnesium is mainly present as Mg^{2+} (aq) in watery solutions, but also as $MgOH^+$(aq) and $Mg(OH)_2$(aq). In seawater it can also be found as $MgSO_4$. Magnesium generally is a slow-reacting element, but reactivity increases with oxygen levels. Furthermore, magnesium reacts with water vapor to form magnesium hydroxide and hydrogen gas:

$$Mg\ (s) + 2H_2O(g) \rightarrow Mg(OH)_2(aq) + H_2(g)$$

A large number of minerals contains magnesium, for example dolomite (calcium magnesium carbonate; $CaMg(CO_3)_2$ and magnesite (magnesium carbonate; $MgCO_3$).

As per BIS standard the most desirable limit for Mg is 30mg/L, permissible limit is 100mg/L and 150mg/l as maximum permissible limit. However as per WHO standard for drinking water quality the most desirable limit is 50mg/L.

4.1.15 Sodium

The sodium content of ground and surface water is mainly dependent upon the nature of geology of the catchment and weathering process of rock and soil.

The concentration of sodium may increased from sewage and industrial effluents, from discharge of waste water, from treatment plants or saline water intrusion from coastal area and from mines. Sodium is essential element to living organism and harmless in small concentration. Elevated sodium in certain soil types can degrade soil structure thereby restricting water movement and affecting plant growth. Sodium is commonly measured where the water is to be used for drinking or agricultural purposes.

The sodium absorption ratio (SAR) is used to evaluate the suitability of water for irrigation. The ratio estimate the degree to which sodium will be absorbed by soil. High value of SAR imply that sodium in the irrigation water may replace the calcium and magnesium ion, potentially causing damage to soil structure.

According to WHO, the limit of general acceptability of sodium in water should not exceed 200 mg/l .

4.1.16 Potassium

Potassium is non-water soluble, but it does react with water. However, potassium compounds may be water soluble. Examples are potassium dichromate with a water solubility of 115 g/L, potassium permanganate with a water solubility of 76 g/L, potassium iodide with a water solubility of 92 g/L, and potassium iodide, of which even up to 1480 g may be dissolved in one litre of water.

Sea water contains about 400 ppm potassium. Rivers generally contains about 2-3 ppm potassium. This difference is mainly caused by a large potassium concentration in oceanic basalts. Calcium rich granite contains up to 2.5% potassium. In water this element is mainly present as K^+ (aq) ions. ^{40}K is a naturally abundant radioactive potassium isotope.

Potassium occurs in various minerals from which it may be dissolved through weathering processes. Rock containing feldspars (orthoclase and microcline),

and chlorine minerals carnalite and sylvite, are the potential source of potassium. Some clay materials also contain potassium.

Potassium from dead plant and animal material is often bound with clay minerals in soils, before it dissolves in water. Consequently, it is readily taken up by plants again. Ploughing may disturb this natural process. Therefore, potassium fertilizer are often added to agricultural soils. Plants contain about 2% potassium (dry mass) on average, but values may vary from 0.1-6.8%.

Potassium is weakly hazardous in water, but it does spread rapidly, because of its relatively high mobility and low transformation potential. Potassium toxicity is usually caused by other components in a compound, for example cyanide in potassium cyanide. However no drinking water limit has been given for K by BIS and WHO standards for drinking water quality.

4.2   HEAVY METALS

4.2.1   Lead

The primary natural source of lead is in the mineral galena (lead sulfide). It also occurs as carbonate, as sulfate and in several other forms. The solubility of these minerals and also of lead oxides and other inorganic salts is low.

Lead reaches water bodies either through urban runoff or discharges such as sewage treatment plants and industrial plants. It may also be transferred from the air to surface water through precipitation (rain or snow). Toxic to both plant and animal life, lead's toxicity depends on its solubility and this in turn depends on pH and is affected by hardness. Lead is not an essential element. In humans it can affect the kidneys, the blood and most importantly the nervous system and brain. Even low levels in the blood have been associated with high blood pressure and reproductive effects. It is stored in the bones.

The required desirable limit for Pb is 0.05mg/L while no relaxation given in permissible limit as per BIS standard. According to WHO standards for drinking water quality the permissible limit is 0.1mg/L for drinking water.

4.2.2 Cadmium

Cadmium is widely distributed in the environment at low concentrations. It can be found in fairly high concentrations in sewage sludge. Primary industrial uses for cadmium are plating, battery manufacture, pigments, and plastics. Cadmium is uniformly distributed in trace amounts in the earth's crust. Generally zinc ores contain small amounts of cadmium. Principle ore is cadmium blende (CdS) and associated with sphelerite (ZnS). The solubility of cadmium in water is influenced by the nature of source of the cadmium and the acidity of water. Surface water that contain more than a few micrograms of cadmium per liter have probably been contaminated by discharge of industrial wastes or by leaching from areas of landfill or from soils to which sewage sludge has been added. The levels of cadmium in public water supplies are normally very slow, but higher levels in tap waters are associated with plated plumbing fittings, silver-base solders, and galvanised iron piping materials. Acute effects have been seen where water has been contaminated by cadmium. Cadmium is readily absorbed through ingestion or though the lungs. The required desirable limit for Cd is 0.01mg/L as per BIS and maximum allowable limit is 0.003mg/l as per WHO guidelines for dirking water quality.

4.2.3 Manganese

The presence of manganese in natural water occurs in both dissolved and suspended forms. Groundwater often contains high levels of dissolved manganese. Freshwater may contain one to several thousand micrograms of manganese per litre depending on the location. Higher levels of manganese sometime found in free flowing river water associated with industrial pollution. The reducing conditions that may exist in underground water and in some lakes and reservoirs are conducive to very high levels of manganese.

The presence of manganese in drinking water supplies may be objectionable for a number of reasons unrelated to health. At

concentrations exceeding 0.15 mg/L manganese imparts an undesirable taste to water and beverages and stains plumbing fixtures and laundry. When manganese compounds in solution undergo oxidation, manganese is precipitated resulting in problems of incrustation. Even at concentration of 0.02mg/L, manganese will form coatings on piping which may slough off as a black precipitate. The growth of certain nuisance organisms is also supported by manganese. These organisms concentrate manganese and give rise to taste, odour and turbidity problems in the distributed water.

Water to be used as a domestic water source should contain less than 0.05mg/L manganese. The required desirable limit for manganese is 0.1mg/L and permissible limit is 0.3mg/L as per BIS and 0.5mg/l as per WHO standard for specification for drinking water (BIS: 10.5, 1991).

4.2.4 Copper

Copper and its compounds are ubiquitous in the environment and are frequently found in surface water. The nature of the copper in water depends on the pH, carbonate concentration and other anions in solution. Various chemical and physical characteristics of the distributed water influence the leaching of copper from the distribution system and house hold plumbing. Water stored in copper vessels tend to maintain the bacterial quality without deterioration. Copper in solution imparts a colour and an undesirable taste to drinking water. The presence of copper in the water supply, may interfere with the intended domestic uses of water. Copper in public water supplies enhance corrosion of aluminium, and zinc utensils and fittings. Staining of laundry and plumbing fixtures occurs when copper concentration in water exceed 1.0 mg/L.

Copper is an essential element in human metabolism, However, intake of excessively large doses by man leads to severe mucosal irritation and corrosion wide spread capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression.

The required desirable limit for Cu is 0.05 mg/L and permissible limit is 1.5mg/L as per BIS and 2mg/L as per WHO guidelines for drinking water quality.

4.2.5 Zinc

Zinc is found naturally in many rock-forming minerals. Zinc is an abundant element and constitutes approximately 0.04g/L of the earth's crust. The most common zinc mineral is sphalerite (ZnS), which is often associated with the sulfides of other metallic elements, The atmospheric concentrations of zinc vary considerably depending on the proximity of point sources. The carbonates, oxides, and sulfides zinc are sparingly soluble in water, while the highly soluble chloride and sulfate salts tend to hydrolyse to form zinc hydroxide and zinc carbonate, as a result the concentration of zinc in natural water is generally low. The concentration of zinc in tap-water can be considerably higher than that in surface water owing to the leaching of zinc from galvanized pipes, brass, and zinc containing fittings. Zinc imparts to water an undesirable astringent taste; in addition water containing zinc at concentration to excess of 5.0 mg/L may appear opalescent to develop a greasy film on boiling.

The required desirable limit of Zn is 5 mg/l and permissible limit for Zn is 15 mg/L as per BIS for drinking water quality and is 3 mg/l as per WHO guidelines for drinking water quality (1993).

4.2.6 Iron

Iron in water occurs mainly in the divalent and trivalent state (ferrous and ferric) and in surface water it generally present in the ferric state. The concentration of iron in well aerated water is seldom high, but under reducing conditions, which may exist in some grounwater, lakes or reservoirs, and in the absence of sulfate and carbonate, high concentration of soluble ferrous iron may be found. The presence of iron in natural water

can be attributed to the dissolution of rocks and minerals, acid mine drainage, landfill leachates, sewage or engineering industries.

The presence of iron in drinking water supplies is objectionable for a number of reasons. Under the less pH condition existing in drinking water supply, ferrous sulfate is unstable and precipitates as insoluble ferric hydroxide, which settles out as a rust coloured silt. Such water often tastes unpalatable even at low concentration (0.3mg/L) and stains laundry and plumbing fixtures. The iron that settles out in the distribution system gradually reduces the flow of water. Iron also promotes, the growth of 'Iron bacteria'. These microorganisms derive their energy from, the oxidation of ferrous to ferric and in the process deposit a slimy coating on the piping. BIS has set desirable limit as 0.3mg/L and permissible limit ss 1.0 mg/L. While WHO has not given any guideline for Fe.

4.2.7 Arsenic

Arsenic occurs naturally in all environmental media and is usually present in the form of compounds with sulfur and with many metals. Arsenic exists in various valency states and in both organic and inorganic forms. The level of environmental arsenic is normally reported in terms of total arsenic. Many arsenic compounds are water soluble, and thus contamination of water can occur. The chemical form of arsenic in water has not been fully elucidated, but both tri and pentavalent forms have been identified, some forms of organic arsenic have been found in water. Most of the arsenic found in water derives form industrial discharges, the higher concentration, other than those occurring naturally in spring-waters are usually in areas of high industrial activity.

The toxicity of arsenic compounds depends on the chemical and physical form of the compounds and the route by which it enters the body. Acute poisoning by arsenic involves the central nervous system leading to coma and for doses of 70-180mg to death. The gastro-

intestinal tract, nervous system, the respiratory tract, and the skin can be severely affected. Adequate evaluation of toxicity hazards, requires arsenic estimation in the micro-gram range. It is recommended that, when water is found to contain arsenic at level of 0.05mg/L, an attempt should be made to ascertain the valency and chemical forms of the elements.

The desirable limit for As is 0.05mg/L and 1.5mg/l as permissible limit as per WHO guidelines but no relaxation is given in BIS guidelines.

4.2.8 Chromium

Chromium is ubiquitous in the environment, occurring naturally in the air, water, rocks and soil. It occurs in several forms, or oxidation states but the most common are chromium VI and chromium III. The form depends on pH. Natural sources of water contain very low concentrations of chromium. It is a micronutrient (or essential trace element). High doses of chromium VI have been associated with birth defects and cancer, however, chromium III is not associated with these effects. Plants and animals do not accumulate chromium, therefore, the potential impact of high chromium levels in the environment is acute toxicity. In animals and humans this toxicity may adversely effects skin, kidney and liver.

The total chromium in a domestic water supply is 0.05mg/L. The aquatic life criteria is less than 0.011mg/L for chromium VI and less than 0.207mg/L for chromium III. (The second value is based on a formula involving hardness).

WHO has given as required desirable limit as 0.05 mg/l while BIS has not given any relaxation in permissible limit.

4.2.9 Nickel

Typical soils contain large quantity of nickel. The main source are arsenides and sulphides. Nickel is used as a component in some alloys

and for metal plating for catalysts, for batteries and in certain fungicides. Many nickel salts are soluble in water. Contamination in water is due to effluent from industries containing Ni compound. Ni in river water is rivers levels are much lower and nearly 1 mg/L have been reported from surface waters.

Nickel is a relatively non toxic element. It is essential for animal nutrition and also to human. Certain nickel compounds have been shown to be carcinogenic in animal experiments. However soluble nickel compounds are not currently regarded as either human or animal carcinogens but high concentrations of nickel can react with DNA, and may damage DNA.

However maximum allowable limit for Ni is 0.02 mg/L as per WHO guidelines.

4.3   BACTERIA AND FAECAL COLIFORM

Bacteria are among the simplest, smallest, and most abundant organisms on earth. Bacteria are "procaryotic" organisms- a term which indicates a cellular structure lacking an organized nucleus and nuclear membrane. Instead of containing genetic information stored on several chromosomes, bacteria contain a single strand of DNA.

4.3.1   Faecal Coliform and Water Quality

Coliform bacteria have been used to assess the quality of water and the likelihood of pathogens being present. Although several of the coliform bacteria are not usually pathogenic themselves, they serve as an indicator of potential bacterial pathogen contamination

Total coliform bacteria are a collection of relatively harmless microorganisms that live in large numbers in the intestines of man and warm- and cold-blooded animals. They aid in the digestion of food. A specific subgroup of this collection is the faecal coliform bacteria, the most common member being

Escherichia coli. These organisms may be separated from the total coliform group by their ability to grow at elevated temperatures and are associated only with the faecal material of warm-blooded animals.

The presence of faecal coliform bacteria in aquatic environments indicates that the water has been contaminated with the faecal material of man or other animals. At the time this occurred, the source water may have been contaminated by pathogens or disease producing bacteria or viruses which can also exist in faecal material. Some waterborne pathogenic diseases include typhoid, diarrhea, viral and bacterial gastroenteritis and hepatitis A. The presence of faecal contamination is an indicator that a potential health risk exists for individuals exposed to this water. Faecal coliform bacteria may occur in ambient water as a result of the overflow of domestic sewage or nonpoint sources of human and animal waste.

Factors affecting faecal coliform

Wastewater and Septic System Effluent - Faecal coliform is present in human waste, so the bacteria goes down the drains in our houses and businesses, and can enter streams from illegal or leaky sanitary sewer connections, poorly functioning septic systems, and poorly functioning wastewater treatment plant (WWTPs) effluent.

Animal Waste - A significant amount of faecal coliform is released in the wastes produced by animals. This can be a serious problem in waters near cattle feedlots, hog farms, dairies, and barnyards that have poor animal keeping practices and waste is not properly contained. In urban areas, faecal coliform can be contributed to surface water by dog, cat, raccoon, and human waste when it is carried into storm drains, creeks, and lakes during storms.

Sediment Load - High amounts of sediments are often related to high concentrations of pathogenic bacteria. The bacteria can attach to sediment particles, escaping invertebrate predators (Murdoch and Cheo, 1996). Fast-running water can carry more sediment, so higher levels of bacteria can occur

during high runoff events. Bacteria are much more abundant in soils than in water.

Temperature - Bacteria grow faster at higher temperatures. The growth rate slows drastically at very low temperatures. E coliform count in 100 ml should be zero and coliform organism should not be exceed more than 10 per 100 ml in any sample as per BIS and WHO standard.

CHAPTER V

SAMPLE COLLECTION AND ANALYTICAL PROCEDURES

This chapter describes the sampling strategies and the analytical procedure adopted for this study. The study area comprising Doon Valley, Risikesh, Haridwar and Roshnabad are too large to sample in detail. Therefore a sampling schedule had to be designed which would be logistically feasible and would provide the relevant samples to achieve the specific objectives of this study. Because of the quantitative significance in assessing the impact of industrial and urban development on water chemistry, samples were collected in upslope (natural unaffected source of water) and down slope (area of the industrial sector receiving industrial effluent directly or indirectly and from within the urban area, away from urban area and agricultural area, area of industrial and urban centers of the two districts. Another aim of this study is to determine seasonal (temporal) variation in the major ion composition of the waters of the study area. In order to achieve this aim samples were collected during lean (summer), peak (post monsoon) and moderate (winter) flows or recharge period of stream or groundwater. The analytical procedure adopted for the chemical analysis of water were selected from the literature and facilities available at water chemistry lab of Wadia Institute of Himalayan Geology WIHG Dehradun and HSE lab UPES, Dehradun and suitably modified for the wide range of concentration encountered.

Three sampling trips were undertaken during December 2007- Jan 2008, May 2008 and October 2008 to collect surface and groundwater samples from the catchment of Asan, Song river and their tributaries and from Ganga river between Risikesh and Haridwar from industrial area of SIDCUL at Selaqui

and Roshnabad and from urban area of Dehradun and Haridwar district. Groundwater samples were collected from tubewells, handpumps, dugwells and springs in such a way that they represent urban, nonurban, industrial and agricultural areas. These sampling period were chosen to represent the typical pattern of annual flow and recharge period in the streams, river viz: lean, peak and moderate flow. Accordingly groundwater samples represent seasonal changes in water table condition and recharging pattern of aquifers. However, only representative samples were collected during lean and peak flow period to understand seasonal and temporal changes in water composition. Samples sites are shown in (Figures 5.1) and the relevant detail of sample collection are given in Table V-1.

All the samples are collected from mid channel of the streams and river thereby avoiding local inhomgeneies along the bank. All samples were collected and stored in 500 ml polyethylene "Tarson mark" bottles. Prior to their use in field all the bottles were soaked in 1 M nitric acid and rinsed several time with deionised (18-2 mega ohm water form milli pore water purification system). Sub sampling was made from this 500 ml sample into pre rinsed 250 ml and 125 ml polyethylene "Tarson Mark" bottles. All the samples for dissolved major constituent were filtered through syringe filter (0.2µm). About 125 ml of filtered unacidified samples were stored in polyethylene bottle until analysed in laboratory for dissolved major ion. The measurement of the temperature, dissolve oxygen and conductivity and TDS were made in situ immediately after sample collection in field. The bicarbonate were measure in the laboratory. The samples for bacteriological analysis (Total coliform and E-Coli) were also processed in the evening on the same day and kept in incubator. Detail methods are described later in this chapter. In all 270 samples from 131 location were collected in three seasons for the present study.

5.1 ANALYTICAL PROCEDURE

The analytical procedure adopted for the chemical and bacteriological analysis of water are described here. The measurement of pH, conductivity, and

dissolve oxygen were made in the "in-situ" in the field. Bicarbonate and bacteriological measurement were made on unfiltered sample within 8 hours of sample collection.

5.1.1 pH

pH measurement were made in-situ by using a pH meter (model pH plus Direct of Lamotte, USA) calibrated with standard buffer solution of 4.0 pH, 7.0 pH and 10 pH supplied by manufacture accuracy of measurement is 0.002.

5.1.2 Conductivity

Conductivity measurement in water were made in situ by using a conductivity meter (Con- 6 model of La Motte USA in μ simen /cm. The conductivity meter was calibrated with standard conductivity solution of 1413μs and 6668μs supplied by manufacturer. The accuracy of measurement of measurement was better then ± 2% full scale for the conductance range observed for all samples.

5.1.3 Dissolve Oxygen

These measurement were made in-situ by using a D.O meter (YSI Company , USA. Model- DO-200). Manufacturer specification were followed for the calibration and accuracy of measurement was ± 2%.

5.1.4 Bicarbonate

Bicarbonate concentration were measured in the field by acid titration within 8 hours of sample collection. About 10 ml of unfiltered sample was titrated with standard solution of 0.01N hydrochloric acid using methyl orange indicator. Titration was done in duplicate or triplicate to get concordant burette reading. Carbonate concentration in all samples was found to be extremely low and could not measured unambiguously by HCl titration method using phenopthiline indicator.
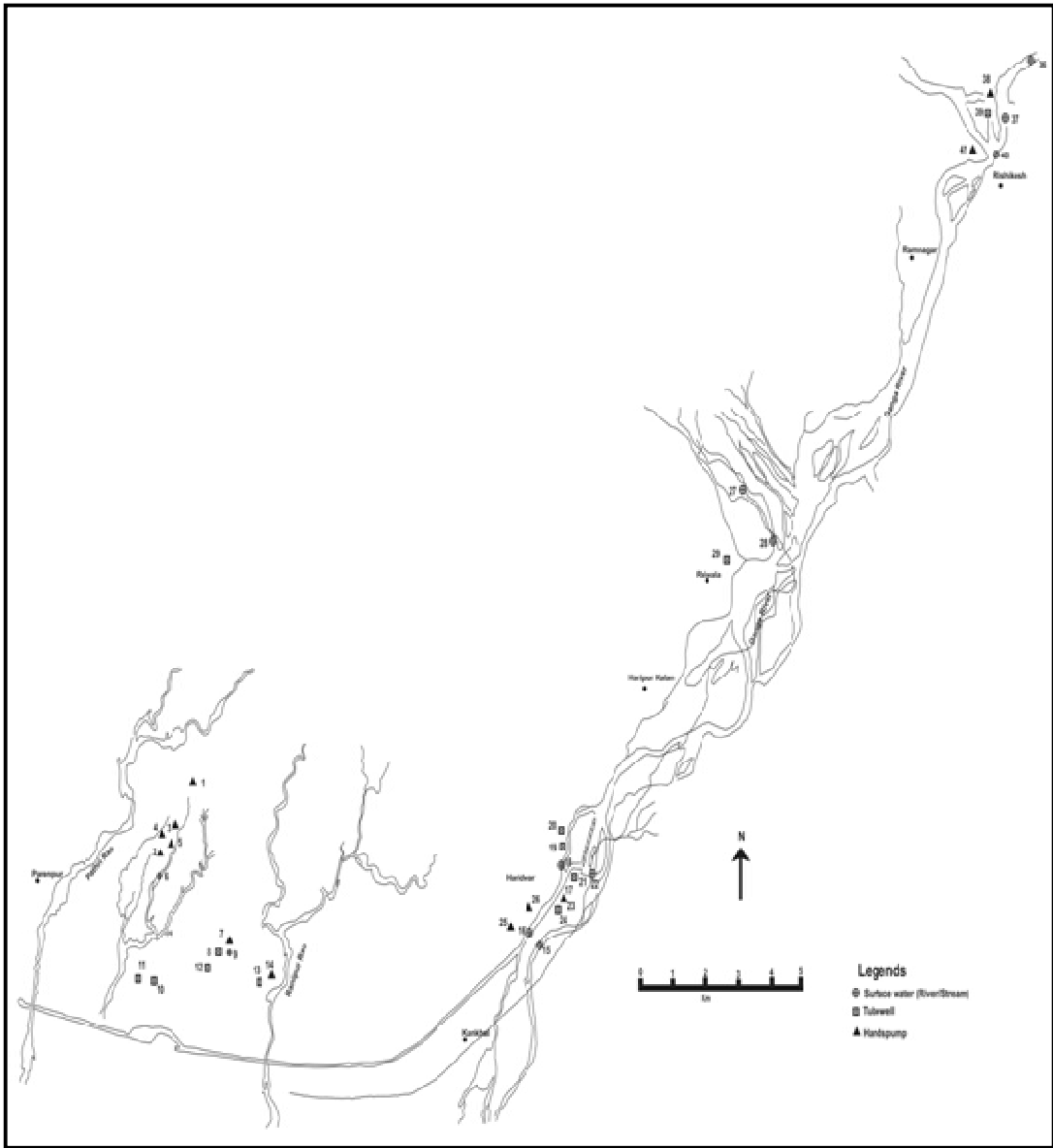
Fig: 5.2: Sampling location Map of Haridwar district

Table 5.1: Sampling Location

Sample	Location	Surface Water	Ground water
RH1	Roshnabad Haridwar, Residential Complex		TubeWell
RH2	Roshnabad Reserve Police Line		Tubewell
RH3	Sidcul Water Supply Satation		
RH4	Sidcul Tubewell -4		Tubewell
RH5	SAB Industries, Sidcul Tubewell 3		Tubewell
RH 6	Seasonal, Sidcul Stream	Surface	
RH7	Ravala Mehdood		Tubewell
RH8	Ravala Mehdood, Chauhan Mohlla		Handpump shallow
RH9	Surface stream near Saleempur	Surface	
RH10	Saleempur		Handpump shallow
RH11	Saleempur, Dandipur, Handpump		Handpump shallow
RH12	Ravala Mehdood		Handpump
RH13	Rampur		
RH14	Ranipur		Tubewell
RH15	Ganga river, upstream Neel Dhara	Surface	
RH16	Ganga river, channel from Har ki padi below bridge	Surface	
RH17	Down Stream, Har ki Padi	Surface	
RH18	Har ki Padi, Upstream	Surface	
RH19	Haridwar Jal Sansthan		Infiltration Well
RH20	Infiltration well 18, Haridwar		
RH21	Parmarth Ashram near shri Gurucharan Asharam		
RH22	Ganga river	Surface	
RH23	Rodi Belwala, Tubewell No-7		Infiltration Well
RH24	Alaknanda Nalkoop , Shakti Chowk		Infiltration Well
RH25	Tubewell 7,		Tubewell
RH26	Ngarpalika office Jal Sansthan Haridwar		Tubewell
RH27	Song River at Raiwala below bridge	Surface	
RH28	Ganga river at Gohri Mafi village after confluence of Song river	Surface	
RH29	Gohri Mafi Raiwala		Handpump
RH 30	Vikasnagar, Jain Athithi Bhawan		Handpump
RH31	Badmawala Road, Vikasnager		Tubewell
RH32a	Office Pump House, near Amar Sweat Shop		Tubewell

Sample	Location	Surface Water	Ground water
RH32b	Yamuna River, Vikasnager	Surface	
RH33	Yamuna River , Vikasnager	Surface	
RH34	Assan River below bridge towards Dharmawala	Surface	
RH35	Asan River at Fatehpur	Surface	
RH36	Laxman Jhula, Risikesh	Surface	
RH37	Ramjula, Risikesh	Surface	
RH38	Jal Nigam Office, Muni Ki Rati, Risikesh	Surface	
RH 39	Muni ke Rati, Risikesh		Handpump
RH40	Triveni Ghaat, Risikesh	Surface	
RH41	Railway Station, Jalkar Compound, Risikesh		Tubewell
RH42	Pump No-5, Bharat Sanchar Limited Nigam Limited, Risikesh Deharadun Road		Tubewell
RH43	Doiwala, Below Bridge	Surface	
RH44	Badowala, Dehradun		Handpump
RH45	Bhuddichowk		Handpump
RH46	Karva Pani, PWD Guest House	Surface	
RH47	Karbari, Dehradun		Handpump
RH48	Assan River below bridge towards Dharmawala	Surface	
RH49	Selaqui Industrial area, PDM Enterprise,		Tubewell
RH50	Selaqui Industrial area near S.S engineering , G88, UPSIDC		Tubewell
RH51	Sealqui Industrial area near Western Crane factory		Tubewell
RH52	, Pharama City, Selaqui Sidcul Water Tubewell		Tubewell
RH53	Akbar Coloney, Selaqui		Tubewell
RH54	Handpump, Syncon , Dev Packaging		Handpump
RH55	Shivnager, Selaqui Industrial area in front of Aromatic Plant,		Handpump
RH56	Suswa river, Kurkawala	Surface	
RH57	Kurkawala		Handpump
RH58	Nangal Jwalapur, towards Doodhli		Handpump
RH59	Thandowala Village, Dhoodli		Handpump
RH60	Suswa River	Surface	
RH61	Khatta Pani		Handpump
RH62	Suswa River, Doodhli	Surface	
RH63	Suswa River, Below Bridge, Noka Ramgarh	Surface	
RH64	Daudwala		Shallow

Sample	Location	Surface Water	Ground water
			Borewell
RH65	Daudwala		Handpump
RH66	Daudwala after the confluence of Bindal and Suswa river		Handpump
RH67	Rispana River	Surface	
RH68	Bindal River	Surface	
RH69	Rispana river at Daurwala near the Confluence point of Bindal, Rispana and Suswa	Surface	
RH70	Mathurawala, (Gururamrai College Compound)		Handpump
RH71	Sarswati Vihar, Ajabpur		Handpump
RH72	Bindal River, Haridwarbypass Road	Surface Water	
RH73	Kargi Chowk		Handpump
RH74	Chandrabani Spring	Spring	
RH75	Pithywala Tubewell		Tubewell
RH76	Assan river near Badowala	Surface	
RH77	Ratanpur		Handpump
RH78	Ratanpur		
RH79	Assan River at Bhuddhapur, Parval Motor Marg	Surface	
RH80	Sherpur		Handpump
RH81	Shekhowala, Gramsabha		Handpump
RH82	Sabhawala		Handpump
RH83	Assan river near Sabhawala	Surface	
RH84	Dandipur		Handpump
RH85	Badripur, Irrigation Tubewell		Tuebwell
RH86	Adhoiwala Tubewell, Dharmawala		Tuebwell
RH87	Assan river near Herbaetpur	Surface	
RH88	Herbaertpur		Handpump-Shallow
RH89	Kushalpur Chowk		Handpump
RH90	Redapur		Dugwell
RH91	Shalow		Tubewell
RH92	Rampur		Tubewell
RH93	Chota Rampur		Handpump
RH94	Sahaspur Chorkhala		Handpump
RH95	Selaqui before market		
RH96	Irrigation T		Tubewell
RH97	Doonga near temple	Spring	
RH98	Kandoli Spring	Surface	
RH99	Nimi Nadi	Surface	
RH100	Nanda ki chowki		Handpump
RH101	Dhoolkot		Handpump

Sample	Location	Surface Water	Ground water
RH102	Vikasnagar Road , Handpump way to Indian Public School		Handpump
RH103	Premnager		Tubewell
RH104	Vasant Vihar		Tubewell
RH105	Tons Nadi at Guchupani, Roberts Cave	Surface	
RH106	Tons Nadi at Tapkashwar Mandir	Surface	
RH107	Nun River after Ganghora near santala devi		
RH108	Nun River downstream of Santala devi	Surface	
RH109	Bhatta water Fall, via Mussoorie	Surface	
RH110	Rispana River on Sahastradhara road below bridge	Surface	
RH111	Sahastradhara stream (Upstream of Picnic spot Namyog Shod Peetham	Surface	
RH112	Sahastradhara, downstream of picnic spot	Surface	
RH113	Rispana River near Nalapani	Surface	
RH114	Anchaal Diary		Tubewell
RH115	Karanpur		Tubewell
RH116	Rispana River near Vidhan Sabha		Tubewell
RH117	Bindal River at Patelnagar	Surface	
RH118	Tubewell Pump House main Bindal Bridge		Tubewell
RH119	Ganndhi Gram near Gurudwara Park Road		
RH120	Gandhi Gram Shri Kalyan Ashram		Handpump
RH121	New Patal Nager		Handpump
RH122	Bhamanwala Chowk		Handpump
RH123	Bhamanwala Chowk		Handpump
RH124	Bharuwala Cant area		Handpump
RH125	Bharuwala Handpump,		Handpump
Rh126	Bindal river, Bharuwala	Surface	
RH127	Rispana River near Kedarpurum	Surface	
RH128	MDDA Coloney		Handpump
RH129	MDDA Coloney		Handpump
RH130	Gorakhpur Chowk, Defecne Coloney		Handpump
RH131	Ajabpur, Uttarakhand Jal Sansthan		Tubewell

5.2   DISSOLVED MAJOR CONSTITUENTS AND TRACE METAL

In the laboratory dissolved major constituent (Na^+, K^+, Mg^{2+}, Ca^{2+}, HCO^-_3, Cl^-, SO^{2-}_4, PO_4 and SiO_2) and trace metals (Pb, Cd, Mn, Cu, Zn, Fe, Co, As, Sr, Ni, Cr, B) were selected from the literature and suitability modified (wherever required) for the wide range of concentration encountered. All glass-ware were leached with 2N nitric acid and rinsed before use with deionized water of 18.2 megha ohm resistance from Milli pore water purification system.

5.2.1   Sodium, Potassium, Magnesium, Calcium, Flouride, Chloride, Nitrate, Phosphate, Sulphate

All the major ions Na, K, Ca, Mg, F, Cl, NO_3, PO_4 and SO_4 were analysed   by ion chromatography using Ion Chromatograph Model D X-500 (DIONEX, USA). The ion chromatography system was consisted of equipped with a gradient pump, conductivity detector, a self regenerating suppressor (ASRS Ultra II – 4 mm for anions and CSRS Ultra II 4 m for cations). Eluent flow rate were set at 1 ml/ min for cations and 1.5 ml /min for anions with an injection volume of 25µl. Anion Pac AG -12A (4m) guard column and Ion Pac AS 12A (4mm) analytical column were used to separate the anions. Similarly for cations analysis, an Ion Pac CG - 5 (4mm) guard analytical columns were used to separate cations. An eluent consisting of mixture of sodium carbonate (2.7µn) and sodium bicarbonate (0.3 µn) was used as mobile phase for anions analysis and an eluent consisting 22 MN H_2SO_4 was used as mobile phase for cation analysis.

The current of suppressor was set at 50 MA and 100 MA for analysis of anions and cations respectively to give a background conductivity of 12.5 µS for anions and 2 µs for cations analysis. All measurement were made at 25^0C.

Deionized water with a resistance better a 18.2 MΩ generated by a Milli –Q plus of Millipore Ltd was used for the preparation of all solution. Working solution for anions were prepared by revival dilution of salt standard (stock

solution of 1000 ppm) prepared in lab from analytical grade reagents. For cations and trace metal reference standard were prepared by dilution of certified reference cations, and trace metal standard from Perkin Elmer.

Separation of anions and cations were performed respectively with mixture of sodium carbonate + sodium bicarbonate and H_2SO_4 as the eluent. The experiment procedure involved choice of column type, eluent concentration and flow rate, reagent concentration and dilution ratio and integration parameters. Most of these parameter were selected. Dionex's operator manual and personnel experience based on replicate analysis. The analytical precision for measurement of cation and anion is generally $^+$ .5%.

5.2.2   Silica

Dissolved silica was measured by Ammonium Molybdate method. A Carrote USA and Spectrophotometer model was used for absorbance measurement at 410 nm wavelength. A calibration curve was made from the series of six standard approximately diluted for reference standard. Overall precision of the analysis is approx ± 5% from replicate analysis.

5.3   TRACE METAL

Trace metal namely Pb, Cu, Ni, Cr, Cd, Zn were determined in January 2008 collection by Atomic Absorption Spectrophotometery (AAS) using Perkin Elemer Model. Whenever required samples were suitably diluted to bring the concentration to the linear proportion of the absorbance curve. Based on replicate analysis the analytical precision for the measurement of these parameter is ± 10%.

The following wavelength was selected for different trace metals, Lead – 283.3 nm, Copper- 324.7nm, Iron – 248.3nm, Chromium- 357.9, Cadmium – 228.8nm, Zinc-213.9 nm and Nickel – 231.6 nm.

5.4   BACTERIOLOGICAL ANALYSIS

The total coliform and E-Coli were measured following Colilert -18 Quanty-Tray procedure as outlined in Standard method for examination of water and waste water (APHA, 2007). It is an 18 hour test for enumeration of coliform and Escherichia coli by Idexx (Colirt -18) Qunaty- Tray procedure. Coliert-18 simultaneously detect Total coliform and E.Coli. It is based on IDEXX's Patented Defined Technology (PDT). Colifrom bacteria produce a yellow colour, due to the presence of B-galactoisdex, following incubation for 18 hours at 37 ^{0}C. *Escheriachia coli* produce yellow colour, due to presence of B-galactosidase and blue – white fluorescence under long wavelength UV light due to presence of B- glucusonidex after incubation for 22 hours at 37 ^{o}C. Coliert -18 can simultaneously detect these bacteria at 1 cfu/100 ml within 18 hours even with as many as 2 million heterotrophic bacteria per sample.

One pack of Coliert -18 added in a 100 ml of sample in sterile transparent nonfluorescing conical flask and caped the vessel and shaked until dissolved completely. In order to dissolved thoroughly the sample is placed in incubator at 35 ^{0}C for 3-5 minutes. The sample is poured in Quanti Tray and sealed in a an IDEXX Quanti –Tray Sealor. Sealed Tray is placed in incubator at 37 ^{o}C for 18 hours. After 18 hours number of positive well were counted and referred to MPN table which give the result of Most Probable Number.

For the measurement of E.coli the sample is incubated for 22 hours and counted with the help of floroscencse light in dark room and florescence colored well were counted. The yellow color will show positive for *Total Colifrom* and yellow and florescence color shows positive for *E-Coli*.

Table 5.2: Analytical Procedure

S No.	Parameter	Instrument / procedure
	Physical Parameter	
1	Temperature	Metallic Thermometer
2	Conductivity	Conductivity meter
3	TDS	TDS meter
4	Dissolve Oxygen	DO Sampler
	Chemical Parameter	
5	pH	pH meter,
6	Anions F, Cl, NO_3, PO_4, SO_4,	Ion Chromatography
7	Cations – Na, K, Ca, Mg	Ion Chromatography and Flame Photometer
8	Si	Spectrophotometer
9	Bicarbonate/ Carbonate	Titrimetric with hydrochemical acid using methyl orange / Phenoptheline indicator
10	Heavy Metals – Pb, Cd, Mn, Cu, Zn, Fe, Co, As, Sr, Ni, Cr, Others: B	ICP- Inductive coupled plasma, AAS–Atomic absorption spectrophotometer
	Biological Parameter	
	Total Coliform and E- Coli Test	Colliert – 18 Quanti Tray procedure using Quanti Tray and incubator

CHAPTER VI

MAJOR IONS CHEMISTRY AND WEATHERING CONTROL ON SURFACE AND GROUNDWATER CHEMISTRY

This chapter gives an account of the major ion chemistry of surface and groundwater of the study area and chemical weathering processes to identify ionic sources and factors controlling the ionic composition of water.

6.1   IONIC VARIATION

The major ions data are given in Table 6.3, 6.4 and 6.5. The temperature of the study area varies from 6.4^{o}C to 26°C in all sampling location in winter, summer and post monsoon season. The pH of surface and groundwater varies from 6 to 8.4 with an average of 7.2 in Dehradun and Haridwar district in winter season. The average pH increases to 7.3 in summer and 7.4 in post monsoon season. The electrical conductivity ranges from 131μs/cm to 1392μs/cm in winter season, 116μs/cm to 1703μs/cm in summer season and 119μs/cm to 986μs/cm in post monsoon season. The concentration of DO ranges from 0.3ppm to 16ppm with an average of 7ppm during winter season, 1.5 ppm to 10.6ppm with an average of 5.3ppm in summer season, during post monsoon it varies from 1.8ppm to 10ppm with an average of 5.7ppm.

Among anions the concentration of bicarbonate varies from 344.3μEq/l to 9395μEq/l with an average of 2984μEq/l in winter season, in summer season it ranges from 1542μEq/l to 7548Eq/l with an average of 3798μEq/l and during post monsoon season it ranges from 574μEq/l to 5525μEq/l with an average of 2809μEq/l. The average concentration of sulfate is 494.3μEq/l, 1500μEq/l and 1084μEq/l respectively in winter, summer and post monsoon season. Similarly the average concentration of chloride is 102.36μEq/l, 396Eq/l and 292μEq/l

respectively in winter, summer and post monsoon season. The concentration of fluoride varies from 0.001µEq/l to 216µEq/l with an average of 22µEq/l in winter season, in summer it varies from 1.79µEq/l to 579µEq/l with an average concentration of 18µEq/l and in post monsoon season it varies from 0.53 µEq/l to 358µEq/l with an average value of 18.7µEq/l.

The nitrate concentration during winter season varies from 0.001µEq/l to 4242µEq/l with an average of 268µEq/l, during summer season it varies from 0.001µEq/l to 3900µEq/l with an average of 345µEq/l and during post monsoon season it varies from 0.001µEq/l to 1087µ Eq/l with an average of 168µEq/l. The phosphate concentration during winter season varies from 0.01µEq/l to 569µEq/l with an average of 18µEq/l, during summer season it varies from 0.001µEq/l to 135µEq/l with an average of 7µEq/l and during post monsoon season it varies from 0.001µEq/l to 695µEq/l with mean value of 11.5µEq/l.

Among the anions bicarbonate is the most dominant (65%) followed by sulphate (23%), chloride (6%) and nitrate (5%), fluoride (0.4 %), phosphate (0.3%) in winter season. This order of dominance continued in summer and postmonsoon collection. Thus the dominance of anions in study in winter, summer and post monsoon season remains as $HCO_3 > SO_4 > Cl > NO_3 > F > PO_4$.

Among cations, the concentration of calcium varies from 180µEq/l to 13323µEq/l with an average of 2901µEq/l during winter season, during summer season it varies from 1297µEq/l to 9081µEq/l with an average of 3218µEq/l and during post monsoon season it varies from 649µEq/l to 5988µEq/l with an average of 2469µq/l. The magnesium concentration ranges from 41µEq/l to 5103µEq/l with an average of 1181µEq/l during winter season, 428 µEq/l to 5597µEq/l with an average of 1785µEq/l in summer season and 82µEq/l to 3391µEq/l with an average of 285µEq/l during post monsoon.

The concentration of sodium during winter season ranges from 61µEq/l to 1725µEq/l with an average of 425µEq/l, during summer it ranges from 4µEq/l to 1484 µEq/l with an average of 412µEq/l and during post monsoon season it

ranges from 34.9µEq/l to1004µEq/l with an average of 285µEq/l. The concentration of potassium ranges from 3µEq/l to 1893µEq/l with an average of 112µEq/l in winter season while in summer it ranges from 5µEq/l to 576µEq/l with an average of 123µEq/l and during post monsoon season it ranges from 5µEq/l to 498µEq/l with an average concentration of 74µEq/l.

Among cations calcium is most dominant ion (63%) in study area followed by Mg (24%), Na(11%) and K (2%) in winter season, during summer season the percentage of various ions are Ca(58%) , Mg (32%), Na(8%) and K (2%) and during post monsoon season the contribution of calcium is (61%) followed by Mg (30%), Na(7%) and K(2%). The order of abundance of major cations in the study area in winter, summer and post monsoon season is Ca>Mg> Na>K. The average concentration of silica is 130µmole/l, 74µmole/l and 129µmole/l respectively in winter, summer and post monsoon season.

6.2   SOURCES OF IONS

6.2.1   TDS vs Ionic Concentration

The relationship between TDS (total dissolved solid) and major ions is studied to understand the spatial distribution of major ion concentration in different landuse categories and relationship between surface and groundwater. The TDS values of groundwater of Doon valley shows systematic control of land use characteristics and tends to increase in urban area (275mg/l) in comparison to agricultural area (149mg/l) and industrial area (148mg/l). The average concentration of TDS in surface water is 388mg/l. The increase in TDS in surface and groundwater is an indicator of surface and groundwater contamination. Thus the TDS value can be effectively used as a indicator of groundwater contamination due to anthropogenic sources.

In Haridwar district the mean TDS is high in groundwater of agricultural area (409mg/l) and industrial area (408.mg/l) in comparison to urban area (381mg/l) whereas in surface water (Ganga river) it is 169mg/l. In Risikesh the average TDS concentration in groundwater is 294 mg/l and in surface water 20 mg/l. Overall cation and anions concentration shows following trend in the study area.

$HCO_3 > SO_4 > NO_3 > Ca > Cl > Mg > Na > Si > K > PO_4 > F$

The coefficients of correlationship computed between various cations and anions during winter, summer, and post monsoon season are given in Table 6.6, 6.7 and 6.8. The TDS has shown positive relationship with HCO_3 ($r^2 = 0.5$), Na ($r^2 = 0.5$), Mg($r^2 = 0.7$), Ca ($r^2 = 0.6$) , SO_4 ($r^2 = 0.5$), Cl ($r^2 = 0.5$), K($r^2 = 0.4$), NO_3 ($r^2 = 0.4$), PO_4($r^2 = 0.4$).

Ca and Mg concentration generally increases with increasing TDS and show a significantly higher concentration in groundwater of Haridwar district. The general trend of Ca and Mg in different landuse categories and surface water is as follow:

Haridwar : Agriculture > Urban > Industrial > surface water

Ca - 39.4 > 23.2 > 22.3 > 15
Mg - 6.55 > 6.2 > 4.4 > 2

Dehradun: Agriculture > Urban > Industrial > surface water

Ca 23 > 17 > 13
Mg 7.17 > 5.4 > 3.5

The spatial variation of Ca follows a pattern similar to that of Mg and show good positive relationship **($r^2 = 0.7$)** indicating same source of Ca and Mg. Good correlation is also observed between TDS and Ca ($r^2 = 0.74$) and between TDS and Mg ($r^2 = 0.611$). The mean ratio of Ca+ Mg **:** Na + K in the entire study area is ~ 3.5 which is greater than worlds average of ~ 2.2 implying that weathering of carbonate lithology is a major source of ions in water.

Considerate excess of Na over Cl and higher Na/Cl molar ratio ranging from 1.4 to 7.3 (mean 3.6) suggest that a much of the Na and K has a source other than precipitation possibly through rock weathering. Since Dehradun and Haridwar district are far away from the sea, the cyclic contribution through precipitation is not of significant importance. This suggests that Na could be derived from either evaporatic dissolution or silicate weathering (Dalai et.al 2002).

Influence of carbonate lithology on water chemistry of Doon valley and Haridwar district is further evident from the high $(Ca^{2+} + Mg^{2+})/HCO_3$ ratio (1.4) and good correlation between HCO_3 and Ca and Mg. However, when sulphate is taken into account along with bicarbonate, the ratio of $(Ca^{2+}+Mg^{2+})/(HCO^-_3+SO_4)$ becomes 0.95 indicating sulphate is another major ions in waters of study area derived from carbonate lithology.

Alkalinity from Silicate weathering may be calculated (where all values are in mill equivalents unit) following method of Raymahasay (1986)

Alkalinity $_{carbonate\ weathering}$ = 0.74 Ca $_{total}$ + 0.4 Mg $_{total}$

Alkalinity $_{silicate}$ = Alka $_{total}$ − Ala. $_{Carb.weathering}$

Based on Ca, Mg and total bicarbonate concentration, it is estimated that on an average 90% of bicarbonate comes from carbonate weathering and ~ 9% bicarbonate comes from silicate weathering in of Dehradun and Haridwar district. Chakrapani (2004) reported that about 5-12% of HCO_3 in the upper Ganga catchment of the Himalaya is derived from silicate lithology implying carbonate weathering account for major amount of HCO_3. This is also evident from the good Ca + Mg and HCO_3 (Fig.6.2) correlations (r^2 = 0.6) in present area of study.

The average ratio (in micro equivalent1) of 9.1 between (Ca+Mg) / (Na+K) in study area further suggest that carbonate lithology is a major source of ions in waters of the study area. The ratio of Ca:Na vary from 2.7 to 496 with an average of 59 (in micro equivalent). The excess Ca over sodium indicate that Ca is also derived from other source such as weathering of gypsum (anhydrite) present in limestone rocks of the Krol belt in northern part of Doon valley whereas sodium may be derived from either precipitation, soil salt or weathering of orthoclase feldspar.

The average SO_4: Cl ratio of 16.9 in study area indicates major contribution of sulphate from dissolution of gypsum as the halites are not reported from the catchment. The presence of pyrites disseminated in shales, quartzites and other

sedimentary rocks of the valley and deposits of gypsum in dolomite of Krol formation is the major source of sulphate in groundwater of Doon valley.

Thus the weathering of rock forming minerals, with minor contribution from cyclic sea salt and pollution, is the major sources of ions in river (Berner and Berner, 1987). The chemical composition of glacial melt water also demonstrate the chemical weathering take place beneath the glacier (Reynold and Johnson) 1972, Rasiwell, 1984). The major source of HCO_3^- in river water is from carbonate and silicate weathering which together account for 95% of global water composition (Berner and Berner 1987). Weathering of both silicate and non- silicate rocks contribute 70% of the river alkalinity while remaining 30% is accounted by river-based biological process due to decomposition of organic matter (Probst et al. 1998).
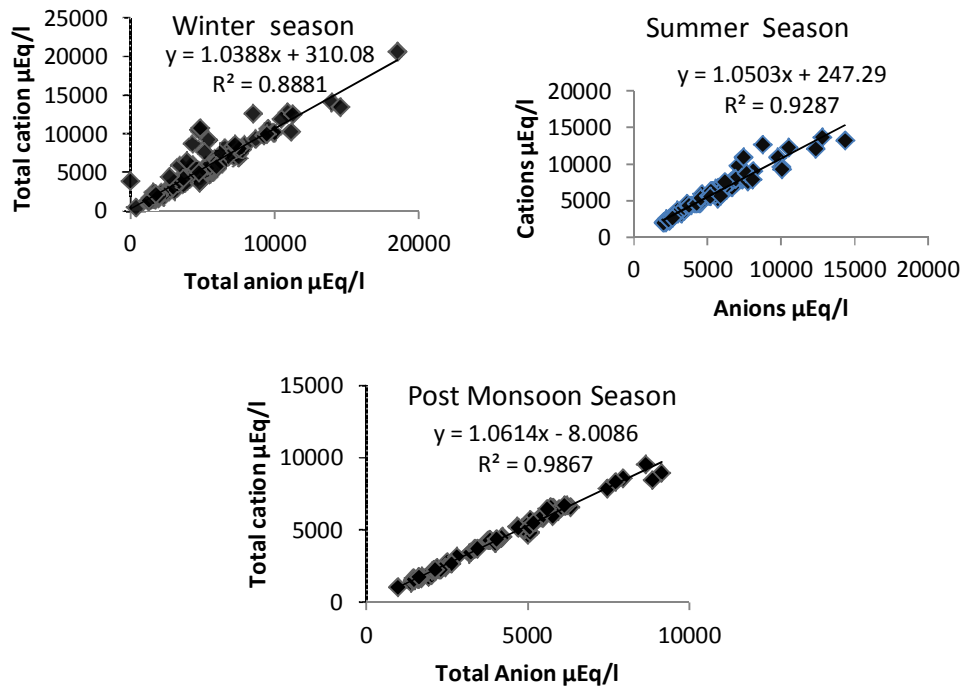
Fig. 6.1: Charge balance between total cations and anions in the waters of study area during winter, summer and monsoon season.
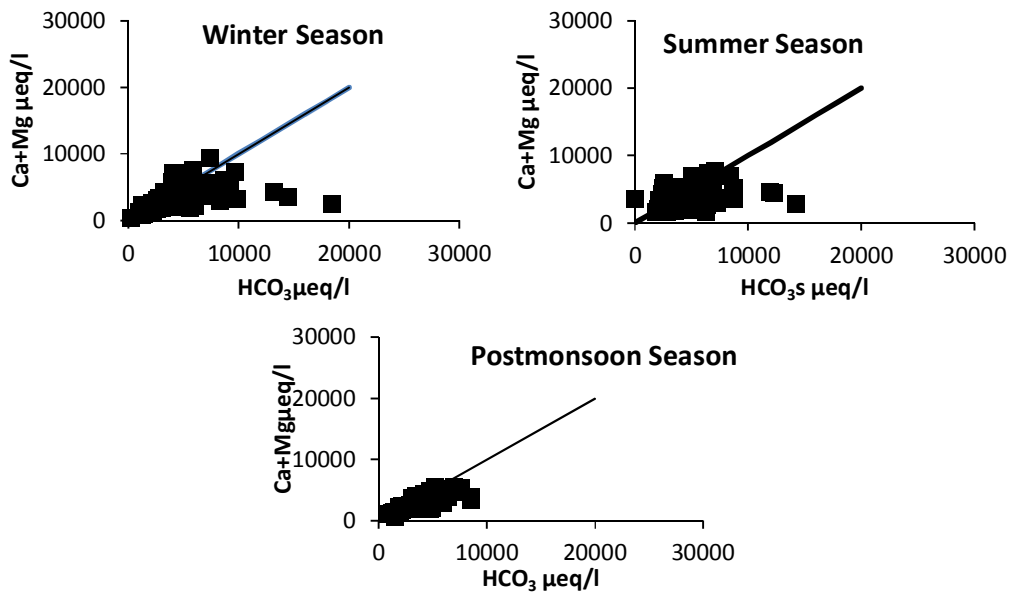
Fig.6.2: Scatter diagram of (Ca+Mg) and HCO$_3$in winter, summer and post monsoon season.
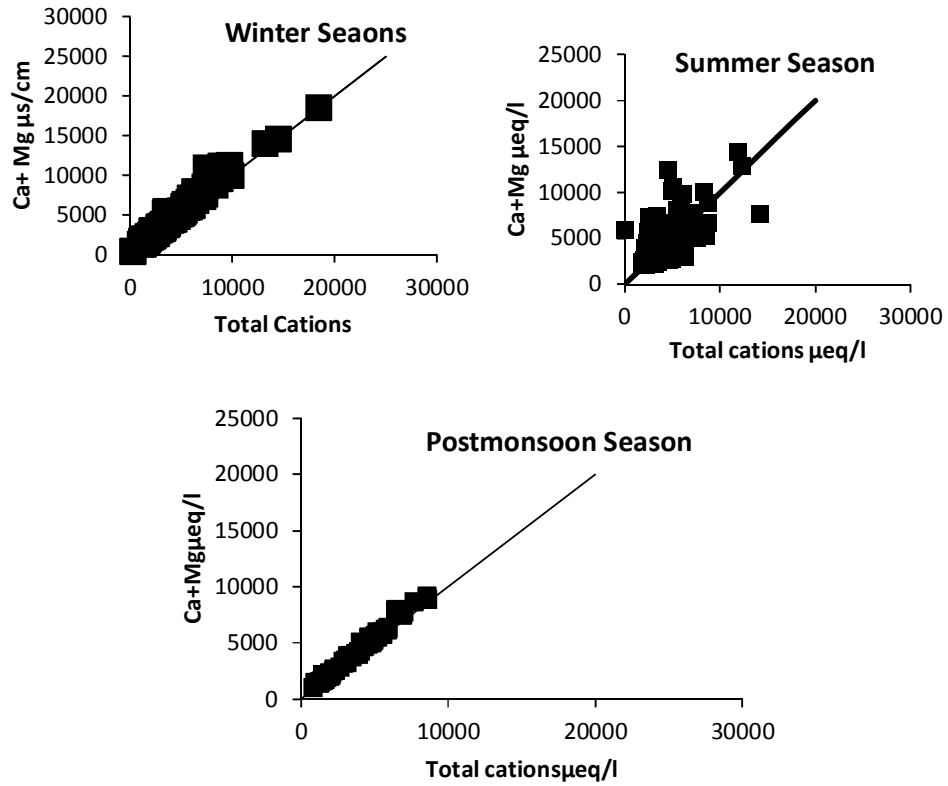
Fig. 6.3: Scatter diagram between (Ca+Mg) and total cations in winter, summer and postmonsoon season.
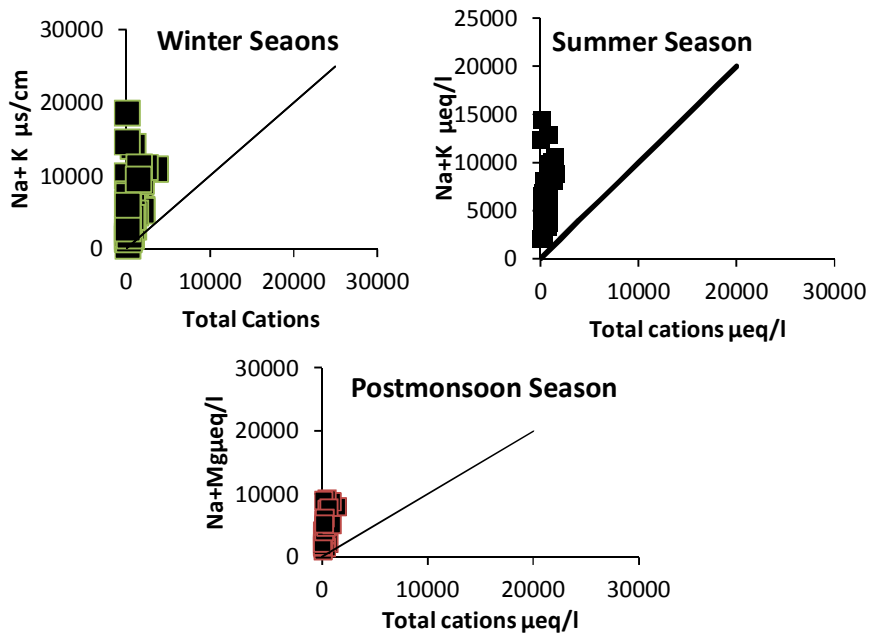
Fig. 6.4: Scatter diagram between (Na+K) and total cations in winter, summer and post monsoon season in study area.
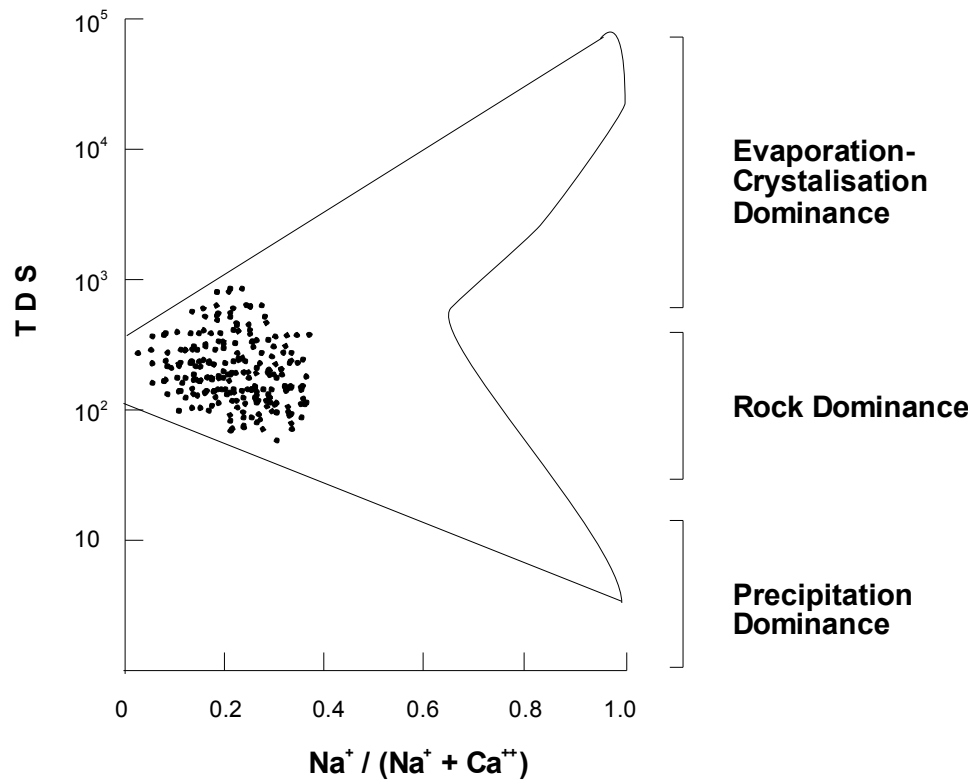
Fig. 6.4.1: Plot of TDS vs Na/Na + Ca (Gibbs, 1970).

Table 6.1: Physico -chemical composition of Surface and groundwater of Dehradun and Haridwar district in Winter Season

Samples	Temp	pH	TDS	EC	DO	HCO_3	F	Cl	NO_3	PO_4	SO_4	Na	K	Mg	Ca	SiO_2	TH
RH1	26.4	7.24	369	558	10	278	0.14	3.3	11.3	0	3.02	10.3	1.5	8.3	75.5	8.54	215.23
RH2	24.7	7.24	346	523	8	256	0.08	4.44	13.68	0	7.3	12	1.8	5.4	88.6	5.33	234.78
RH3	25.7	7.1	405	618	9	280	0.14	6.3	22.5	0	3.04	7.5	0.6	7.2	92	4.62	250.32
RH4	26	7	380	582	13	295	0.2	3.44	11.6	0	1.3	8.3	0.8	9	79	7	226.5
RH5	26	7.12	395	605	14.1	326	0.145	1.6	13.9	0	0.9	8.5	1.1	7.8	98	8.18	267.18
RH6	2 0	7.7	555	862	2.6	412	2.5	39	0	4.8	0.01	15.3	8.4	11.2	95.2	9.83	274.4
RH7	25.2	7.2	423	645	11	291	0.2	13.4	35	0.02	9.3	8.6	1.3	11.4	77	3.74	231.54
RH8	25.3	6.93	740	1225	12	304	0.1	70.4	263	0.2	66.4	26.2	2.8	21.4	111	3.72	354.14
RH9	18.3	7.44	493	753	10.6	323	0.2	18.45	50	3	13.8	14.7	8.2	10	88.6	7.4	253.64
RH10	24.3	6.85	396	603	15	262	0.24	39.6	8.5	0	18.2	7.2	0.6	11.8	87	5.3	257.18
RH11	25.3	7.1	288	414	7.3	170	0.22	35.5	7.7	0	14.3	10.2	3.1	6.4	58	8.2	165.44
RH12	23	6.9	796	1330	7.5	463	0.1	10.4	20	0	5.8	26.6	2.8	21.4	83	8.4	286.94
RH13	26	7.1	381	590	16	239	0.1	14	38	0	17.4	15.6	1.8	10.6	72.8	9.7	218.18
RH14	25	7	332	500	14	212	0.2	12.62	31.4	0	15.1	15.2	1.6	8.4	61	7	180.84
RH15	15.9	7.7	129	185	13.5	79	0.5	1.3	1.3	0	21.8	1.64	1.8	4.3	25.6	4.4	79.07
RH16	14.6	7.8	136	192	11.4	81	0.44	1.2	1.3	0	21.5	1.63	1.8	4.2	24.8	7.4	76.74
RH17	16	8.3	157	227	14.1	98	0.5	1.5	1.8	0	27.8	3.8	3.6	5.4	29.6	6.6	93.18
RH18	14.4	8.3	143	205	12.5	96	0.5	1.7	1.9	0	28	4	3.6	4.5	30.8	6.7	92.37
RH19	21.4	7.4	280	415	10.1	190	0.3	5.74	1	0	21.7	3.91	4.6	5.4	48	8.2	137.34
RH20	20.07	7.2	470	700	11	315	0.1	17.31	9	0	24.3	10.6	5.7	8.94	97.6	6.5	270.894
RH21	20	7.2	370	558	11.3	123	0.1	1.2	1.92	0	23	9.1	2.8	6.7	28.6	8.3	96.11
RH22	17	8.54	254	377	12	153	0.1	9.7	16	0	20	3.2	1.73	12.2	41.7	8.5	150.1
RH23	20.5	8.54	254	377	12.4	115	0.22	2.3	2.84	0	24.5	2.3	3	6	38.6	7	117.24
RH24	19	7.9	236	166	12.1	104	0.2	1.5	1.8	0	25.6	1.8	2.3	5.2	35	8	105.32
RH25	20.6	7.4	419	286	12.4	115	0.2	6.7	9.8	0	27.6	5.6	2.2	11.2	27.6	6.8	112.16
RH26	21	7.33	346	517	12	246	0.12	11	13.73	0	29.1	6.1	7.71	11.2	79.4	3	236.48
RH27	22.1	8.1	615	385	14.5	151	0.13	4	6.6	0	98.7	3.4	1.4	18.2	56.4	5	209.98
RH28	21.4	8.24	329	494	12.6	195	0.1	3.5	6.2	0	93.2	3.5	1.64	17.6	71.2	6.2	243.04
RH29	21.1	7.6	370	555	15.4	240	0.1	2.7	4.3	0.019	102	3.7	1.2	18.4	90	4	291.44
RH30	23	6.4	155	232	6	91	0.51	4.7	10	0	20	4.8	1.5	5.1	30.4	6.68	93.87
RH31	24	6.31	125	181	7	65	0.8	5	7.2	0	17	4.3	0.9	3.7	23	6	70.37

Samples	Temp	pH	TDS	EC	DO	HCO$_3$	F	Cl	NO$_3$	PO$_4$	SO$_4$	Na	K	Mg	Ca	SiO$_2$	TH
RH32A	23	6.2	119	173	6.72	67	0.1	3.2	9.4	0	16.5	2.1	2.4	4	23	6.06	71.6
RH33	13..5	8.36	180	252	8.36	73	1	4	1.1	0	41.3	2.7	2	6.7	31	2.2	101.87
RH34	20	7.4	201	299	13	143	0.4	3.7	7.8	0	27	5	1.3	7.7	45.7	4.84	141.25
RH35	20	7.5	202	295	13	140	1.5	4	8	0	27.2	5	1.3	7.4	44.6	9.1	137.38
RH36	17	7.76	103	148	8	66	0.5	2.8	0.006	0	20	1.4	3.84	3	20.1	2	60.54
RH37	17	7.73	105	156	6.8	67	0.5	2.2	0.8	0	22.4	1.5	1.82	3.1	20.4	2.3	61.67
RH38	23.4	7.36	365	552	7.49	163	0.14	3.2	4.7	0	99	6.5	2.5	23.3	46.6	1.8	207.37
RH39	26	7.28	392	600	3.8	183	0.13	3.6	6	0	60	5	2.8	22.2	47.5	7.74	205.02
RH40	19.4	8.01	201	315	8.24	101	0.3	9.3	4.6	0	29.2	3.8	2.3	6.8	33	3.5	107.08
RH41	24.7	7.1	244	367	5.6	136	0.11	9.9	17.8	0	36.2	9.1	1.8	10.8	41.2	5.53	143.16
RH42	25.8	7.22	175	256	5.5	105	0.2	1.3	9.3	0	38.7	2.6	0.9	11.5	32	2.71	123.95
RH43	22	8.38	429	614	8.2	134	0.1	1.9	5.2	0	201	2.2	1.6	41	53	2.2	295.3
RH44	23.4	7.35	384	595	11	144	0.5	7.5	14.3	0	35.1	12	2.5	22	21.2	2.3	141.08
RH45	22	7.2	390	595	8	203	1.4	5.7	4.1	0	0	12	2.5	20	23.6	21	138.64
RH46	15	7.6	159	234	12	153	0.6	4	0	0	0	18	3.6	6.2	32	5.4	102.22
RH47	23.4	6.9	366	446	5	203	0.9	3.9	6.3	0	26	11.2	2.4	14.3	41	5.3	157.03
RH48	17.4	7.3	440	684	12.5	134	0.76	14.1	13.9	0	77	10	2.3	13.6	39.6	5.6	150.8
RH49	23.5	6.47	214	323	6.5	116	0.47	8.2	21.4	0	30	7.3	2.05	11.5	32	6.73	123.95
RH50	24.6	6.43	125	179	4	61	0.3	1.7	8.4	0	21	6.3	1.05	4.5	20.5	4.9	67.65
RH51	23.3	6.53	219	340	5.32	78	1	6	19.2	0	31	10	1.5	3	29	5	81.9
RH52	22	7.38	133	195	5	73	0.6	1.8	5.6	0	26.3	9.1	3.1	4.1	29	7	86.41
RH53	25.1	6.84	114	168	4.4	73	0.81	2	0.2	0	22	9.1	4.4	4.2	21.5	9.11	68.82
RH54	23.8	6.2	116	171	4.42	67	0.5	3.6	17	0	12.6	12.5	0.9	3.4	18.2	7.8	57.62
RH55	24.4	6.42	121	179	5.7	79	0	2.1	9	0	23.3	11.8	2	3.4	22	7.2	66.74
RH56	15.3	8.74	447	703	14	165	0.1	21.6	20.8	1	84.8	7.14	3.8	21	63	8.59	237.3
RH57	22.6	7	335	528	4.3	205	0.1	4.21	2.8	0	76	8	2.4	14.8	65	6.75	216.68
RH58	22.3	7.3	434	695	5.3	108	0.1	16	6.8	0	65.1	10.2	3.2	21.4	25.6	6.48	149.18
RH59	16.5	6.61	309	476	7.28	262	0.1	7.7	6.4	0	31	7.9	3.2	12	65.4	7.8	206.16
RH60	19.9	8.27	464	729	7	268	0.1	19.8	22.1	0.9	84.3	14.8	7.2	23.5	88.2	8.72	308.03
RH61	21	6.8	312	480	7.5	244	0.11	10.15	3.6	0	33.2	9.2	4.9	11.5	72	7	219.95
RH62	19.5	8.14	464	728	7	284	0.1	19.86	18.72	0.77	81.4	15	7.6	22.5	88	7.44	303.45
RH63	21	7.5	469	737	7.2	260	0.1	20.11	27.5	1.08	85.3	14.6	7.8	22.1	90	7.56	306.61
RH64	20	6.7	337	516	7	194	0.1	12.6	20.08	0	60.8	8	8.8	14.8	72.1	5.4	233.72
RH65	21.6	6.49	153	245	2	85	0.1	1.3	0.2	0	0.2	2.4	1.1	3.8	18.1	10.2	59.02

Samples	Temp	pH	TDS	EC	DO	HCO₃	F	Cl	NO₃	PO₄	SO₄	Na	K	Mg	Ca	SiO₂	TH
RH66	20.7	7.33	477	763	4.5	242	0.1	21.33	1.94	0	110	16	11.5	23.5	92	7.41	317.15
RH67	18.3	7.66	521	850	4.1	236	0.1	30.18	83.8	5.07	111	25.2	21	22.5	88.4	7	304.41
RH68	20.6	7.58	501	817	3	290	0.1	25.83	40.14	1.93	88.1	18	12.4	24	94.1	7.4	324.24
RH69	21.2	6.65	358	572	6	114	0.06	7.61	11	0	182	7	3.6	21	76.3	7	269.22
RH70	21.6	6.59	359	587	4.95	122	0.07	7.4	9.31	0.009	193	6.8	2.8	20.8	77.6	6.5	271.52
RH71	23	7.15	413	662	6.1	133	0.1	10	21	0	52.5	8.4	2.2	23.5	24.6	6.9	155.39
RH72	16.7	7.62	761	1309	0.5	567	0.05	54.6	0	18	63.3	37	74	26.2	105	7	359.42
RH73	21	7.25	455	750	2.53		0.2	24	9.3	0	144					8.55	
RH74	17.8	7.64	553	903	11	366	0.12	22.1	29.3	0.28	169	14.2	7.5	34.2	119	8.8	425.34
RH75	17	7.6	366	466	10	346	0.05	21.8	31.4	0	165	14	2.1	31	134	13.7	448.7
RH76	17.4	7.3	440	684	12.5	241	0.8	14.1	13.9	0	77	19.5	4.2	26.1	64	5.6	260.61
RH77	20.02	7.17	310	446	2.3	256	0.8	3.6	0.1	0	49	10	3	15	70	7.5	229.5
RH78	18.7	6.5	307	441	3.1	158	0.6	15.19	24.39	0	57	12	10.2	12	61.3	5.9	196.32
RH79	18.8	7.9	405	589	7.8	305	0.6	7.5	13.5	0	77.4	8.4	2.4	19.8	95.4	10.4	310.14
RH80	21.8	7.03	323	466	3.1	195	0.64	5.1	8.1	0.02	0.03	9	2.1	15.2	38.7	13.14	155.2
RH81	23.2	6.16	157	222	2.5	138	2.5	1.3	2.1	0.016	0.03	9	1.6	6	30	6.7	96.6
RH82	6.35	6.17	251	358	2.4	176	0.515	0.3	0.05	0.003	0.01	4.5	0.85	4.9	43	15.2	123.29
RH83	20.5	7.68	311	449	6.6	177	0.1	4.83	9.55	0.018	61.2	8.1	2	12.3	64.9	12	206.19
RH84	23.11	6.34	165	232	3.65	115	0.1	0.34	1.9	0	0.01	4.5	0.55	2.5	28	17	77.45
RH85	23.4	6.65	195	275	4.2	145	0.1	0.2	0.1	0	0.03	5	6.7	3.5	18	18	57.55
RH86	21.6	6.67	159	221	4.3	105	0.1	1.9	3.6	0.008	0.04	5.6	0.75	2.6	23.5	21	67.06
RH87	24.3	6.12	323	471	2.9	165	0.1	3.44	7.24	0	32.8	9.5	1.5	8	44	14.4	138.4
RH88	24.3	6.12	323	471	2.9	176	0.1	40.95	41	0	29	33.5	16	9	55	9.07	168.9
RH89	23.3	6	136	190	3.4	61	0.05	8.6	33.13	0	0	11.5	2	2.6	18	15.9	53.86
RH90	17.3	7.14	549	840	2.02	158	0.1	57.84	25.5	0	44.5	39.5	4.9	9	53.3	14.1	164.82
RH91	19.9	6.29	296	429	3.5	68	0.1	34.9	33.4	0	22	15.5	2.5	6.5	34.2	14.34	108.73
RH92	22.7	6.25	117	165	5.7	65	0.1	3.16	12.7	0.2	18.1	5.4	0.1	2	20.4	17.6	57.16
RH93	23.2	6.55	115	164	4.5	63	0.53	2.45	6.53	0	20.1	4.4	0.76	3.63	20.4	14.04	63.843
RH94	23.7	6.3	99	137	4.5	58	0.092	3.7	0.78	0	15	4.7	0.7	2.8	16	17.6	49.88
RH95	23.4	6.14	141	195	4.3	61	2.1	10.7	10	0	18	6.8	0.81	2.2	21.6	18.2	60.86
RH96	24.2	6.49	128	178	4.5	67	0.7	2.1	3	0	30	5.1	1.35	1.7	25.2	15	67.45
RH97	19.5	6.66	91	131	5.3	49	4.1	1.7	2.2	0	37	5.7	2.4	2.2	22.4	17.1	62.78
RH98	17.6	6.39	336	451	4.7	21	0.8	0.02	0	0	0.9	3.42	0.85	0.5	3.6	16	10.69
RH99	15.7	8.66	185	133	6.6	69	0.6	5	0.3	0	2.4	5.9	1.55	1.9	16.5	7.5	47.39

Samples	Temp	pH	TDS	EC	DO	HCO$_3$	F	Cl	NO$_3$	PO$_4$	SO$_4$	Na	K	Mg	Ca	SiO$_2$	TH
RH100	23.8	6.87	247	358	3.4	63	0.9	24	6	0	6.9	4.5	0.95	2.9	29.8	7.6	83.41
RH101	21.6	6.34	120	170	3.1	116	1.3	3.5	2.9	0	1.3	7.9	1.4	4.2	21	13.2	67.62
RH102	23.6	6.11	257	382	3.1	145	0.1	19.7	14.09	0	75.4	20.4	8.1	13.8	53.9	6.49	185.94
RH103	22.2	7.21	463	715	5.8	128	0.1	10.3	24.2	0	92.2	13	10.15	15	49	6.12	179.1
RH104	19.2	7.16	412	631	6.5	122	0.9	8	13	0	92.5	4	1.11	16	57.5	4.6	203.6
RH105	7.22	7.3	336	500	7.9	219	0.5	3	6	0	59	6.9	3.6	21.6	52.5	2.2	214.56
RH106	12.4	8.42	503	776	9.7	178	0.8	4.6	3.7	0	298	6.8	3.3	35.5	108	3	404.75
RH107	11.2	8.51	400	588	13.5	168	0.14	13.4	0	0	210	16.3	2.6	16.8	80.4	2.3	261.84
RH108	18.8	7.52	293	430	2.8	213	0.31	1.3	0.1	0	4.3	7.8	1.85	13.8	66	3	214.98
RH109	14.4	8.27	762	1353	9.5	146	2.3	6	2.5	0	861	1.7	1.05	62	267	11.8	895
RH110a	16.5	8.46	393	608	10.2	135	0.3	2.42	2	0	331	3.6	1.5	23.7	65	3	253.17
RH110b	16.1	8.5	545	858	9.3	195	0.3	2.6	2	0	329	2.6	1.1	36.4	137	3	477.56
RH111	16.2	8.1	783	1380	9.6	256	0.2	0.7	0.004	0	475	18.2	1.2	44.2	191	3.1	639.62
RH112	16.1	8.12	787	1392	7.8	214	0.3	0.72	0	0	477	1.6	1.6	47.2	212	3.44	702.32
RH113	16.1	7.39	656	1065	2.3	244	0.2	48	79	8.2	240	29.4	19.8	29.4	125	12.03	421.5
RH114	21.9	7.2	365	551	5.2	156	0.2	6.5	12	0	47	6	4	20	27.2	3.44	147.28
RH115	24.1	7.3	377	577	5.3	336	0.15	5.8	12.5	0	104	5.2	2.2	41.4	77.4	3.5	355.5
RH116	17	7.63	603	956	0.44	293	0.1	49	79	7.3	101	25.6	26	26	107	7.23	363.88
RH117	15.4	7.62	725	1177	0.9	325	0.1	55.5	46.7	17	101	30.2	36.8	29.6	129	6.24	430.96
RH118	13.8	7.14	432	655	15	259	0.1	14.2	33.4	0	35.3	4.4	1.4	22	28	6.02	157.4
RH119	18.3	7.14	510	804	2.5	344	0.02	36.2	55	0	56.5	7.6	1.6	29	31	3	193.3
RH120	23.3	7	538	877	5	427	0.1	44	75.4	0	51	11	1.4	29	37.6	4	209.14
RH121	23	6.93	597	982	4.8	427	0.02	47.23	69.45	0	62	17.6	2.6	35	23	9.54	198.7
RH122	22.5	7.16	443	701	2.5	251	0.1	6.1	11	0	149	5.7	1.2	22	61.3	9.05	237.32
RH123	21.4	7.4	495	804	2.8	222	0.1	4.4	19	0	218	4.4	1.4	29	93.3	4.2	342.82
RH124	22	7	483	785	1.4	213	0.1	47	14.2	0	43.2	13.4	1.6	26	30.4	4.8	179.56
RH125	22	7.1	429	693	5.3	227	0.1	22.6	39.53	0	70.5	6	1	28	27	6.67	179.6
RH126	15.7	7.5	626	1053	0.3	439	0.1	45.71	5.33	6.1	180	19.6	27.4	30	145	6.67	471
RH127	15.4	7.81	568	929	3.5	338	0.12	42	45	9.2	105	21	22	25	119	3.48	388.1
RH128	23.1	7.31	319	493	6.02	151	0.1	4.3	8.6	0	69	3	1.3	16	44	7.01	171.2
RH129	20.9	7.37	293	462	2.5	156	0.1	4	2.5	0	109	3.3	1.1	16.8	64	7.3	222.48
RH130	23	7.15	296	466	3.5	189	0.1	3.8	9.2	0	49.5	3.6	1	16	24.4	7.2	124.16
RH131	22	7.18	381	650	5.4	220	0.12	12.3	27	0	64	4	1	22	79	7.2	279.8

Table 6.2: Physico -chemical composition of Surface and groundwater of Dehradun and Haridwar district in summer season

Sample	Tem.	pH	TDS	EC	DO	HCO$_3$	F	Cl	NO$_3$	PO$_4$	SO$_4$	Na	K	Mg	Ca	SiO$_2$
RHII	27	6.8	378	608	5.5	324	0.14	2	14.8	0	1.6	6.9	1.7	11	77	4.07
RHII2	27.6	7.3	339	533	5.1	326	0.37	2.7	17.42	0	1.1	11	2	8.6	88	3.49
RHII3	26.9	6.86	350	558	2.5	289	0.5	1.8	3.6	0	2.7	17	0.9	19	47	4
RHII 4	27.6	6.8	378	610	4	306	0.1	1.9	4.5	0	3.9	8.9	0.9	15	81	4.5
RH5	27.6	6.79	378	610	4.01	453	0.1	3.8	14.24	0	3.8	5	10.6	19	96	4.1
RHII6	29.1	4.42	527	881	2.3	460	0.16	54	28.18	1.7	7.2	12	3.4	19	98	15.8
RH7	26.4	6.67	881	1703	5.7	316	0.1	61	241		88	32	11.2	22	105	3.88
RHII8	26.3	6.7	736	1355	4.2	301	0.08	57	241.2	0	85	34	10	33	122	8.3
RHII10	27.2	6.86	486	695	8	304	0.15	45	2.36	0	14	8.1	1.8	14	81	8.01
RHII11	25.3	6.75	380	624	4.27	314	0.4	20	1.6	0	45	5.9	10	22	69	3.2
RHII15	25.6	8.22	121	179	5.06	132	0.3	2.1	0.8	0	25	1.9	1.8	9	35	1.8
RHII16	21.4	8.18	111	166	7.11	126	0.3	1.3	0.5	0	22	2	1.9	8.7	34	1.65
RHII17	23	8.35	119	178	5	113	0.3	1.8	2.4	0	23	2.1	2	5.5	32	1.9
RHII18	22.2	8.32	118	174	5.35	113	0.28	1.4	1.14	0	24	3.1	4.2	5.2	31	1.15
RH1II9	23	7.46	247	386	3.81	240	0.4	4.4	0.003	0	24	4.8	5.1	9.8	49	2.19
RHII22	21.2	8.16	110	165	5.6	176	0.3	1.3	0.47	0	22	0.1	2.1	13	41	0.72
RHII23	20.2	8.05	134	199	5.9	171	0.32	1.5	0.27	0	24	3.1	5.2	9.2	44	1.3
RHII24	19.2	8.06	129	193	5.2	106	0.31	1.3	0.65	0	24	2.3	1.5	7	34	1.3
RHII25	21.6	7.33	257	403	5.05	206	0.38	6.8	9.03	0	29	8.4	1.8	15	45	3.4
RHII30	23.9	6.25	135	198	3.4	100	0.2	4	8.93	0	17	3.2	7.5	8	29	4.2
RHII31	24	6.26	114	170	3.81	94.1	0.08	2.9	6.5	0	13	5.9	0.5	5.8	28	10.79
RHII32A	20	6.2	93	145	4.7	94.1	0.1	3.2	9.4	0	17	2.2	2.4	7.2	26	1.9
RHII36	21.6	8.3	103	150	10.6	94.1	0.2	1	1	0	15	0.4	4.7	5.8	28	1.88
RHII37	21.2	8.28	99	152	6.3	107	0.1	5.5	10.74	0	37	5.2	3.4	8.6	33	1.7
RHII39	27.5	7.24	266	420	5.03	326	0.32	0	0.001	0	43	4.7	3.5	26	58	1.11
RHII40	22.5	8	119	173	6	165	0.32	0	0.014	0	46	1.3	9.3	8.7	39	1.17
RH43	25	8.6	357	576	6.4	182	11	2.3	3.66	0	154	1.8	3	40	61	2.7
RHII44	25.3	7.23	142	744	1.75	208	0.03	17	33.5	0	7.3	2.2	3.3	26	36	5.9
RH45	25	7.6	390	595	8	256	0.08	3.6	5.4	0	9.4	11	3.5	27	33	6
RH46	25	7.6	158	233	8	188	0.08	1.7	0.002	0	0.3	16	3.6	9	34	9.6
RHII48	26.4	8.04	410	735	4.6	164	0.1	21	10.73	0.1	117	15	1.2	18	49	6.2
RHII49	24.5	6.11	119	173	4	175	0.06	3.9	20.3	0	11	6.2	3.7	17	34	6.7
RHII51	24.8	6.53	196	131	3.5	94.1	0.07	1.2	5	0	29	5.3	0.5	8.9	28	5.5

Sample	Tem.	pH	TDS	EC	DO	HCO$_3$	F	Cl	NO$_3$	PO$_4$	SO$_4$	Na	K	Mg	Ca	SiO$_2$
RHII52	25.8	7.46	130	199	3.96	100	0.07	1.3	5.5	0	27	4.5	0.2	9.2	27	10.6
RHII55	24.7	6.7	115	176	5.6	97	0.27	41	60.9	0.1	28	14	10	13	36	5.96
RH57	22	6.8	81.2	116	5.5	212	0.1	61	241.8	0	88	18	12.3	29	79	2.16
RHII58	24	6.84	362	592	4.71	164	0.06	16	9.07	0	63	16	3.1	23	31	3.2
RH59	23.7	6.86	348	567	5.4	302	0.1	13	2.7	0	38	8.6	3.5	15	69	3.8
RHI61	28.8	7.14	368	615	4.2	259	0.08	3.2	11	0	136	13	5.8	26	73	
RH62	29.4	7.87	415	698	5.7	365	0.1	19	3.86	0.4	60	12	11.8	28	85	3.6
RHII63	24	7.65	453	777	2.69	337	0.09	24	19.19	1.7	91	14	9.8	26	95	3.8
RHII64	23.4	6.76	137	209	3.25	169	0.27	7.4	9.3	0	174	10	9.1	29	72	9.6
RHII65	24	7.28	381	635	6.35	208	0.08	16	14.5	0	59	2.2	9.5	25	43	6.88
RHII67	23	7.15	376	630	6.12	319	0.04	31	35.9	2.7	109	27	22.5	29	79	3.2
RHII69	27.6	6.79	336	480	1.5	219	0.37	33	38.82	2.9	112	13	7.5	26	76	4.8
RHII74	24	7.03	508	888	9.84	416	0.06	28	27.8	0	134	18	8.1	33	121	4.2
RHII77	23.2	7.4	358	598	5.2	333	0.28	10	14.6		88	12	3.7	28	76	
RHII79	22.8	8.26	348	564	3.25	357	0.14	7.5	7.8	0	91	9.6	2.7	25	96	2.9
RHII93	27.7	6.25	234	377	2	132	0.21	12	4.8	0	30	9.6	2.1	13	29	
RHII100	24.4	7.18	168	264	3.8	147	0.13	4.3	3.6	0	15	8	0.8	9	32	11.2
RHII102	26.4	6.29	74.4	117	2.13	155	0.07	1.6	1.25	0	0.1	8	1.4	5.7	35	12.6
RHII103	25.7	7.15	402	714	3.7	201	0.16	9.4	13.75	0	93	18	2	22	57	2.44
RH104	28.1	7.6	350	647	5.02	216	0.08	16	17.5	0	112	5.9	2.5	29	68	4.3
RHII105	21.2	7.58	414	591	7	227	0.11	30	0	0	160	7.9	3.9	37	68	11
RHII106	23.4	7.94	454	826	8.7	182	0.22	6.8	1.86	0	212	6.4	2.3	38	85	4.1
RHII107	23.9	8.23	437	757	9.4	169	0.16	33	0	0	238	8.3	3.1	31	93	3.66
RHII109	18.7	8.31	729	1041	9.3	276	0.16	2.8	1.9	0	413	2.2	1.2	68	173	3.8
RHII111	23.1	8.18	792	1693	7.3	266	0.22	1.1	0.15	0	443	20	1.8	54	149	3.6
RHII112	22.9	8.26	791	1682	8.29	288	0.3	1.2	0.19	0	349	0.1	1.8	39	182	8.9
RHII114	26.2	7.5	365	644	5.4	226	0.16	5.9	11.7	0	75	9.4	3	30	42	1.99
RHII115	25	7.68	372	622	6.5	344	0.15	5.9	11.96	0	88	8.2	2.1	46	78	1.8
RH124	28	7.65	356	654	5.5	235	0.09	40	85.4	1.3	55	14	1.7	38	48	1.4
RH125	27.9	7.25	426	808	5.18	255	0.07	39	8.9	0	40	8	1.8	35	39	2.3
RH126	27.6	7.27	394	731	5.4	420	0.07	25	38.3	0	65	21	20.3	36	113	2.24
RH127	27.9	7.19	481	920	6.5	425	0.1	38	0.75	4.3	50	26	21.7	32	115	4.9
RH 128	26	7.32	319	493	6.4	259	0.63	4.2	1E-04	0	54	3.5	1.3	28	54	6.5
RH131	25	7.2	650	381	5.4	220	0.15	15	29	0	54	5	1.3	21	78	6.4

Table 6.3: Physico -chemical composition of Surface and groundwater of Dehradun and Haridwar district in post monsoon season.

Sample	Tem.	pH	TDS	EC	DO	HCO3	F	Cl	NO₃	PO₄	SO₄	Na	K	Mg	Ca	SiO₂
RHIII	27.2	7.2	348	626	4.5	238	0.5	3.1	12.5	0	4.2	6	1.5	6.5	59	10.2
RHIII 2	26.8	7.8	301	524	5.5	236	2.44	17	0.04	0	2.2	3.6	0.8	5	73	4.2
RH3	26.9	7.2	305	536	4.6	274	0	1.2	5.85	0	2.1	4	0.2	7	85	3.3
RH4	26.8	6.96	389	769	10	243	0.14	65	13.83	0	1.5	17.3	3	12	73	6.3
RH5	27.6	6.9	370	528	7.6	290	0.07	13	8.9	0	5	6	1.5	11	78	7
RH6	27	6.9	351	625	4.3	321	0.18	38	1.97	0	7.8	11.1	2	11	87	8.2
RH7	27.1	7.25	343	614	5	262	0.09	30	2.4	0	4.5	9.5	1.8	10	68	3.8
RH8	27.1	7.22	341	613	8.7	278	0.27	14	33.6	0	11	4	2.6	8.5	83	3.5
RH10	27.2	6.86	413	695	2.8	263	0.23	16	9.8	0	5.6	6.8	1.2	12	72	3.6
RH11	26.9	6.9	354	646	5.1	162	0.22	50	3.19	0	11	10	2.4	6.1	57	4.08
RH15	24	8.18	97	157	5	81.5	0.58	1.3	1.3	0	15	3.5	1.5	9	20	3.97
RH16	26	8.29	107	157	6	82.8	0.04	1.6	1.73	0	18	1.4	1.6	8.2	19	3.04
RH17	23	8.34	119	178	5	109	0.04	1	1.22	0	20	1.1	2.2	9	25	5
RH18	22.2	8.34	118	174	5.35	112	0.05	1.9	2.8	0	20	2.6	3.4	9	25	8.84
RH19	26.4	7.47	292	512	8.7	155	0	11	6.39	0	19	3.72	4.4	11	41	8
RH22	23	8.22	107	162	7	140	0.68	1.4	2.03	0	19	3	1.9	7.2	35	1.2
RH23	23	8.1	133	195	7.2	121	2.9	3.2	3.3	22	9	2.5	2.2	8.5	39	1.4
RH24	22	7.9	169	266	10	101	0.07	3.2	4.58	0	3.2	0.8	1.9	4.3	32	3.3
RH25	21.6	7.33	257	403	5.05	101	0.2	5.8	7.8	0	23	4.8	1.9	9.8	28	6.1
RH30	25.3	6.87	123	181	6.09	72	0.2	3	6.8	0	14	2.1	2.5	4.9	23	14.1
RH31	25	7.3	124	189	6	62	0	3.5	10.5	0	16	2	1	4.9	22	2.3
RH32A	27.5	8.07	79	124	5.2	63	0.01	1.1	1.14	0	11	1.8	1.9	3.7	19	3.6
RH33	23	8.1	78	126	5.2	80	0.02	1	1.3	0	11	3.5	1.7	4.5	21	2.4
RH36	23	8.2	78	125	5.2	70	0.03	0.7	1.07		15	2.7	2.1	3.8	19	2.6
RH37	33.5	8.16	121	186	9.17	61.5	0.05	2.3	3.9	0	17	5.9	0.5	3	20	2.3
RH39	30.8	7.22	239	394	4.6	143	0	5.1	11.47	0	38	1.7	0.8	18	33	6.5
RH40	24	8.27	139	221	7.5	108	0.05	2.3	3.9	0	18	2.6	2.5	7.9	29	7.7
RH43	25	8.2	119	175	7.6	114	0.12	1.1	3.2	0	138	5.6	2.2	32	43	11.9
RH44	25.3	7.4	521	745	6	108	0.05	16	33.6	0	73	12.6	2.8	25	23	18.14
RH45	24.2	7.23	335	574	6	138	0.08	3.4	6.4	0	10	8.2	1.9	16	18	8.43
RH46	26.7	7.9	124	190	6.5	129	0.08	1.7	0.002	0	0.4	2.7	1.2	6.9	27	3.7
RH48	27.8	6.3	107	160	2.42	114	0.06	10	20.8	0	59	9.7	2.8	13	36	12.32
RH49	24.9	6	114	174	4.9	80	0.06	4.2	22.5	0	16	14.9	1.5	6.2	19	6.8

Sample	Tem.	pH	TDS	EC	DO	HCO3	F	Cl	NO$_3$	PO$_4$	SO$_4$	Na	K	Mg	Ca	SiO$_2$
RH51	25	6.3	107	160	2.4	66.6	0.07	3.8	13.11	0	12	9.2	3	1.9	17	9.92
RH52	27	7	132	206	3.6	96.8	0.12	1.6	12.2	0	20	7.5	0.9	8	26	12.3
RH61	28	6.99	368	617	4.1	196	0	1.9	4.5	0	156	6.3	12	23	65	5.6
RH62	27	6.9	312	589	5.11	222	0	1.6	0.24	0	1.1	5.6	4.3	2.9	57	19.3
RH63	26	7.7	453	777	2.5	212	0.09	19	19.19	1.7	91	12.9	7.4	22	68	5.3
RH64	23.5	6.9	137	210	3.5	170	0.16	22	20.67	0	65	7	7.8	22	51	5.5
RH65	25	7.3	380	636	6.4	61	0.15	1.4	0.3	0	0.2	3.3	1.1	2	13	9.8
RH67	25	7.4	370	625	6.2	225	0.05	11	21.07	0	204	23	20	31	78	6.5
RH68	27	7.25	198	318	5	181	0.11	4	7.2	0	41	1.4	1.2	20	45	5.13
RH69	26	6.8	336	479	1.8	206	0.1	3.5	3.24	0	43	5.2	1.4	18	49	30.81
RH70	25	6.5	315	530	4	175	0.14	9	0.1	0	106	5.9	1.8	19	62	8.2
RH74	26.6	7.25	407	851	6	316	0.05	32	39.93	0.6	134	18	7.3	34	98	3.21
RH75	26.7	7.39	336	600	7.24	306	0.11	9.1	18.54	0	42	8.6	3	21	76	14
RH79	28.2	7.83	344	595	7.04	282	0.18	8.3	12.6	0	75	7.8	3.8	24	75	12.05
RH80	25.6	7.27	302	507	5	168	0.15	5.5	11.3	0	58	5.8	1.4	19	44	13.3
RH94	27.5	6.75	126	197	3.2	70	0.87	11	3.04	0	1	3.5	0.5	1	25	19
RH100	25.4	6.77	217	353	5.47	35	0.19	20	10.49	0	21	2.1	0.6	2.8	26	12
RH102	26	6.3	75	119	2	121	0.18	1.4	1.1	0	9.8	1.9	0.4	7.2	29	4.3
RH103	24.4	7	405	742	7.7	236	0.14	11	30.02	0	90	8.8	1	21	84	13.2
RH104	24	7.23	372	668	8.5	120	6.8	9.4	17.65	0	129	5.8	1.3	25	58	4.8
RH105	24.4	7.9	355	637	7	203	0.18	4	8.21	0	108	4.9	1.2	30	56	2.94
RH106	26.7	8.44	334	581	8	174	0.28	2.3	3.8	0	179	5.2	2.1	41	51	4.9
RH107	26.8	8.6	243	393	8	230	0.34	2.9	0	0	96	7.2	2.7	21	66	2.5
RH111	27.4	8.19	439	888	6.5	232	0.24	0.7	1.09	0	246	12	1.8	36	112	6.6
RH112	27.3	8.22	448	908	7.1	200	0.25	0.7	1.09	0	246	4.6	1.2	32	120	3.6
RH114	27.3	7.55	332	623	8	175	0.24	7.7	17.7	0	48	5.2	2.1	28	29	3.7
RH115	25	7.7	371	625		226	0.23	7.3	11.9	0	89	4.9	0.4	34	55	3.8
RH116	27.3	7.8	355	652		278	0.24	11	6.3	0	140	9.4	5	36	79	7.3
RH124	27	7.44	482	986	3	201	0.04	41	67.4	0	43	12.7	1.2	28	54	8.8
RH125	27	7.18	423	833	4	176	0.06	43	13.42	0	41	8.7	1.6	32	33	8.8
RH126	27.8	7.16	383	748	5	337	0.07	24	35.8	0	75	11.2	9.2	28	94	6.8
RH127	27	7.2	483	925	6.5	220	0.05	12	9.5	0	53	18	9.5	23	43	33.08
RH128	26	7.4	321	495	6.4	230	0.11	4.8	0	0	134	1.7	8.9	35	59	6.7
RH131	22	7.18	651	382	5.2	220	0.21	12	23.4	0	55	4.5	3.5	19	66	7.2

Table 6.4: Coefficient of correlationship between various ions in Winter Season

	TDS	EC	HCO$_3$	Si	F	Cl	NO$_3$	PO$_4$	SO$_4$	Na	K	Mg	Ca	(Ca+Mg)
TDS	1	0.97	0.736	-0.2	-0	0.57	0.4	0.432	0.55	0.53	0.42	0.79	0.74	
EC	0.97	1	0.737	-0.2	-0	0.58	0.41	0.447	0.58	0.54	0.44	0.8	0.77	
HCO$_3$	0.736	0.737	1	-0.2	-0	0.56	0.34	0.458	0.12	0.52	0.48	0.54	0.57	0.5894
Si	-0.24	-0.23	-0.19	1	0.2	-0	-0.08	-0.03	-0.2	0.05	-0.1	-0.3	-0.2	
F	-0.21	-0.19	-0.24	0.24	1	-0.2	-0.2	-0.07	0.07	-0.2	-0.1	-0.1	-0.1	
Cl	0.572	0.578	0.556	-0	-0	1	0.64	0.563	0.03	0.75	0.57	0.31	0.29	
NO$_3$	0.403	0.408	0.342	-0.1	-0	0.64	1	0.201	-0	0.47	0.16	0.22	0.19	
PO$_4$	0.432	0.447	0.458	-0	-0	0.56	0.21	0.1	0.08	0.58	0.91	0.23	0.33	
SO$_4$	0.547	0.581	0.124	-0	0.1	0.03	-0	0.075	1	0	0.06	0.77	0.76	
Na	0.528	0.54	0.521	0.05	-0	0.75	0.47	0.576	0	1	0.64	0.22	0.31	
K	0.42	0.439	0.482	-0.1	-0	0.57	0.16	0.909	0.06	0.64	1	0.23	0.31	
Mg	0.792	0.805	0.539	-0.3	-0	0.31	0.22	0.234	0.77	0.22	0.23	1	0.71	
Ca	0.744	0.769	0.565	-0.2	-0	0.29	0.19	0.335	0.76	0.31	0.31	0.71	1	

Table 6.5: Coefficient of correlationship between various ions in summer season

	TDS	EC	HCO3	F	Cl	NO3	PO4	SO4	Na	K	Mg	Ca
TDS	1	0.9	0.6	0.01	0.4	0.28	0.18	0.603	0.482	0.134	0.678	0.813
EC	0.93	1	0.6	-0	0.4	0.31	0.183	0.623	0.509	0.17	0.68	0.794
HCO$_3$	0.62	0.6	1	-0.1	0.4	0.14	0.35	0.131	0.45	0.42	0.473	0.687
F	0.01	0.9	0.6	1	-0	-0.1	-0.05	0.112	-0.155	-0.06	0.164	-0.02
Cl	0.4	0.4	0.4	-0.1	1	0.7	0.429	0.035	0.639	0.469	0.272	0.308
NO$_3$	0.28	0.3	0.1	-0.1	0.7	1	0.065	0.008	0.615	0.35	0.15	0.232
PO$_4$	0.19	0.2	0.3	-0	0.4	0.07	1	0.004	0.441	0.552	0.162	0.229
SO$_4$	0.62	0.6	0.1	0.11	0	0.01	0.004	1	0.118	-0	0.776	0.718
Na	0.51	0.5	0.4	-0.2	0.6	0.61	0.441	0.118	1	0.543	0.297	0.384
K	0.16	0.2	0.4	-0.1	0.5	0.35	0.552	-0	0.543	1	0.178	0.298
Mg	0.7	0.7	0.5	0.16	0.3	0.15	0.162	0.776	0.297	0.178	1	0.703
Ca	0.82	0.8	0.7	-0	0.3	0.23	0.229	0.718	0.384	0.298	0.703	1

Table 6.6: Coefficient of correlationship between various ions in Post Monsoon Season

	TDS	EC	HCO3	F	Cl	NO$_3$	PO$_4$	SO$_4$	Na	K	Mg	Ca
TDS	1	0.84	0.627	0.012	0.414	0.396	-0.125	0.373	0.452	0.256	0.534	0.5987
EC	0.84	1	0.694	0.0424	0.497	0.427	-0.117	0.457	0.583	0.244	0.6079	0.6932
HCO$_3$	0.63	0.69	1	-0.071	0.388	0.289	-0.072	0.3	0.438	0.315	0.4994	0.8693
F	0.01	0.84	0.627	1	-0.021	-0.018	0.3405	0.078	-0.1	-0.12	0.0139	0.059
Cl	0.41	0.5	0.388	-0.021	1	0.43	-0.058	-0.1	0.54	0.117	0.1359	0.3206
NO$_3$	0.38	0.44	0.282	-0.016	0.432	1	-0.058	0.105	0.523	0.208	0.3235	0.2234
PO$_4$	-0.13	-0.1	-0.071	0.3403	-0.058	-0.058	1	-0.079	-0.09	-0.01	-0.075	-0.038
SO$_4$	0.39	0.46	0.3	0.0779	-0.1	0.105	-0.079	1	0.337	0.437	0.8309	0.5592
Na	0.5	0.58	0.444	-0.104	0.542	0.523	-0.089	0.337	1	0.545	0.3988	0.4184
K	0.26	0.25	0.314	-0.124	0.116	0.208	-0.008	0.437	0.545	1	0.3753	0.2855
Mg	0.55	0.61	0.498	0.0145	0.135	0.323	-0.075	0.831	0.399	0.375	1	0.5202
Ca	0.61	0.7	0.869	0.0604	0.32	0.223	-0.038	0.559	0.418	0.286	0.5202	1

6.3 CHEMICAL WEATHERING PROCESS

The control on the abundances of dissolved major cations (Na, K, Mg and Ca) and anions (HCO_3, SO_4 and Cl) in the water can be explained in terms of weathering of various rocks in the drainage basin. The dissolved concentrations in river water are derived from various sources including rock weathering, rainfall, glacial melt water, wind-blown dust but among all these sources, rock weathering dominate the resultant water composition. Plotting of the data as per the Gibb's schemes (1970) also shows that the water chemistry of the study area is controlled by rock weathering (Fig. 6.4.1)

Rock weathering involves congruent and incongruent dissolution as per the following reactions (Chakrapani, 2005).

1. $Na \rightarrow Na^+ + Cl^-$

2. $CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$

3. $CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$

4. $CaCO_3 + H_2SO_4 \rightarrow Ca^{2+} + SO_4^{2-} + H_2CO_3^-$

5. $Ca\,Mg(CO_3)_2 + H_2SO_4 \rightarrow Ca^{2+} + Mg^{2+} + 2\,SO_4^{2-} + 2\,H_2CO_3^-$

6. $Ca\,Mg(CO_3)_2 + 2H_2SO_4 \rightarrow 2Ca^{2+} + 2\,Mg^{2+} + 2\,SO_4^{2-} + 42\,H_2CO_3^-$

7. $2\,Na\,AlSi_3O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O5(OH)_4 + 2Na^+ + 4H_4SiO_4$

8. $2KAlSi_3O_8 + 2H_2O \rightarrow 4OH^- + Al_4Si_4O_{10}(OH)_8 + 8H_4SiO_4$

9. $CaAlSi_2O_8 + 2CO_2 + 3H_2O \rightarrow Ca^{2+} + Al_2Si_2O_5(OH)_4 + 2HCO_3^-$

A source of proton is necessary for the rapid weathering of these carbonate minerals and the most common source of protons is carbonic acid (H_2CO_3 , reaction 3). The relative proportion of ions in water dependent on their relative abundances in the host rock. The two major anions HCO_3 and SO_4 in surface water are mainly derived from dissolution of atmospheric CO_2 in water and the oxidation of sulphides (Garrels and Mackenzie 1971). These two reaction provide the bulk of protons which chemically weather carbonate, and silicates in the drainage basin (Singh 1999). The dissolution of carbonates rocks

proceeds more rapidly than silicate rocks. Some of the weathering reactions for carbonate minerals such as calcite ($CaCO_3$), dolomite $CaMg(CO_3)_2$ and gypsum or anhydrite ($CaSO_4.2H_2O$, $CaSO_4$) associated with sedimentary rocks are as follows (Garrels and Christ, 1965, Garrels and Mackenzie, 1971, Holland, 1978):

1. $CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^-$
2. $CaMg(CO_3)_2 + 2H_2CO_3 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$
3. $CaCO_3 + H_2SO_4 \rightarrow Ca^{2+} + SO^{2-}_4 + H_2CO_3^-$
4. $Ca Mg(CO_3)_2 + H_2SO_4 \rightarrow Ca^{2+} + Mg^{2+} + 2SO_4^{2-} + 2 H_2CO_3^-$
5. $CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$

The equivalent ratio of Ca:HCO_3 in entire study area (surface and groundwater) is 1.2 and that of surface water of Haridwar and Dehradun district is 1.09 and 0.95 respectively suggesting of calcite weathering as their source. The equivalent ratio of Ca: HCO_3 of Ganga river at Haridwar and Risikesh is 1.09 and in Dehradun surface water it is 0.95.

The sulphuric acid is mainly derived from the oxidation of sulphate minerals such as gypsum and pyrites and from anthropogenic sources (Holland, 1978, Jickells etal, 1982). Pyrite which oxidized in a carbonate environment yields H_2SO_4 which is neutralized largely by Ca^{2+}, Mg^2, Na^+ and K^+ in the solution. However, the solution products of silicate weathering are not well defined because the degradation of silicates generate a variety of solid phases (mostly clays) along with the dissolve species. Thus the weathering of silicate rocks with carbonic acid is written as (Sarin1983);

(Na, K, Mg, Ca+CO_2 +H_2O) Silicate $\rightarrow$ H_4SiO_4 + HCO_3^- +Na^+ +K^++Mg^{2+} +Ca^{2++} Solid products
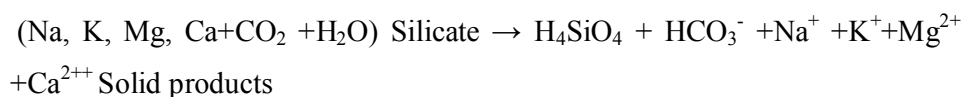
Since the abundance of cations and anions released to the solution are determined by the bulk composition of the parent rock and the availability of protons for rock weathering, the relative proportion of Ca^{2+} and HCO^-_3, released during the weathering of calcium silicate (Ca feldspar) can be same as

that resulting from calcite dissolution (Garrels and Mackenzie 1971). Therefore it is difficult to find out the origin of Ca in the water based on water chemistry alone. Additional information on geology of the terrains is required to distinguish the relative inputs of Ca and Mg from weathering of carbonate and silicates. In addition to the inputs of Ca, Mg and HCO_3 , there are other reaction product such as SiO_2, Na and K which are released to the solution during silicate weathering.

In case of silicate weathering all of the alkalinity produced is of atmospheric origin whereas in case of carbonate weathering only half of it is. Therefore, silicate weathering on land represents an important sink for atmospheric CO_2 and is of special interest within the context of controlling the concentration of CO_2 in the atmosphere and ocean over geological time scales (Berner et al. 1983, Wollast and Mackenzie 1983, Brady and Carrol 1994). Silicate weathering is dependent on temperature and precipitation (white and Blum, 1995) and possibly would be enhanced through global warming. The ratio of (Ca+Mg)**:**(Na+K) is 6 in Indus river which is more than twice the world average (2.2) implying that weathering of carbonate lithology is major factor in water composition in the basin. (Ahmad, et al. 1998).

Another factor affecting weathering is the erosion rate, i.e the delivery of potentially weatherable material. In Outer and Lesser Himalaya abundant supply of and resulting eroded material is not a limiting factor in case of Himalayan rivers due to steep relief.

6.4   MAJOR ION CHEMISTRY OF SURFACE AND GROUNDWATER OF DEHRADUN AND HARIDWAR DISTRICTS

Despite the complexity of weathering environment, it is possible to evaluate the major ion chemistry of rivers and groundwater in terms of chemical weathering in their catchment by studying abundance ratios of various cations, anions and silica in waters and with the knowledge of lithology of the basin. Thus based on the weathering reaction and observed geographical variability of dissolved major constituents, the surface and groundwater chemistry of

Dehradun and Haridwar district has been evaluated in terms of chemical weathering in their drainage basin. The chemistry of surface and groundwater of Dehradun and Haridwar district have been discussed separately.

6.4.1 Dehradun Surface Water

The major ions chemistry of Bindal, Rispana, Asan, Nun, Ganga and Yamuna rivers have been described here. The geology of the drainage basin is discussed in detail in Chapter III. The salient features of the major ion chemistry of the Dehradun surface water are:

i) The order of abundance of major anion in surface water of Dehradun is as: HCO_3(56%)>SO_4(32 %)>Cl(6%)>NO_3 (3%)>F(1%)>PO_4 (0.5 %) and the order of abundance of major cations in surface water of Dehradun is Ca (63 %) > Mg (25%) > Na (9%) > K (2.7%)

ii) Calcium and Magnesium are major cations, together they account for 56 to 99% of cations. The Mg : Ca equivalent ratios varies from 0.3 to 2.4 with mean value of 0.53 in winter season, during summer season it ranges from 0.3 to 1.3 with an average of 0.7 and during post monsoon season it varies from 0.01 to 2.4 with an average of 0.50. During summer season the contribution of sodium and potassium to the total cation is relatively high in comparison to post monsoon season (Fig. 6.6). This trend is evident from the plot of Ca+Mg versus total cations (TZ+) of summer season (Fig. 6.5) which show that at higher TZ+ concentration Ca +Mg fall below the 1:1 trend reflecting increases contribution of sodium and potassium.

iii) The K:Na ratios varies from 0.03 to 0.7 with mean vlaue of 0.3 in winter season, during summer the ratio varies from 0.05 to 10 with mean value of 1.03 and in post monsoon mean value is 0.3.

iv) Among the anions bicarbonate is the most dominant and account for 11 % to 96% of the anions in winter season and ranges from 344µeq/l to 6000µeq/l with an average of 3218µeq/l in winter season. The average concentration of sulphate and chloride is 2931µeq/l and 424µeq/l respectively. The SO_4: Cl ratio are generally high and varies from 0.1 to

500 with mean value of 43 in winter and post monsoon season and 42 during summer season.

v) The silica concentration of these river ranges from 12μmole/l to 263μmole/l with mean value of 53μmole/l during winter season and summer season and in post monsoon it varies from 41 μmole/l to 321μmole/l with an average of 98μmole/l.

vi) The scatter diagram of (Ca + Mg) versus bicarbonate (Fig. 6.7) shows that all the Ca+Mg in the surface water of Dehradun district is not balanced by bicarbonate which gives an indication that the chemistry of surface water of Doon is not only limited to weathering of limestone and dolomite exposed in northern part of the valley but also from different sources. Further the plot of Ca+Mg and HCO_3+SO_4, (Fig. 6.12) in which all the samples are falling close to 1:1 line, indicating SO_4 is the other ion in balancing the chemical equilibrium. Sulphate is derived from weathering of gypsum present in limestone and dolomite of Krol formation of Lesser Himalaya and from oxidation of pyrite.

However, the contribution of other ions like chloride, nitrite and phosphate were found to be very high at several places along the course of Bindal and Rispana river, possibly from anthropogenic sources. A closer look at scatter diagram (Fig. 6.7) shows that most of the sample collected during winter season falls above the equiline of (Ca+Mg) **:** HCO_3. This require a high fraction, about 70% of the (Ca+Mg) in these waters has to be balance by others anions.

vii) The relative importance of silicate weathering to the major ion composition of surface water can be understood from abundance of sodium, potassium and silica in these waters. On an average (Na+K) account for almost less than 12% of the total cations in winter season, during summer it account for 8% and during winter season it account for 10%. The average (Na+K) **:** Cl is about 4:1 suggesting that about 75% of the (Na+K) in these water has a source other than marine cyclic salts and halite deposit. The present study area of Dehradun and Haridwar district is far away from the sea, thus the cyclic contribution of sodium is less significant thus indicating anthropogenic activity may be the other

source of (Na+K) in the study area . The sodium concentration in the surface water of Doon is relatively high as compared to chloride concentration and the average Na:Cl equivalent ratio is 3:1 in winter and summer which increases to 4:1 in post monsoon season. This increases may be attributed to rain.

viii) The (Na*+K) : TZ+ equivalent ratio (Na* signifies sodium corrected for chloride) range between 0.005 to 0.23 in winter season, 0.004 to 0.21 in premonsoon season and 0.026 to 0.20 during post monsoon season suggesting that the contribution of sodium and potassium in these river waters comes from silicate weathering which may account on an average of less than 12 %.

ix) On a ternary anion plot (Fig.6.15) relating HCO_3, SO_4 and $(Cl+NO_3+PO_4)$ most of the data falls close to HCO_3 vertex and on a ternary cation diagram of Ca, Mg and (Na+K), most of the data falls close to Ca vertex or towards the centre of the field. (Fig. 6.18) indicating dominance of carbonate weathering as a source of ion in surface water of Dehradun district.

Basin wise characteristics of major ion chemistry in different rivers of Doon valley are discussed below:

6.4.2   Asan River

The Asan river water is characterized by relatively high TDS content (333.2 mg/l) where bicarbonate constitutes ~71% of the anions and calcium and magnesium constitute 70% and 20% of cations respectively. The SO_4**:**Cl equivalent ratio is also high (6.8) indicating leaching of sulphate either from dissolution of gypsum or from oxidation of pyrite or from anthropogenic sources. The SiO_2 concentration ranges from 79.3μmole/l to 236.05μmole/l with a mean value of 166μmole/l.

Calcium and magnesium together constitute about 90% of the cations and magnesium and calcium equivalent ratio is 0.3. Already high (2.5) ratio of Na**:**Cl in water of Asan river suggest less significant contribution of Na from

other than marine source. The contribution from silicate weathering is limited to 8% as Na+K **:** TZ+ is 0.08 only. This indicates possibility of Na from anthropogenic source.

The scatter diagram of (Ca+Mg) verses bicarbonate (Fig. 6. 12a) shows that almost all of the Ca+Mg in Asan river is balanced by bicarbonate which can also be understood from 1.2 ratio between Ca+Mg**:** HCO_3. This suggests that the chemistry of Asan river is dominated by weathering of carbonate. This is consistent with the geology of river basin dominated by limestone and dolomite in northern part and Siwalik sandstone in southern part of the valley.

6.4.3   Suswa River

The TDS content in Suswa river varies from 429mg/l to 469mg/l with mean value of 455 mg/l. Among anions bicarbonate contribute ~ 53% followed by sulphate (27%), Cl (7%), NO_3 (4.5%) and PO_4 (0.3%) in Suswa river. Among cations calcium is found to be most dominating cation constituting 58% followed by Mg 33% sodium 7% and potassium ~ 2.1%. The SiO_2 concentration ranges from 37μmole/l to 145μmole/l with mean value of 113.14μmole/l.

The low 0.09 ratio of (Na* + K)**:** TZ+ indicate that contribution of alkali metals from silicate weathering is ~ 9%. The (Ca+Mg)**:** TZ+ ratio is 0.9 and Ca**:** Mg ratio is 1.9. The Ca**:** HCO_3 ratio is 1.07 indicating same source of Ca and HCO_3 possibly from weathering of carbonate.

6.4.4   Rispana River

The average pH of the river is 7.7 indicating slightly alkaline nature of water. The TDS varies from 393mg/l to 656mg/l with mean value of 548mg/l. Among anions bicarbonate is the dominant anions but accounts only 41% followed by sulpahte (37%), chloride (10%), nitrate (9%) and phosphate (2%) of total anions. Among cations , calcium is the most dominant and account for 59% followed by Mg(26%), Na(10%) and K(5%) of total cations. The SiO_2

concentration is relatively low in Rispana river and varies from 49 µmole/l to 197 µmole/l with a mean value of 108 µmole/l.

The (Na* +K):TZ+ equivalent ratio is 0.15 suggests that the contribution of sodium and potassium in this river water from silicate weathering is limited to about 15%. SO_4 : Cl ratio ranges from 1.5 to 101. The ratio of (Ca+Mg) :HCO_3 is 1.8 indicating that the chemistry of water is dominant by weathering of carbonate particularly weathering of gypsum, and or pyrite mineral present in the Krol limestone is very prominent .

6.4.5   Bindal River

The pH value of Bindal river vary from 7.5 to 7.6. The TDS ranges from 501mg/l to 725 mg/l with a mean value of 613mg/l. The bicarbonate is the most dominant anion accounting for 55% of total anions followed by SO_4 (22%), Cl(12%), NO_3(8%), PO_4(3%) and F(0.05%). Ca constitute 59% of total cations followed by Mg(24%), Na(11%) and K(6.2%).   The SiO_2 concentration in Bindal river ranges from 103 µmole/l to 123µmole/l.

The average (Ca+Mg)/HCO_3 equivalent ratio of 1.5 suggest relatively high contribution of (Ca+Mg) to the cations and high (Ca+Mg) : (Na+K) ratio of 5:1 indicate carbonate weathering could be the primary source of major ions to these water. Alkalinity from silicate weathering may also be calculated (where all values are in milli equivalent units) following Raymahasay (1986);

$$\text{Alkalinty }_{\text{(Carbonate Weathering)}} = 0.74 \text{ Ca }_{\text{total}} + 0.04 \text{ Mg }_{\text{total}}$$

and

$$\text{Alkalinity }_{\text{silicate weathering}} = \text{Alka. }_{\text{Total}} - \text{Alk. }_{\text{Carb. weathering}}$$

The total alkalinity in Bindal river is 4754 µEq/l. Based on Raymahasay formula the alkalinity due to bicarbonate weathering is estimated 4265 µEq/l and due to silicate weathering is 89 µEq/l. This further substantiates the dominance of carbonate weathering over silicate weathering in Bindal basin.

Table 6.7: Comparison of ion composition in surface water of Dehradun and Haridwar districts.

Dehradun	Temp	pH	TDS	EC	DO	HCO$_3$	F	Cl	NO$_3$	PO$_4$	SO$_4$	Na	K	Mg	Ca	Si
Suswa River	19.54	8.2	454.6	702.2	8.68	222.2	0.1	16.7	18.86	0.75	107	10.7	5.6	26.02	76.44	6.9
Assan	19.02	7.5	333.2	500	10.9	195.2	0.58	6.26	9.998	0.003	50.4	9.25	2.12	13.55	59.77	9.4
Rispana	16.66	7.8	548.2	881.6	4.11	249.2	0.16	34.3	57.76	5.954	178	21	18.1	25.32	101	6.5
Bindal	18	7.6	613	997	1.95	307.5	0.1	40.7	43.42	9.465	94.5	24.1	24.6	26.8	111.6	6.8
Sahastradhara	16.15	8.1	785	1386	8.7	235	0.25	0.71	0.002	0	476	9.9	1.4	45.7	201.5	3.3
Nimi Nadi	15.7	8.7	185	133	6.6	69	0.6	5	0.3	0	2.4	5.9	1.55	1.9	16.5	7.5
Haridwar Ganga river	16.4	7.9	169	245	13.0	109	0.5	2.2	1.4	0	24.16	3.0	3.0	4.8	38.8	6.6

6.4.6 Song River

The Song river is characterized by alkaline water (pH- 8) and relatively high TDS value of 346 mg/l. The bicarbonate is found to be most dominant anions accounting 52% of total anions followed by SO_4 (43%), Cl (2%), NO_3 (2%) and F (0.1%) while phosphate were found to be absent in Song river. Calcium constitutes about 63% of total cations followed by Mg (12%), Na (3%) and K (0.7%). The Ca:HCO_3 ratio is 1.1, Na:Cl ratio is 1.3 and Ca+Mg:HCO_3 is 1.7. Based on Raymahasay formula the alkalinity due to bicarbonate weathering is 2142µEq/l and due to silicate weathering is 333µeq/l. The high Ca+Mg: Na+K ratio (23) and low ratio of Na+K : TZ (0.04) indicate weathering of carbonate rocks (limestone and dolomite) as the major source of solute in these water.

6.4.7 Nimi Nadi

The water of Nimi Nadi are characterized by alkaline nature (pH ~8.6) and relatively low TDS (185 mg/l). Among anions bicarbonate constitutes 83% followed by chloride (10%) and sulphate (3.6%) of the total anion. Based on the dominance of ions the water belongs to calcium bicarbonate ($CaHCO_3$) hydrochemical facies (Back 1966). Among cations, calcium account for 64% followed by magnesium 12% and SiO_2 is 122 µmole/l. The Calcium and Magnesium together account for 77 % and the Mg/Ca ratio is 0.18. These observation suggests, ionic concentration in water of Nimi nadi is due to carbonate weathering of limestone and dolomite rocks and the 0.26 ratio of the (Na*+K): TZ+ ratio indicate contribution of silicate weathering in ionic concentration is about 26%.

6.4.8 Nun River

Nun river is characterized by relatively high TDS content with mean value of 383mg/l. The SiO_2 concentration in this water ranges from 36µmole/l to 49µmole/l. Bicarbonate account for 58% followed by SO_4 (38%) among anions and calcium is (62%) followed by magnesium (29%) among cations. Calcium and Magnesium together constitute ~ 91% . This together with

bicarbonate and sulphate indicate that ionic source in waters of the Nun river are controlled by carbonate weathering particularly dolomite and limestone of of the Krol formation of Lesser Himalaya.

6.4.9   Seasonal variation in Dehradun Surface water

The samples collected in winter, summer and post monsoon season from the Rispana, Bindal, Suswa, and Asan rivers have been used to evaluate the seasonal variation in the major ion composition of these rivers. The data are given in Table 6.9. The salient features of the seasonal variation are:

1. During winter season on an average Ca+Mg account for 88% of total cations, in summer it constitute 91.5 % and during post monsoon it constitute 90 % of the total cations. The (Ca+Mg) **:** (Na +K) equivalent ratio are high in summer season in comparison to post monsoon and winter season. In winter the average ratio of (Ca+ Mg)/(Na+K) is 19.3, in summer 30 and in postmonsoon season it is 13.2.

2. Mg **:** Ca ratio is about 0.7 during summer and post monsoon season but decreases to 0.4 in winter season.

3. The SO_4 **:** Cl equivalent ratio tend to slightly increase during winter and post monsoon season (43) in comparison to summer season (42).

4. The average Na **:** Cl ratio is 3.1 in winter season, 2.9 in premonsoon and 4.2 in post monsoon season.

5. The average TDS concentration in winter season ranges from 91mg/l to 787mg/l with a mean of 440mg/l, during summer season from137mg/l to 792mg/l with a mean of 460mg/l and from 137mg/l to 483mg/l with a mean of 369.6mg/l during post monsoon season.

6. The bicarbonate is the dominant anion (56%, 54%, 59%) followed by sulphate (32%, 37% and 37%), chloride (6%, 5.9% and 4.8%), nitrate (6%, 3% and 3%) and phosphate (0.09%, 2.8% and 3.5%) respectively in winter, summer and post monsoon season in surface water of Dehradun. Fluoride is generally low in concentration and account ~ 1% in winter season, 0.09% in summer season and 0.6 % in post monsoon season among anions.

7. Among cations calcium were found to be most dominant cation (54%, 63% and 54%) followed by magnesium (24%, 12% and 17%), sodium (6%, 6% and 18% and potassium (2%, 2% and 11%) respectively in winter, summer and postmonsoon season.

8. The ions HCO_3, F, Cl, PO_4, SO_4 and Mg are generally tend to decrease in post monsoon season when compared with summer season due to recharge from rain in monsoon season.

6.4.10 Springs (Sahastradhara and Chandrabani)

Sample of two springs namely Sahastradhara and Chandrabani were collected from Doon valley. Both the springs are alkaline in nature (pH -7) and have relatively high TDS of 553mg/l (Chandrabani) and 787 mg/l (Sahastradhara). Among cations, calcium constitute 68% and 62% followed by magnesium 26% and 29% respectively in Sahastradhara and Chandrabani spring. Among anions sulphate ion is most dominant anion (70%) followed by bicarbonate (30%) in Sahastradhara and bicarbonate (56%) followed by sulphate (33%) in Chandrabani Spring.

The ratio of Ca: HCO_3 is 2.2 and 0.9 respectively in Sahastradhara and Chandrabani spring and ratio of (Ca+Mg):(Na+K) is 73 and 11 in Sahastradhara and Chandrabani spring. The high concentration of sulphate is due to weathering of gypsum present in pockets in limestone and dolomite rocks of Krol formation. The relatively high contribution of (Ca+Mg) to total cations, high (Ca+Mg:(Na+K) ratio (72) and low (Na+K):TZ+ ratio of 0.05 indicates carbonate rocks are the major source of solutes in these waters. However in Chandrabani spring, sulphate may also have been added from sulpahte rich fertilizer applied in agriculture field present in the surrounding area. The extent of silicate weathering borne out from (Na^*+K) : TZ^+ ratio (0.10) indicates contribution of silicate weathering is limited to ~ 10 %.

a) Dehradun Groundwater

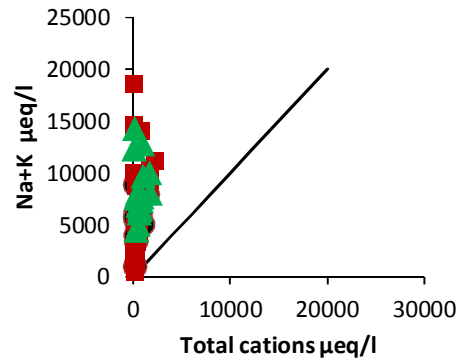b) Surface waetr of Dehradun
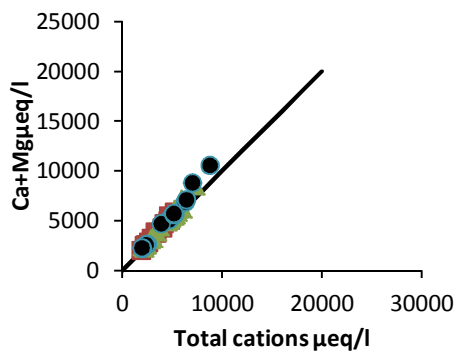
c) Haridwar Groundwater
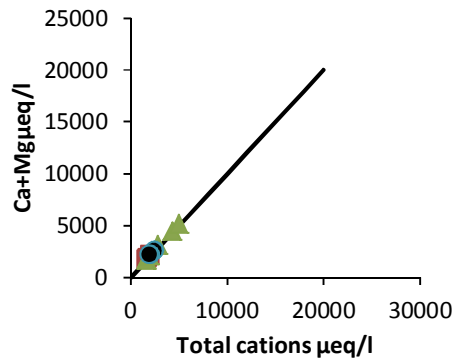
d) Ganga river at Haridwar

Fig. 6.5: Scatter diagram between (Ca+Mg) and total cations in the surface and groundwater of Dehradun and Haridwar district during winter, summer and post monsoon season.
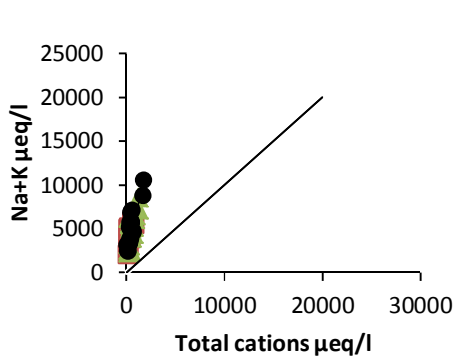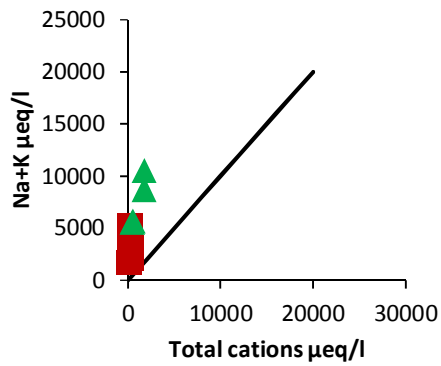
a) Groundwater of Dehradun

b) Surface water of Dehradun

c) Groundwater of Haridwar

d) Surface Water of Haridwar
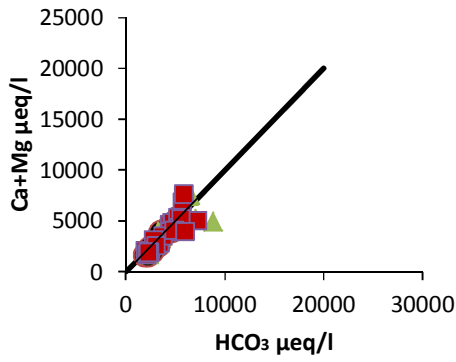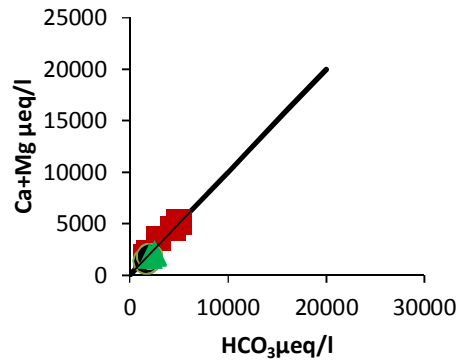
Fig. 6.6: Scatter diagram of (Na+K) and total cations in the surface and ground water of study area during winter, summer and monsoon season.

■ Winter Season

● Post Monsoon Season

▲ Summer Season
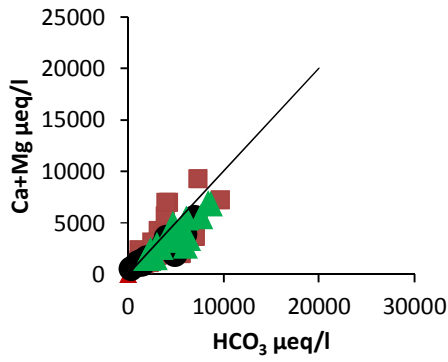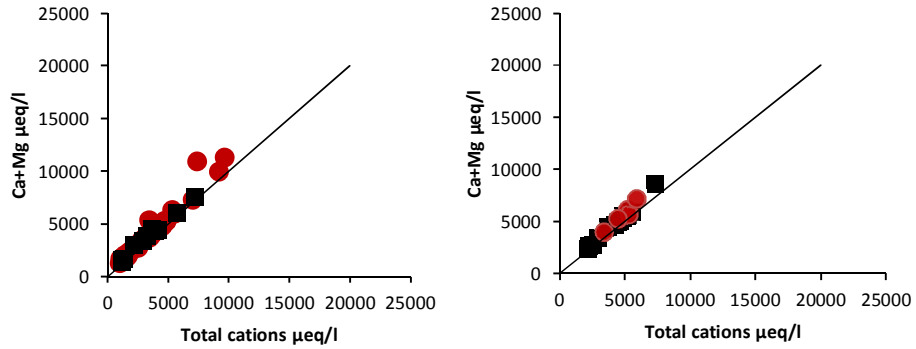
a) Groundwater of Dehradun
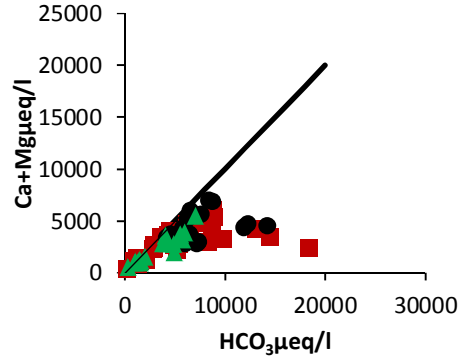
b) Surface water of Dehradun

c) Groundwater of Haridwar

d) Surface water of Haridwar

Fig. 6.7: Equivalent ratio of Ca+Mg and (HCO₃) and in surface and groundwater of Dehradun and Haridwar district.

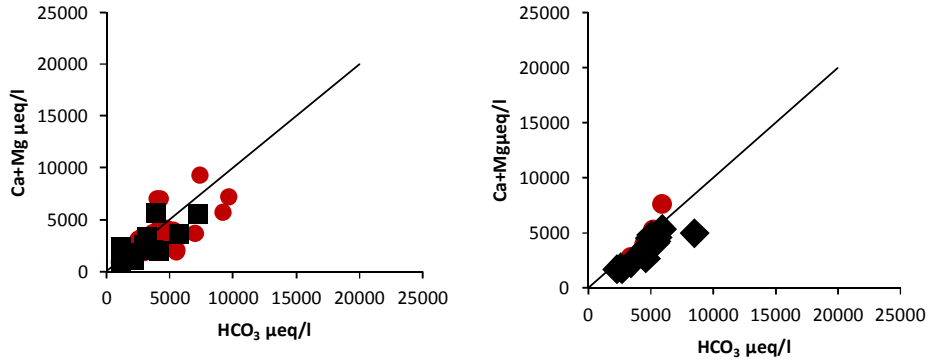a) Dehradun Tubewell and Handpump   b) Haridwar Tubewell and Handpump

Fig. 6.8: Scatter diagram showing equivalent ratio of Ca+Mg and total cations in tubewell and handpump of Dehradun and Haridwar district.
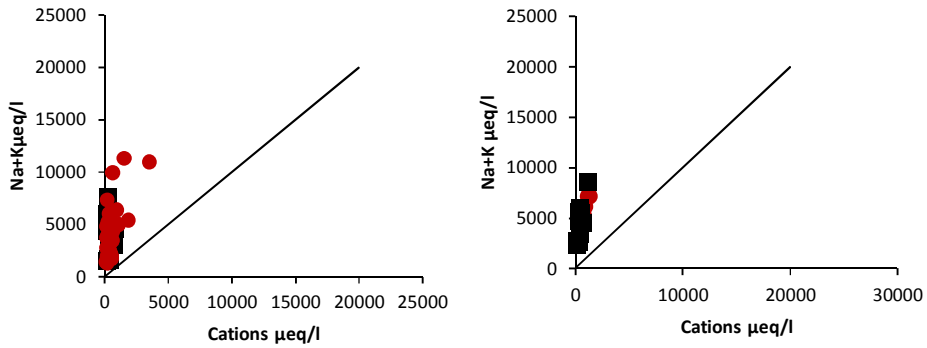
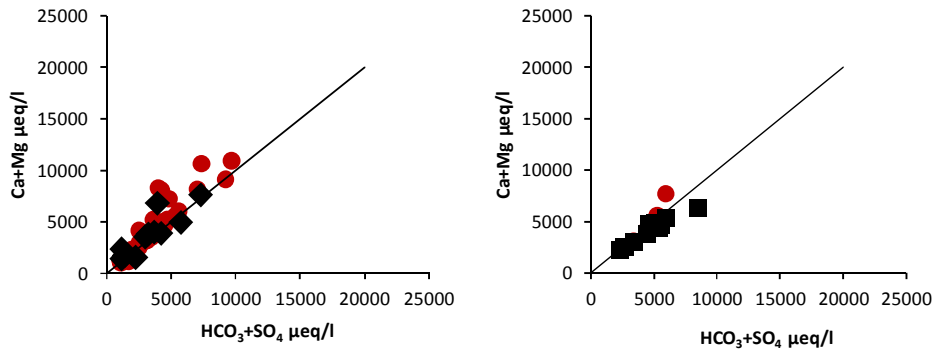a) Dehradun Tubewell and Handpump   b) Haridwar Tubewell and Handpump

Fig. 6.9: Scatter diagram showing equivalent ratio of Na+K and total bicarbonate in tubewell and handpump of Dehradun and Haridwar district.

a) Dehradun Tubewell and Handpump   b) Haridwar Tubewell and Handpump

Fig. 6.10: Scatter diagram showing equivalent ratio of Ca+Mg and total bicarbonate in tubewell and handpump of Dehradun and Haridwar district.
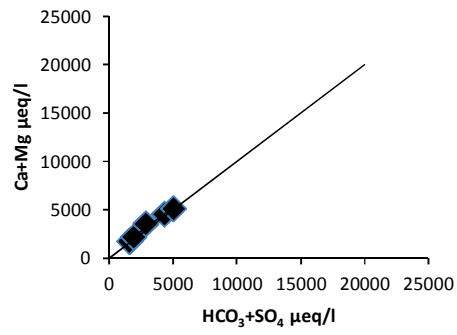

a) Dehradun Tubewell and Handpump   b) Haridwar Tubewell and Handpump

Fig. 6.11: Scatter diagram showing equivalent ratio of Ca+Mg and (HCO$_3$+SO$_4$) and in tubewell and handpump of Dehradun and Haridwar district.
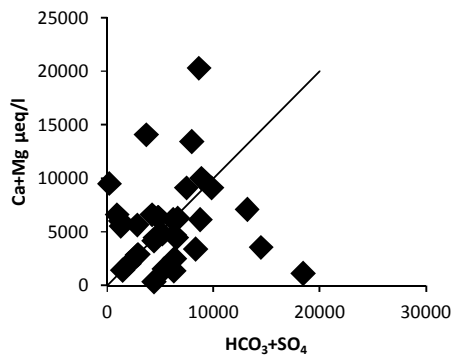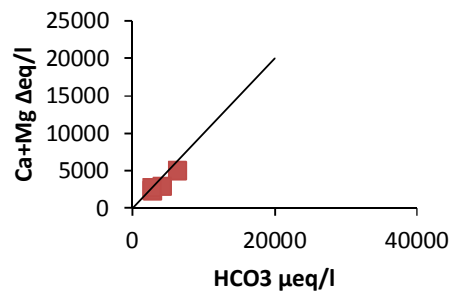
a) Surface water of Dehradun   b) Surface water of Haridwar

Fig. 6.12: Scatter diagram showing equivalent ratio of Ca+Mg and (HCO$_3$+SO$_4$) and in surface water of Dehradun and Haridwar district.

Fig. 6.12a: Scatter diagram showing equivalent ratio of (Ca+Mg) and HCO$_3$ in Asan river of Dehradun district.

6.5 MAJOR ION CHEMISTRY OF DEHRADUN GROUNDWATER

Since more than 80% of drinking water supply in Dehradun district is from groundwater, it is important to understand the controls on the ionic composition of groundwater. The groundwater in Dehradun district is extracted through tubewells and handpumps. The salient features of the major ion chemistry of Dehradun groundwater are as follows;

The order of abundance of major anions in groundwater of Dehradun is as:

HCO_3 (65%)>SO_4 (21%)>Cl (74%) NO_3 (6%)>F (0.7%) >PO_4 (0.1%)

and the order of abundance of major cations is as:

Ca (58%)>Mg (27%)>Na (13%)>K (2.5%).

The bicarbonate accounts 64% to 66% of the total anions and Ca+Mg contribute 85% of the total cations supports the earlier observation of carbonate weathering as the major source of dissolved constituents in groundwater of Dehradun district.

The average (Ca+Mg)**:**HCO_3 equivalent ratio of 1.2, a relatively high contribution of (Ca+Mg) to total cations (Ca+Mg: TZ+ = 0.8) and high (Ca +Mg) **:** (Na+K) equivalent ratio ~9 in groundwater indicate that carbonate weathering could be primary source of major ions in groundwater of Dehradun district. The (Ca+Mg) vs TZ+ plot (Fig. 6.5) shows that in groundwater of Dehradun most of the points approach 1**:**1 equiline i.e. suggesting large fraction of total cations are balanced by (Ca+Mg), and equivalent ratio of (Na+K) vs TZ+ (Fig. 6.6) suggests less contribution of (Na+K) to total cations. Further, the plotting of data on a ternary cation diagram (Fig. 6.14) and anion diagram relating HCO_3, SO_4 and (Cl, NO_3, PO_4) (Fig.6.13) shows that most of the samples cluster around Ca apex and along the alkalinity apex, respectively, indicating dominance of carbonate weathering to major ion composition in groundwater of Dehradun district.

6.5.1 Seasonal variation in groundwater of Dehradun

There is wide seasonal variation found in TDS concentration of groundwater. In winter season the TDS varies from 99mg/l to 761 mg/l with an average of 314.5mg/l, during summer season it ranges from 81mg/l to 381mg/l with a mean value of 232.9mg/l and during post monsoon season it ranges from 79 mg/l to 483 mg/l with mean of 265mg/l. The TDS values are found higher in post monsoon season in compare to summer season. The increased concentration is due to percolation of rain water to downward leaching of ions from the soil and rocks, thereby increasing the ion concentration in groundwater samples.

The bicarbonate concentration is 2809 Eq/l, 3759µEq/l, 2348µEq/l respectively in winter, summer and post monsoon season. Bicarbonate constitute (64%, 65% and 63.8%) of total anions followed by sulphate (23%, 22.4% and 23%), chloride (6.1%, 6.3% and 6.1%) nitrate (6.3%, 5.8% and 6.3%) and fluoride (0.5%, 0.2% and 0.5%) respectively in winter season, summer and post monsoon season.

Calcium and magnesium are the major cations together they constitute ~ 84% in winter season and ~ 88% in both summer and post monsoon season. Individually, calcium varies from 798 µEq/l to 7235 µEq/l with an average of 2156 µEq/l in the winter season, 1347 µEq/l to 3942 µEq/l with an average of 2499 during summer season and 648.7 µEq/l to 4690 µEq/l with an average of 1976 µEq/l during post monsoon season. Ca constitute about (58%, 55% and 55%) of the total cations followed by Mg(27%, 33% and 31%) , Na (12.6%, 8.8% and 11.2) and K(2.5%, 2.5% and 11.25) respectively during winter, summer and post monsoon season.

Ca:Mg ratio is 2.9, 1.8 and 2.2 respectively in winter season, summer and post monsoon season. The SO_4:Cl equivalent ratio is 5.4, 8.2 and 8 respectively in winter, summer and post monsoon season. The (Ca+Mg):(Na+K) equivalent ratio is 8.8 in winter season, 10 in summer season and 9.4 in post monsoon season.

Na **:** Cl ratio increases to 3.7 in winter season compared to 2.2 summer season and 2.7 in post monsoon season.. The Ca+Mg **:** HCO_3 is 1.2 in winter season, 1.3 in summer and in post monsoon. It has been observed that the ratio such as SO_4**:**Cl, and (Ca+Mg)**:**(Na:K) are lowest in post monsoon and tend to increase in summer season indicating dilution effect from recharge during rainy season.

6.5.2 Dehradun Tubewell and Handpump

The TDS value in tubewell varies from 117mg/l to 510mg/l with a mean of 314mg/l while in handpump it ranges from 99mg/l to 761mg/l with mean of 340mg/l. The HCO_3 concentration ranges from 1066µEq/l to 5639µEq/l with an average of 2676µEq/l in tubewell while in handpump it ranges from 1066 µEq/l to 5639 µEq/l with an average of 2676µEq/l which constitute about 65% of total anions in tubewell and 68% of total anions in handpump while the average concentration of F, Cl, NO_3, PO_4 and SO_4 are respectively 0.4%, 6.8%, 6.3%, 0.0001%, 21.2% in tubewell water and 0.4%, 7.6%, 6.4%, 0.1%, 22% of the total anions in hand pump water.

The ions like SO_4, Cl and PO_4 tend to increase in shallow aquifer (handpump water) in comparison to deep aquifers (tubewell water) of Dehradun. The contribution of Ca, Mg, Na and K are 58%, 28%, 11% and 2% respectively in tubewell and 60%, 29%, 10% and 2.3% in handpump water respectively**.**

The order of abundance of anions and cations in groundwater of Dehradun during winter season is as follows:

The Anions:

Tubewell**:** HCO_3 (65%)>SO_4 (21.2%)>NO_3 (6.7%)>Cl (6.5%)>F (0.07%)

Handpump**:** HCO_3 (66%)>SO_4 (23%)>Cl (8%)>NO_3 (5%)>F (0.5%)>PO_4 (0.1%)

The Cation:

Tubewell **:** Ca (58%)>Mg (28%)>Na (11%) > K(2%)

Handpump**:** Ca (56%) > Mg (30%)> Na (11%)> K (2%)

6.6   SURFACE WATER OF HARIDWAR

In Haridwar district the surface water is mainly represented by the river Ganga. The Ganga river originate from Gangotri Glacier near Gaumukh travel and through the crystalline rocks of Higher Himalayan, meta-sedimentary and crystalline rocks of Lesser Himalaya and sedimentary rocks of Siwalik belt. These rocks are cut by several faults and thrusts. The local geology is described in Chapter III.

The plot of (Ca+Mg) versus TZ^+ shows the dominance of Ca and Mg among cations (Fig.6.5). Bicarbonate is the major anion in Ganga waters and account for 73% followed by sulphate and chloride which together constitute about 25% of anions. The SO_4 : Cl equivalent ratios varies from 2.7 to 13.6 with mean value of 10.8 in winter season. The plot of (Ca+Mg) versus bicarbonate (Fig. 6.7) show that most of the sample during winter, summer and post monsoon season falls slightly below 1:1 trend indicating that a significant fraction of bicarbonate has to be balanced by (Na+K). On a ternary cation diagram of Ca, Mg and Na+K (Fig. 6.20) most of the data fall either close to Ca vertex or towards the centre of the field and also on the ternary anions diagram of HCO_3, SO_4 and (Cl+NO_3) (Fig. 6.15), most of the data falls close to HCO_3 vertex indicating carbonate weathering as the major source of ions in Ganga river. The earlier studies of Sarin (1983) and Sarin and Krishnaswamy (1984) also substantiate the present observations.

6.6.1   Seasonal Variation in Ganga River at Haridwar

The abundance of cations and anions and their ratios in these river waters have been used to evaluate the seasonal variation in the major ion chemistry of the Ganga rivers. In Ganga water of Haridwar the bicarbonate constitute (73%, 77% and 77%) followed by SO_4 (22%, 19.3% and 19%) chloride (2.4%, 2%, 2%) and nitrate (1%, 0.7%, 1%) respectively during winter, summer and post monsoon seasons. Calcium constitute (72%, 69% and 55%) followed by Mg (18%, 24% and 36%) of cations respectively in winter, summer and post monsoon season. The (Ca+Mg) account for more than 90% of the cation and

HCO_3 constitute about 73% of the anions. It has been observed that equivalent ratio of (Ca+Mg):(Na+K) increases considerably during summer season (19.6) in comparison to winter (6.7) and post monsoon season (13.5). However, the ratio of SO_4 : Cl (8.8) in summer in comparison to winter (10.8) and post monsoon season (9.7). It has been observed that the Ca and SO_4 ions tend to increase in summer season whereas the ions like Cl, NO_3, Mg, Na tend to increase in post monsoon season with respect to summer season. A good relationship between SO_4 and Ca is ($r^2 = 0.85$, Table 6.6) indicate same source of ions in Ganga water possibly due to weathering of gypsum, pyrite and calcium rich feldspar in the basin. These observations seems to favour the carbonate weathering as a major source of dissolved constituent in all three season in Ganga water.

It is difficult to estimate contribution of cations through silicate weathering. A rough estimate of the contribution from silicates obtained using the (Na*+K):TZ ratios (Na signifies sodium corrected for chloride) as a index of silicate weathering indicates that the sodium and potassium derived from silicate weathering can account about 9 % in all three season viz. summer, winter and post monsoon season. The Na+K : TZ+ ratio varies from 0.7 to 0.9 in all three season. The low abundance of SiO_2, 73 µmole/l to 136 µmole/l with mean value of 110 µmole/l and low SiO_2 : HCO_3 molar ratios (0.044 to 0.09 with mean value of 0.06) also indicate the contribution of ions from silicate weathering is very less in Ganga basin.

Na^+ and Cl^- when derived from rainfall or halite deposit, show a molar ratio of 1. The molar ratio of Na/Cl of Ganga water at Haridwar vary from 0.3 to 1.4 with mean value of 1.05 indicating either rainfall or halite dissolution as their source. (Ahmad et al., 1998)

6.7   MAJOR ION CHEMISTRY OF HARIDWAR GROUNDWATER

The TDS found to be maximum 398 mg/l in winter season, moderate 265mg/l in post monsoon season and minimum 232mg/l in summer season. The pH vary from 6.8 to 8.5 with an average of 7.3 in winter season, 6 to 8 with an

average of 7 during summer season and during post monsoon it vary from 6 to 8.7 with an average of 7.

Calcium and Magnesium are major cations together they account for 90% of total cations. Calcium constitute 72% of total cation followed Mg (17%), Na (86%) and K (1.6%). Among anions, bicarbonate is most dominant and account for 77% of total anions followed by SO_4 (9%), Cl (7%) and NO_3 (6%).

On a ternary anion plot (Fig. 6.13) relating HCO_3, SO_4 and $(Cl+NO_3+PO_4)$ most of the data falls close to HCO_3 vertex and on a cation diagram (Fig. 6.14) of Ca, Mg and (Na+K), most of the data falls close to Ca vertex and towards the centre of the field. A plot of (Ca+Mg) vs HCO_3 (Fig. 6.7) shows that in most of the samples the (Ca+Mg) contents are slightly inexcess of HCO_3 suggesting that excess of (Ca+Mg) in these water should be balanced by SO_4 and Cl. The plot of (Ca+Mg) versus bicarbonate (Fig. 6.7) shows that almost all the samples falls slightly below 1:1 trend indicating that a significant fraction of bicarbonate has to be balance by (Na+K) in groundwater of Haridwar district.

The average ratio of (Ca+Mg) **:** (Na+K) is ~10 (in micro equivalent) in groundwater of Haridwar district further suggest that carbonate lithologies are the major source of ions in water composition. The average Ca+Mg **:** HCO_3 equivalent ratio of 1, a relatively high contribution of (Ca+Mg) to total cations (Ca+Mg: TZ+ = 0.8) and high (Ca +Mg) **:** (Na+K) equivalent ratio of ~10 indicate that carbonate weathering could be primary source of major ions in groundwater of Haridwar district.

6.7.1   Seasonal Variation

The HCO_3 concentration is highest 4071µEq/l in winter season, found moderate 3159 µEq/l in summer season and lowest 2348µEq/l in post monsoon season. The silica concentration is highest 659µmole/l in post monsoon season, lowest 69µmole/l in summer season and moderate 113µmole/l in winter season.

In groundwater of Haridwar district bicarbonate constitute (77%, 79% and 79%) followed by Cl (7%, 6% and 10%), NO_3 (6%, 6%, 3%), SO_4 (9.2%, 8.5% and 5%) respectively in winter, summer and post monsoon season. Among cation Ca constitute (72%, 66% and 74%) followed by Mg (17%, 24%, 18.4%) Na (9%, 7% and 6%) and K (2%, 2% and 1.3%), respectively in winter, summer and post monsoon season.

Among the ionic ratios the Na **:** Cl ratio is 2.4, 3.1 and 1.2 respectively in winter, summer and during post monsoon season. Ca **:** HCO_3 ratio is 0.8 in both winter and post monsoon season and 0.7 in summer season. HCO_3 is almost balanced by Ca and Mg in post monsoon season (Fig. 6.7). The equivalent ratio of Ca+Mg **:** HCO_3 is ~ 1.1 in all three season viz winter, summer and post monsoon seasons. However, Ca and Mg together do not show much variation in three season and account for 89 %, 88% and 81.4% respectively in winter season, summer and post monsoon season. Na and K together constitute 10.2% in winter season, 9.5% in summer and 7.7% of total cation in post monsoon season. Similar to Ca+Mg contribution the ratio of Ca+Mg **:** TZ+ in winter, summer and post monsoon season remained same ~ 0.9 in all three season . The ratio of HCO_3 **:** TZ^- is ~ 0.7 in all three season.

Most of the ions like Cl, NO_3, SO_4, K and Mg are tend to increase in post monsoon season in comparison to summer season possibly due to dissolution of ions attached with clay minerals present in the soil due to recharge during monsoon season thereby increasing the ionic concentration in post-monsoon season.

6.7.2   Haridwar Tubewell and Handpump

The TDS value in tubewell varies from 175mg/l to 740mg/l with an average of 365mg/l and in handpump it varies from 288mg/l to 796mg/l with an average of 471mg/l. Among anions the bicarbonate concentration varies from 1705µEq/l to 5344µEq/l with a mean value of 3556µEq/l in tubewell, however in handpump its concentration increases from 2287µEq/l to 7590µEq/l with an average of 4777µEq/l. The SiO_2 concentration in tubewell varies from

142µmole/l to 299µmole/l with an average of 92µmole/l while in handpump water it varies from 88µmole/l to 161µmole/l with an average of 130µmole/l.

The abundance of anions and cations in tubewells and handpumps of Haridwar districts is in the following order:

The Anions:

Tubewell:
$HCO_3(74.7\%)>SO_4(13\%)>NO_3(7\%)>Cl(4.5\%)>F(0.2\%)>PO_4(0.004\%)$

Handpump: $HCO_3(75\%)>Cl(12\%)>NO_3(6.4\%)>SO_4(5.4\%)>PO_4(0.3\%)>F(0.16\%)$

The Cations :

Tubewell: Ca (69%)>Mg(21%)>Na(8%)> K(1%)

Handpump: Ca(70%)>Mg(17%)>Na(11%)>K(2%)

It has been observed that the concentration of ions (F, Cl, PO_4, Na, K, Mg and Ca) in waters of handpump of Haridwar tend to increase in comparison to water of tubewell.

In Haridwar district the handpumps are generally drilled to a depth of 40 m and draw water from shallow aquifers in comparison to tubewells which are drilled to a depth of more than 40 m and draw water from relatively deep aquifer located between 40m to 100 m in Haridwar district. Thus increase in ionic concentration in water of handpumps in comparison to tubewells could be because of contamination of shallow aquifer from the urban waste water, which includes sewage, domestic and agricultural waste, which discharges directly in streams recharging the aquifers and soil. Another source in village area could be contamination of shallow aquifer from leaching of industrial effluent generated from Sidcul Industrial area located upstream of handpumps in village area which is discharged in open drainage and in soil without any treatment.
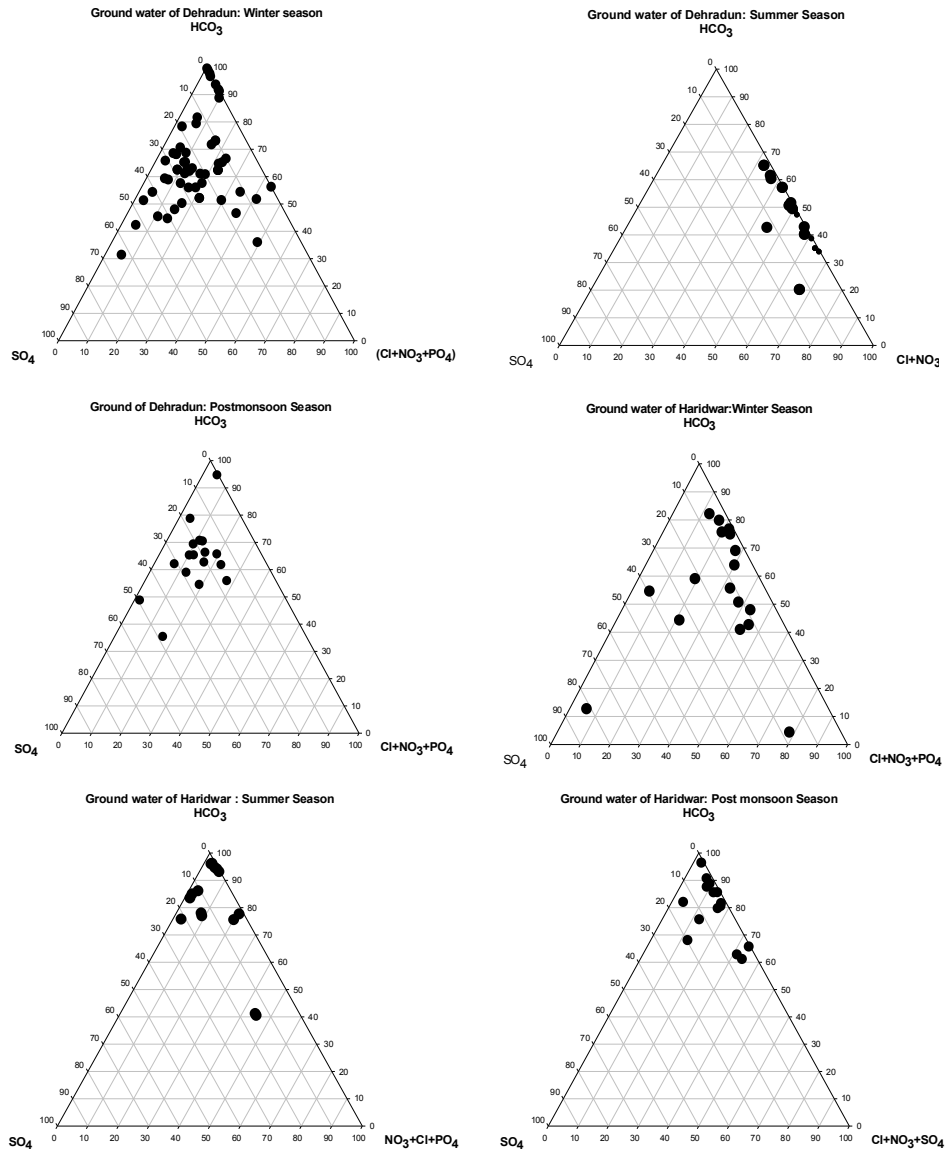
Fig. 6.13: The Ternary anion diagram showing relationship between HCO₃, SO₄ and (Cl+NO₃+PO₄) in Dehradun and Haridwar groundwater during winter, summer and post monsoon season.
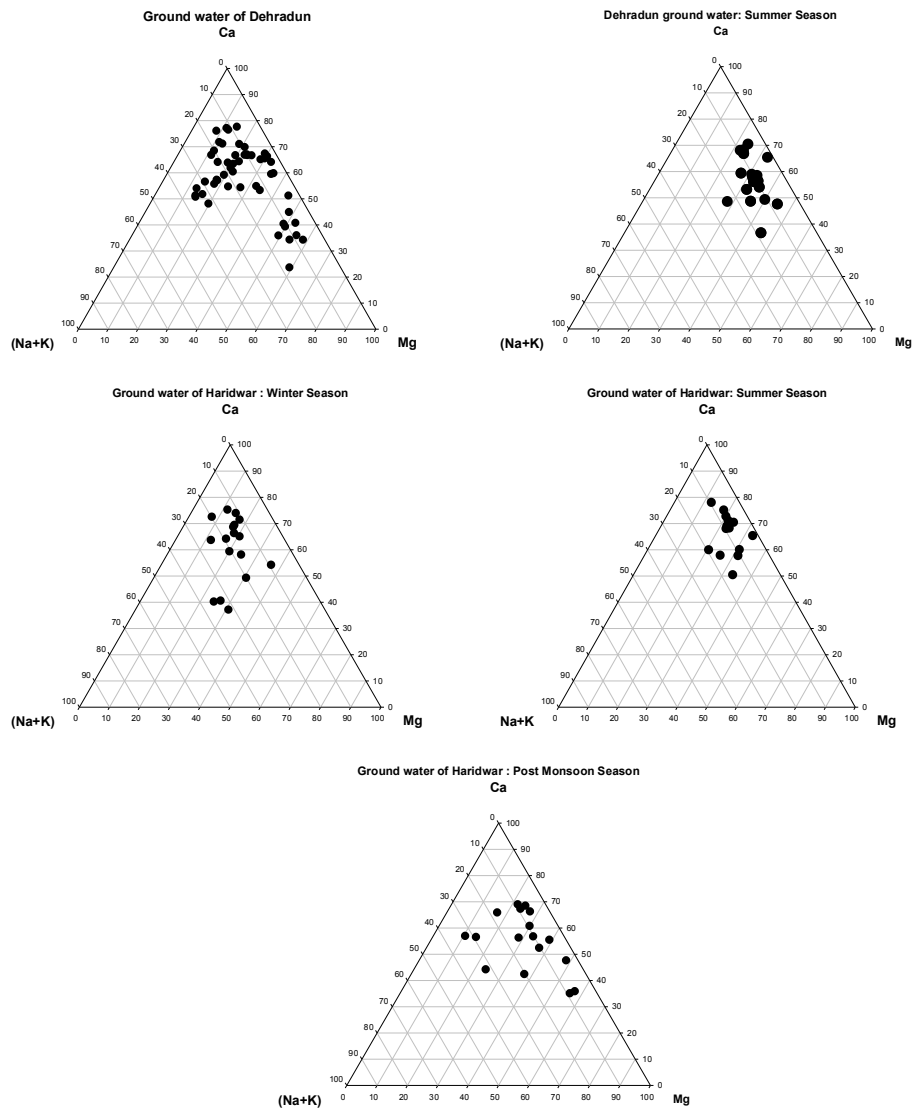
Fig. 6.14: The Ternary cation diagram showing relationship between Ca, Mg and (Na+K) in Dehradun and Haridwar groundwater during winter, summer and post monsoon season.

Dehradun District

Industrial area of Doon

Agricultural area of Doon Ground Water

Urban Area of Doon

Surface Water of Doon- Winter Season

Haridwar District

Induatrial area of Haridwar

Ganga river - Haridwar

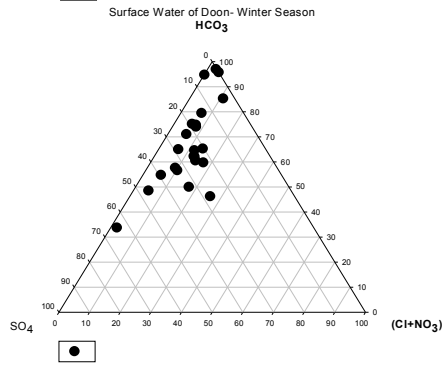Urban area of Haridwar

Gnaga river at Risikesh
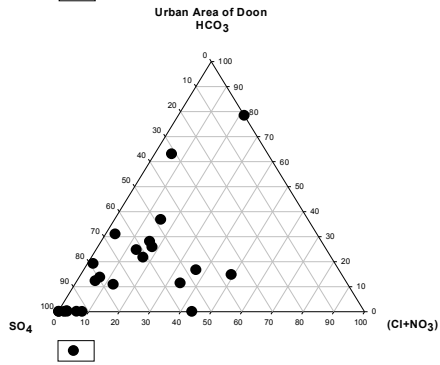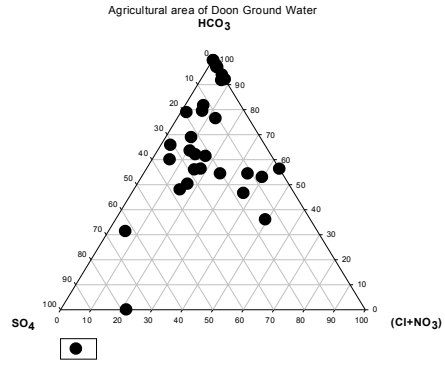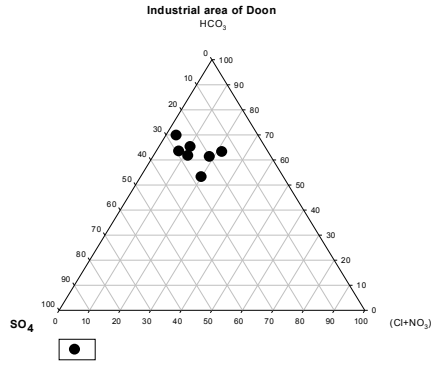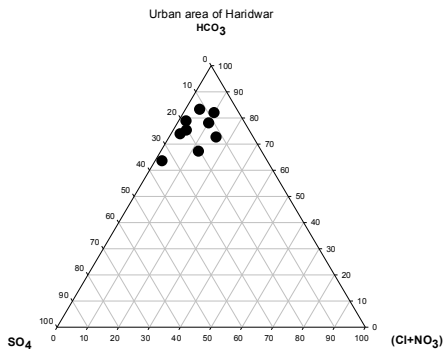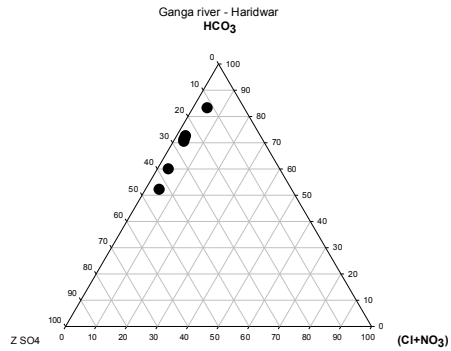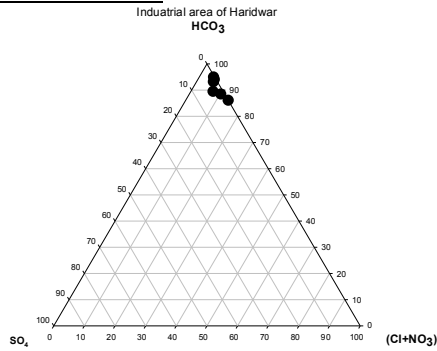
Fig. 6.15: The ternary anion diagram showing the relationship between SO_4, HCO_3 and $(Cl + NO_3)$ (µeq/l) winter Season of Dehradun and Haridwar district.

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Dehradun District

Industrial area of Doon(SS)

Agricultural area of Doon-SS

Urban area of Doon

Surface water of Doon

Haridwar District

Industrial area of Haridwar

Agricultural area of Haridwar

Urban area of Haridwar

Ganga river at Haridwar

Fig. 6.16: The ternary diagram show relationship between HCO_3, SO_4, (Cl +NO_3) in summer season of Dehradun and Haridwar district.

Dehradun District

Industrial area of Dehradun : P
HCO₃

SO₄   Cl+NO₃+F

Agricultural area of Dehradun: P
HCO₃

SO₄   Cl+NO₃+SO₄

Urban area of Dehradun
HCO₃

SO₄   Cl+NO₃+F

Surface water of Dehradun
HCO₃

SO₄   Cl+NO₃+F

Col 2 vs Col 3 vs Col 4

Haridwar District

Industrial area of Haridwar
HCO₃

SO₄   Cl+NO₃+F

Agricultural area of Haridwar
HCO₃

SO₄   Cl+NO₃+F

Urban water of Haridwar distrcit
HCO₃
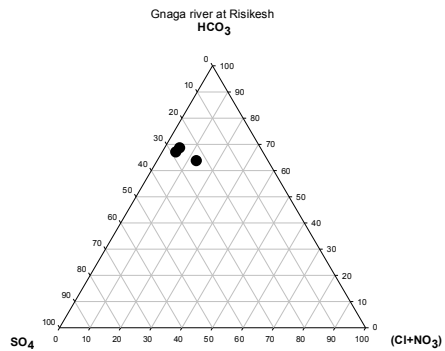

SO₄   (Cl+NO₃+F)

Ganga river at Haridwar
HCO₃
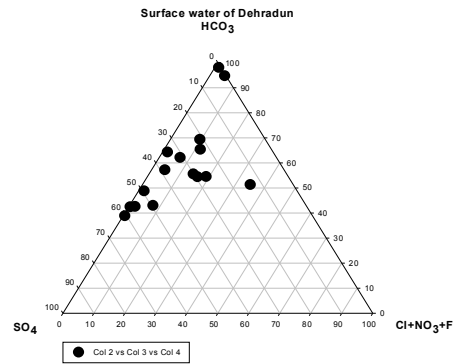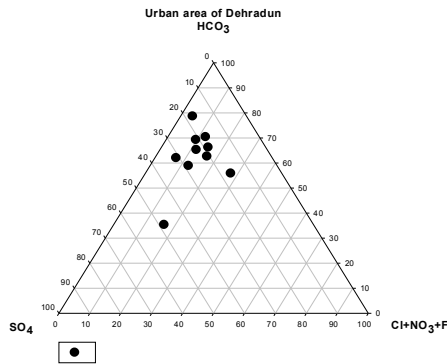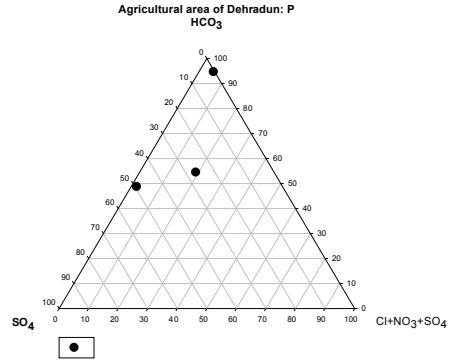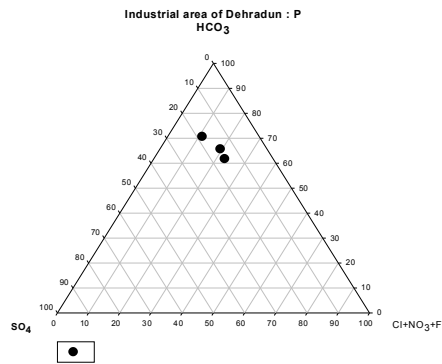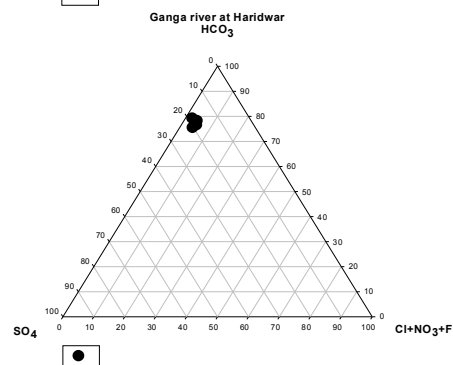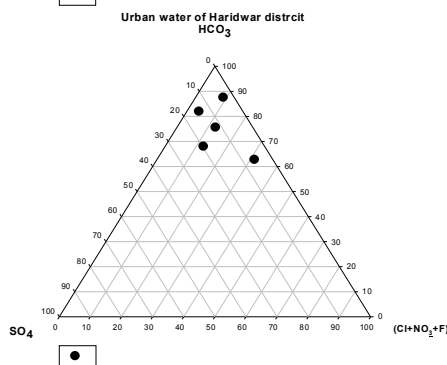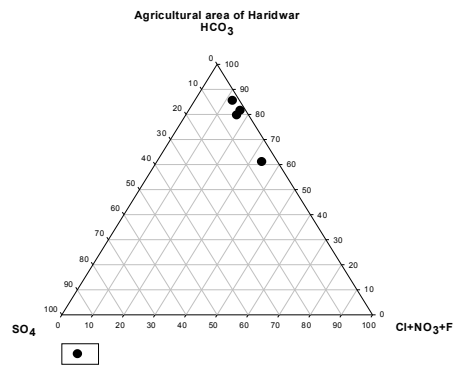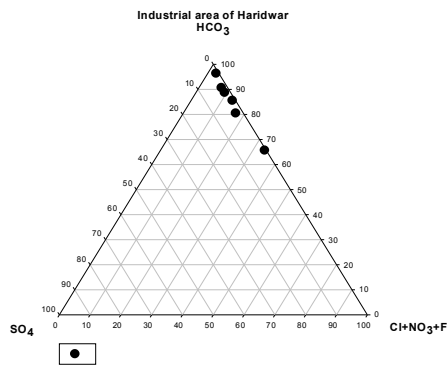
SO₄   Cl+NO₃+F

Fig. 6.17: The ternary diagram show relationship between HCO₃, SO₄, (Cl +NO₃) in postmonsoon season of Dehradun and Haridwar district.

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Dehradun District

Ternary Plot of Industrial area of Dehraun ground water

Ternary Plot of Dehradun Agricultural area of ground water

Surface water of Dehradun

Ternary Plot of Dehradun urban ground water

Haridwar District

Haridwar agricultural area

Ternary Plot of Industrial area of Haridwar

Ganga river at Haridwar

Urban area of Haridwar

Fig. 6.18: Teranary plot showing the relationship between Ca, Mg and (Na+K) in winter season of Dehradun and Haridwar district.

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Dehradun District

Summer Season: Industrial area of Doon

Summer Season: Agricultural area of Doon

Summer Season- Surface Water of Doon

Summer Season : Urban area of Dehradun

Haridwar District

Summer Season : Urban area of Haridwar

Summer Season: Industrial area of Haridwar

Summer Season : Ganga river at Haridwar

Village area of Haridwar

Fig. 6.19: Teranary plot showing the relationship between Ca, Mg and (Na+K) in summer season of Dehradun and Haridwar district.

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Dehradun District

Post Monsoon : Industrial area of Doon

Post Monsoon : Agricultural area of Doon

Post Monsoon: Surface Water of Doon

Post Monsoon : Industrial area of Haridwar

Haridwar District

Post Monsoon : Village area of Haridwar

Post Monsoon Urban area of Haridwar

Post Monsoon : Surface Water of Haridwar

Industrial area of Haridwar

Col 2 vs Col 3 vs Col 4

Fig. 6.20: The ternary diagram showing the relationship between Ca, Mg and (Na+K) in post monsoon of Dehradun and Haridwar district.

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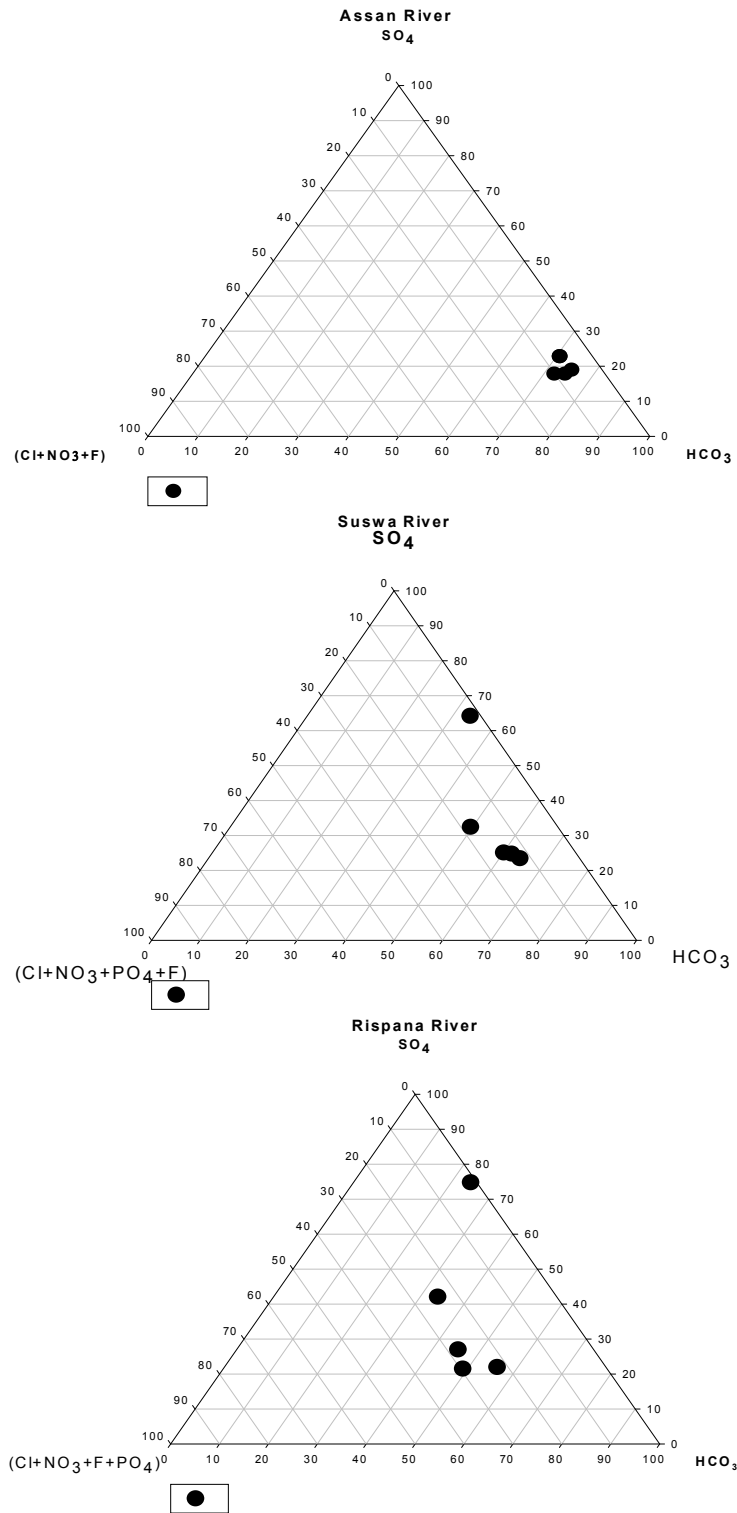
Fig. 6.21: The ternary diagram showing the relationship between SO₄ HCO₃ and (Cl + NO₃ + PO₄) of Assan, Suswa and Rispana river in winter season.
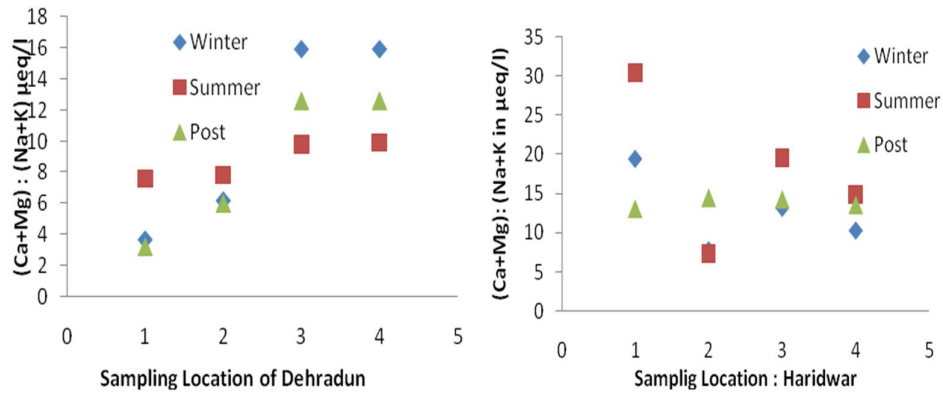
Fig. 6.22: Variation in (Ca+Mg) : (Na+K) equivalent ratio in Dehradun and Haridwar district

Note: Sampling Location 1,2,3 indicate (groundwater) and 4 location indicate surface water.
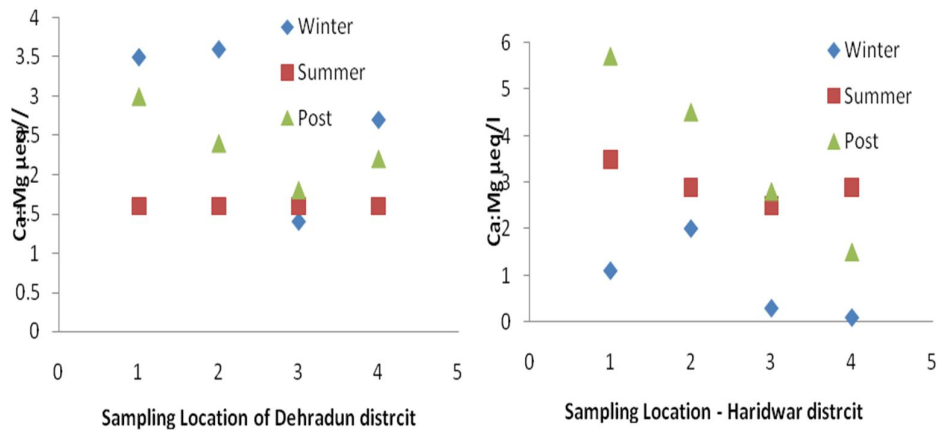
Fig. 6.23: Variation in Ca:Mg equivalent ratio
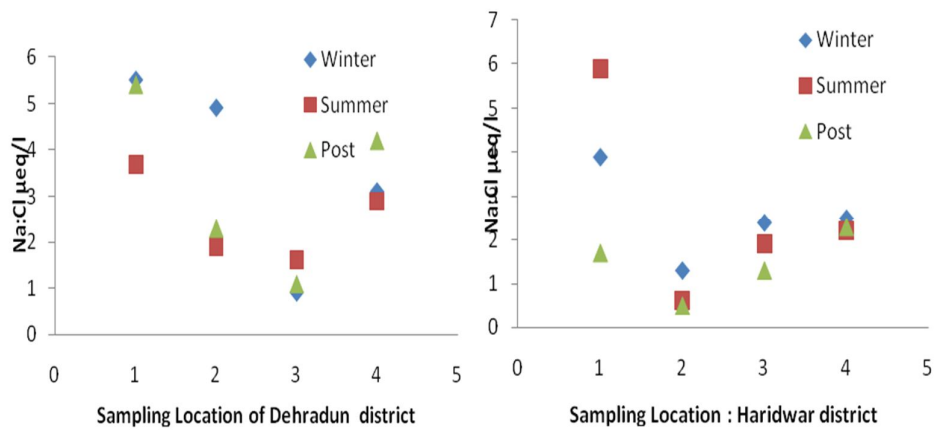
Fig. 6.24: Variation in Na:Cl equivalent ratio

139
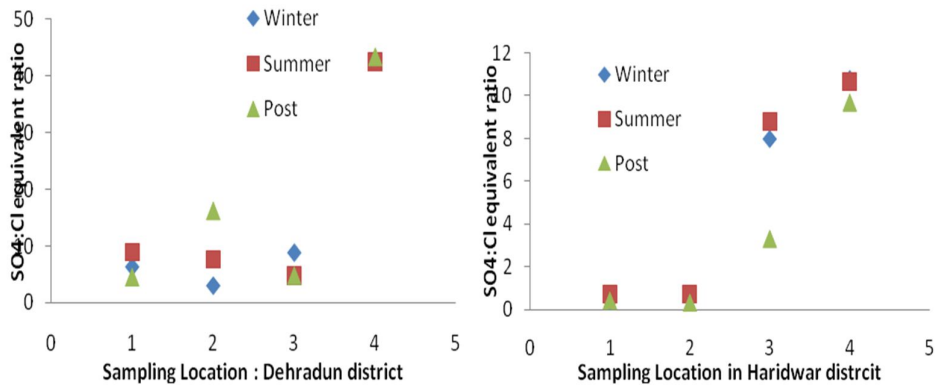
1- Industrial, 2. Agricultural, 3. Urban, 4. Surface water

Fig. 6.25: Variation in SO₄: Cl equivalent ratio
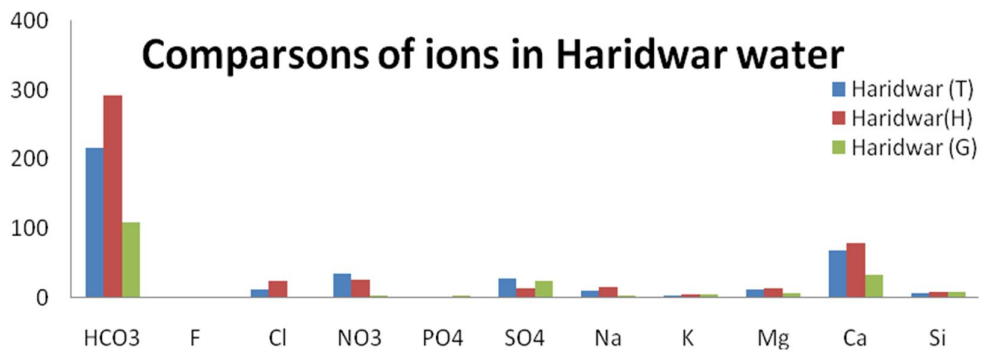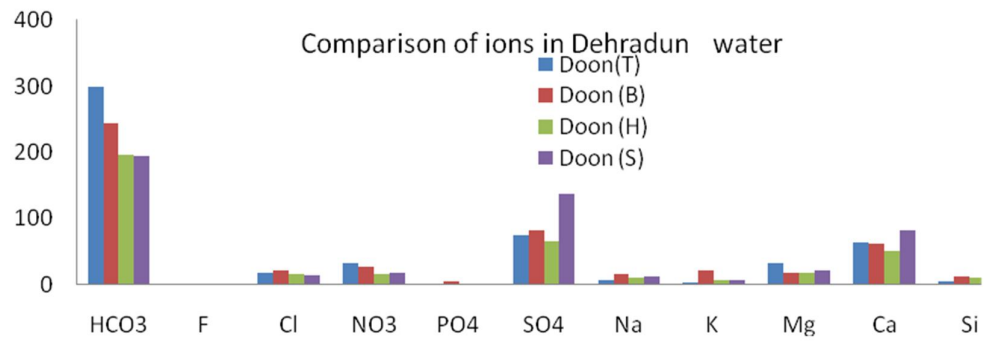
Fig. 6.26: Comparison of various ions in Tubewell(T), Borewells(B), Handpump(H) and Surface water (S) in Dehradun and Haridwar district

T= Tubewell

H= Handpump

B= Borewell

S= Surface Water

G= Ganga river

Spatial variability of water quality:

The spatial distribution of water quality parameter presented in Fig. VI-25.
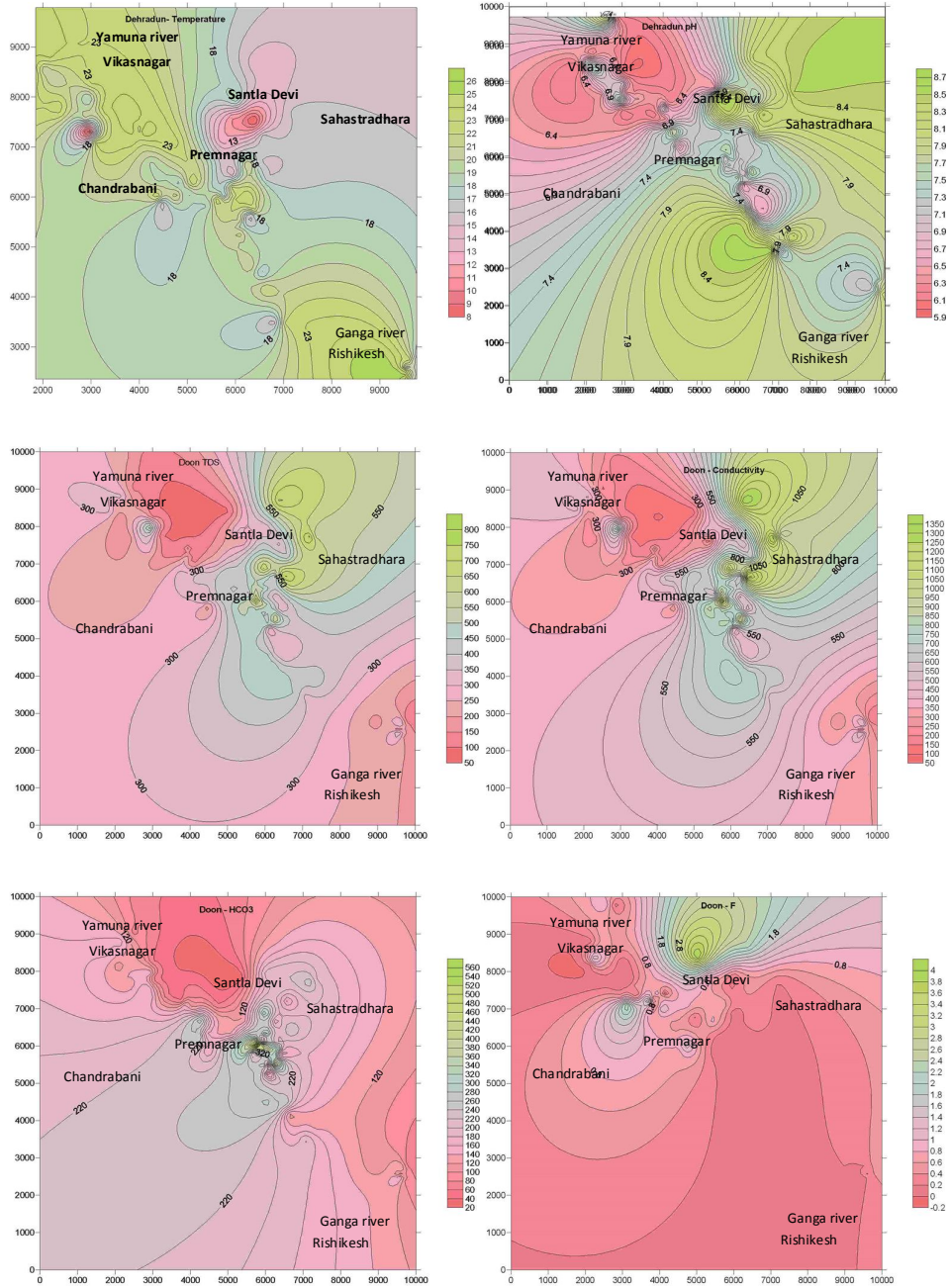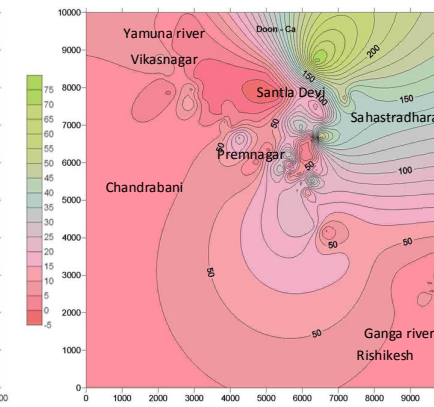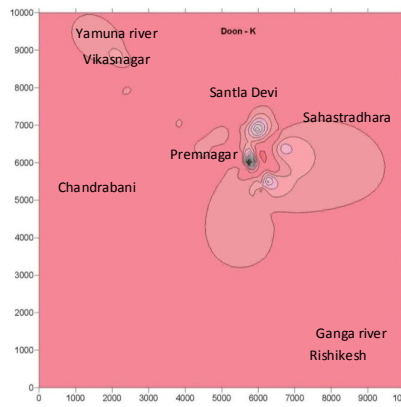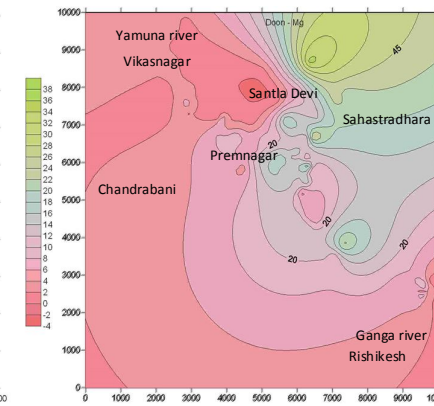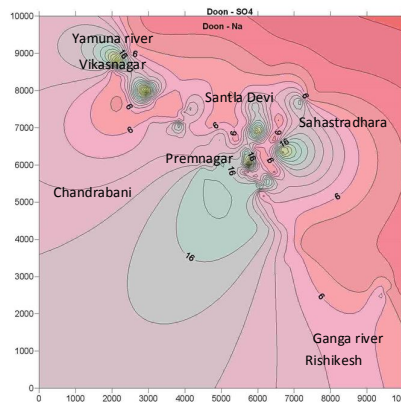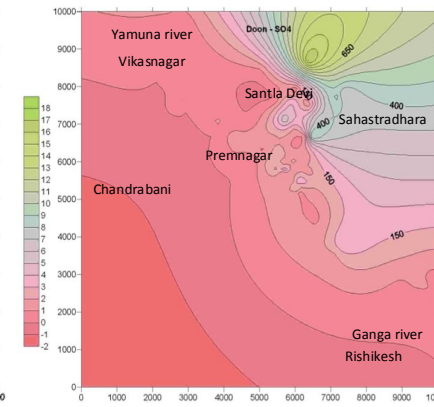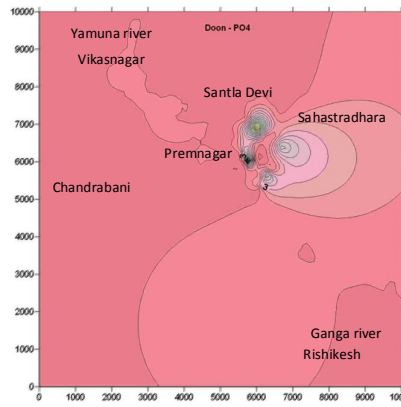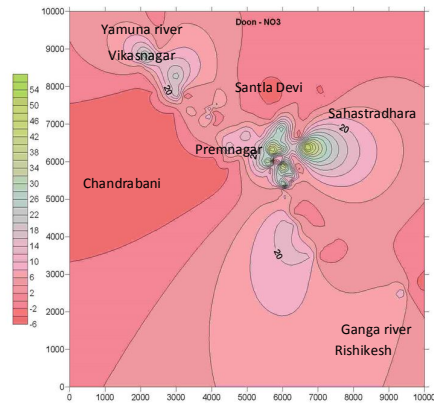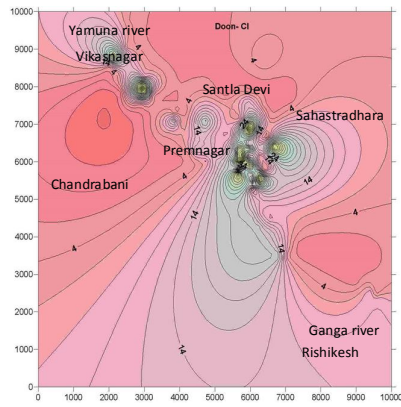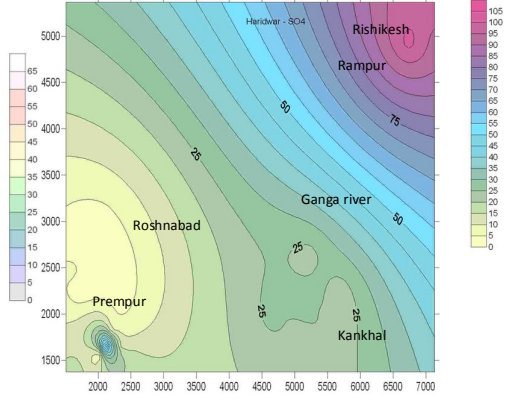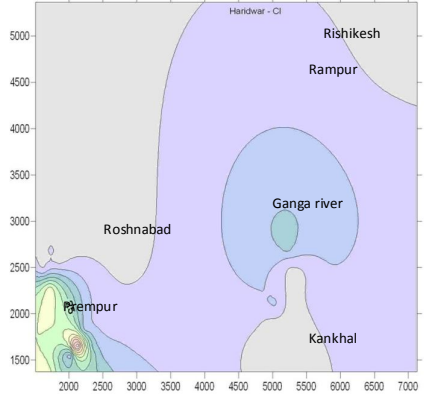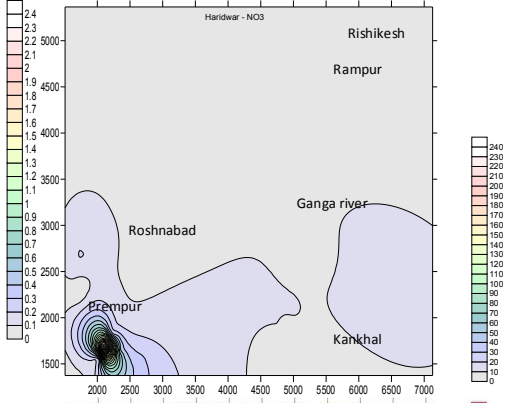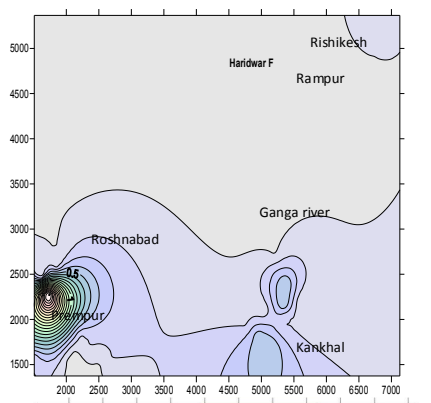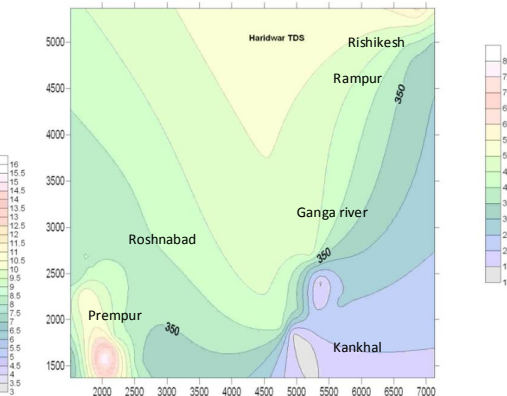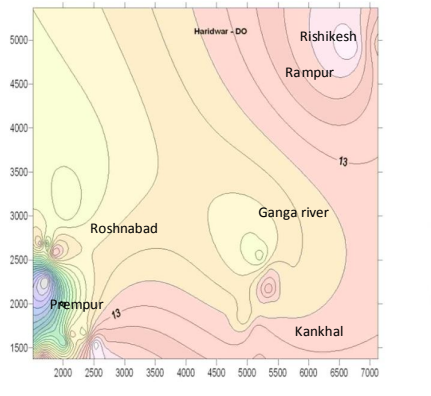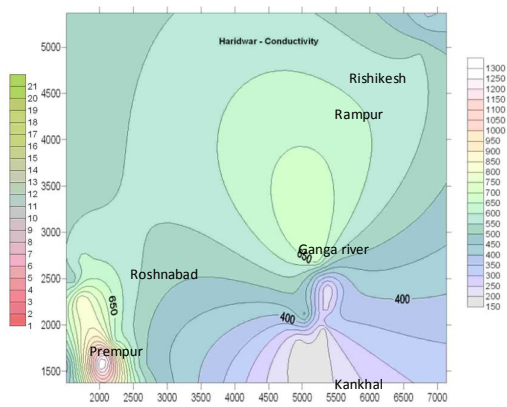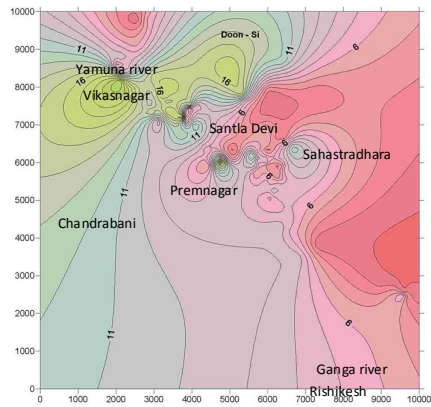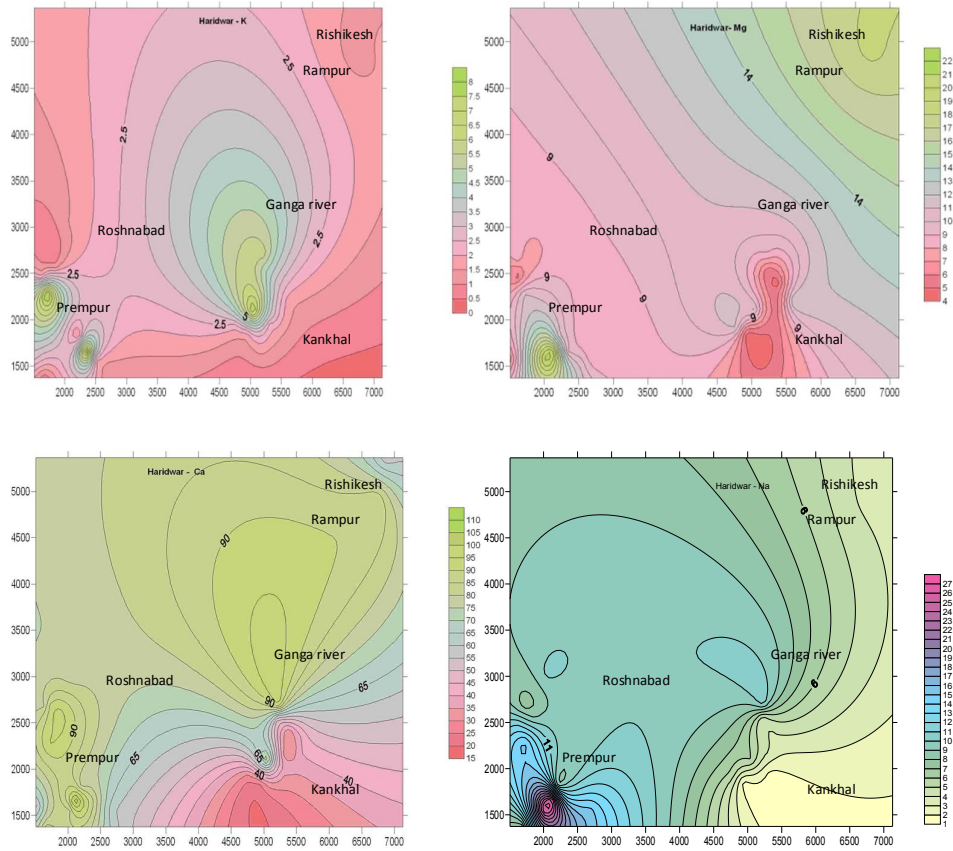
Fig. 6.27: Spatial Variation of Ions in Dehradun and Haridwar district

CHAPTER VII

IMPACT ASSESSMENT OF URBANIZATION AND INDUSTRIALIZATION ON WATER CHEMISTRY OF DEHRADUN AND HARIDWAR DISTRICT

The excess use of water, deforestation, urbanization and industrialization caused depletion and deterioration of groundwater resources. The quality of surface water has deteriorated due to discharge of industrial, sewage and domestic effluents directly into water bodies resulting in eutrophication by adding excess nutrients such as NO_3 and PO_4. The water quality of river has depleted severely at several places along their courses to oceans.

This chapter gives an account of impact of urbanization and industrialization on water chemistry. An attempt has been made to identify the sources of pollutant, if any. A comparison is also made with previous data to assess the temporal change that has taken place.

Deforestation, urbanization and industrialization have adversely affected hydrological regime and environment of the NW –SE trending intermontane Doon Valley in the Sub Himalaya region. The rate of the recharge of natural spring is depleting continuously causing lowering of water table. The quality of water has severely deteriorated township of Rishikesh and at various places of Dehradun, Haridwar district including township of Risikesh, Vikasnager, Selaqui and Roshnabad (Industrial area in Dehradun and Haridwar district respectively).

During the last ten years there has been phenomenal growth of industries in Dehradun and Haridwar districts. Among them Pharmaceutical industry forms a major part of industrial area.

In Haridwar alone (in Roshnabad industrial area) there are about 127 pharmaceutical industries may contribute large amount of waste in water system. Various physical and chemical process in pharmaceutical industries generate large amount of solid and liquid waste. Waste may be generated from floor and equipment washing, leaking of valves / machine, cooling water, laboratory and, faecal waste, acid and alkali waste (from regeneration of Ion-exchanger, floor and equipment washing, microbial suspension, Antitoxin, preparation include animal tissue, leather, blood, fats, fluid and shell, biological culture media, solvent, salt and antiseptic agent. Acidic and alkaline effluent contain mineral acid HCl, H_2SO_4, organic acid like acetic and formic acid. Some pharmaceutical effluent contain toxic waste – antic septic, germicidal agent and organic solvent like phenol, cresol and benzene etc. Total textile industries in Roshnabad - BHEL industrial area of Haridwar district are about 15. The industrial effluent discharge form textile industries may have high pH, BOD and COD. There are about 43 industries which synthesis rubber and plastic. Effluent contain high amount of BOD, COD, high acidity, alkalinity, TDS and high level of chloride and sulphate.

There are about 11 tanneries industry in Roshnabad - BHEL industrial area. The waste water generated from the tanneries industries are highly alkaline, containing BOD and COD. If untreated waste discharge into ground it may affect physical, chemical and biological characteristics of water and deplete DO from water. There are about 6 food processing and 10 Iron and steel industries in Haridwar area. The solid waste generated from the steel industries, if not properly disposed, may contribute certain toxic compound in the environment e.g hydrocarbon residue, soluble salt, sulphur compound and heavy metals. Similarly industrial area of Selaqui in Dehradun district have several pharmaceutical (31 No.), textile and rubber industries.

7.1 SEASONAL (TEMPORAL) VARIABILITY OF PHYSICAL PARAMETER, MAJOR IONS, AND HEAVY METALS

Seasonal or Temporal variation trend

The seasonal variation in water quality parameters was assessed by examining variations in summer season (May), post monsoon (September - October) and

winter season (December to January). The parameters include temperature, conductivity, TDS, and DO, anions and cations and heavy metals (Cd, Al, Cu, Pb, Hg). The min. max and mean value of these parameters (Table 7.1, 7.2) were examined in surface and groundwater of industrial, agricultural and urban areas of Dehradun and Haridwar districts with respect to mean value pristine or undisturbed areas to assess the impact of urbanization and industrialization on water quality.

7.1.1 Temperature

The temperature in waters of entire study area in winter season ranges from 6.4^0C to 29.6^0C with an average of 21^0C, during summer season it varies from 19^0C to 29^0C with a mean value of 25^0C and in post monsoon season it varies 8^0C to 34^0C with mean value of 26^0C.

The average temperature in industrial area of groundwater of Dehradun district is 24^0C in winter season, 26^0C in summer and post monsoon season. In groundwater of agricultural area of Dehradun, the average temperature is 24^0C, 26^oC and 22^0C in winter, summer and post monsoon season respectively. In urban area of groundwater of Dehradun the mean temperature is 20^0C, 24^0C and 26^0C respectively in winter, summer and post monsoon season. In surface water of Doon valley, the temperature varies from 7^0C to 29^0C in all the season with an average of 24^0C during summer monsoon, 26^0C during post monsoon and 18^0C during winter season (Fig. 7.1).

In groundwater of industrial area of Haridwar district, the average temperature is 26^0C, 28^0C and 28^0C during winter, summer and post monsoon season. In groundwater of agricultural area of Haridwar the average temperature is 27^0C in summer and post monsoon season and 24^0C in summer season. In urban area of Haridwar groundwater, the average temperature during winter, summer and post monsoon season is of 23^0C, 21^0C and 24^0C and does not show much variation. The average temperature in the Ganga river at Haridwar does not show much variation and varies from 23^0C to 24^0C in the three season. The temperature of Ganga water at Risikesh varies from 18^0C to 29^0C in winter and post monsoon season (Fig. 7.1).
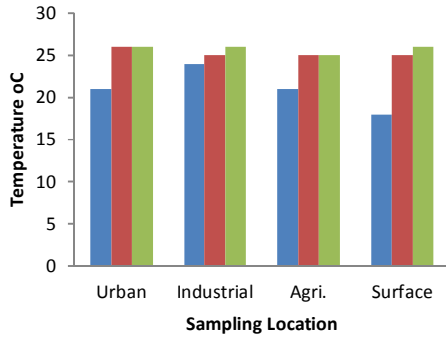
a) Temp. in different land use categories in Dehradun district
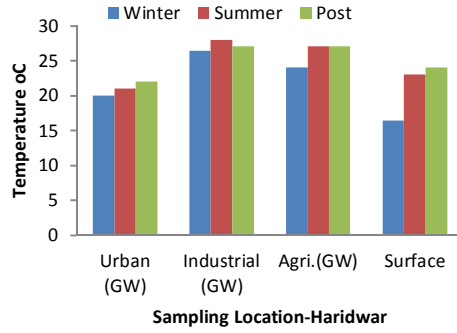
b) Temp. in different land use categories in Haridwar district
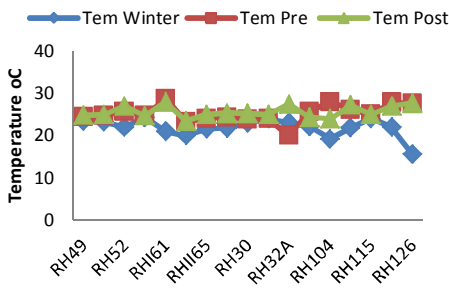
c) Groundwater of Dehradun
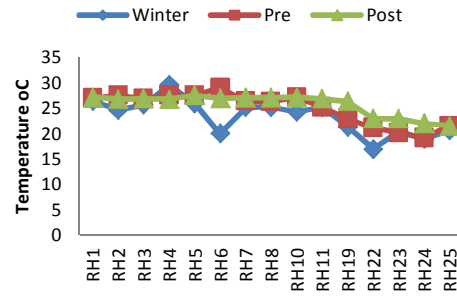
d) Groundwater of Haridwar
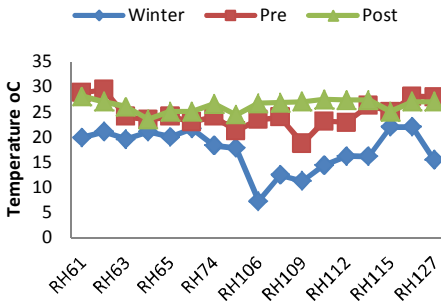
e) Surface water of Dehradun
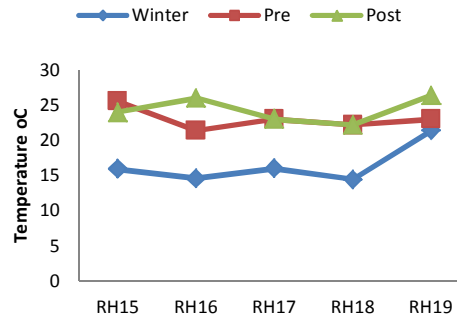
f) Surface water of Haridwar

Fig. 7.1: Variation in temperature of surface water and groundwater of Dehradun and Haridwar District

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7.1.2 pH

The pH in study area varies from 6 to 9 with an average of 7.2 in winter season, from 4 to 9 with an average of 7 in summer and during post monsoon season it vary from 6 to 9 with an average of 7.4.

The average pH of groundwater in industrial area of Dehradun district does not show much variation and remains at 6.7, 6.4 and 7.2 respectively in summer, post monsoon and winter season except that of Selaqui industrial area where groundwater becomes slightly acidic in post monsoon possibly due to leaching of acids from soil into ground water. Similar variation were observed in agricultural area (Fig 7.2). In urban area pH tend to be alkaline in nature with an average pH remains at 7.6 and 8 during summer and post monsoon season and does not show much changes in winter season possibly due to higher dissolution of carbonate rocks during post monsoon season (Fig. 7.1c, 7.1e).

The average pH of groundwater in industrial area of Haridwar is slightly acidic in nature during post monsoon season. However in certain locations such as at Selaqui industrial area and Bhuddi Chowk (RH49, RH51 and RH45). In Dehradun pH of 4.4 indicates leaching of acids from soil or sub surface to groundwater.
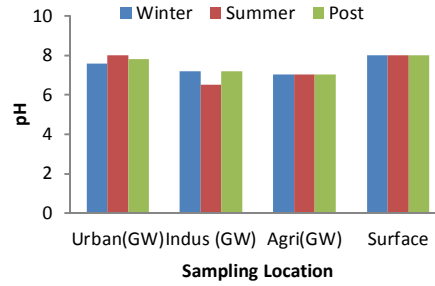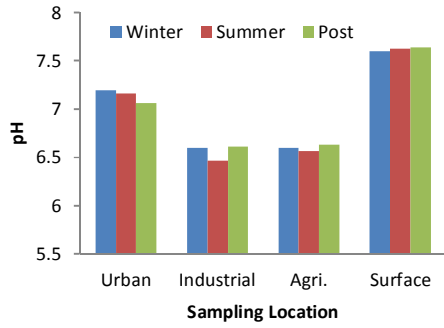
a) pH in different land use
   categories in Dehradun district

b) pH in different land use
   categories in Haridwar district
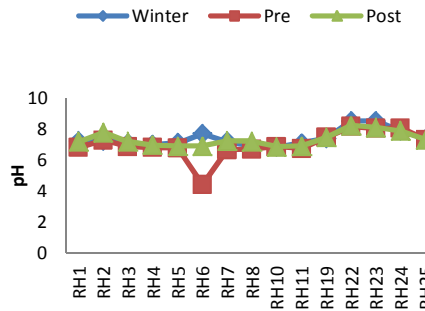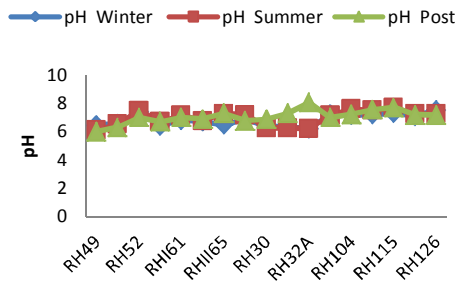
c) Groundwater of Dehradun

d) Groundwater of Haridwar
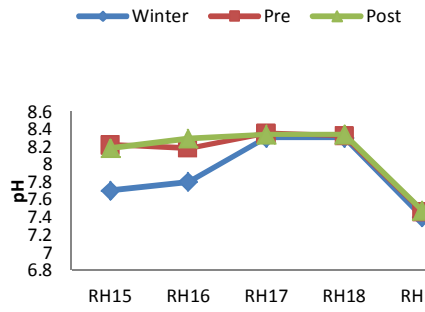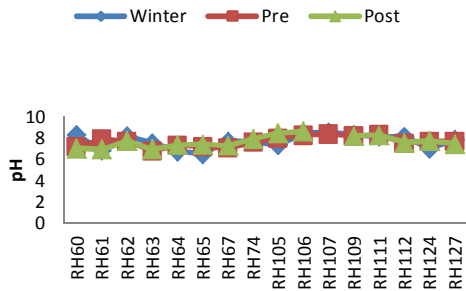
e) Surface water of Dehradun

f) Surface water of Haridwar

Fig: 7.2: Variation in pH of surface water and groundwater of Dehradun and Haridwar District

7.1.3 Total Dissolved Solid and Electric Conductivity

The seasonal variation in TDS and EC shows that the ionic concentration is maximum in winter and minimum in post monsoon season in surface and groundwater of Dehradun and Haridwar district. The dilution of water due to recharge during monsoon season possibly lower the ionic concentration while evaporation during summer and winter season and enhanced rock water interaction increases ionic concentration which in turn increases TDS and EC concentration in winter season in comparison to summer and post monsoon season.

The high ionic concentration in summer as compared to post monsoon period reflecting the concentration effect due to elevated temperature and increased evaporation during the low water level period of the summer season.

The highest concentration of TDS is found in winter season which varies from 91 mg/l to 796 mg/l with an average of 353 mg/l. The lowest TDS are found in post monsoon season and varies from 75 mg/l to 651 mg/l with an average of 276mg/l while moderate concentration of TDS is found in summer season which varies from 74mg/l to 881mg/l with an average concentration of 276mg/l.

The average EC in surface water of Dehradun district is 662µs/cm in winter season, 816 µs/cm in summer season and 679µs/cm in post monsoon season.

The average electric conductivity which also reflect TDS in surface and groundwater varies from 533 µs/cm in winter season, 545 µs/cm in summer season and 469 µs/cm in post monsoon season. The groundwater of industrial area of Dehradun district shows high EC (222µs/cm) in winter season and low EC (169 µs/cm) in summer season and moderate EC of 180µs/cm in post monsoon season. In groundwater of agriculture area, the average EC in summer season increases to 442 µs/cm as compared to 220µs/cm in post monsoon season. However in groundwater of urban area, the average EC remain high 694 µs/cm in winter season as compared to 359 µs/cm and 566

μs/cm in summer and post monsoon season respectively. In Haridwar district, the groundwater of Roshnabad industrial area shows average EC of 624μs/cm, 633μs/cm and 601μs/cm respectively in winter, summer and post monsoon season and does not shows much seasonal variation. However in agricultural area the EC show significant seasonal variation in winter (758μs/cm), summer (1251μs/cm) and post monsoon season (642μs/cm) (Fig 7.3).

Table 7.1: Max, minimum and mean value of ions in urban, agricultural, urban area and surface water of Dehradun district

Parameter	Industrial area			Agricultural area			Urban area			Surface water		
	Max	Min	Average	Max	Min	Average	Max	Min	Average	Max	Min	Average
Tem	25.1	22	23.8	24.3	6.3	21	24	14	21	23	7.2	18
pH	7.3	6.2	6.6	7.6	6	6.6	7.5	6.9	7.2	8.7	6.2	7.6
TDS	219	114	149	761	99	275	626	293	436	787	91	420
DO	6.5	4	5.0	7.5	0.5	3.9	15	0.3	4.9	14	0.4	7.3
HCO$_3$	116	61	78	567	58	149	439	122	253	366	21	195
F	1	0.001	0.5	2.5	0.05	0.42	0.9	0.02	0.15	4	0.06	0.46
Cl	8.2	1.7	3.6	57.8	0.2	12.9	47	3.8	17.22	55	0.02	14
NO$_3$	21	0.2	12	41	0.1	11	75	2.5	26	84	0.002	17
PO$_4$	Nd	Nd	Nd	18	0.002	Nd	75	2.5	26	84	0.002	1.3
SO$_4$	31	13	24	193	0.002	37	218	35	91	861	0.002	137
Na	13	6	9.4	40	2.4	11	20	3	7.4	30	2	11
K	4.4	0.9	2	74	0.1	6	27	1	4	37	0.8	6.3
Mg	12	3	5	26	2	9.3	41.4	15	24	62	0.5	21
Ca	32	18	25	105	16	42	145	23	54	267	4	82
Si	9.1	5	7	21	5.4	11.3	9.5	3	6	17	2.2	7
Hardness	124	58	79	359	50	138	471	124	229	895	11	283

Table 7.2: Max, minimum and mean value of ions in urban, agricultural, urban area and surface water of Haridwar district

Parameter	Industrial area			Agricultural area			Urban area			Surface water		
	Max	Min	Average	Max	Min	Average	Max	Min	Average	Max	Min	Average
Tem	29.6	24.7	26.5	26	18.3	24.5	21.4	17	20.7	21.4	14.4	16.5
pH	7.7	7	7.23	7.44	6.85	7.0	8.54	7.2	7.6	8.3	7.4	7.9
TDS	555	346	408.3	796	288	481	470	236	318	280	129	169
DO	14.1	2.6	7.48	16	4.5	10	15.4	6	9.5	14.1	11.4	12.9
HCO$_3$	412	256	308	463	170	283	315	104	177	190	79	109
F	2.5	0.08	0.53	0.24	0.1	0.17	0.3	0.1	0.16	0.5	0.3	0.45
Cl	39	1.6	9.68	70.4	10.4	268	17.3	1.2	6.4	5.74	1.2	2.29
NO$_3$	23	0.002	12	263	7.7	56.7	16	1	6.7	1.9	1	1.5
PO$_4$	4.8	0.001	0.8	3	0.002	0.4	0.02	0.001	0.002	Nd	Nd	Nd
SO$_4$	7.3	0.01	2.6	66.4	5.8	20.4	102	20	33	28	21.5	24.2
Na	15.3	7.5	10.3	26.6	7.2	15.5	10.6	1.8	5.1	4	1.63	3
K	8.4	0.6	2.37	8.2	0.6	2.7	7.71	1.2	3.4	4.6	1.8	3.08
Mg	11.2	5.4	8.15	21.4	6.4	13	18.4	5.2	9.5	5.4	4.2	4.76
Ca	98	76	88	111	58	80	98	28	54	48	25	32
Si	9.83	4.62	7.25	9.7	3.72	6.7	3.72	7.19	6.7	8.2	4.4	6.66
Hardness	274	215	245	354	165	243	165	254	168	137	76.7	95.7
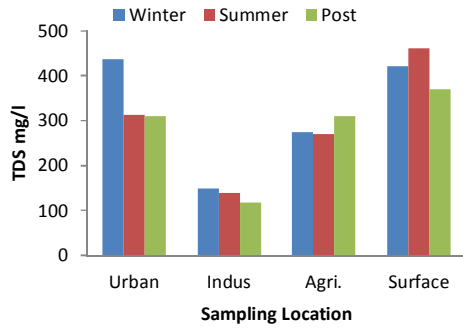
a) Dehradun district
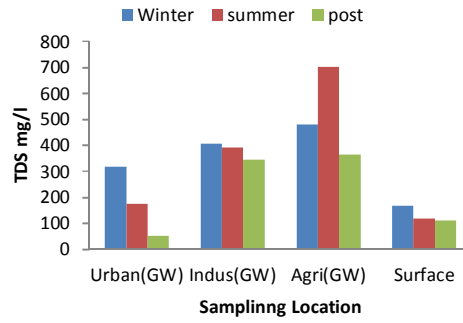
b) Haridwar district
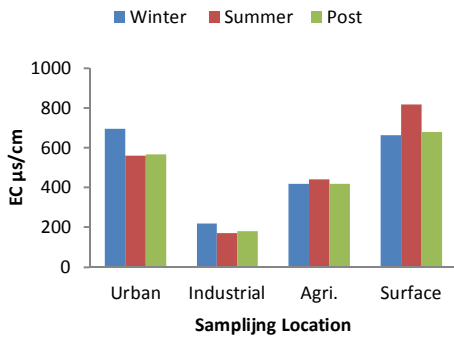
c) Dehradun district
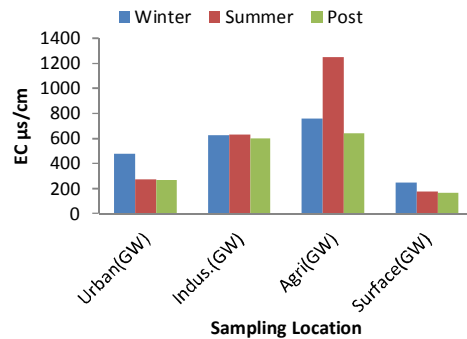
d) Haridwar district
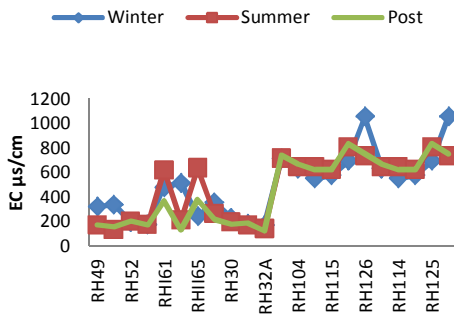
e) Groundwater of Dehradun
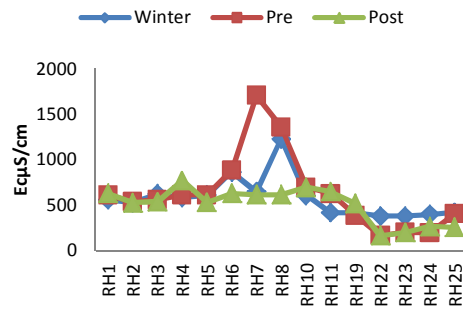
f) Groundwater Haridwar
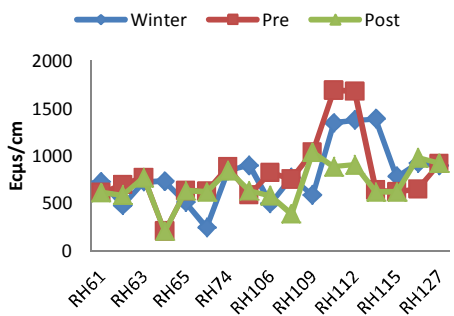
g) Surface water of Dehradun

h) Surface water of Haridwar

Fig. 7.3: Variation in TDS and EC of Surface and Groundwater of Dehradun and Haridwar District

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7.1.4 Dissolve Oxygen (DO)

The dissolve oxygen in surface and groundwater of Dehradun district range between 0.3 mg/l and 14 mg/l in all three season viz winter, summer and post monsoon season. In surface water of Dehradun the DO concentrations varies from 2.7 mg/l to 14 mg/l in all three season with mean value an average of 6.5 mg/l during summer, 5.9mg/l during post monsoon and 7mg/l during winter season.

The average DO in groundwater of industrial area of Dehradun district is 4.2mg/l, 3.6mg/l, and 5 mg/l respectively in summer, post monsoon and winter season

Table 7.3: Average DO concentration in surface and groundwater of Dehradun and Haridwar district

DO	Summer Season		Post Monsoon		Winter season	
	Dehradun	Haridwar	Dehradun	Haridwar	Dehradun	Haridwar
Industrial Area	4.2	3.9	3.6	6	5	7.4
Urban Area	5	5.1	6.3	7.5	4.9	9.5
Agricultural Area	4.4	5.9	4.8	5.5	3.9	9.9
Surface Water Area	6.5	5.6	5.8	5.3	7.3	5.6

In groundwater of industrial area of Dehradun the DO concentration was varies from 3.5 mg/l to 6.5 in summer, winter and post monsoon season. In groundwater of agricultural area average DO is found almost same in summer and post monsoon season with a mean value of 4.4 mg/l and 4.8mg/l and during winter it decreased to 3.9mg/l. The DO concentration in groundwater of urban area of Dehradun is 5mg/l in winter and summer season and 6mg/l in post monsoon season (Fig. 7.4).

The mean concentration of DO in surface water (Ganga river) of Haridwar area varies from 5.3 mg/l in summer season, 6mg/l in post monsoon season

and 13 mg/l in winter season, but its concentration is slightly less in surface (Ganga water) and groundwater of Risikesh area. In groundwater of industrial area of Haridwar district the DO varies from 2.3 mg/l to 14 mg/l in all three season with an average of 7.4mg/l, 3.9 mg/l and 6 mg/l respectively in winter, summer and post monsoon season. In agricultural area of Haridwar, the average DO varies from 6mg/l in summer, 7.3mg/l in post monsoon and 10.6mg/l winter season. Similarly in urban area the DO range from 3.1mg/l in summer season, 7.3mg/l in post monsoon and 10.7mg/l in winter season.

The above data shows that the surface water has higher concentration of DO in comparison to ground water in the study area and higher values in winter and lower values in summer. The oxygen content result from oxygen usage and supply. The oxidation of organic matter and of reduced inorganic substance lead to lower oxygen content in groundwater. High content of oxygen in the infiltration water and the supply from the ground air enrich the groundwater oxygen (Mathers, 1994). In Dehradun and Haridwar districts most of the groundwater recharge take place in monsoon and partly during winter season and since solubility of oxygen is temperature sensitive, being lower in warm water than cold water, relatively high content of DO are observed in winter season than in summer season.

a) Dehradun district   b) Haridwar district
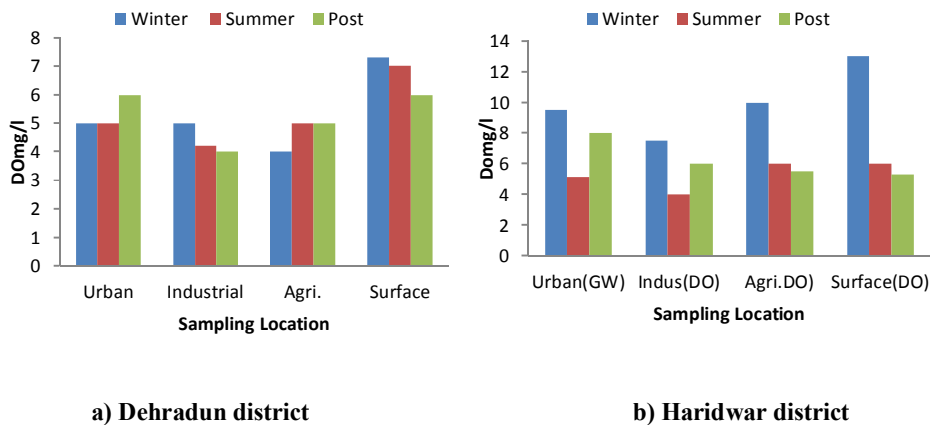
Fig. 7.4: Variation in DO of Surface and Groundwater of Dehradun and Haridwar District

7.1.5 Bicarbonate

The overall bicarbonate concentration, which is also a measure of total alkalinity as carbonates are absent in waters of the study area, varies from 21mg/l to 708mg/l with mean concentration of 259mg/l. Seasonally its average concentration varies from 231mg/l in summer season, 171 mg/l in post monsoon season and 259mg/l in winter season.

In groundwater of industrial area of Dehradun district (Selaqui) the average HCO_3 concentration varies from 78 mg/l in winter, 116 mg/l in summer and in 81 mg/l post monsoon season. In agricultural area of Dehradun district, the average bicarbonate concentration in ground water is 148mg/l, 213 mg/l, 115mg/l respectively in winter, summer and post monsoon season. The average bicarbonate concentration in groundwater of urban area of Dehradun district varies from 253 mg/l in winter, 238 mg/l during summer and 169 mg/l during post monsoon season. In surface water of Dehradun, the average concentration of HCO_3 is 195 mg/l in winter, 277mg/l in and 204 mg/l in post monsoon season (Fig. 7.5a).

In Haridwar district, the HCO_3 concentration in groundwater of industrial area varies from 307mg/l during winter, 359mg/l in summer and 267mg/l in post monsoon season. In groundwater of agricultural area, the average HCO_3 concentration is 283 mg/l in winter, 307 mg/l in summer and 268 mg/l in post monsoon season. However, in groundwater of urban area the average HCO_3 concentration varies from 178 mg/l in winter, 179 mg/l in summer and 124mg/l in post monsoon season (Fig. 7.5b).

The concentration of HCO_3 in surface water of Haridwar which is mainly represented by Ganga river varies from 108mg/l in winter, 121mg/l in summer and 97 mg/l in post monsoon season.

The average HCO_3 concentration in groundwater of Risikesh area varies from 150 mg/l in winter season, 326 mg/l in summer and 143 mg/l in post monsoon season. The HCO_3 concentration in Ganga river at Rishikesh during pre

monsoon was 136 mg/l which reduces to109 mg/l in winter season and 89 mg/l in post monsoon season.

Seasonal variation in river water composition due to chemical weathering has been documented by Raymond and Cole (2003) for Mississipi river, Stallard and Edmond (1981) for Amazon river and by Subramanian (2000) for several rivers in the Indian subcontinent. The weathering of silicate rocks and its product such as clay are the main causes of alkalinity variation in river water and the process of weathering depend upon temperature, precipitation and human activities (Subramanian, 2006).
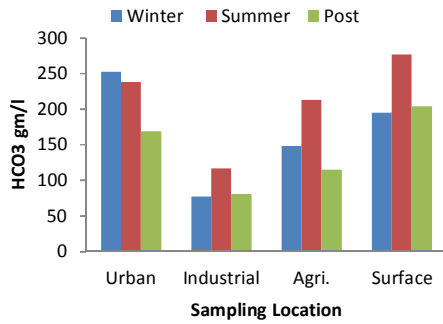
a) HCO₃ in different land use categories in Dehradun district
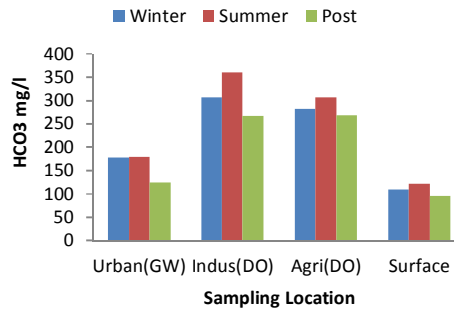
b) HCO₃ in different land use categories in Haridwar district
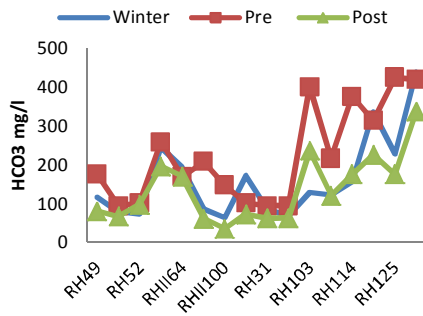
c) Groundwater of Dehradun
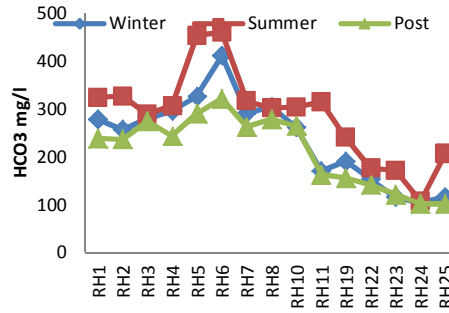
d) Groundwater of Haridwar
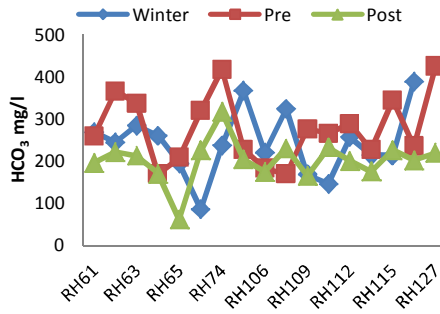
e) Surface water of Dehradun

f) Surface water of Haridwar

Fig. 7.5: Variation in bicarbonate concentration in Surface and Groundwater of Dehradun and Haridwar District

7.1.6 Flouride

The Fluoride concentration in study area during winter season ranges from 0.1 mg/l to 4.1mg/l with an average of 0.4 mg/l, during summer season it varies from 0.03 mg/l to 11 mg/l with an average of 0.344 mg/l and in post monsoon season it varies from 0.004 mg/l to 6.8 mg/l with an average of 0.347 mg/l.

In groundwater of industrial area of Dehradun the average fluoride concentration varies from 0.12 mg/l in summer and post monsoon season to 0.53mg/l in winter season. In groundwater of agricultural area the mean fluoride concentration is 0.38mg/l, 1.33 mg/l and 0.32mg/l respectively in winter, summer and post monsoon season. In ground water of urban area of Dehradun the average fluoride concentration varies from 0.1mg/l in summer, 0.8mg/l in post monsoon and 0.3 mg/l in winter season. In surface water of Dehradun the average fluoride concentration is 0.32 mg/l, 0.14mg/l and 0.2mg/l respectively in winter, summer and post monsoon season (Fig 7.6a).

In Haridwar district the flouride concentration found to be maximum 0.5 mg/l in winter season, minimum 0.2 mg/l during post monsoon in groundwater of industrial area . However at one location (RH6) in down slope of industrial area fluoride (2.4mg/l) was found in excess of BIS and WHO permissible limit. This may be because of direct discharge of industrial effluent in soil. In groundwater of agricultural area of Haridwar the average F concentration is 0.11mg/l in all three season. In groundwater of urban area of Haridwar district the average fluoride concentration varies from 0.2mg/l in post monsoon, 0.34mg/l in summer and 0.14 mg/l in winter season (Fig. 7.6b).

In Surface water of Ganga river at Haridwar district, the fluoride concentration found to be maximum 0.4mg/l in winter season, minimum 0.1mg/l in post monsoon season and moderate 0.3 mg/l in summer season (Fig. 7.6f) and almost similar pattern of fluoride concentration.
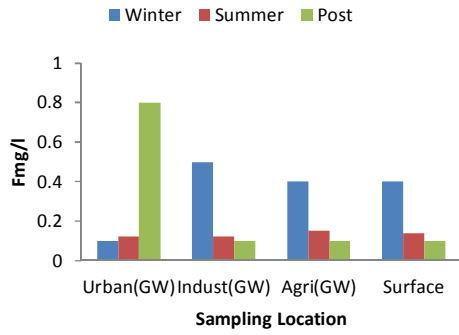
a) F in different land use categories
in Dehradun district
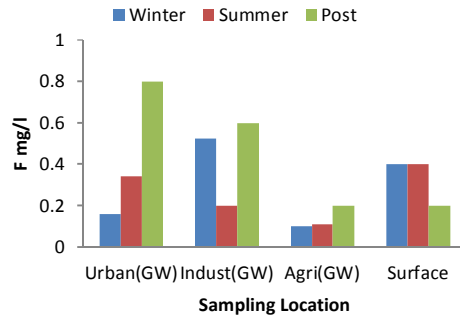
b) F in different land use categories
in Haridwar district
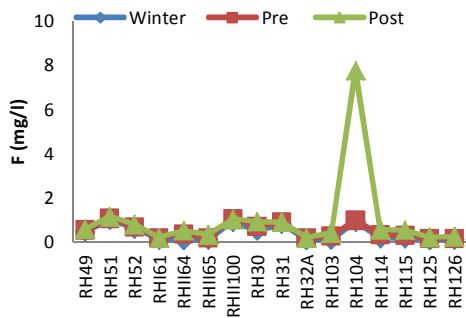
c) Groundwater of Dehradun
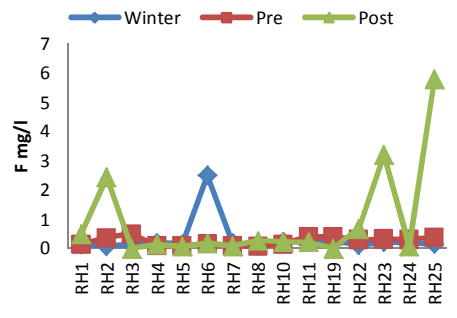
d) Groundwater of Haridwar
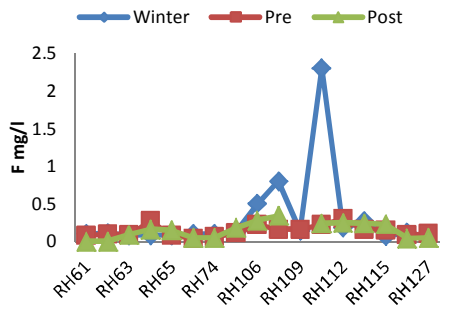
e) Surface water of Dehradun

f) Surface water of Haridwar

Fig. 7.6: Variation in fluoride concentration Surface and Groundwater of Dehradun and Haridwar District

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7.1.7   Chloride

The chloride concentration in entire study area in winter season varies from 0.02 mg/l to 70.0 mg/l with an average of 12.5 mg/l, during summer season it varies from 0.01 mg/l to 61 mg/l with an average of 14 mg/l and during post monsoon it ranges from 0.74 mg/l to 65 mg/l with an average of 10.3 mg/l (Fig. 7.7)

In Dehradun district, the average chloride concentration varies from 11.8 mg/l, in summer season 3.2 mg/l during post monsoon season and 3.6 mg/l during winter season in groundwater of the industrial area. The concentration of chloride in groundwater of agricultural area is 15.8mg/l, 11mg/l and 12.9 mg/l respectively in summer, post-monsoon and winter season. In urban area, the average chloride concentration is 15mg/l, 12 mg/l and 17.2mg/l respectively in summer, winter and post monsoon season (7.7a).

In surface water of Dehradun district the average chloride concentration varies from 17mg/l in summer season, 11mg/l in post- monsoon season and 14mg/l in winter season.

In Haridwar district the average chloride concentration in groundwater of industrial area varies from 10.7 mg/l in summer season, 23mg/l in post monsoon season and 9.7mg/l in winter season (7.7b). In groundwater of agricultural area of Haridwar district, the average chloride concentration found to be maximum 54 mg/l in summer season and minimum 20 mg/l in post-monsoon season. However in contrast to agricultural area, the chloride concentration in groundwater of urban area was low and variation found between 5.3mg/l (maximum) in post- monsoon season and minimum 3.1mg/l in summer season. This indicate groundwater contamination in village area of Haridwar district is due to improper disposal of industrial and sewage effluent in upstream area.

Higher concentration (> 44 mg/l) of chloride in Dehradun district were found at Redapur (RH - 907), Ganndhigram (RH -120), New Patel Nagar (RH-121),

Bharuwala Deep Handpump (RH-126), Rispana river at Nalapani (RH-113) and Bindal river at Lalpul Patelnagar (RH-117) Bhamanwala and in Cantt area (RH-124 mainly due to discharge of urban and municipal waste directly, without any treatment into river.

High chloride concentration in Hand pump of Gandhigram and new Patelnagar of urban area is mainly attributed to leakage from septic tank whereas higher concentration of chloride in a handpump located close to Bindal river (RH - 129) indicate recharge of shallow aquifer by polluted Bindal river.

In the surface water (Ganga river) of Haridwar district the average chloride concentration is 1.5mg/l in summer season and does not vary much and remains almost static at 1.4mg/l to 1.6mg/l in post monsoon and winter season.

In groundwater of Rishikesh area, the chloride concentration was found maximum 5.1mg/l in post monsoon season and minimum 0.007mg/l in summer season. In the Ganga river at Rishikesh the mean chloride concentration varies from 2.7mg/l in summer season, 5.1mg/l in post monsoon season and 4.7mg/l in winter season.
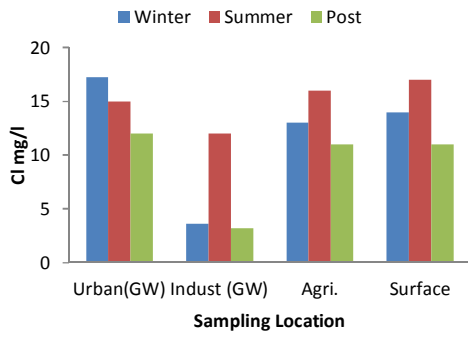
a) Cl in different land use categories in Dehradun district
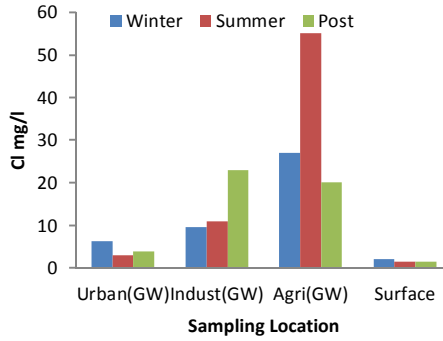
b) Cl in different land use categories in Haridwar district
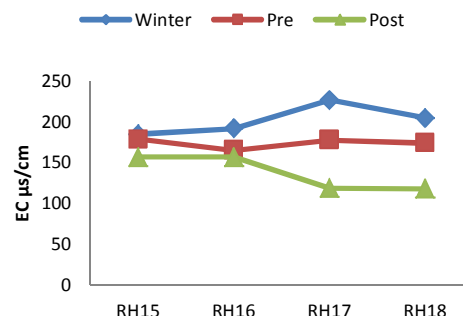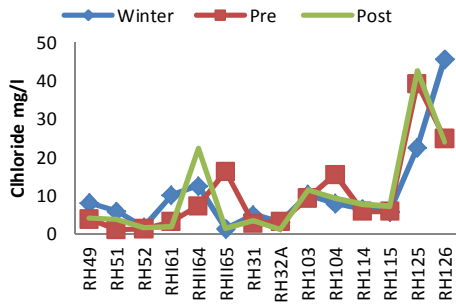
c) Groundwater of Dehradun
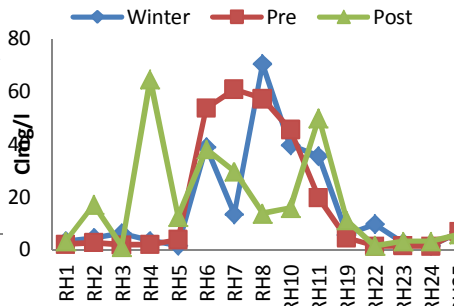
d) Groundwater of Haridwar
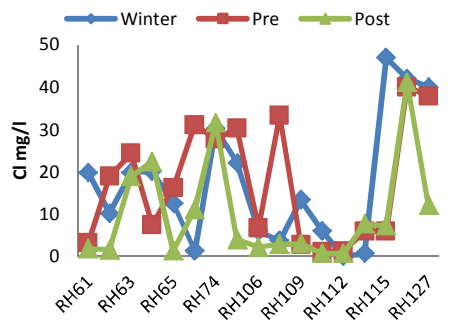
e) Surface water of Dehradun
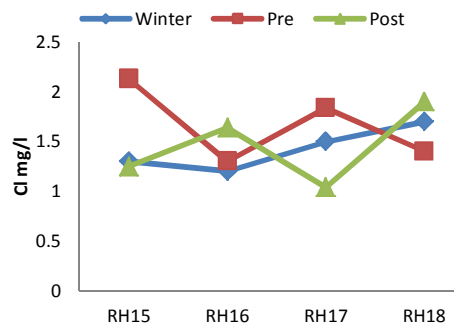
f) Surface water of Haridwar

Fig. 7.7: Variation in chloride concentration of Surface and Groundwater of Dehradun and Haridwar District

7.1.8   Nitrate

The nitrate concentration in study area varies from 0.004mg/l to 263mg/l with an average of 16.3mg/l in winter season, during summer season it ranges from 0 .0001 mg/l to 242 mg/l with an average concentration of 21.3 mg/l and in post monsoon it ranged from 0.04 to 67.4 mg/l with an average concentration of 10.4 mg/l.

In groundwater of industrial area of Dehradun district the average nitrate concentration varies from 22.9mg/l in summer, 15.9mg/l in post monsoon and 11.5mg/l in winter season.(Fig 7.8a)The average concentration of nitrate in groundwater of agricultural area of 34.6 mg/l in summer season, 8.9mg/l in post monsoon season and 10.6mg/l in winter season. In groundwater of urban area of Dehradun district the average nitrate concentration varies from 13 mg/l in summer season, 15.4mg/l in post monsoon season and 26mg/l in winter season. In surface water of Dehradun district, the average concentration of nitrate varies from 13.8 mg/l in summer season, 15mg/l in post monsoon season and 17.9mg/l in winter season.

In Haridwar district, the average nitrate concentration in groundwater was found to be maximum14.6mg/l in winter season and minimum 7.1mg/l in post monsoon season and it was 13.7mg/l in summer season (Fig. 7.8b). However, the average nitrate concentration in urban area was found maximum 6.5mg/l in winter season and minimum 2.1 mg/l in summer season and moderate 4.8mg/l in post - monsoon season. In groundwater of agricultural area of, the average nitrate concentration was maximum 161 mg/l in summer season and minimum 15.3mg/l in post monsoon season and moderate 56.7mg/l in winter season.

In surface water (Ganga river in Haridwar district), the concentration of nitrate doest not show much variation and was found minimum at 1.0mg/l during summer season and maximum 1.7mg/l during post monsoon season. However, it indicate that the input of nitrate from local sources slightly increased its concentration in Ganga water during post monsoon season (Fig. 7.8f)

The average nitrate concentration in Rishikesh groundwater varies from 5.3 mg/l during summer season, 11.5mg/l in post monsoon season and 9.4mg/l in winter season. Seasonal variation in ground water of urban area of Rishikesh could not be established due to insufficient number of samples. However in surface water (Ganga river) at Rishikesh the nitrate was maximum 4.8mg/l in winter season and minimum 2.3mg/l in post - monsoon season.

According to BIS for drinking water quality, the desirable limit for nitrate is 45 mg/l and maximum permissible limit is 100 mg/l for drinking water beyond this a disease called methanmogrbenimia occur. WHO has given the most desirable limit for NO_3 as 50 mg/l for drinking water. Higher concentration of nitrate (>45mg/l) was observed in local stream (RH-8) carrying waste from Sidcul industrial area,   Rispana river (84mg/l), confluence point of Bindal, Suswa and Rispana river (RH113), Bindal river at Nalapani and in Hand pump water of Patel Nager, Dehradun (RH121).

Significant positive correlation between of nitrate and chloride ($r^2 = 0.6$) is also observed (Table V-5) indicating same anthropogenic source of chloride and nitrate i.e. sewage, chemical fertilizer etc. due to surface runoff and leaching of pollutants in shallow and deep aquifers.

The analytical result of surface and groundwater quality shows that the high concentration of nitrate was found in Rispana and Bindal river of Dehradun where Dehradun city waste- urban runoff is discharged.

In Haridwar, the highest concentration of nitrate was found in stream carrying waste from Sidcul industrial area. In some places the concentration of NO_3 is higher than the desirable limit of BIS standard of 45 mg/L. It has been observed that leakage from ~ 6 to 20 feet deep soak pits (Sewage pit), constructed underground, are the possible source of nitrate in handpump water (shallow aquifer). The water from these aquifer contribute to discharge of adjacent river which also recharge shallow aquifers in down slope thus causing higher nitrate in river water and in handpumps drawing water from shallow aquifer.

Level of nitrate at some sampling points is however too high and is attributed to the seepage of contaminated water from the urban area directly into river. Application of fertilizer in agricultural area is another artificial source of NO_3 into the handpumps and river water. Thus nitrate has been found as a significant indicator of pollution in view of its association with human activity.


**a) NO_3 in different land use categories in Dehradun district**

b) NO_3 in different land use categories in Haridwar district
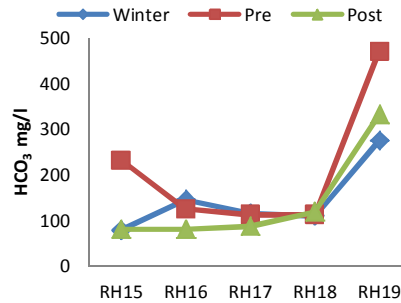
c) Groundwater of Dehradun

d) Groundwater of Haridwar

e) Surface water of Dehradun

f) Surface water of Haridwar
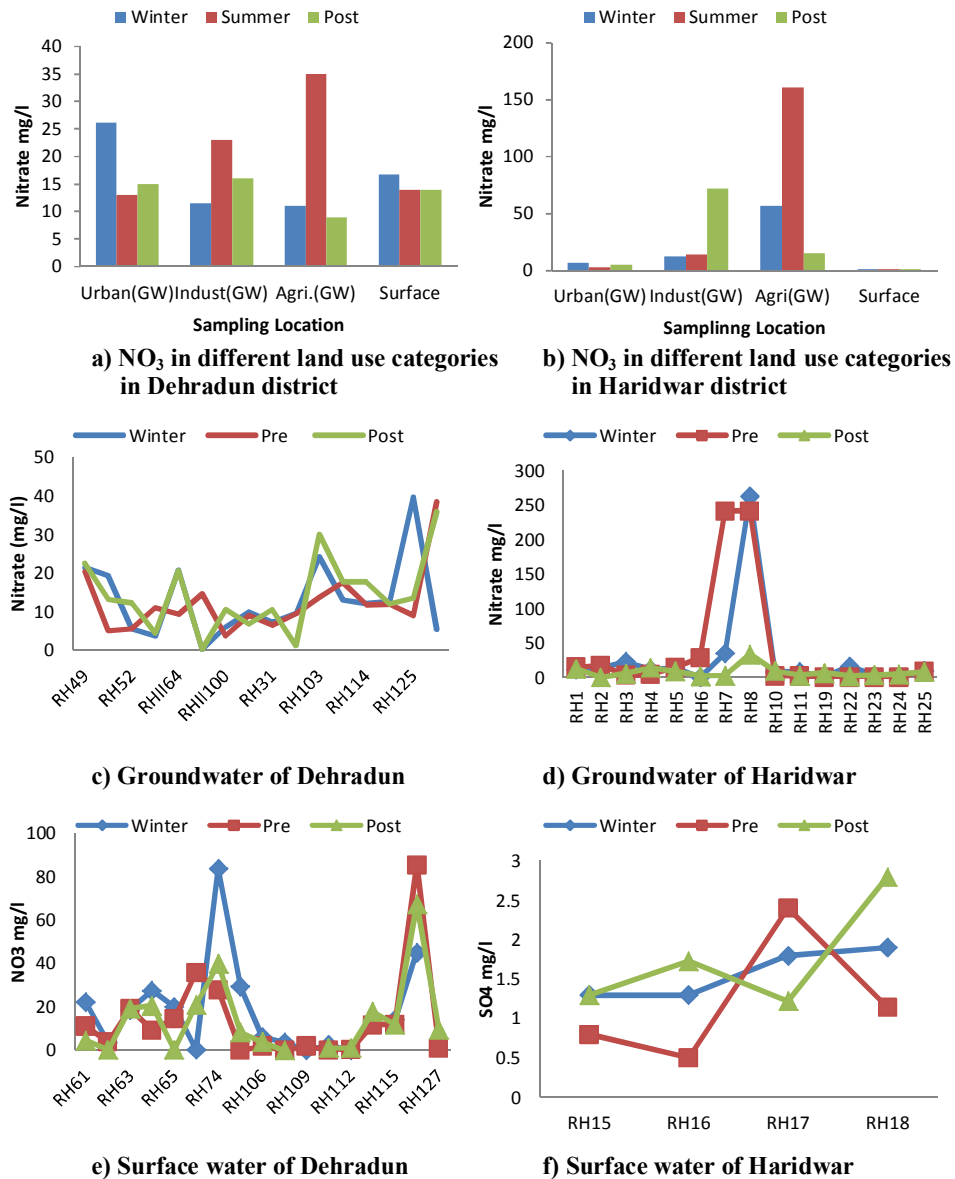
**Fig. 7.8: Variation in Nitrate concentration Surface and Groundwater of Dehradun and Haridwar District**

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7.1.9 Phosphate

P does not exist as the free element in nature but is widely distributed in rock minerals, plants and animals. It is the 12th most abundant element in the earth crust at approximately 0.12%. The phosphate concentration in study area varies from 0.01 mg/l to 18 mg/l with an average of 0.65 mg/l in winter season, 0.03 mg/l to 4.3 mg/l with an average of 0.24 mg/l during summer season and from 0.002 mg/l to 22 mg/l with an average of 0.4 mg/l post-monsoon in entire study area.

In groundwater of Dehradun district phosphate concentration was almost negligible in industrial and agricultural area and therefore no variation was observed. However in groundwater of urban area, the average phosphate concentration varies from 0.3 mg/l in winter season, 0.4 mg/l in summer season and 0.002mg/l in post monsoon season. In surface water of Dehradun the average phosphate concentration is 1.3mg/l, 0.5mg/l and 0.2 mg/l respectively in winter, summer and post monsoon season. (Fig. 7.9 a, c, d)

In groundwater of industrial area of Haridwar, the average phosphate concentration is 0.3mg/l in summer season but phosphate is absent in all sampling location in post monsoon and summer season except at one location (4.8mg/l) that is in a seasonal stream in Roshnabad industrial area (RH 6). In agricultural area of Haridwar, the phosphate was absent during summer and post monsoon season however in winter season it varies from 0.002 mg/l to 3.0 mg/l with an average of 1.1 mg/l. In groundwater of urban area and in surface water (Ganga river) of Haridwar and Risikesh area the phosphate was not detected in all the three season (Fig 7.9.a, b).

WHO has given maximum permissible limit of phosphate indicating water as 0.3mg/l. Although phosphate was not detected in study area at number of location in all the three season, it has been found that phosphate in water of few location is above permissible limit of WHO.

In Haridwar district these include a seasonal streams in industrial area of Haridwar district (RH 6 and RH 9) and handpumps (RH 11) extracting water

from shallow aquifers in Saleempur and Ravala Mehdood village. It has been observed that domestic waste and effluents from industrial area of Haridwar (Sidcul) are directly discharged into the stream in unslope direction near Saleempur and Ravala Mehdood village which infiltrate into shallow aquifers.

In Dehradun district, higher PO_4 concentration that is above WHO drinking water limit has been found in Bindal river at Bhamanwala (18mg/l), Suswa, Rispana and Bindal river in their lower reaches. The presence of Phosphate and nitrate at these location indicate adverse impact of urbanization on water quality.
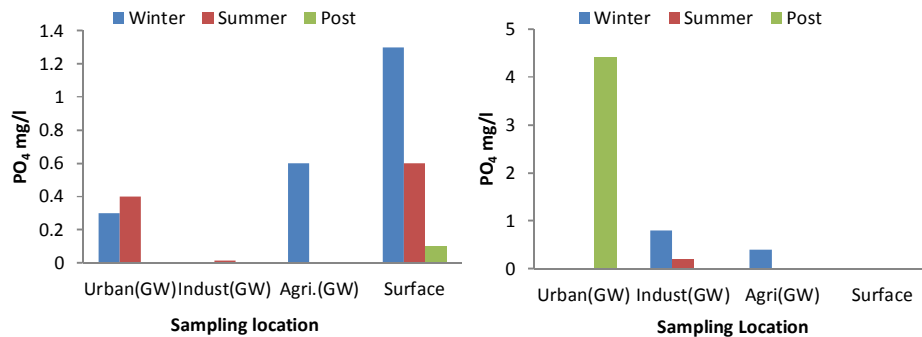

a) PO_4 in different land use categories in Dehradun district

b) PO_4 in different land use categories in Haridwar district
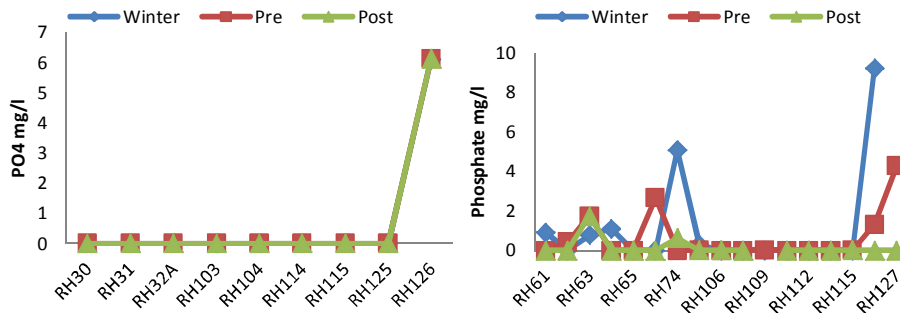
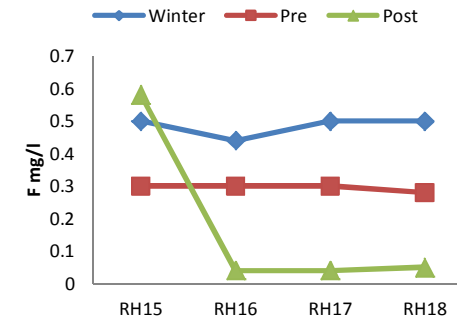c) Groundwater of Dehradun

d) Surface water of Dehradun

Fig. 7.9: Variation in Phosphate concentration in Surface and Groundwater of Dehradun and Haridwar District

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7.1.10 Sulphate

The SO_4 concentration in study area varies from 0.01 mg/l to 861 mg/l with an average of 71 mg/l in winter season, during summer season it varies from 0.12 mg/l to 443 mg/l with an average of 71.1 mg/l and in post monsoon it varies from 0.2 mg/l to 246 mg/l with an average of 52 mg/l (Fig. 7.10a and 7.10b).

In industrial area of Dehradun district average sulphate concentration in groundwater is 23mg/l in winter season, 24mg/l in summer season and 16 mg/l in post monsoon season. In agricultural area of, average sulphate concentration in groundwater is 77mg/l in summer season, 61 mg/l in post monsoon season and 37mg/l in winter season. In urban area, average sulphate concentration in groundwater was found maximum 91mg/l in winter season and minimum 56mg/l in post monsoon season. In surface water of Dehradun the sulphate concentration was higher than groundwater and varies from 167mg/l in summer season, 110mg/l in post monsoon season and 146mg/l in winter season (Fig. 7.10e).

In groundwater of industrial area of district Haridwar the sulphate concentration doest not show much variation and maximum concentration of 3.7mg/l was observed in winter season and minimum 3.2mg/l in summer season. However in comparison to industrial area the agricultural area of the Haridwar shows relatively higher mean sulphate concentration and varies from 20.4 mg/l, 62mg/l, 6.8 15mg/l respectively in summer, post monsoon and winter season. In groundwater of urban area of Haridwar district average sulphate concentration is 24mg/l in summer season, 14.7 mg/l in post monsoon season and 33mg/l in winter season (7.10d). In surface water (Ganga river) of Haridwar district, no significant variation was observed in sulphate concentration and it remain between 24.2mg/l (maximum) in winter season and 18 mg/l (minimum) in post monsoon season. The concentration in summer season was similar to that winter season. The average sulphate concentration in ground water of Rishikesh groundwater is 43mg/l in summer season, 38.4mg/l in post monsoon season and 49.3mg/l in winter season. In surface water (Ganga river) of Risikesh area the sulphate concentration varies

from 41.5mg/l in summer season, 17mg/l in post monsoon season and 29mg/l in post monsoon season.

According to BIS standards for drinking water quality, the maximum desirable limit of sulphate is 200 mg/L and permissible limit is 400 mg/L. When the concentration of sulphate increases to 200 mg/L it causes gastrointestinal irritation, if Mg and Na are present.

Of the 34 surface water sample collected from Asan, Rispana, Bindal, Yamuna, Suswa, Nimi, Bhuddi and Song river of Dehradun district, 8 samples (RH 106, RH 107, RH 108, RH 109, RH 110, RH 111, RH 112, RH 113) have shown high concentration of sulphate exceeding the desirable limit, that is > 200mg/l of BIS standards for drinking water quality. The highest concentration of 860 mg/l was recorded in Bhattafall a stream near Mussoorie. The higher concentration of sulphate at these sampling location is probably due to weathering of gypsum bearing carbonate rock of krol formation present in northern part of Doon valley. Significant positive correlation of sulphate r^2 = 0.76 and r^2 = 0.77) with Ca and Mg (Table 6.4) respectively further corroborate the above observation.
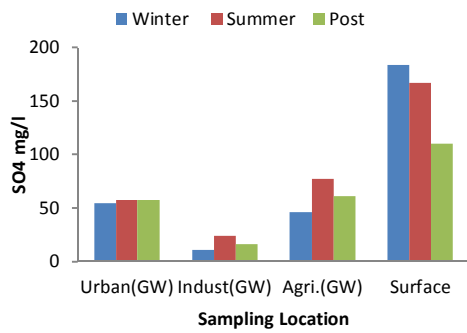
a) SO₄ in different land use categories in Dehradun district
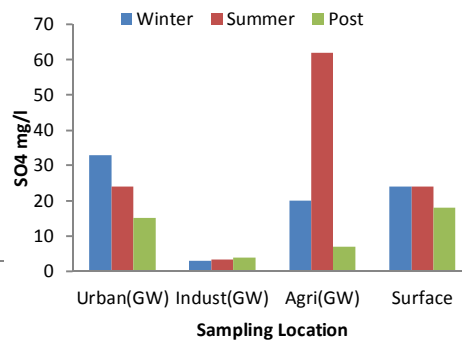
b) SO₄ in different land use categories in Haridwar district
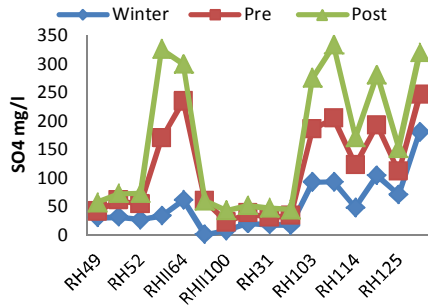
c) Groundwater of Dehradun
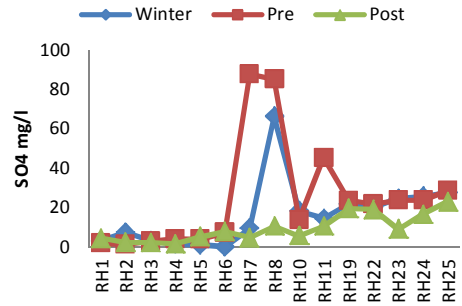
d) Groundwater of Haridwar
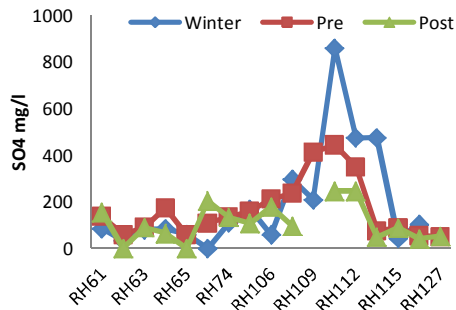
e) Surface water of Dehradun

f) Surface water of Haridwar

Fig: 7.10: Variation in Sulpahte concentration Surface and Groundwater of Dehradun and Haridwar District

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7.1.11 Silica

The SiO_2 concentration in study area during winter season ranges form 1.7 mg/l to 21 mg/l with an average of 7.6 mg/l, during summer monsoon it ranges from 0.7 mg/l to 15.8 mg/l with an average of 4.6 mg/l and during post monsoon it ranged from 1.2 mg/l to 33.08 mg/l with an average concentration of 7.7 mg/l (Fig. 7.12a and 7.12b).

In groundwater of industrial area of Dehradun the average SiO_2 concentration is 7.19mg/l in summer season, during post monsoon season it is 9.6 mg/l and during winter season it is 6.8 mg/l. The average concentration of SiO_2 in agricultural area of Dehradun is 6.1mg/l, 8.2mg/l and 11.3 respectively in summer, pre monsoon and winter season. In groundwater of urban area of Dehradun, the average concentration of silica is 3.6mg/l, 46mg/l and 5.9mg/l respectively in summer, post monsoon and winter season.

In surface water of Dehradun the Si concentration is slightly increased (6.9mg/l) in winter season as compare to summer (4.6mg/l) and post monsoon season (5.9mg/l).

In groundwater of Haridwar industrial area the average silica concentration is 6mg/l, 5.7mg/l and 7.3mg/l respectively in summer, post monsoon and in winter season. In ground water of agricultural area of Haridwar the Si concentration during summer season is slightly Increase 6.7mg/l as compare to post monsoon season 3.6 mg/l and winter season 6.6mg/l. The average concentration of Si in ground water of urban area of Haridwar is 1.7mg/l in summer season, 4.0 mg/l in post monsoon season and 6.7 mg/l in winter season and in surface water (Ganga river) of Haridwar district, the average silica concentration is 1.6 mg/l, 3.04 mg/l and 6.6 mg/l respectively in summer, winter and post monsoon season. The average Silica concentration in Risikesh groundwater during summer season is 1.1 mg/l, in post monsoon it is 6.5 mg/l , and during winter season it is 4.4 mg/l. The average silica concentration in Ganga river at Rishikesh during summer is 1.4 mg/l, during post monsoon season 6.5 mg/l and during winter season it is 2.6 mg/l.

a) Si in different land use categories in Dehradun district

b) Si in different land use categories in Haridwar district

Fig: 7.11: Variation in Silica concentration in Surface and Ground water of Dehradun and Haridwar District

7.1.12 Sodium

The Na concentration during winter season varies from 1.4mg/l to 39.5mg/l with mean value of 4.5 mg/l, during summer season it varies from 0.1mg/l to 34mg/l with mean concentration of 4.8mg/l and during post monsoon season it varies from 0.8mg/l to 23mg/l with an average of 6.5mg/l.

In Dehradun district, the mean sodium concentration is 7.6 mg/l, 10.5 mg/L and 9.4 mg/L during summer, post monsoon and winter season, respectively in groundwater of industrial area. The average concentration of sodium in groundwater of agricultural area is 11mg/l, 4.6mg/l and 10.9mg/l respectively in summer, post monsoon and winter season and in urban area, the average sodium concentration is 11mg/l, 6.8mg/l and 7.4mg/l respectively in summer, post monsoon and winter season. In surface water of Dehradun the mean sodium concentration is 12mg/l, 9.4mg/l and 11.3mg/l respectively in summer, post-monsoon and winter season. (Fig. 7.12.a)

In Haridwar district, the mean sodium concentration is 10 mg/L during summer season, 10.3 mg/L in winter season and 8 mg/L during post-monsoon season. In groundwater of industrial area of Haridwar, the mean sodium concentration in summer, post monsoon and winter season is respectively

25mg/l, 1.8mg/l and 15.5 mg/l. However, in groundwater of urban area the sodium concentration is 3.7mg/l, 2.9mg/l and 5.15mg/l respectively in summer, winter and post monsoon season. (Fig.7.12.b)

In the surface water (Ganga river) of Haridwar district, the average sodium concentration varies from 2.3 mg/l in summer season, 2.1 mg/l in post monsoon and marginally increased to 3.0 mg/l during winter season. The average sodium concentration in groundwater of Rishikesh area during winter and summer season is 5 mg/l, 4.7 mg/l respectively, which decreased to 1.7 mg/l in post monsoon indicating dilution due to recharge during rainy season. The mean sodium concentration in the surface water (Ganga river) at Rishikesh is 3.3 mg/l in summer, 2.2 mg/l in winter and 4.2 mg/l in post-monsoon season.
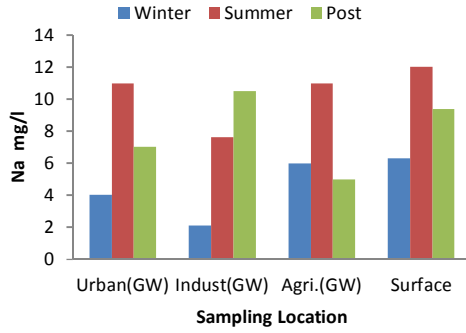
a) Na in different land use categories in Dehradun district
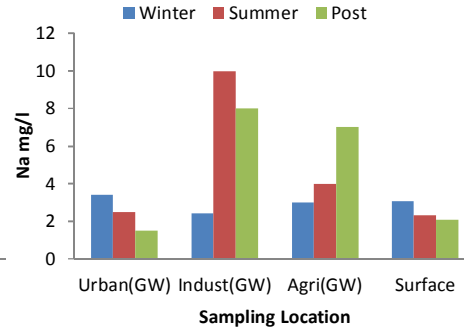
b) Na in different land use categories in Haridwar district
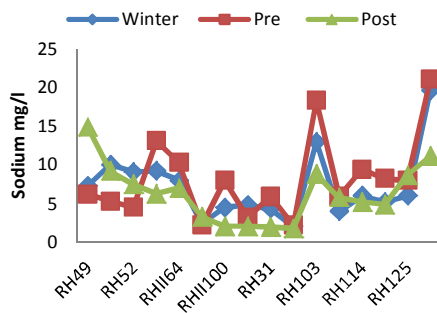
c) Groundwater of Dehradun
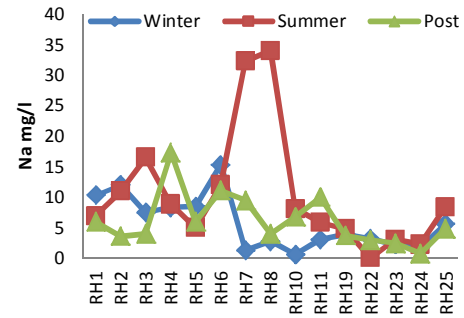
d) Groundwater of Haridwar
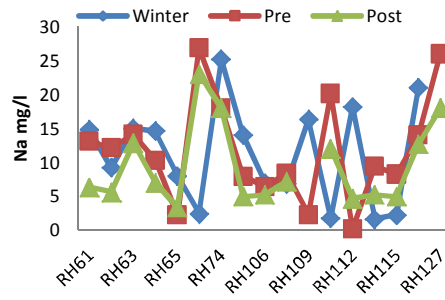
e) Surface water of Dehradun
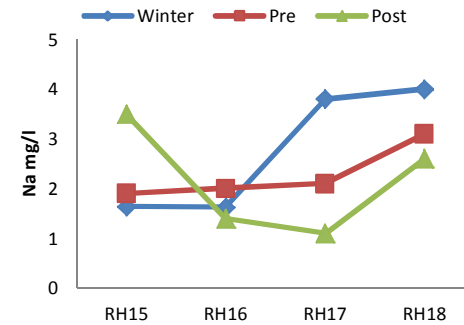
f) Surface water of Haridwar

Fig. 7.12: Variation in Sodium concentration of Surface and ground water of Dehradun and Haridwar District

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7.1.13 Potassium

The potassium concentration in study area varies from 0.1mg/l to 74mg/l with an average of 4.9 mg/l in winter season, during summer season it ranges from 0.2mg/l to 22.5 mg/l with an average of 4.8mg/l and in post monsoon it ranges from 0.2mg/l to 19.5 mg/l with an average of 2.8mg/l (Fig. 7.13a and 7.13b).

In groundwater of industrial area of Dehradun, the average potassium concentration in all three season is 3.6 mg/l, 10.5 mg/l and 2.14 mg/l respectively in summer, post monsoon and winter season. In groundwater of agricultural area the average potassium concentration is 5.5mg/l, 12.5mg/l and 5.7mg/l respectively in summer, post monsoon and during winter season. In urban area , the average potassium concentration varies from 6.3 mg/l in summer to 6.8 mg/l during post monsoon and during winter season it is 3.7mg/l. In comparison to groundwater, the average concentration of potassium in surface water is found to be 7.0 mg/l in summer season as compared to 5 mg/l in post monsoon season 5mg/l and in winter season it is moderate 6.3mg/l.

In Haridwar district the average potassium concentration is 3.2mg/l, 1.5mg/l and 2.3mg/l respectively in summer, post-monsoon   and winter season in groundwater of industrial area . In groundwater of agricultural area, the average potassium concentration during summer season is 7.6mg/l which decreases to 1.8mg/l in post monsoon season and 2.7mg/l in winter season. In groundwater of urban area, the average potassium concentration is 3.0 mg/l, 2.4mg/l and 3.4 respectively in summer, post monsoon and winter season. In the surface water (Ganga river) of Haridwar the mean potassium concentration during summer is 2.5 mg/l, 2.2 mg/l in post – monsoon and 3.1 mg/l during winter season.

The average potassium concentration in groundwater of Rishikesh area is **3.5** mg/l in summer season and 0.8mg/l in post monsoon   and during winter season its average value is 2mg/l. The average potassium concentration in the

Ganga river at Rishikesh during summer season is 3.3 mg/l, 1.5 mg/l in post monsoon and 2.6 mg/l during winter season.

A relatively higher concentration of potassium in Bindal (RH 72, RH 117) and Rispana river (RH113, RH127) and in handpump at Bahruwala close to Bindal river (RH 26) further indicates the adverse impact of urbanisation on the surface and groundwater quality at few placesin Dehradun district x Similarly elevated then average concentration of K in stream receiving discharge of industrial area (Sidcul) of Haridwar district and in handpumps in the vicinity (RH 6, RH 8) possibly indicate the impact of industrialization and domestic and sewage waste on water quality.

Higher than average concentration of potassium in groundwater of agricultural area of Haridwar district is possibly result of application of potash-rich fertilizer on the subsurface water.

a) K in different land use categories
in Dehradun district

b) K in different land use categories
in Haridwar district
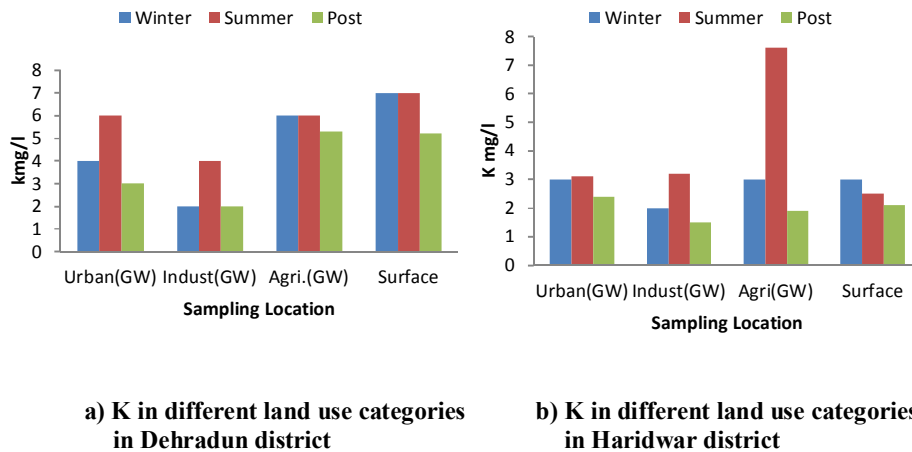
Fig. 7.13: Variation in K in Surface and Ground water of Dehradun and Haridwar District

7.1.14 Magnesium

The Mg concentration in entire study area ranges from 0.5mg/l to 62 mg/l with an average of 15mg/l in winter season, during summer season it ranges from 5.2 mg/l to 68 mg/l with an average of 21.6 mg/l and in post monsoon it ranges from 1mg/l to 41.2 mg/l with an average of 15.9 mg/l. In groundwater of industrial area of Dehradun the average magnesium concentration is 11.5mg/l in summer season, 5.3 mg/l during post monsoon season and 4.9 mg/l during winter season. The average concentration of Mg in groundwater of agricultural area of Dehradun is 21.9 mg/l, 12.5mg/l and 9.3mg/l respectively in summer, post monsoon and winter season. In groundwater of urban area the Mg concentration is 25mg/l in summer season, 3.1 mg/l in post monsoon it is and 24 mg/l during winter season it is. In surface water of Dehradun district, the average magnesium concentration is 36mg/l in summer season, 25mg/l in post monsoon season and 21mg/l in winter season (Fig. 7.14a and 7.14b).

In groundwater of industrial area of Haridwar district, the average magnesium concentration is 8.2mg/l, 8.7mg/l and 8.2mg/l respectively in summer, post monsoon and winter season. In agricultural area the average magnesium concentration during summer season is 22.8 mg/l, 10.2 mg/l during post monsoon and 13 mg/l during winter season. In of urban area of Haridwar the mean magnesium concentration is 10.7 mg/l, 8.07 mg/l and 9.5 mg/l respectively in summer, winter and post-monsoon season. In the surface water (Ganga river) of the Haridwar, the average Mg concentration is 7.1 mg/l in summer season, 8.8 mg/l during post monsoon season and remain 4.8 mg/l in winter season.

The average Mg concentration in groundwater of Rishikesh area during summer season is 26 mg/l which decreased to 18.4 mg/l in postmonsoon season and 17 mg/l during winter season. The average magnesium concentration in Ganga river at Risikesh is 8.6mg/l during summer and post monsoon season and in winter season it is 4.3mg/l. The Mg concentrations at all sampling locations were found under the permissible limit of BIS and

WHO standard for drinking water quality. The Mg has shown good of relationship with Ca ($r^2 = 0.7$) and SO_4 ($r^2 = 0.77$) and with EC ($r^2 = 0.7$), TDS ($r^2 = 0.70$) indicating an important ion among total dissolved solids and have similar ionic sources to that of calcium and sulpahte (Table 6.4)

a) Groundwater of Dehradun   **b) Groundwater of Haridwar**

c) Surface water of Dehradun   **d) Surface water of Haridwar**
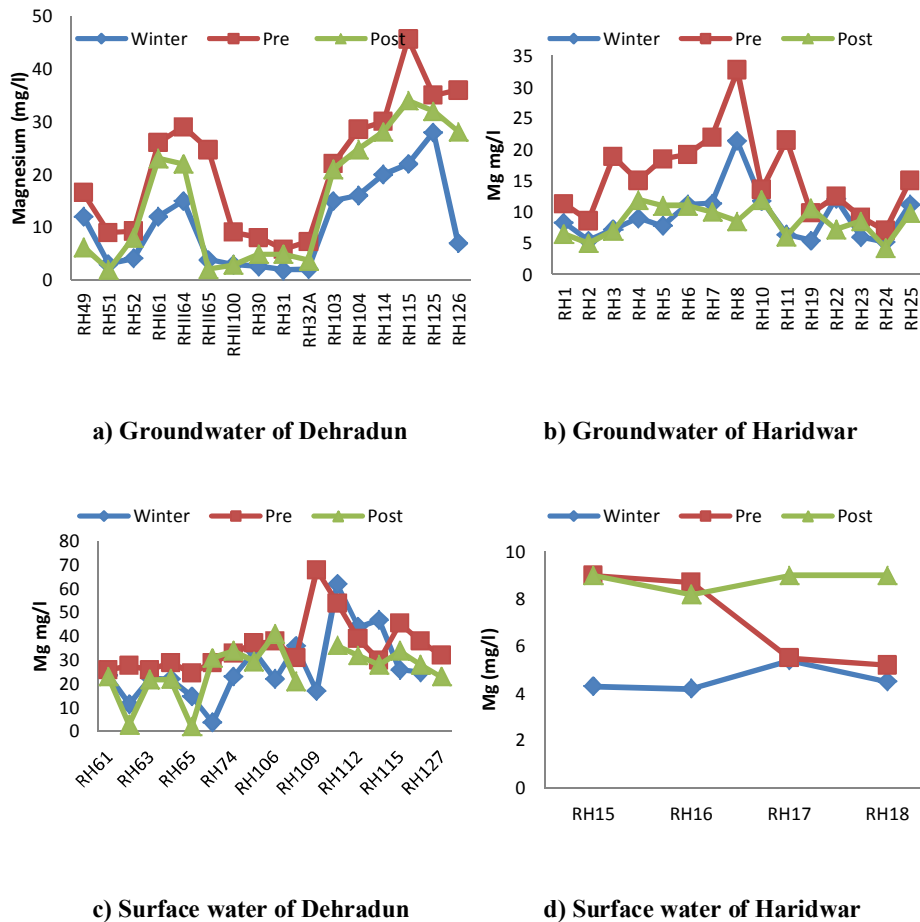
Fig: 7.14: Variation in Magnesium concentration in Surface water and Ground water of Dehradun and Haridwar District

7.1.15 Calcium

The calcium concentration in waters of the study area varies from 3.6 mg/l to 267 mg/l with an average concentration of 58.9 mg/l in winter season, during summer season it ranges from 26 mg/l to 182mg/l with an average of 64.4 mg/l and in post monsoon it ranges from 13mg/l to 120 mg/l with an average of 49.5 mg/l. In groundwater of Dehradun district, the average calcium

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concentration summer season is 31mg/l in summer season and 20.6mg/l in both post monsoon and winter season. The average calcium concentration in agricultural area, is 56mg/l, 38.7mg/l and 41.6mg/l respectively in summer, post monsoon and winter season. In groundwater of urban area, the average concentration of calcium is 60mg/l, 20.4 mg/l 54mg/l respectively in summer, post monsoon and during winter season. In surface water of Dehradun district the mean calcium concentration varies from 94 mg/l during summer season, 63.5 mg/l during post monsoon and 81.8 mg/l during winter season (Fig. 7.15).

In groundwater of Haridwar district, the average calcium concentration is 81mg/l, 75mg/l and 88mg/l respectively in summer, post monsoon and winter season in industrial area. In agricultural area, the average concentration of calcium is 103mg/l in summer season, 74.3 mg/l during post monsoon and 79 mg/l during winter season. In groundwater of urban area , the average calcium concentration is 43mg/l in summer season, 35mg/l in post monsoon season and 54.1mg/l in winter season. The average calcium concentration in the surface water (Ganga river) of Haridwar district is 33 mg/l during summer season which slightly decreased to 22.3 mg/l in post monsoon season and remain 31.8 mg/l in winter season. In groundwater of Rishikesh area the average calcium concentration during all three season is 58mg/l, 32mg/l and 42mg/l respectively in summer, winter and in post monsoon season.

The WHO has prescribed 75 mg Ca/l as a limit of acceptability and 200 mg/l as a maximum permissible amount in drinking water. Alekin (1970) state the concentration of Ca in world's river water varies between 3 mg/l and 110 mg/l. The Ca concentration varies from 3.6mg/l to 267mg/l with a mean value of 58.9mg/l in the study area of Dehradun and Haridwar district indicating higher than the permissible Ca concentration at few locations. For example higher concentration of Ca was found at Bhatta fall near Mussoorie (RH - 109), in a deep handpump in Bharuwala in Dehradun and Roshnabad in Haridwar (RH 8), Chandrabadni Spring (RH 75), in tubewell of Pitthowala (RH 110) and Anchal Diary (RH114) , in Rispana river (RH111, RH 127) and in Sahashtradhara stream (RH112).
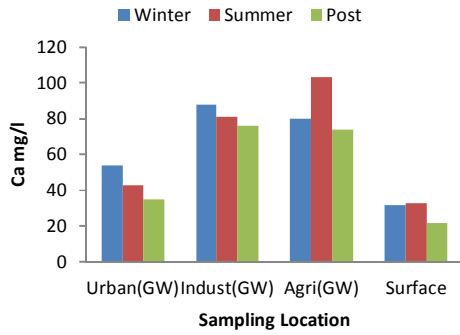
**a) Ca in different land use categories in Dehradun district**
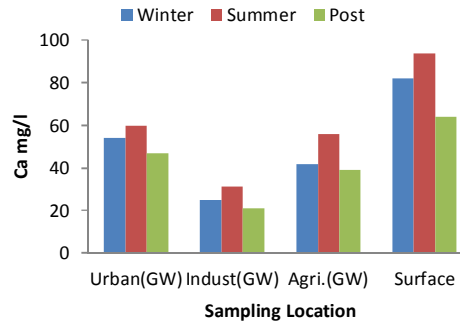
b) Ca in different land use categories in Haridwar district
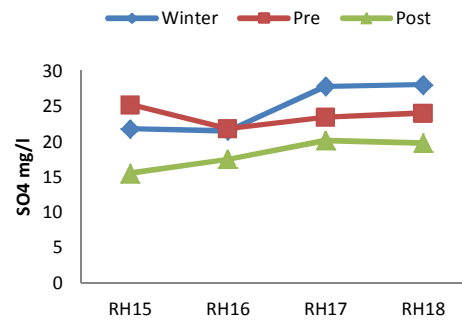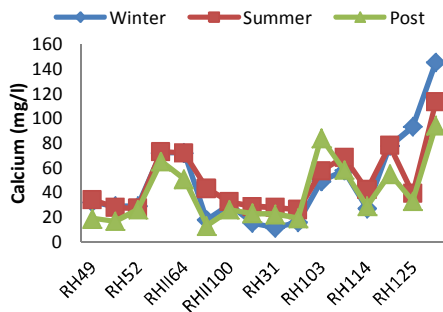
c) Groundwater of Dehradun
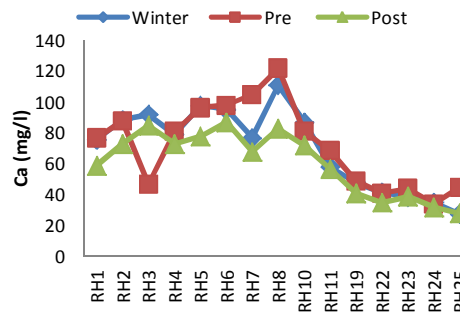
d) Groundwater of Haridwar
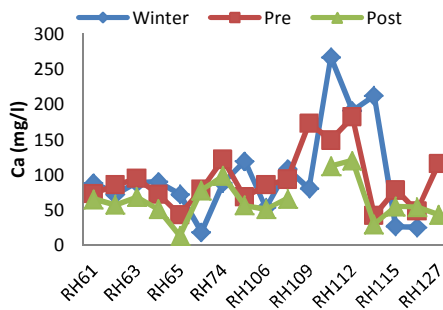
e) Surface water of Dehradun
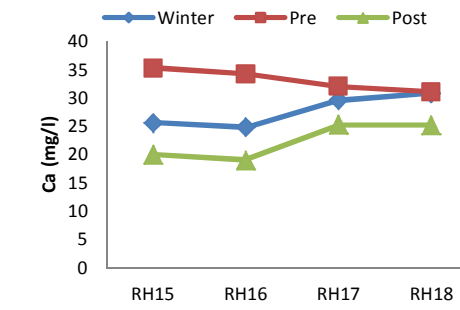
f) Surface water of Haridwar

Fig. 7.15: Variation in Calcium concentration in Surface water and Groundwater of Dehradun and Haridwar District.
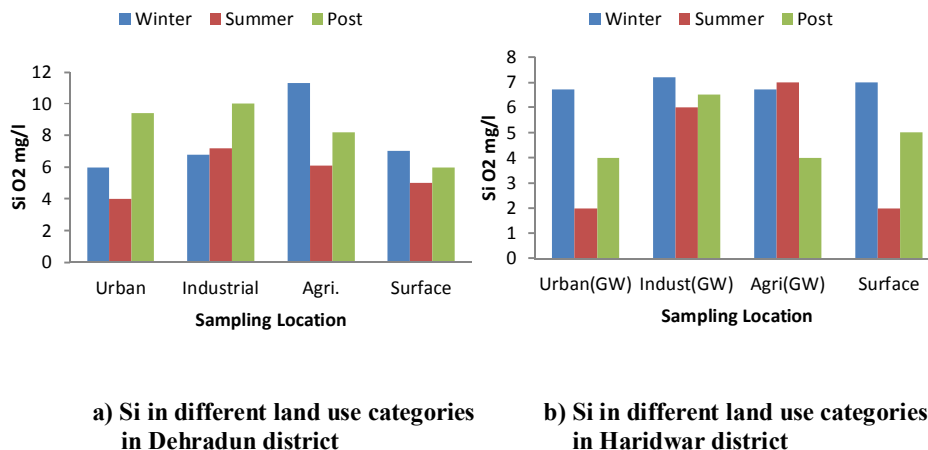
7.2   ASSESSMENT OF DRINKING WATER QUALITY OF THE STUDY AREA

The assessment of drinking water quality of the study area was carried out by comparing the chemical data with BIS (1997) and WHO (1990) standards for drinking purposes(Fig. 7.16, 7.17, 7.18, 7.19). Majority of the chemical parameter falls below the permissible limit of drinking water but few samples shows higher concentration of F, K, NO_3 and SO_4.   These include fluoride in handpumps of Shekhowala (RH 81), Patel Nagar (RH 124), (RH 109) and in Bindal river at Bharuwala (RH 72) in a stream called Bhattafall and a spring near Doonga (RH 99) in Dehradun district and in handpump at Roshnabad (RH 18) of Haridwar district.

In Bindal river at Bharuwala (RH 72) K has exceeded the permissible limit of WHO (50 mg/l). Similarly, NO_3 has exceeded the permissible limit of WHO and BIS in a handpump at Patelnager (RH 121) in Dehradun district and at Rewala Mehdood (RH 48) in Haridwar district.

Among the surface water, Rispana river near (RH 67, RH 113, RH 116) and Bindal river near Patel Nagar (RH 117) in Dehradun district and a local stream (RH 9) in Haridwar district shows higher concentration of NO_3 exceeding the permissible limit of WHO standards. SO_4 has also exceeded the maximum permissible limit of WHO and BIS for drinking purpose at Bhattafall near Mussoorie (RH109) and at Sahastradhara (RH 112) in Dehradun district.

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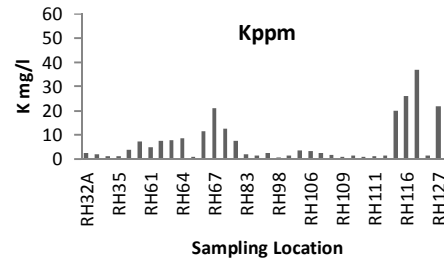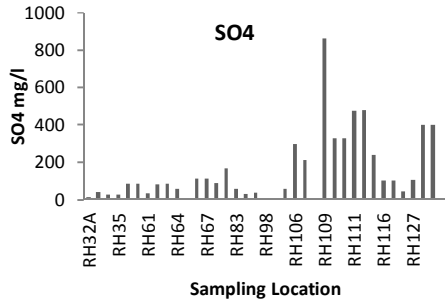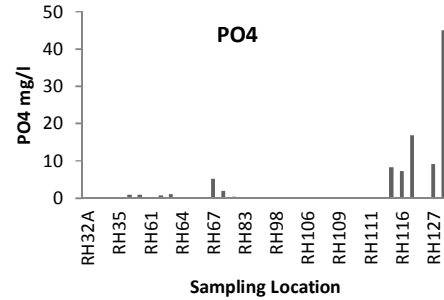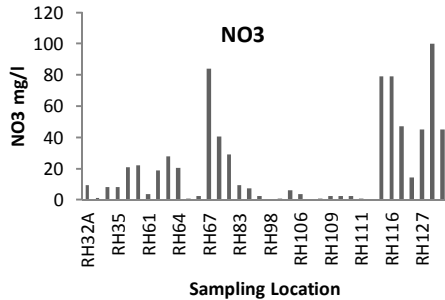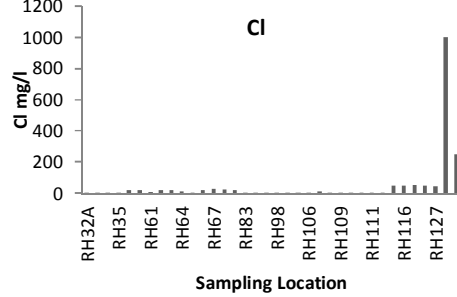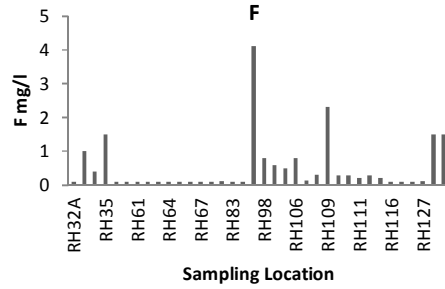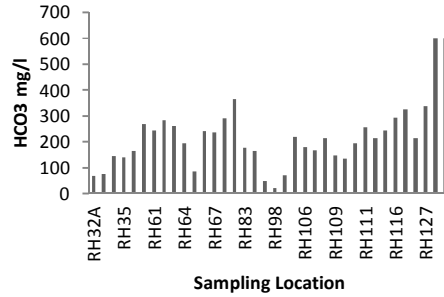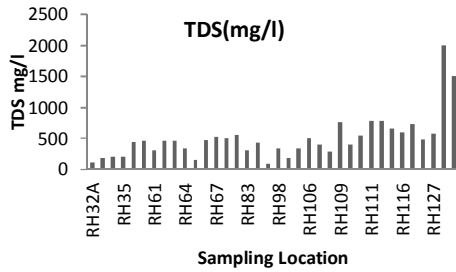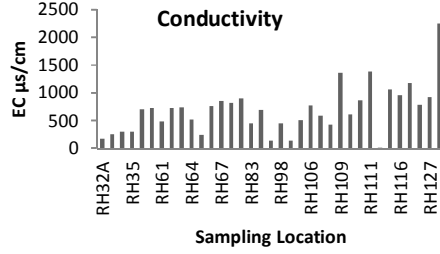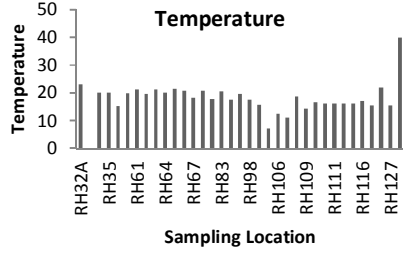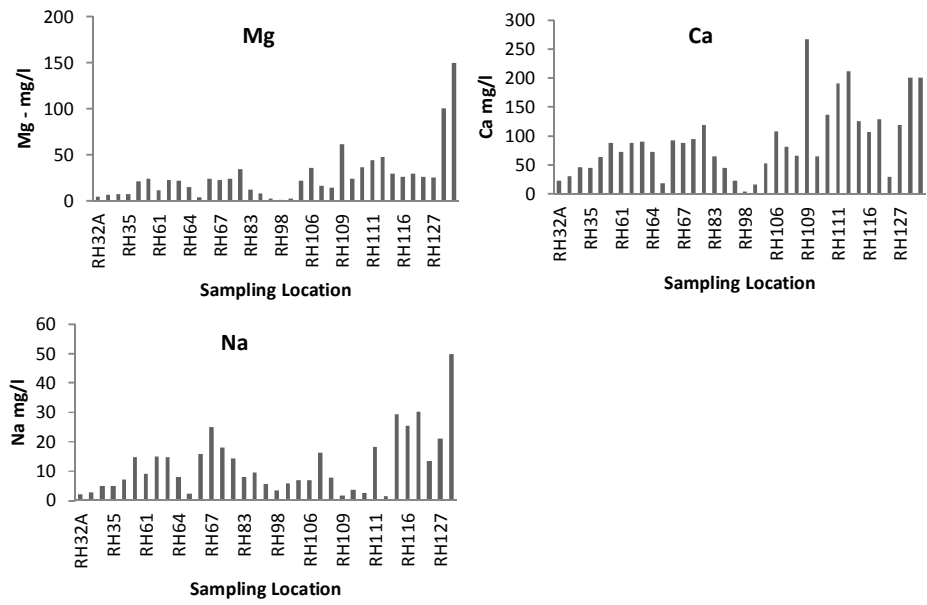
Fig. 7.16: Comparison of water chemistry data with WHO and BIS drinking standard of Surface water of Dehradun district.
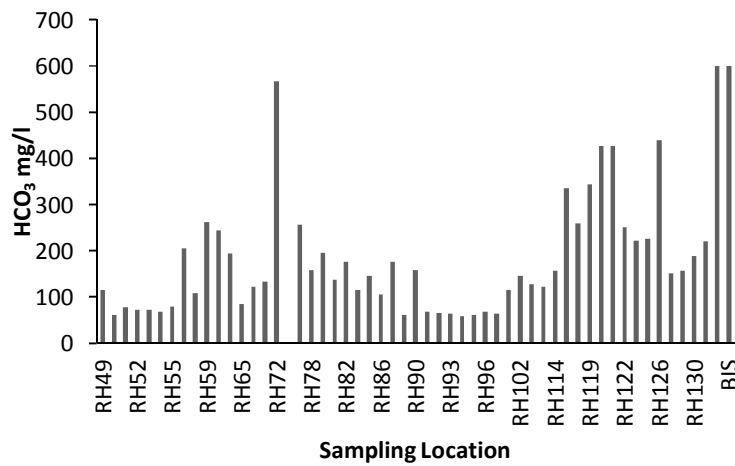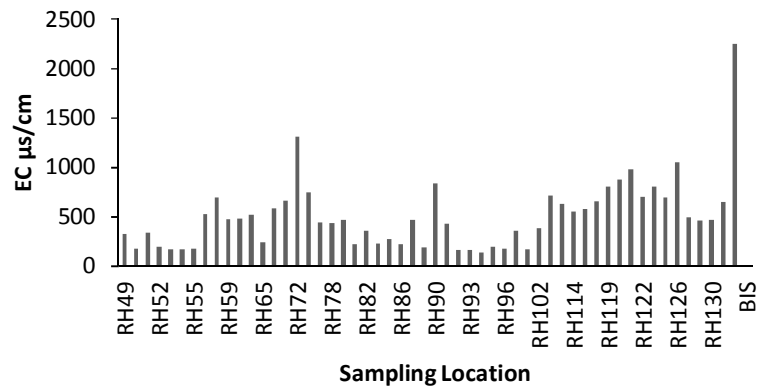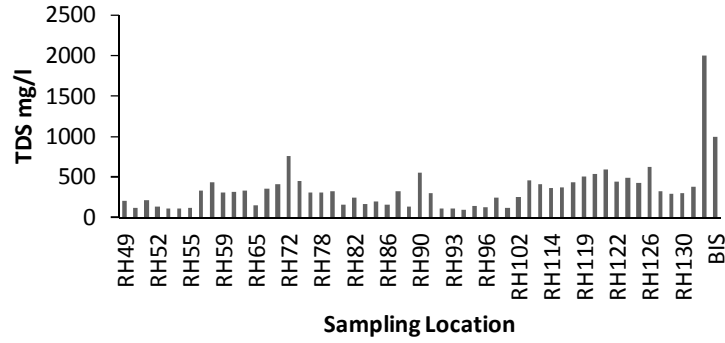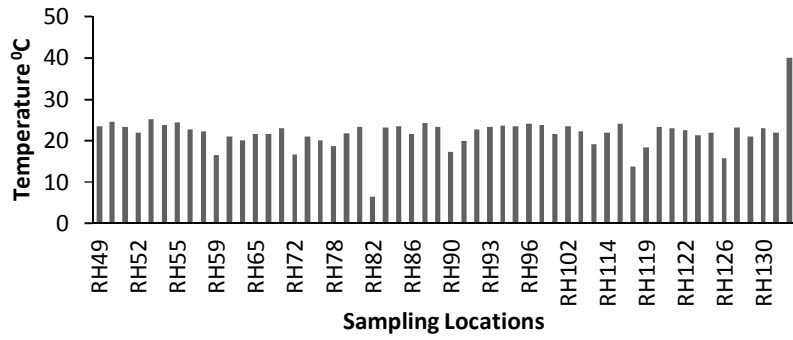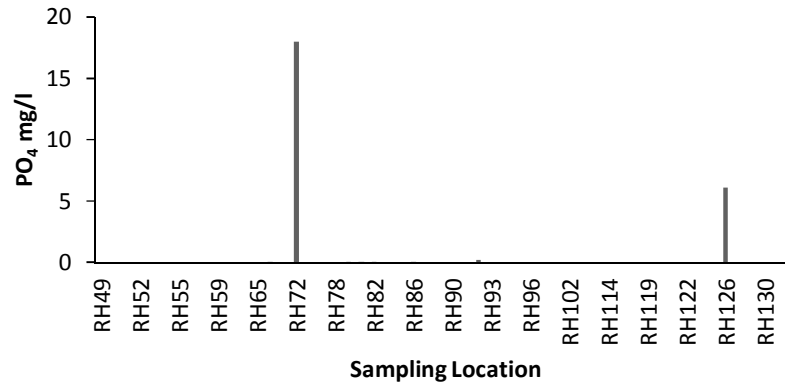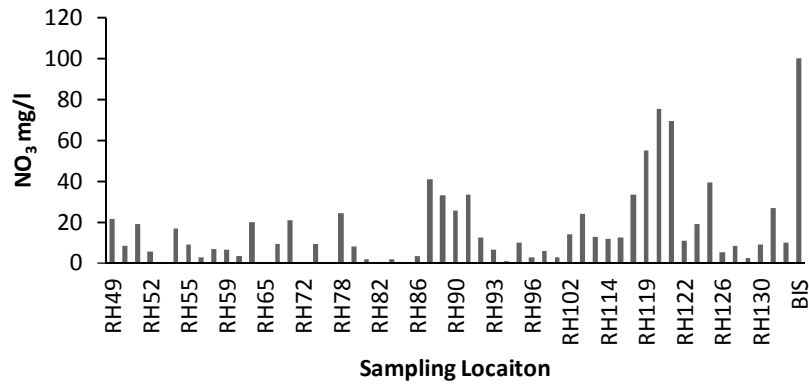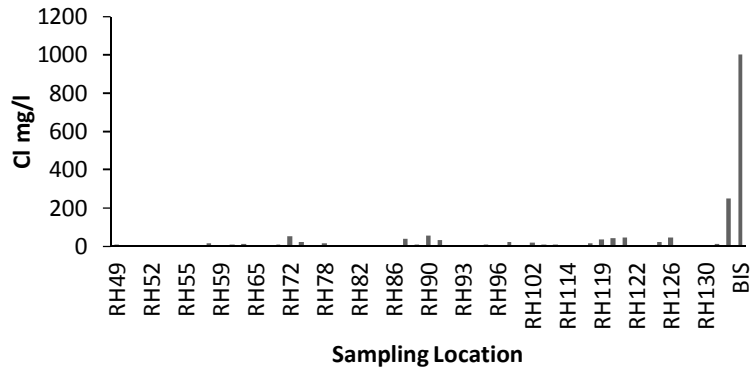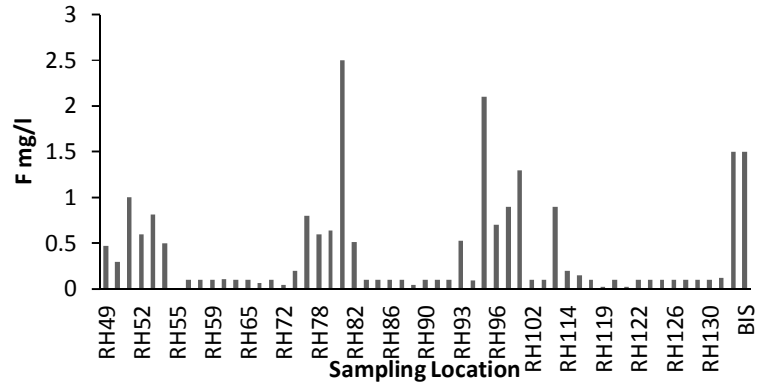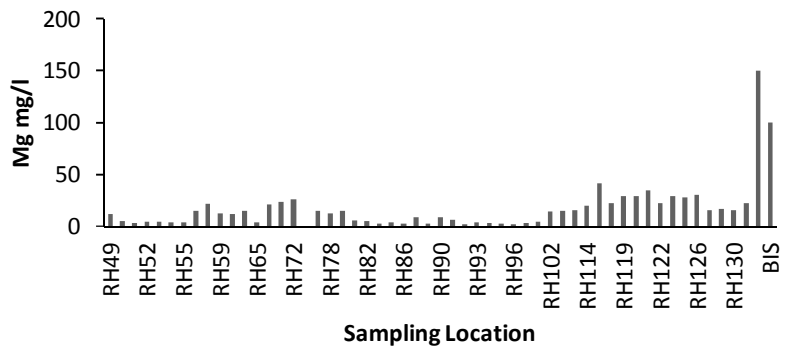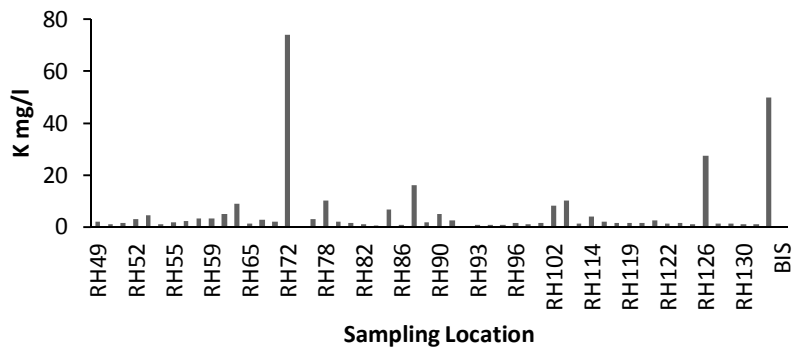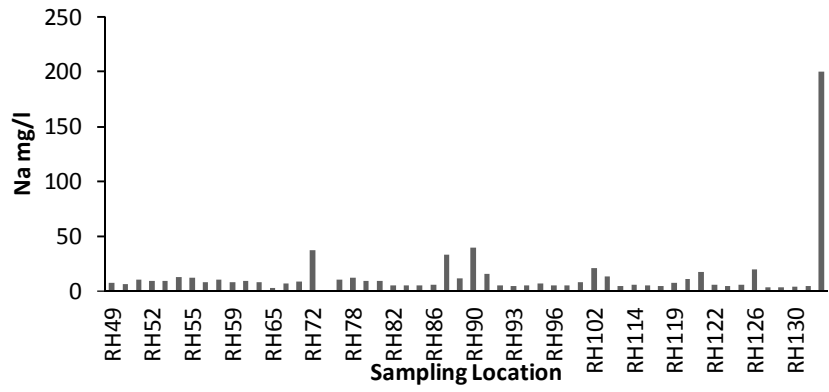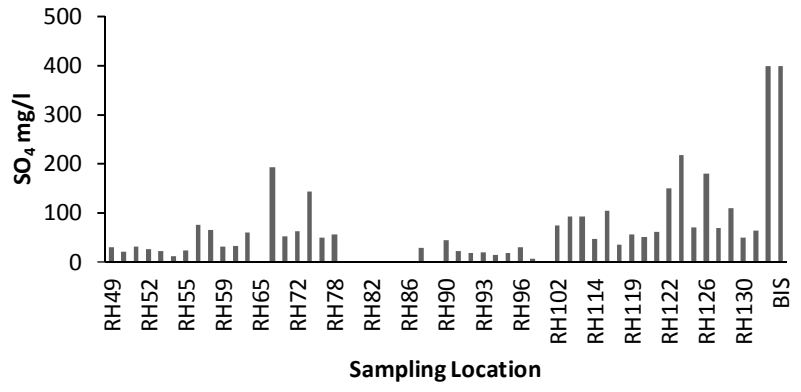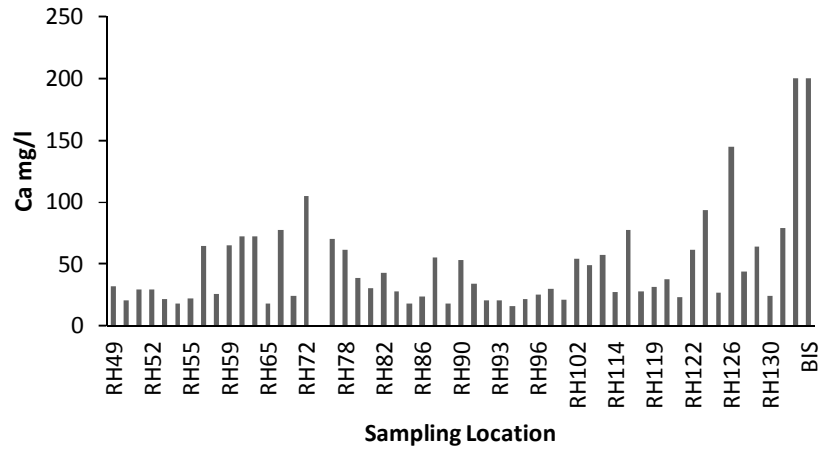
Fig. 7.17: Comparison of water chemistry data with WHO and BIS standard of ground water of Dehradun district
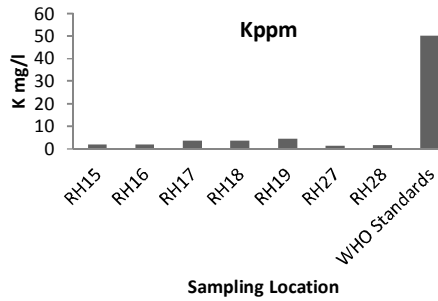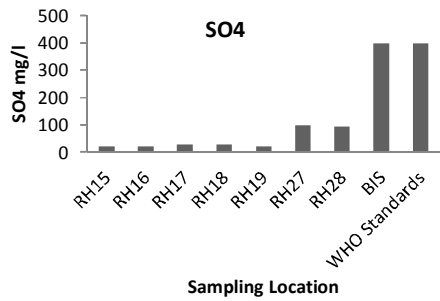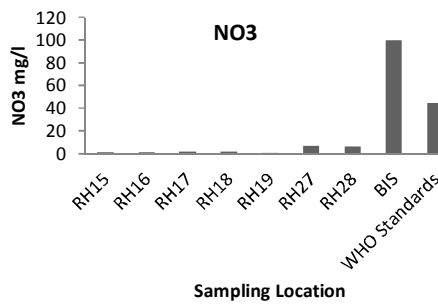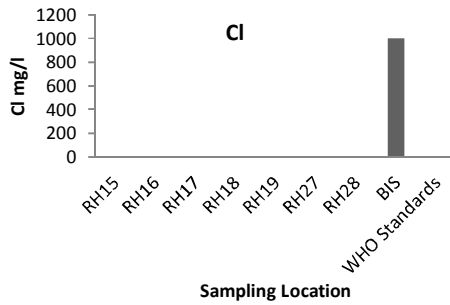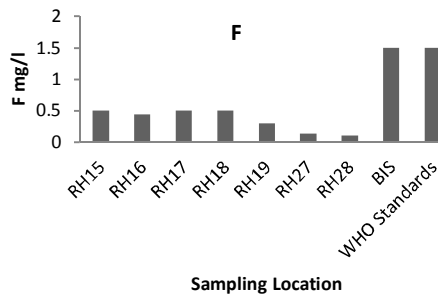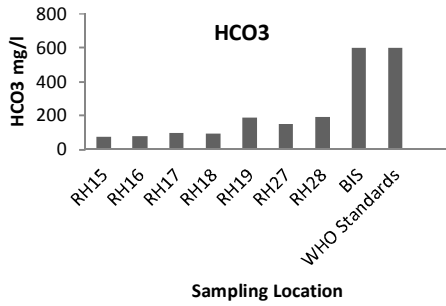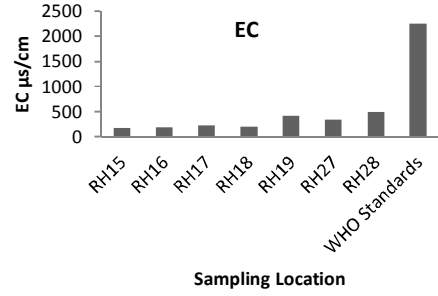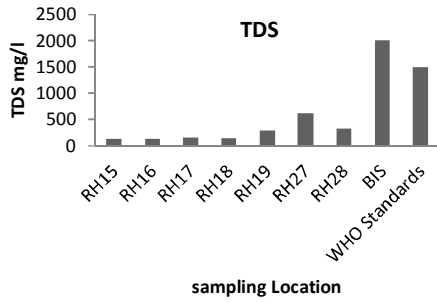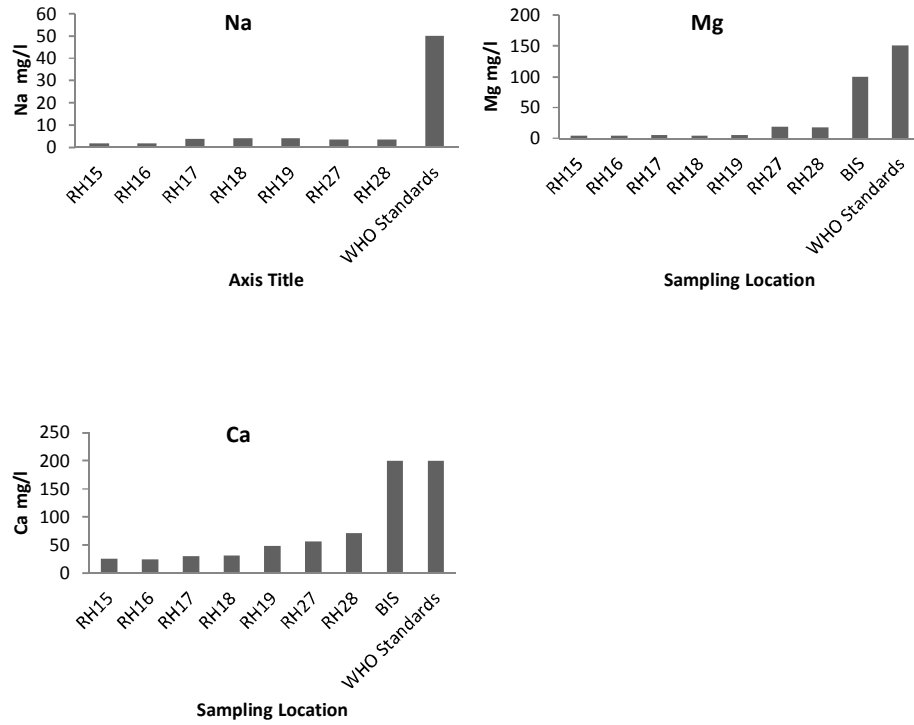
Fig. 7.18: Comparison of water chemistry data with WHO and BIS standard of Ganga river at Haridwar district
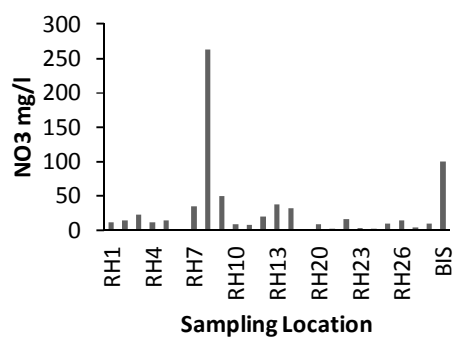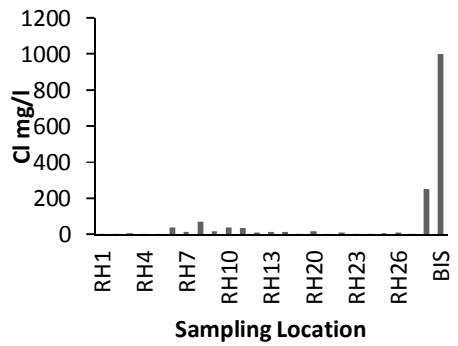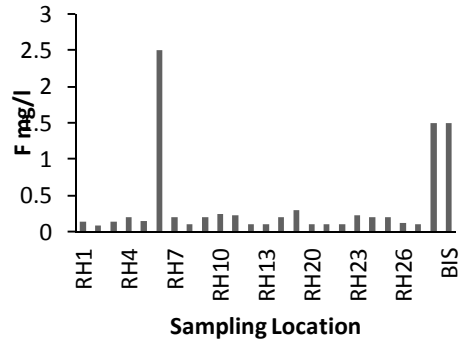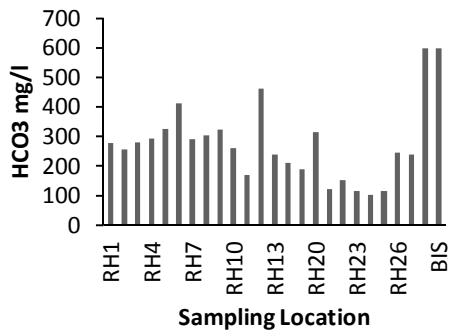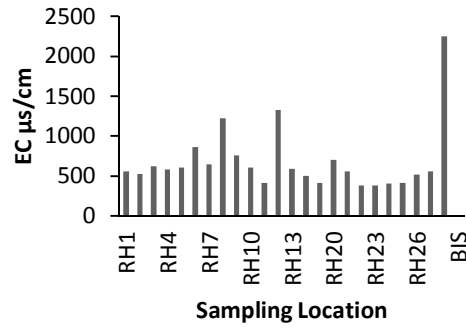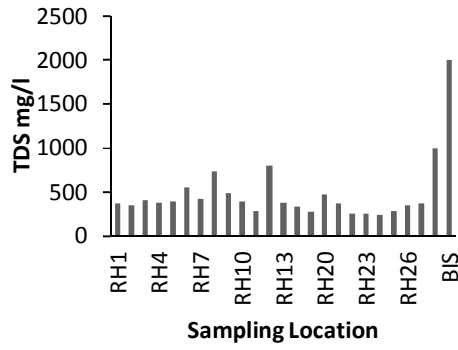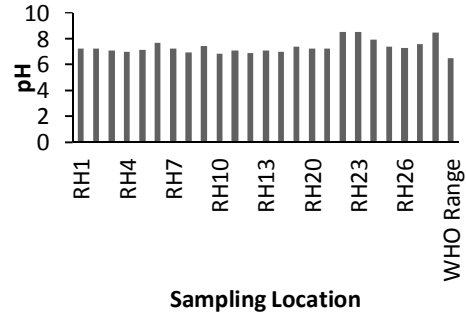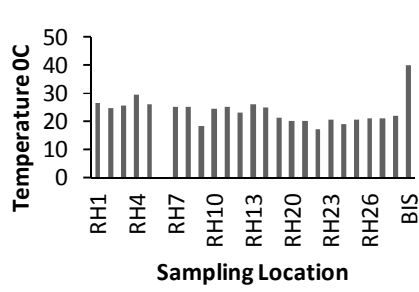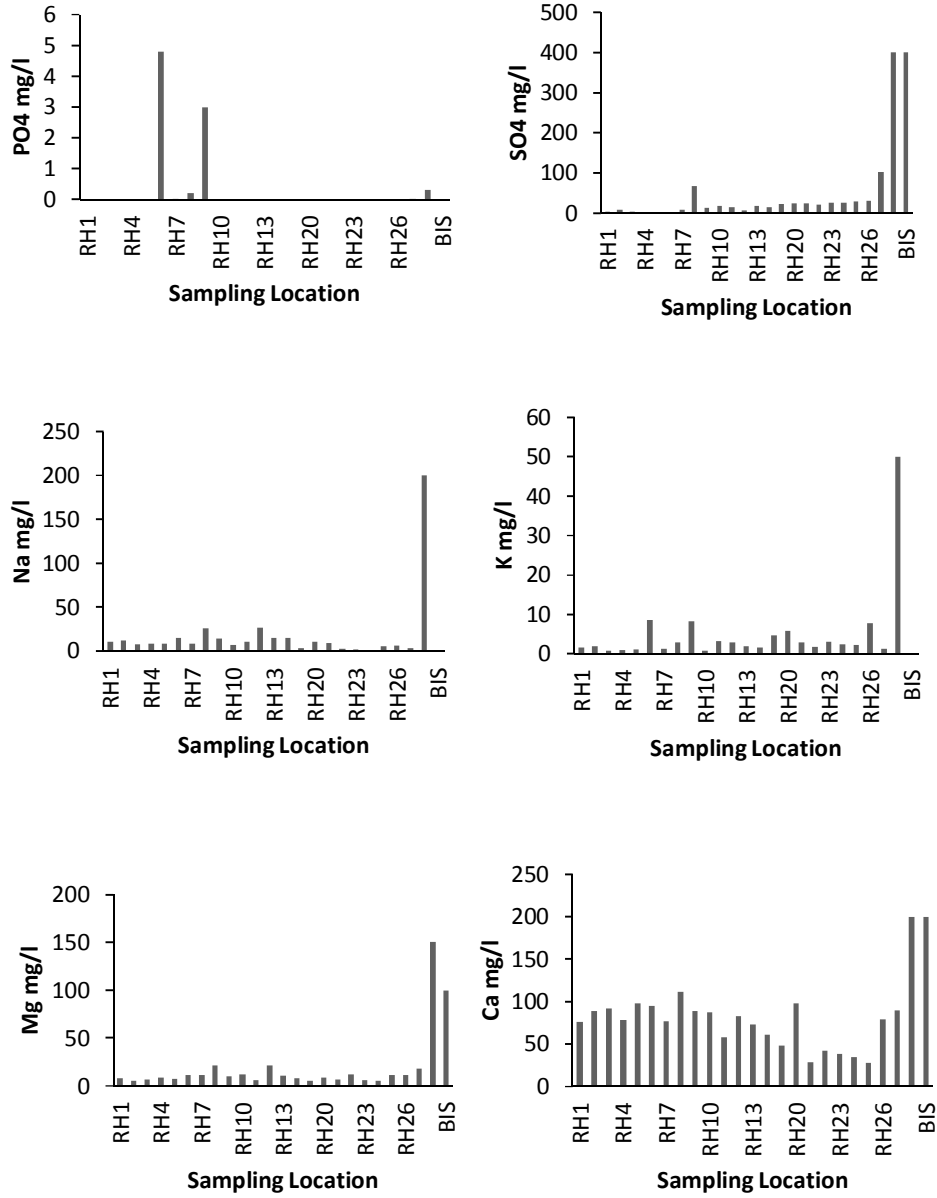
Fig. 7.19: Comparison of Ions With BIS and WHO standards for drinking water quality of Haridwar ground water

7.3   HEAVY METALS

7. 3.1   Lead

The concentration of lead in all sampling location (5 samples) were found to be less the 1 ppb (Table 7.5).

7.3.2   Nickel

The Ni concentration in winter season varies from 0 ppb to 0.396ppb with an average of 0.396 ppb, during summer season it varies from 0 to 0.38 ppb with an average of 0.396 ppb and in post monsoon it varies from 0 ppb to 0.39 ppb with an average of 0.39 ppb in entire study area (Table 7.4).

 In industrial area of district Haridwar ground water the average Ni concentration is 480ppb, 0.49ppb and 0.48ppb respectively in winter, summer and in post monsoon season. The concentration of Ni in agricultural area of ground water of Haridwar district 0.43ppb, 0.47ppb and 0.54ppb respectively in summer, post monsoon and in winter season. In urban area of Haridwar ground water the Ni concentration did not much variation and found almost same 0.4ppb in all three season.

In the Ganga river at Haridwar the Ni concentration did show much variation found to be almost 0.25 in all three season.

 In Dehradun industrial area of ground water of Doon the Ni concentration found to be almost same ~ 0.46 in all three season. In agricultural area of Dehradun ground water the Ni concentration did not show much variation found almost ~0.54ppb in all three season.

In urban area of Dehradun ground water the average Ni concentration is ~ 0.24 in all three season. In surface water of Dehradun the nickel concentration did not show much variation and found to be almost same ~ 0.4ppb in summer, post monsoon and in winter season. The Ni concentration in Ganga river at Risikesh was ~ 0.3 in all three season summer, post monsoon and in winter

season. In ground water sample of Risikesh the average of nickel is 0.23ppb in summer and post monsoon season and 0.38ppb was found in winter season. The Ni concentration is found high at sampling location RH69-9ppb and RH124 & RH119- 2ppb. No permissible and desirable limits of Ni are given by BIS and WHO drinking water quality standards.

7.3.3 Cadmium

In industrial, agricultural, urban of groundwater of Dehradun and Haridwar district and in surface the amount of Cd at all sampling location were found to be under below detectable limit. The maximum permissible limit for Cd is 5ppb by BIS for Drinking water. All samples are found to be under permissible limit of BIS standard (Table 7.4).

7.3.4 Chromium

The Cr concentration in industrial area of district Haridwar ground water in all sampling location except in few location RH3- summer (0.023 ppb), post – (0.021 ppb), winter (0.02 ppb) and RH5 (summer 0.023, post – 1540ppb and winter – 0.07) were found to be below the detectable limit. In village area of Haridwar the Cd concentration at all sampling location except (RH- 0.5 ppbb during winter season) were found to be below detectible limit at all sampling location in three season winter season, summer and post monsoon season. In urban area of Haridwar ground water and in Ganga river at Haridwar except one sampling location RH15 (0.75ppb, winter season) the Cd concentration were found to be under below detectable limit (Table 7.4).

In industrial area of Dehradun ground water the Cr were found at the sampling location RH51(5889ppb) during winter season and at RH 51(Cr 5990ppb) during summer season and at sampling location RH55(1.2ppb) during winter season and summer 1.3ppb while in rest of the sampling location it was below the detectable limit. In urban area of Doon the Cr were found only at the sampling location RH32B during winter season 0.08ppb and during post monsoon season it is 0.084 ppb.

In surface water of Doon the Cr is found at the sampling location of RH67 (winter season 16.9 ppb and summer season 17.8 ppb) and at RH 63 (winter season – 987ppb) and during (summer 1.97ppb) whereas in rest of the ther sampling locations it was found below the detectable limit. In the Ganga river at Risikesh the Cr were found at sampling location RH40 (winter season 0.03ppb and during summer season 0.027 ppb) and in ground water of Risikesh the Cr were under the below detectable limit. The higher concentration of Cr also found at the sampling locations RH69- 11ppb, RH124-26ppb, RH19- 6ppb, RH49-5ppm and RH69 31ppb. Except two sample locations RH 51 Selaqui Industrial area (5889ppb during winter and summer season), RH 63 Suswa river (987ppb in winter season) the Cr concentrations in all sampling location found to be under maximum permissible limit 50 ppb of BIS and WHO standards for drinking water quality.

The possible sources of Cr in ground water of industrial area is leaching of effluents that may contain toxic metals in surface water of Suswa river, it may come from urban waste that may contain (E-waste i.e. batteries, cells and other waste of electronic devices).

7.3.5   Copper

The average copper concentration was 13ppb in winter season, 12ppb in summer season and 19ppb in post monsoon season. In industrial area of Haridwar ground water the average Cu concentration is ~ 3ppb in all three season viz summer, winter and in post monsoon season. The average concentration of Cu in agricultural area of district Haridwar ground water is 19.7ppb, 3.9ppb and 3.8ppb respectively in winter season, summer and in post monsoon season (Table 7.4).

In urban area of Haridwar ground water the average concentration of copper is 45.7ppb, 22ppb and 22.6ppb respectively in winter, summer and post monsoon season. In the Ganga river at Haridwar district no seasonal variation is found in copper concentration and it is found to be almost same ~ 48mg/l in all three season.

In Dehradun industrial area the copper copper concentration is 25ppb,24.7ppb and 0.6ppb respectively in summer, post monsoon and in winter season. In agricultural area of Dehradun ground water the average concentration of the Cu is 4.08 ppb, 13.4 ppb and 5.33ppb respectively in summer, post monsoon and in winter season. In urban area of Dehradun ground water the Cu concentration doest not show much variation found to be almost same ~ 20.7 in all three season. In surface water Dehradun also the Cu concentration doest not show much variation and found to be almost same ~ 0.4ppb in all three season

The average Cu concentration in Ganga river is almost same~ 8.5ppb in all three season. In ground water sample of Risikesh the average copper concentration is 10.5ppb, 12.5ppb and 11ppb in all three season. The concentrations of Cu found to be highest at sampling location RH69II -144ppb (Confluence point of Bindal, Rispana and Suswa river). The Cu concentration has crossed the maximum desirable limit 50ppb of BIS standard at few sampling location but found to be under maximum permissible limit 1500ppb BIS standards for drinking water quality.

7.3.6 Manganese

For the analysis of Mn total five samples were taken from Dehradun and Haridwar district. The concentration of Mn vary from <1ppb to 142ppb, highest concentration of Mn is found very high at the sampling location RH124 (142ppb Bharuwala Cant area, shallow handpump), RH 69 (17ppb confluence point of Bindal, Rispana and Suswa river). One samples at Bahruwala RH124(142ppb) has crossed the maximum permissible limit of WHO standards while according to BIS standard few samples crossed the maximum desirable limit – 100ppb of BIS but under the permissible limit-300ppb of BIS for Drinking Water Quality (Table 7.5).

7.3.7 Cobalt

At sampling location of RH19, RH69, RH124, RH49and RH 68 the concentration of cobalt found to be less then one ppb and high concentration of Co is found at the sampling location RH124- 1ppb (Table 7.5). No

permissible limit or desirable limits are given for Co by WHO and BIS standards.

7.3.8 Zinc

The Zn concentration vary from RH19- 17 ppb to RH69- 170 ppb in study area. Higher concentration is also found at the sampling location of RH49-44ppb, RH69-95ppb (Table 7.5). All the samples are under permissible limit (15000ppb) of BIS standards for drinking water quality.

7.3.9 Iron

The Fe concentrations in study area vary from 37 ppb (RH49) to 228ppb(RH124). The higher concentration of Fe is also found at the sampling location RH 69I- 207ppb, RH69II- 236ppb (Table 7.5). The Fe concentration is found under the permissible limit (1000ppb) of BIS standards and WHO standards (300ppb).

7.3.10 Arsenic

The As concentrations vary from 2ppb to 8ppb in study area and found to be under permissible limit (50ppb) of BIS standards of drinking water quality (Table 7.5).

7.3.11 Stronisium

The concentration of Sr is found high in all sampling locations i.e RHI 19 – 104ppb, RH69- 367ppb, RH124-371ppb, RH69-262ppb and RH49-75ppb (Table 7.5). No limits are given for Sr by BIS and WHO standards for drinking water quality.

7.3.12 Boron

The B concentration is found maximum at sampling location RH69- 335ppb and minimum RH49-8ppb. The higher concentration is also found at sampling location RHI69-32ppb and RH124- 31ppb (Table 7.5). No limits are given by BIS and WHO standards for drinking water quality.

Table 7.4: Trace Metals in Winter, Summer and post monsoon season

Sample Code	Ni	Ni	Ni	Cd	Cd	Cd	Cr	Cr	Cr	Cu	Cu	Cu
	Winter	Pre	Post	Winter	Pre	Post	Winter	Pre	Post	Winter	Pre	Post
RH1	0.246	0.171	0.17	<DL	<DL	<DL	<DL	<DL	3080	4	5	11
RH2	0.21	0.211	0.24	<DL	<DL	<DL	<DL	<DL	<DL	2.9	3	
RH3	0.458	0.46	0.44	<DL	<DL	<DL	0.022	0.02	0.021	3.8	4	5
RH4	1.15	1.17	1.15	<DL	<DL	<DL	<DL	<DL	<DL	2.9	3	2.8
RH5	0.47	0.653	0.64	<DL	<DL	<DL	0.114	<DL	<DL	4	3.6	3.4
RH6	0.29	0.3	0.27	<DL	<DL	<DL	<DL	<DL	<DL	0	0	7
RH7	0.591	0.5	0.49	<DL	<DL	<DL	<DL	<DL	<DL	4	3.8	3.6
RH8	0.62	0.49	0.56	<DL	<DL	<DL	<DL	<DL	<DL	7	6	5.8
RH11	0.302	0.31	0.36	<DL	<DL	<DL	0.503	<DL	<DL	48	2	2
RH15	0.356	0.34	0.35	<DL	<DL	<DL	<DL	<DL	<DL	1	1	0.8
RH16	0.167	0.158	0.23	<DL	<DL	<DL	<DL	<DL	<DL	73	69	70
RH18	0.38	0.29	0.38	<DL	<DL	<DL	<DL	<DL	<DL	12	13	12
RH19	0.196	0.18	0.2	<DL	<DL	<DL	<DL	<DL	<DL	60	60	62
RH22	0.894	0.598	0.6	<DL	<DL	<DL	<DL	<DL	<DL	73	2	1.8
RH23	0.39	0.391	0.41	<DL	<DL	<DL	0.754	0.75		4	4	3.9
RH30	0.445	0.447	0.43	<DL	<DL	<DL	<DL	<DL	<DL	37	37	36
RH31	0.298	0.31	0.22	<DL	<DL	<DL	<DL	<DL	<DL	3	11	11

Sample Code	Ni Winter	Ni Pre	Ni Post	Cd Winter	Cd Pre	Cd Post	Cr Winter	Cr Pre	Cr Post	Cu Winter	Cu Pre	Cu Post
RH32A	0.599	0.56	0.61	<DL	<DL	<DL	<DL	<DL	<DL	11	11	12
32 B	0.599	0.58	0.56	<DL	<DL	<DL	0.081		0.084	32	32	33
RH35	0	0	0	<DL	<DL	<DL	<DL	<DL	<DL	ND	ND	ND
RH37	0.361	0.318	0.31	<DL	<DL	<DL	<DL	<DL	<DL	3	2.8	3
RH39	0.51		0.29	<DL	<DL	<DL	<DL	<DL	<DL	14	18	17
RH40	0.291	0.296	0.31	<DL	<DL	<DL	0.027	0.03		14	15	15
RH41	0.249	0.23	0.24	<DL	<DL	<DL	<DL	<DL	<DL	7	6.9	6.8
RH44	0.34	0.343	0.33	<DL	<DL	<DL	<DL	<DL	<DL	15	4	3.9
RH45	0.398	0.402	0.42	<DL	<DL	<DL	<DL	<DL	<DL	4.2	4.1	3.9
RH46	0.25	0.27	0.26	<DL	<DL	<DL	<DL	<DL	<DL	8.4	8.6	9
RH47	ND	ND	ND	<DL	<DL	<DL		<DL	<DL	ND	ND	ND
RH48	0.321	0.322	0.31	<DL	<DL	<DL	<DL	<DL	<DL	31	0.9	1
RH49	0.432	0.437	0.44	<DL	<DL	<DL	<DL	<DL	<DL	0	73	72
RH51	0.255	0.26	0.39	<DL	<DL	<DL	5889	5990	<DL	0.9	0.9	1
RH52	ND	ND	ND	<DL	<DL	<DL	1.3		<DL	ND	ND	ND
RH53	0.668	0.66	0.67	<DL	<DL	<DL	<DL		<DL	1	1	1
RH55	0.452	0.458	0.46	<DL	<DL	<DL	1.2	1.3		ND	ND	ND
RH57	0.464	0.311	0.32	<DL	<DL	<DL	<DL	8.68		12	ND	ND
RH62	0.609	0.34	0.09	<DL	<DL	<DL	<DL		<DL	3	0	290

Sample Code	Ni Winter	Ni Pre	Ni Post	Cd Winter	Cd Pre	Cd Post	Cr Winter	Cr Pre	Cr Post	Cu Winter	Cu Pre	Cu Post
RH63	0.571	0.237	0.3	<DL	<DL	<DL	987	1.97	<DL	6.3	6	0
RH67	0.833	0.839	0.78	<DL	<DL	<DL	16.9	17.8		1	0	0
RH70	0.9	0.91	0.94	<DL	<DL	<DL	19		19	1.8	2	2
RH73	0.459	0.44	0.47	<DL	<DL	<DL	1.06		<DL	1	1	1.6
RH74	0.094	0.96	0.94	<DL	<DL	<DL	<DL			3	2.8	2.7
RH76	0.02	0.019	0.02	<DL	<DL	<DL	<DL		<DL	2.7	2.5	3
RH77	0.512	0.497	0.51	<DL	<DL	<DL	4.9	5.12		8.3	8	68
RH80	0.778	0.79	0.78	<DL	<DL	<DL	<DL		19	1.3	1.3	2
RH83	ND	ND	ND	<DL	<DL	<DL	<DL	<DL	<DL	ND	ND	ND
RH95	0.34	0.333	0.34	<DL	<DL	<DL	0.89	0.96		2.9	3	2.8
RH100	0.296	0.41	0.42	<DL	<DL	<DL	<DL	<DL	6.41	10	9.2	4
RH103	0.2	0.206	0.21	<DL	<DL	<DL	<DL	<DL	<DL	ND	ND	ND
RH104	0.456	0.123	0.14	<DL	<DL	<DL	<DL	<DL	<DL	27	27	26
RH105	0.53	0.536	0.5	<DL	<DL	<DL	<DL	<DL	<DL	7.4	7	7.3
RH106	0.451	0.587	0.51	<DL	<DL	<DL	<DL	<DL	<DL	5.4	5	5.2
RH107	0.112	0.501	0.52	<DL	<DL	<DL	<DL	<DL	<DL	20	21	22
RH109	0.442	0.41	0.42	<DL	<DL	<DL	<DL	<DL	<DL	2	1.8	1.7
RH111	0.401	0.42	0.41	<DL	<DL	<DL	<DL	<DL	<DL	21	22	23
RH112	0.428	0.16	0.19	<DL	<DL	<DL	<DL	<DL	<DL	16	4	16

Sample Code	Ni Winter	Ni Pre	Ni Post	Cd Winter	Cd Pre	Cd Post	Cr Winter	Cr Pre	Cr Post	Cu Winter	Cu Pre	Cu Post
RH114	0.198	0.202		<DL	<DL	<DL	<DL	<DL	<DL	4.3	2	2.3
RH116	0.28	0.27	0.29	<DL	<DL	<DL	<DL	<DL	<DL	3.7	3.6	4
RH118	0.225	0.23	0.23	<DL	<DL	<DL	<DL	<DL	<DL	114	113	115
RH124	0.164	0.142	0.19	<DL	<DL	<DL	<DL	<DL	<DL	2	1.8	0
RH125	0.12	0.11	0.13	<DL	<DL	<DL	<DL	<DL	<DL	7	1	1
RH127	ND	ND	ND	<DL	<DL	<DL	<DL	<DL	<DL	0	1	1
RH128	0.103	0.13	0.12	<DL	<DL	<DL	<DL	<DL	<DL	1.8	1.6	2
RH131	0.171	0.16	0.18	<DL	<DL	<DL	<DL	<DL	<DL	0	1.9	2

Table 7.5: Trace metals (ppb) in winter season

Element	Pb	Cd	Mn	Cu	Zn	Fe	Co	As	Sr	Ni	Cr	Si	B
RH-19	<1	<1	<1	2	17	61	<1	2	104	2	6	1.5	21
RH-69	<1	<1	17	13	170	207	<1	3	367	9	11	3.0	32
RH-124	<1	<1	142	1	16	228	1	8	371	2	26	4.5	31
RH-49H	<1	<1	<1	2	44	37	<1	0	75	<1	5	7.3	8
RH-6	<1	<1	4	144	95	236	<1	2	262	4	31	5.0	335

Table 7.6: WHO and BIS standards for drinking water quality

S. No.	Parameter	WHO Guidelines (World health Organization)		BIS Guidelines: (IS 10500:1991)		Winter		Summer		Post	
		Desirable limit	Maximum permissible limit	Desirable limit	Maximum permissible limit	Range	Mean	Range	Mean	Range	Mean
1	Colour			5 HZ(Hazen Unit)	5 HZ(Hazen Unit)						
2	Odour			Unobjectionable	Unobjectionable						
1.	Temperature	-	40^0C	-	-	6.3 -26.4	20.5	18.7-29.4	25	21.6-33.5	26
2.	pH	-	6.5-8.5	6.5 -8.5	No Relaxation	6- 8.74	7.2	4.4-8.6	7.3	6-8.6	7.4
3.	Conductivity	-	2250	-	-	131-1392	351.3	116-1703	545	119-986	469
4.	TDS	-	1000mg/l	500mg/l	2000mg/l	91-796	351	74 - 881	325	75-651	277
5.	DO	-	-	-		0.3-16	7	1.5 – 10.6	5.3	1.8 - 10	5.7
6.	Hardness total			300	600mg/l	10.7-895	203	90-694	243	33 - 320	135
7.	Alkalinity	200	600	200	600mg/l	21-567	186	94 - 460	232	35 - 337	171
8.	Ca	75	200	-	200mg/l	3.6-267	59	26 - 182	64	13 - 120	50
9.	Mg	-	150	-	100mg/l	0.5-62	15	5.2 - 68	22	1 - 41	16
10	Na	-	200	--	-	1.4-39.5	9.6	0.1 - 34	9.4	0.8 - 23	6.5
11	K	-	50	-	-	0.1-74	4.4	0.2 – 22.5	4.8	0.2 - 19.5	3
12.	Si	-	-	-		1.8-21	7.7	0.7 – 15.8	4.6	1.2 - 33	7.7
13	F	-	1.5	1mg/l	1.5 mg/l	0.001-4.1	0.3	0.03 - 11	0.3	0.001- 6.8	0.3
14	Cl	-	250 mg/l	250 mg/l	1000 mg/l	0.02-70.4	12.5	0.007- 61	14	0.7 - 65	10.3
15	NO_3		10 mg/l	45 mg/l	100 mg/l	0.001-263	16.3	0.001- 242	21.3	0.001 – 67.4	10.4
16	PO_4	-	0.3mg/l	-	-	0.001-18	0.65	0.02-4.2	0.24	0.001-22	0.4
17	SO_4	-	400 mg/l	200 mg/l	400 mg/l	0.01-861	71	0.12 – 443.2	72	0.2 - 246	52
18	Fe	0.3 mg/l	1.0or 1000ppb	0.3mgl	1 mg/l or 1000ppb	37-236 (ppb)	154				
19	Zn		5 mg/l or (5000ppb)	5 mg/l	15 mg/l	16-170 (ppb)	68				
20	Cd		0.005 mg/l or 5ppb	0.01 mg/l or 10ppb	10ppb	<DL	<DL				

S. No.	Parameter	WHO Guidelines (World health Organization)		BIS Guidelines: (IS 10500:1991)		Winter		Summer		Post	
		Desirable limit	Maximum permissible limit	Desirable limit	Maximum permissible limit	Range	Mean	Range	Mean	Range	Mean
21	Pb	0.05	-	0.05mg/l or 50 ppb	No Relaxation	<1	<1				
22	Cr	0.05 mg/l or 50ppb)	-	0.05mg/l	No Relaxation	0.022-461 (ppb)	461 (ppb)	0.02- 603	603	0.21-521	520
23.	Cu	0.05 mg/l(50ppb)	1.5 mg/l or 1500 ppb	0.05mg/l	1.5 mg/l or (1500ppb)	1-13.4	13.4	1-12 (ppb)	12	1-19	19
25.	Mn	0.1 mg/l (100ppb)	0.3 or 300 ppb	0.1mg/l	0.3 mg/l or 300mg/l 100 ppb	4-142	54.3				
26	Al				200ppb						
27	As			50ppb	No Relaxation	2-8	3				
28	Hg			1ppb	No Relaxation						
30	CN			0.05mg/l	No Relaxation						
	Total Coliform Bacterial			95% of samples should not contain coliform in 100 ml – 10 coliform/100ml		3.1->2419		3.1- > 2419		2-1011	
	E- Coliform			Nil/100 ml of water		1.5->2419		3.1 - > 2419		1-1668	

Table 7.7: Water quality classes for Agricultural Used of Dehradun and Haridwar district during three different seasons (Sundaray S.K., 2009).

Parameter	Rate of Hazard	Range Present Study	Mean Value Present Study	Water Class
1. pH	6.5-8.4, 5.1- 6.4 and 8.5 to 9.5, 0-5.0 and 9.5	6 – 8.7	7.2	No problem Moderate Severe
2. EC µs/cm (Salinity hazard)	<250 250- 750 750 – 2250 2250- 5000	131- 1392	541	Excellent Good Permissible Unsuitable
3. TDS Mg/l	200- 500 500 – 1,500 1,500 – 3,000	91 - 796	354	Good Permissible Unsuitable
4. Cl Meq/l	< 4 4 – 10 >10	7 – 7.9	3.5	No Problem Moderate Severe
5. NO_3–N (mg/l)	<5 5-30 >30	0.004- 263	18	No Problem Moderate Severe
6. Hardness (mg/l)	0-60 60-120 120- 1800 >1800	10- 895	207	Soft Moderate soft Hard Very hard
7. Na % When Na, K, Ca, Mg ions in meq/l	<20 20-40 40- 60 60- 80 >80	0.5 - 43	12.8	Excellent Good Permissible Doubtful Unsuitable
8. SAR Where Na, Ca, Mg as meq/l	<10 10- 18 18- 26 >26	0.5 - 31	7.6	Excellent Good Fair Poor
9. R.S.C. Meq/l	< 1.25 1.25-2.50 >2.50	5.3 – 8.6	1.3	Soft Permissible Unsuitable
10. PI	Class I >75% Class II50-75% Class iii < 25%	99% -8.7 %	55%	Excellent Good Unsuitable

Table 7.8: The tolerance limit (IS 100500-1991) for agricultural use

S.N.	Parameter	Tolerance Limit	Range (Present Study)
1.	pH	5.5-9.0	6 – 8.7
2.	EC	3,000 µs/cm	131 - 1392
3.	Cl	600 mg/l	0.02 – 70.4
4.	TDS	2100 mg/l	91 – 796
5.	SO_4	1,000 mg/l	0.01 – 860.7
6.	Na%	60 mg/l	0.5 - 43

7.4 WATER QUALITY FOR IRRIGATION USE

The suitability of surface and ground water samples for irrigation use depend upon the minerals constituents present in water. The major physico- chemical parameters, which control the suitability of river water for irrigation are pH, EC, TDS, Hardness, chloride, sulphate, carbonate, bicarbonate, nitrate, sodium, potassium, calcium magnesium etc. Silica, iron, boron are usually present in very small amounts and analyzed under special circumstances, for example when industrial waste alone to be used for irrigation.

7.4.1   pH

The normal pH range for irrigation water is from 5.5 to 8.4. Irrigation water with a pH outside the normal range may cause nutritional imbalance or may contain a toxic ion. The pH of the water of study area is slightly alkaline in nature in most of the places. The pH in surface and groundwater area ranges from 6 to 8.7 with an average value of 7.2 in winter season, 7.3 during summer season and 7.4 during post monsoon season . The water for irrigation use in the study area found under moderate to no problem category (Table 7.10).

7.4.2   EC (Salinity Hazard)

Electrical conductivity is an important measure of salinity hazard for crops in determining the suitability of water for irrigation use as it reflect the TDS in water. (Rajanath 1987 and Irrigation using river water with high TDS can add salt concentration to the soil and problem enhance, if the added salt

accumulate to concentration that is harmful to a crop or landscape. Salinity of surface and groundwater used for irrigation water can be determined by EC. According to Langenegger (1990), the importance of EC is its measure of salinity. The EC for water is expressed as micro siemens per centimeter. The tolerance limit of EC according to (ISI 1974 Standard) is 3,000 µs/cm.

Excess salinity reduce the osmotic activity of plants and thus interferes with the adsorption of water and nutrient from the soil (Saleh et al. 1999).

Table 7.9: Quality of irrigation water based on electrical conductivity.

EC (µs/cm)	Water class
>250	Excellent
250-750	Good
750-2000	Permissible
2000-3000	Doubtful
>3000	Unsuitable

Based on above classification (Table 7.9) of irrigation quality, 5 samples were found to be in excellent category and 2 samples are categorized under good category in Dehradun industrial area. In agricultural area of Dehradun 17 samples falls under good, 11 samples under excellent and 2 samples falls under permissible class.

In urban area of Dehradun district, 11samples falls in good category and 5 samples falls under permissible category. In surface water of Dehradun 5 samples falls in excellent category, 19 samples falls in good category and 13 samples falls in permissible category of irrigation purposes.

In Rishikesh all 4 samples of groundwater falls under good category. Among surface water (Ganga river) 2 samples are categorized under excellent and one samples categorized under good category for irrigation quality.

In industrial area of Haridwar district, 5 samples of groundwater falls under good category and one under permissible category for irrigation purposes. In

the agricultural area of Haridwar district 6 samples falls under good category and 2 samples falls under permissible category for irrigation purposes.

Among groundwater of urban area of Haridwar district 10 samples falls under good category and one sample falls under excellent category. Among surface water of (Ganga river) Haridwar, 4 samples falls under good and one sample fall under excellent category of irrigation quality.

The EC value in all sampling locations in all three season found under excellent to permissible category of irrigation water quality as per BIS guidelines (1991)

7.4.3   TDS

The TDS concentration in study area varies from 74mg/l to 818 mg/l in all three season with mean value of 351 mg/l in winter season, 325 mg/l in summer season and 276mg/l in post monsoon season. In comparison to BIS standards for irrigation water quality TDS in all sampling location falls under good to permissible limit and water is suitable for irrigation purposes (Table 7.10).

7.4.4   Chloride

The most common toxicity in the irrigation water is from Chloride. Chloride is not adsorbed or held back by the soils, therefore it moves readily with the soil water. From soil water it is taken up by the crops and moves in the transpiration stream and accumulates in the leaves. If the chloride concentration in the leaves exceed the tolerance of crop, injury symptoms develop such as leaf burn or drying of leaf tissue.

According to irrigation water quality BIS standard, the water having the chloride concentration less than 4meq/l is suitable for irrigation purposes. It has been observed that the chloride concentration in all sampling location of the study area are less than 4meq/l indicating its suitability for irrigation purposes.

This is further substantiated by the chloride concentration falling under tolerance limit of BSI 1991 standards for irrigation purposes in all the sampling location of the study area.

7.4.5 Sulphate

A source of sulphate ion in water environment is mainly from acid mine drainage. A number of crops show sensitivity to very high concentration of sulphate in the irrigation water, but it is likely that this sensitivity is related to the tendency of high sulphate concentration to limit the uptake of calcium by plants. This decrease in the uptake of calcium is associated, on the other hand, with relative increase in the absorption of sodium and potassium (Tiwari and Manzoor 1988 a).

In the entire study area, the sulphate concentration in winter varies from 0.001mg/l to 861mg/l with a mean value of 71mg/l. Although its concentration varies from 0.12mg/l to 443mg/l during summer season, its mean concentration remained 72mg/l. However, in post monsoon season its concentration varies from 0.2mg/l to 246mg/l with mean value of 52mg/l. Thus the sulphate content are within tolerance limit of or BIS (1991) standards for irrigation water quality in entire study area during three season.

7.4.6 Nitrate

The source of N_2 are natural soil nitrogen or added fertilizer, but nitrogen in irrigation water has much the same effect as soil applied fertilizer nitrogen and an excess will cause problems, just as too much fertilizer would. . If excessive quantities are present or applied production of several commonly grown crops may be upset because of over –stimulation of growth, delayed maturity or poor quality. Sensitive crops may be affected by nitrogen concentration above 5 mg/l. Most of the crop relatively unaffected until nitrogen exceeds 30 mg/l (Ayres and Westcot 1994).

The nitrate concentration in study area varies from 0.004 mg/l to 263 mg/l with a mean value of 16.5 mg/l in winter season, 21mg/l during summer and 11mg/l in post monsoon season.

In industrial area of Dehradun one sample was found to be under no problem category (NO_3<5mg/l), 6 samples falls under moderate category (5mg/l-30mg/l). In agricultural area of Dehradun, 11 samples of groundwater falls under no problem category, 17 samples falls under moderate category and 2 samples (RH91 and RH89) falls under severe category (NO_3 >30 mg/L). In urban area of Doon , 1 sample falls under no problem category, 10 samples falls under moderate category and 6 samples falls under severe category as per BIS standards for irrigation water quality.

In surface water of Dehradun, 14 samples falls under no problem category, 23 samples falls under moderate category and 6 samples falls under severe category.

In Haridwar industrial area, all 5 samples falls under moderate category and one samples falls under no problem category while in agricultural area, 3 ground water samples falls under moderate category. In urban area of Haridwar district, 5 samples falls under no problem category and 4 samples falls under moderate category of irrigation water quality.

Among the surface water (Ganga river) at Haridwar, all 5 samples falls under no problem category and two samples falls under moderate category. In Rishikesh groundwater one samples falls under no problem category and 3 samples fall under moderate category while in Ganga river at Rishikesh all 4 samples falls under no problem category.

7.4.7   Hardness

The groundwater of industrial area of Dehradun, is classified as soft to moderately soft water. In agricultural area of Dehradun district, 5 samples falls under soft and moderately soft water category, 6 samples falls under hard water category and 8 samples under very hard water (Table 7.10).

In urban area, 10 samples of groundwater are categorized under very hard and 5 samples falls under hard water category. Among surface water of Dehradun, 2 samples are categorized as soft water, 5 samples as moderately soft, 3

samples are categorized under hard and 25 samples under very hard water category.

In industrial area of Haridwar district, all 6 samples falls under very hard water category and in agricultural area of Haridwar district, 4 samples falls under moderately hard category and 7 samples falls under very hard category and 1 samples under hard water. In urban area of Haridwar, 4 samples falls under moderately hard water category, 2 samples falls under very hard category and 1 samples falls under hard water category.

7.5   SODIUM (Na)

The sodium hazard of irrigation water is usually specified as two sodium related indices named as Sodium Absorption Ratio (SAR) and sodium percent (Na%).

7.5.1   Sodium Percent (Na%)

Wilcox (1948) proposed a method for rating irrigation waters quality based on percentage of sodium and electric conductivity. The water is classified into five categories for irrigation purpose i.e. excellent to good, good to permissible, permissible to doubtful, doubtful to unsuitable. The Na percentage is calculated on the basis of electrical conductivity and sodium percentage in study area as per the following formula. Where all the ionic concentration are express in μeq./L.

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

The Na % in all sampling location of Dehradun and Haridwar district are found to be less then 40% indicating excellent to good category of irrigation water (Table 7.10, Fig. 7.21).

7.5.2   Sodium Absorption Ratio (SAR)

The sodium adsorption ratio (SAR) of groundwater is an important parameter for determining the suitability for irrigation purposes because it is a measure of alkali/sodium hazard to crop.

The SAR has been recommended by the U.S. salinity laboratory staff (1954) for assessing the suitability of water for irrigation purpose. Excess sodium in water produces the undesirable effect of changing soil properties and reducing soil permeability (Kelly 1951).

High sodium concentration lead to development of an alkaline soil. The sodium or alkali hazard of water for irrigation purposes is determined by the absolute and relative concentration of cations (Na, Ca and Mg) and is expressed in terms of sodium absorption ratio. High concentration of sodium in soil affects its physical condition and soil structure resulting in formation of crusts, water logging and reduced soil permeability. The excessive concentration of sodium in soil may also be toxic to certain types of crops.

SAR gives a reliable assessment of water quality for irrigation purposes with respect to sodium hazard since it is more closely related to exchangeable sodium percentage in soil than the simple sodium percentage (Tiwari and Manzoor 1988).

The SAR can be computed as (Karanath, 1987).

$$SAR = \frac{Na^+}{\left(\dfrac{Ca^{2+} + Mg^{2+}}{2}\right)^{\frac{1}{2}}}$$

Where the concentrations are in meq./L.

The water in Dehradun and Haridwar district has been classified in relation to irrigation based on ranges of SAR values (Table 7.10, Fig. 7.20).

The SAR value at all the sampling location in surface and ground water is less than 18 at R H90(SAR -31), RH 72- (SAR- 20) and RH88-(SAR- 26) and thus belong to good to excellent category for irrigation purposes.

7.5.3   Residual Sodium Carbonate (RSC)

When total carbonate levels exceed the total amount of calcium and magnesium, the water quality may be deteriorated. The excess carbonate

(residual) combines with calcium and magnesium and form a solid material (scale) which settle down, as in case of waters of Dehradun district. The relative abundance of sodium with respect to alkaline earths and boron and the quantity of bicarbonate and carbonate in excess of alkaline earth also influence the suitability of water for irrigation. This excess is denoted by "Residual Sodium Carbonate" (RSC) and is determined by the following equation, suggested by Ricahrds (1954).

RSC given by this relation:

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

The water with high RSC has high pH and land irrigated by such waters becomes infertile owing to deposition of sodium carbonate as evident from the black color of soil. (Eaton 1950). Negative RSC at some locations indicate in complete precipitation of calcium and magnesium (Tiwari and Manzoor 1988b)

In Dehradun district, out of 85 samples 27 samples falls under unsuitable category and rest under permissible category for irrigation. In Haridwar district 22 samples, particularly of in the industrial area, falls under unsuitable category and rest under permissible category.

7.5.4 Permeability Index (PI)

The long term use of irrigation water having high Na, Ca and bicarbonate content affect soil permeability. The suitability of water for irrigation purpose can also be assessed using permeability index developed by Doneer (1984) as expressed below.

$$PI = \frac{Na + \sqrt{HCO_3}}{Ca + Mg + Na} \times 100$$

Where ionic concentrations are expressed in µeq./L.

Accordingly water can be classified as Class I, Class II and Class III. Class I and Class II water with 50 -75% or more of permeability index   are

categorized as good for irrigation. Class III waters with 25% of maximum permeability index are unsuitable. (Fig. 7.26)

The PI values at all the sampling locations in Dehradun and Haridwar district found to between 25%- 100% indicating good and excellent and good category of irrigation purposes except 5 sampling locations (RH107, RH111, RH112, RH110) which are found to be under class III (<25%) category.

7.5.5 Chloroalkaline indices (CAI)

The changes brought about in the chemical composition of the ground water during its underground movement is essential to know the dissolution of undesirable constituents in water and various changes undergone by water during its underground flow (Johnson 1979 and Sastri 1994).

The ion exchange between the ground water and its surrounding rocks during residence or travel can be understood by studying the chloroalkaline indices developed by Schollor (1967).

$$CAI - I = \frac{Cl - Na + K}{Cl}$$

$$CAI - II = \frac{Cl - (Na + K)}{SO_4 + HCO_3 + CO_3 + NO_3}$$

CAI are negative when there is exchange between sodium and potassium (Na + K) in water with calcium and magnesium (Ca+Mg) in rocks. The positive CAI indicate no base exchange.

In urban area of Dehradun, the ratio of CAI - I and CAI – II is negative in all sampling location. However in agricultural area of Dehradun the ratio of CAI-I and CAI – II is found positive in 10 sampling location and in surface water ratio is positive in 9 sampling location.

In Haridwar the ratio of CAI – I and CAI – II is found positive in 3 sampling locations in industrial area, 1 sampling location in urban area and in surface

water the ratio is negative in all sampling locations indicating base exchange between Na, K and Ca and Mg.

In surface and ground water of Rishikesh the ratio is negative in all sampling locations.

7.5.6 Graphical Methods of Representing Analysis

Many graphical methods are available to assess the water quality for irrigation purposes using total dissolved solid concentration and relative proportion of certain major ions (Hem 1989, Guler et al 2002). Of the several diagrams Wilcox and U.S. Salinity diagram are used in the present study to assess the suitability of water of Dehradun and Haridwar district for irrigation purposes.

1. **U.S. Salinity Diagram:** The US salinity diagram is based on the integrated effect of EC and SAR, in which EC is taken as salinity hazard and SAR is taken as alkalinity hazards. The SAR and EC values of water samples of Dehradun and Haridwar district were plotted in the graphical diagram (Fig 7.20) of irrigation water (US Salinity Laboratory 1954). Based on the graphical representation of US salinity diagram most of the samples falls into C1S1(low salinity with low sodium) and C2S2(medium salinity with medium sodium) categories. However, 5 samples falls under C3S3 (high salinity and high sodium) possibly due to contamination of water from the anthropogenic sources i.e urban waste, industrial waste and chemical fertilizers etc.

2. **Wilcox Diagram:** The Na% is plotted against conductivity, which is designated as a Wilcox diagram (Wilcox 1955). According to Wilcox diagram (Fig 7.23) almost all the samples of Dehradun and Haridwar district falls into "Excellent to Good" category.
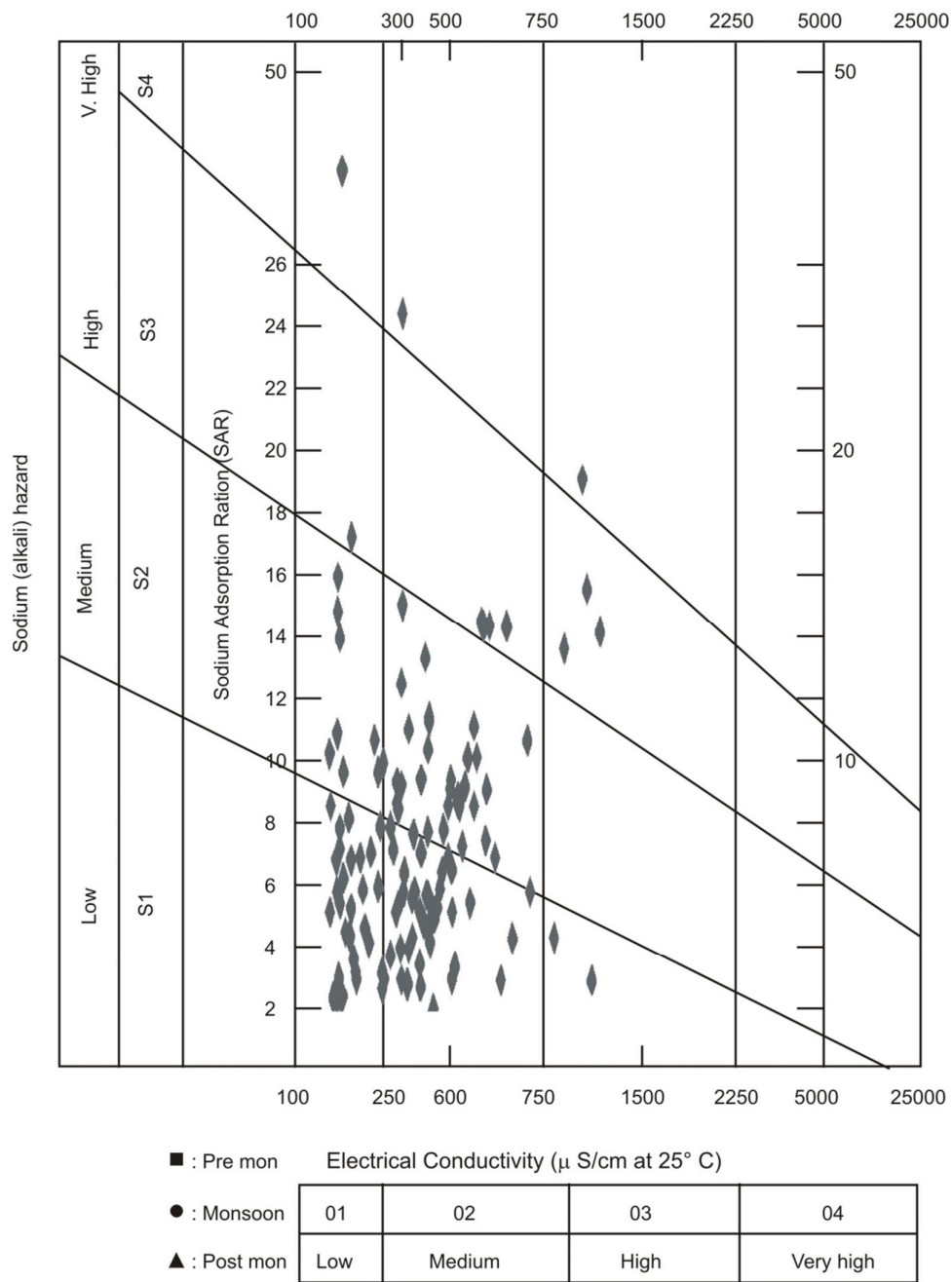
Fig. 7.20: US Salinity Laboratory classification of Surface and Ground water of Dehradun and Haridwar districts.
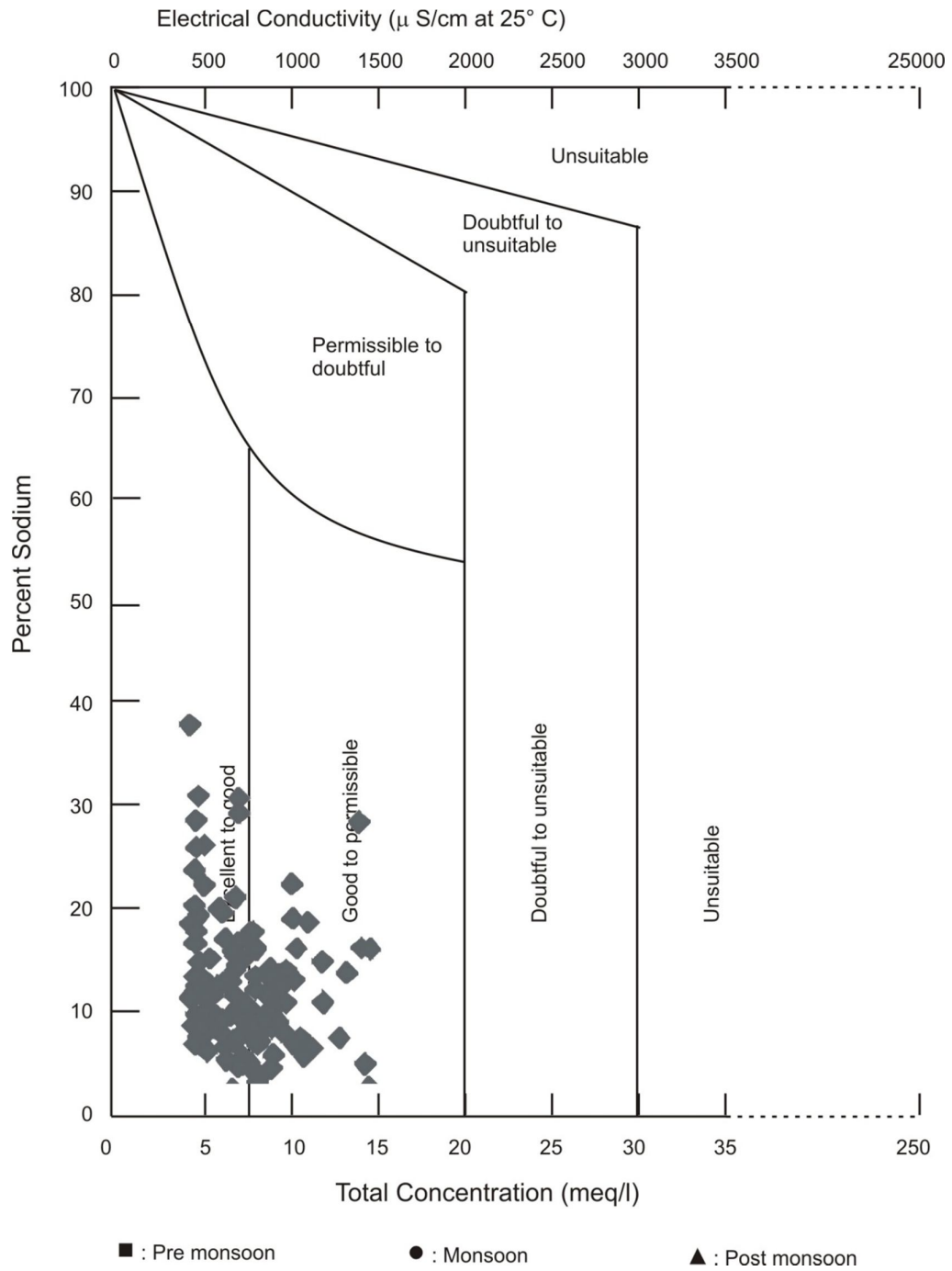
Fig. 7.21: Wilcox diagram for classification of Surface and Ground water of Dehradun and Haridwar districts.
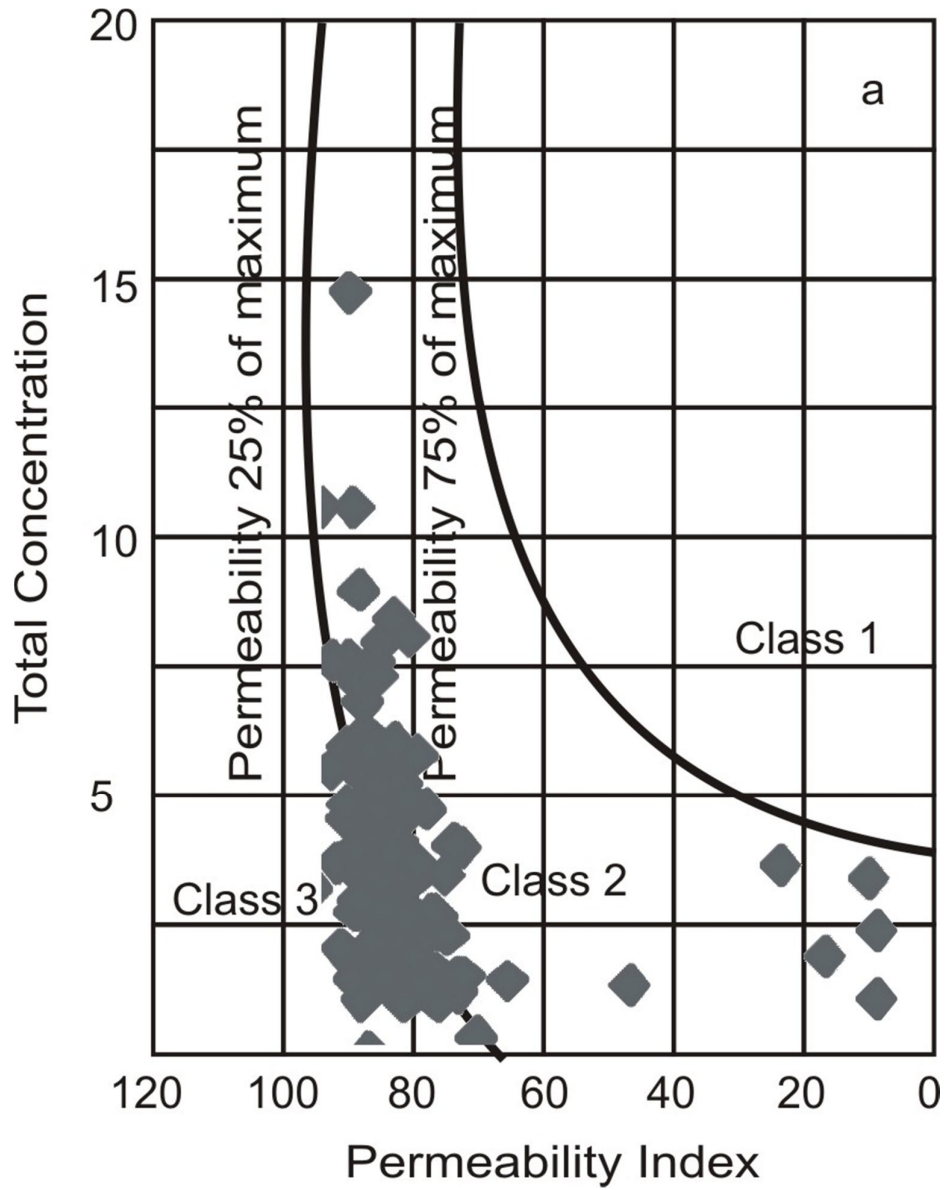
Fig. 7.22: Permeability Index Diagram for classification of Surface and Ground water of Dehradun and Haridwar districts.

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Table 7.10: Irrigation water quality parameter

Sample	pH	Ecμs/cm	TDS(mg/l)	Cl meq/l	NO3(mg/l)	SO4 mg/l	Hardness mg/l	Na%	RSC	PI %	CAI I	CAI II	SAR %
RH1	7.24	558	369	3.69	11.3	3.02	215.23	9.884179	1.453912	47.73264	87.8	92.987	7.017
RH2	7.24	523	346	3.46	13.68	7.3	234.78	10.48749	0.207564	44.81968	121	125.12	7.69
RH3	7.1	618	405	4.05	22.5	3.04	250.32	6.204186	0.575346	50.77102	176	177.65	4.685
RH4	7	582	380	3.8	11.6	1.3	226.5	7.558796	1.61395	45.44766	93.1	96.962	5.519
RH5	7.12	605	395	3.95	13.9	0.9	267.18	6.732164	1.078043	51.52625	36.3	45.063	5.142
RH6	7.7	862	555	5.55	0	0.01	274.4	13.47014	2.899599	49.64363	1099	1100	9.255
RH7	7.2	645	423	4.23	35	9.3	231.54	7.87766	1.840176	39.98539	377	377.92	5.719
RH8	6.93	1225	740	7.4	263	66.4	354.14	14.27593	1.156684	49.99938	1985	1985.8	14.28
RH9	7.44	753	493	4.93	50	13.78	253.64	13.97159	1.673924	42.41873	519	520.32	9.234
RH10	6.85	603	396	3.96	8.5	18.2	257.18	5.84445	0.897765	54.69752	1117	1117	4.525
RH11	7.1	414	288	2.88	7.7	14.32	165.44	13.29857	0.404674	55.43972	1001	1001.2	7.927
RH12	6.9	1330	796	7.96	20	5.8	286.94	17.28084	5.160447	51.30018	289	293.22	16.39
RH13	7.1	590	381	3.81	38	17.4	218.18	13.89928	1.133298	57.46728	393	394.77	10.68
RH14	7	500	332	3.32	31.4	15.1	180.84	15.87148	1.103498	71.03074	354	355.83	11.4
RH15	7.7	185	129	1.29	1.3	21.8	79.07	6.727393	0.361637	73.95573	33.5	36.605	1.878
RH16	7.8	192	136	1.36	1.3	21.5	76.74	6.893938	0.426344	68.67008	30.4	33.785	1.895
RH17	8.3	227	157	1.57	1.8	27.8	93.18	11.83901	0.561511	68.64524	36.2	42.197	4.025
RH18	8.3	205	143	1.43	1.9	28	92.37	12.27046	0.396844	64.29748	42.4	47.833	4.209
RH19	7.4	415	280	2.8	1	21.7	137.34	9.220356	1.151545	45.08643	160	161.84	3.337
RH20	7.2	700	470	4.7	9	24.3	270.894	9.81976	1.008875	76.49005	487	488.19	6.42
RH21	7.2	558	370	3.7	1.92	23	96.11	19.16205	1.125248	53.44594	20	33.665	9.63
RH22	8.54	377	254	2.54	16	20	150.1	5.628563	1.403358	58.46185	273	273.57	2.75
RH23	8.54	377	254	2.54	2.84	24.5	117.24	6.822176	0.439098	61.44121	62.1	64.808	2.155
RH24	7.9	166	236	2.36	1.8	25.6	105.32	5.944864	0.374411	63.59434	39.1	42.252	1.775
RH25	7.4	286	419	4.19	9.8	27.6	112.16	11.57061	1.404	44.16388	187	188.88	5.704
RH26	7.33	517	346	3.46	13.73	29.14	236.48	8.66971	0.966711	38.59892	309	310.2	4.005
RH27	8.1	385	615	6.15	6.6	98.7	209.98	4.09835	1.117039	37.65359	111	112.8	2.487

Sample	pH	Ecµs/cm	TDS(mg/l)	Cl meq/l	NO3(mg/l)	SO4 mg/l	Hardness mg/l	Na%	RSC	PI %	CAI I	CAI II	SAR %
RH28	8.24	494	329	3.29	6.2	93.2	243.04	3.748723	1.051827	34.78374	96.8	98.693	2.337
RH29	7.6	555	370	3.7	4.3	101.6	291.44	3.102291	0.915408	66.67211	73.6	76.132	2.23
RH30	6.4	232	155	1.55	10	20	93.87	11.35076	0.382837	74.39244	131	132.46	5.044
RH31	6.31	181	125	1.25	7.2	17	70.37	12.67548	0.213869	72.65787	140	140.91	5.208
RH32A	6.2	173	119	1.19	9.4	16.5	71.6	9.392498	0.270656	54.68026	88.6	90.172	2.531
RH33	8.36	252	180	1.8	1.1	41.3	101.87	7.456419	0.185815	55.84757	111	112.75	2.762
RH34	7.4	299	201	2.01	7.8	27	141.25	7.947397	0.679823	56.77451	102	104.29	4.284
RH35	7.5	295	202	2.02	8	27.2	137.38	8.152331	0.661533	84.00273	111	112.75	4.341
RH36	7.76	148	103	1.03	0.006	20	60.54	11.30864	0.318973	83.18547	77	78.878	1.822
RH37	7.73	156	105	1.05	0.8	22.4	61.67	8.090086	0.328397	82	60.3	61.988	1.935
RH38	7.36	552	365	3.65			207.37	7.575903	0	42.38029	86.4	90.196	4.953
RH39	7.28	600	392	3.92	4.7	99	205.02	6.461889	2.210782	44.16887	98.7	101.48	3.81
RH40	8.01	315	201	2.01	6	60	107.08	9.245707	2.405741	61.23524	261	262.25	3.781
RH41	7.1	367	244	2.44	4.6	29.24	143.16	13.08739	0.553031	56.56627	278	279.13	7.947
RH42	7.22	256	175	1.75	17.8	36.2	123.95	5.095805	1.03762	53.65478	32.9	36.62	2.495
RH 43	8.38	614	429	4.29	9.3	38.7	295.3	2.225417	1.044505	25.80761	51	53.575	1.46
RH44	7.35	595	384	3.84	5.2	201	141.08	17.01035	2.832011	60.73393	209	211.39	11.83
RH45	7.2	595	390	3.9	14.3	35.1	138.64	17.23396	3.062772	70.14443	157	160.62	11.72
RH46	7.6	234	159	1.59	4.1	0	102.22	29.41567	3.750224	81.90999	105	112.48	18.27
RH47	6.9	446	366	3.66	0	0.003	157.03	14.58865	1.40739	62.32116	105	109.88	9.529
RH48	7.3	684	440	4.4	6.3	26	150.8	13.79928	2.425961	54.32551	396	397.62	8.672
RH49	6.47	323	214	2.14	13.9	77	123.95	12.73689	1.308673	59.31956	230	231.18	7.006
RH50	6.43	179	125	1.25	21.4	30	67.65	17.81226	1.224833	76.42553	41.7	47.763	7.915
RH51	6.53	340	219	2.19	8.4	21	81.9	21.90125	0.337046	73.56605	166	169.04	11.02
RH52	7.38	195	133	1.33	19.2	31	86.41	21.08066	0.071583	68.34887	41.4	50.516	9.886
RH53	6.84	168	114	1.14	5.6	26.3	68.82	26.4427	0.077616	82.12548	47.4	56.11	11.26
RH54	6.2	171	116	1.16	0.2	22	57.62	32.3796	0.459867	91.92604	95.9	101.2	16.86
RH55	6.42	179	121	1.21	17	12.6	66.74	29.13695	0.462177	87.34111	49.7	58.944	14.65

Sample	pH	Ecµs/cm	TDS(mg/l)	Cl meq/l	NO3(mg/l)	SO4 mg/l	Hardness mg/l	Na%	RSC	PI %	CAI I	CAI II	SAR %
RH56	8.74	703	447	4.47	9	23.3	237.3	7.744622	0.469278	37.74098	609	609.22	4.925
RH57	7	528	335	3.35	20.8	84.8	216.68	8.430034	1.241205	45.36624	115	118.68	5.628
RH58	7.3	695	434	4.34	2.8	76	149.18	14.78607	1.301143	50.97368	450	451.18	9.588
RH59	6.61	476	309	3.09	6.8	65.13	206.16	9.124486	2.205047	52.59749	215	217.12	5.628
RH60	8.27	729	464	4.64	6.4	31	308.03	11.58942	1.991609	39.27933	557	558.41	8.821
RH61	6.8	480	312	3.12	22.1	84.32	219.95	10.40378	1.872245	48.60789	284	286.21	6.3
RH62	8.14	728	464	4.64	3.6	33.2	303.45	11.97664	1.327186	40.77559	559	560.1	8.983
RH63	7.5	737	469	4.69	18.72	81.38	306.61	11.71246	2.06452	38.89293	566	567.15	8.676
RH64	6.7	516	337	3.37	27.5	85.3	233.72	10.65726	1.539277	41.28919	354	355.31	5.386
RH65	6.49	245	153	1.53	20.08	60.8	59.02	9.855751	0.766523	97.31145	33	36.576	3.22
RH66	7.33	763	477	4.77	0.2	0.2	317.15	13.20699	0.794249	37.24531	600	601.53	9.372
RH67	7.66	850	521	5.21	1.94	110.04	304.41	20.72805	1.256395	41.65669	849	851.12	15.06
RH68	7.58	817	501	5.01	83.8	110.63	324.24	14.19115	1.257675	39.78058	727	728.48	10.43
RH69	6.65	572	358	3.58	40.14	88.07	269.22	6.703775	1.97849	28.63561	213	214.6	4.472
RH70	6.59	587	359	3.59	11	182	271.52	6.191626	-0.25853	29.0957	207	208.68	4.318
RH71	7.15	662	413	4.13	9.31	193	155.39	11.80242	-0.20826	52.24312	281	281.97	7.83
RH72	7.62	1309	761	7.61	21	52.46	359.42	32.17688	2.832783	51.76099	1538	1539.9	20.33
RH74	7.25	750	455	4.55	0	63.3		8.497748	6.151561	#DIV/0!	622	623.33	7.24
RH75	7.64	903	553	5.53	9.3	144	425.34	6.715806	0	32.78396	614	614.88	6.851
RH76	7.6	466	366	3.66	29.3	168.5	448.7	15.22002	2.807856	30.38734	395	397.58	13.03
RH77	7.3	684	440	4.4	31.4	164.5	260.61	9.796342	1.465504	45.84309	96.5	101.45	6.811
RH78	7.17	446	310	3.1	13.9	77	229.5	16.24662	2.845207	48.12441	427	428.3	8.792
RH79	6.5	441	307	3.07	0.1	49.02	196.32	6.280274	1.903707	46.67741	210	211.5	4.913
RH80	7.9	589	405	4.05	24.39	57	310.14	12.31048	0.491282	38.52169	141	143.73	7.773
RH81	7.03	466	323	3.23	13.5	77.4	155.2	17.89625	1.823521	61.00255	24.8	36.482	9.411
RH82	6.16	222	157	1.57	8.1	0.03	96.6	7.88693	2.481584	79.58172	-17.3	8.387	4.056
RH83	6.17	358	251	2.51	2.1	0.03	123.29	8.696263	1.245289	69.02578	133	136.15	5.78
RH84	7.68	449	311	3.11	0.05	0.009	206.19	11.61134	1.131537	44.67577	-12.4	9.4811	5.074

Sample	pH	Ecµs/cm	TDS(mg/l)	Cl meq/l	NO3(mg/l)	SO4 mg/l	Hardness mg/l	Na%	RSC	PI %	CAI I	CAI II	SAR %
RH85	6.34	232	165	1.65	9.55	61.2	77.45	24.72954	0.647116	87.22269	-63.4	5.4779	6.763
RH86	6.65	275	195	1.95	1.9	0.01	57.55	15.97989	0.68804	125.3094	48.7	53.448	6.836
RH87	6.67	221	159	1.59	0.1	0.03	67.06	13.70377	1.758846	95.42304	92.4	96.909	8.256
RH88	6.12	471	323	3.23	3.6	0.04	138.4	34.94564	0.756657	63.00332	1154	1154.7	26.21
RH89	6.12	471	323	3.23	7.24	32.84	168.9	33.22325	1.149309	63.89244	240	242.23	15.84
RH90	6	190	136	1.36	41	29	53.86	35.23826	0.860735	93.05025	1630	1631.1	31.34
RH91	7.14	840	549	5.49	33.13	0.001	164.82	24.83961	0.309796	65.05534	984	984.13	15.23
RH92	6.29	429	296	2.96	25.5	44.48	108.73	16.77525	0.650483	59.37027	86.5	88.995	7.109
RH93	6.25	165	117	1.17	33.4	21.96	57.16	13.84417	-0.07183	89.40293	66	68.975	5.624
RH94	6.55	164	115	1.15	12.7	18.1	63.843	17.82324	0.20761	80.08653	102	104.2	6.79
RH95	6.3	137	99	0.99	6.53	20.1	49.88	20.14898	0.305223	95.6441	301	301.63	8.687
RH96	6.14	195	141	1.41	0.78	15	60.86	15.54672	0.376416	83.35874	54.9	59.093	6.113
RH97	6.49	178	128	1.28	10	18	67.45	19.28391	0.098156	78.43507	41.5	47.762	7.161
RH98	6.66	131	91	0.91	3	30	62.78	43.65839	-0.02312	73.98946	-303	0.0929	10.55
RH99	6.39	451	336	3.36	2.2	37	10.69	23.28019	-0.13849	198.8674	139	140.79	8.581
RH100	8.66	133	185	1.85	0	0.9	47.39	11.34381	0.204622	106.7742	677	676.84	4.903
RH101	6.87	358	247	2.47	0.3	2.4	83.41	21.46067	0.459794	63.09218	94.9	98.538	9.874
RH102	6.34	170	120	1.2	6	6.9	67.62	22.30225	-0.22224	99.16116	554	555.45	15.61
RH103	6.11	382	257	2.57	2.9	1.3	185.94	18.31719	1.189735	51.57904	288	290.36	10.22
RH104	7.21	715	463	4.63	14.09	75.368	179.1	4.626547	0.791428	47.44379	225	225.62	2.941
RH105	7.16	631	412	4.12	24.2	92.2	203.6	8.211435	0.853251	36.4356	80	84.546	5.087
RH106	7.3	500	336	3.36	13	92.5	214.56	4.387327	0.410739	46.73662	127	129.72	3.588
RH107	8.42	776	503	5.03	6	59	404.75	12.6082	2.698403	23.29431	376	377.89	10.38
RH108	8.51	588	400	4	3.7	298	261.84	8.053263	0.368811	38.83313	26.1	36.563	5.481
RH109	7.52	430	293	2.93	0	210	214.98	0.545664	0.086122	46.31715	169	169.25	0.589
RH110a	8.27	1353	762	7.62	0.1	4.3	895	3.628735	1.30239	8.763622	65.4	68.244	2.42
RH110b	8.46	608	393	3.93	2.5	860.7	253.17	1.421905	-5.96991	30.73736	71.4	73.329	1.244
RH111	8.5	858	545	5.45	2	331	477.56	5.89855	0.865602	19.13767	-22.1	19.687	7.46

Sample	pH	Ecµs/cm	TDS(mg/l)	Cl meq/l	NO3(mg/l)	SO4 mg/l	Hardness mg/l	Na%	RSC	PI %	CAI I	CAI II	SAR %
RH112	8.1	1380	783	7.83	2	329	639.62	0.760238	-0.71763	20.36265	14.9	20.302	0.624
RH113	8.12	1392	787	7.87	0.004	474.5	702.32	17.10388	-1.79822	13.36835	1353	1353.8	14.86
RH114	7.39	1065	656	6.56	0	476.6	421.5	10.81852	-3.29465	32.96673	181	183.26	5.611
RH115	7.2	551	365	3.65	79	240.4	147.28	3.751532	0.094515	56.99754	162	163.57	3.044
RH116	7.3	577	377	3.77	12	47	355.5	19.2298	2.800092	34.33523	1381	1382	13.95
RH117	7.63	956	603	6.03	12.5	104	363.88	20.30078	4.957921	38.4512	1564	1565.3	15.07
RH118	7.62	1177	725	7.25	79	101	430.96	6.63457	1.533977	35.58628	400	400.52	4.004
RH119	7.14	655	432	4.32	46.7	101	157.4	8.656796	1.258743	66.25496	1021	1021.1	6.34
RH120	7.14	804	510	5.1	33.4	35.33	193.3	10.80012	4.608696	63.45176	1241	1241.1	8.67
RH121	7	877	538	5.38	55	56.5	209.14	17.17042	6.412438	65.90383	1332	1332.2	15.11
RH122	6.93	982	597	5.97	75.4	51	198.7	5.430112	7.443752	71.17711	170	172.04	3.953
RH123	7.16	701	443	4.43	69.45	62	237.32	3.135346	8.652295	44.49347	122	124.09	2.512
RH124	7.4	804	495	4.95	11	149.4	342.82	14.618	2.815872	29.02481	1325	1325.7	11.5
RH125	7	785	483	4.83	19	218	179.56	7.300326	1.303656	57.84461	637	637.47	5.241
RH126	7.1	693	429	4.29	14.2	43.2	179.6	13.82445	4.054837	55.98283	1288	1289.3	9.3
RH127	7.5	1053	626	6.26	39.53	70.45	471	15.61736	4.614006	33.50737	1184	1184.6	10.99
RH128	7.81	929	568	5.68	5.33	180	388.1	4.467568	2.361192	36.69971	120	121.26	2.452
RH129	7.31	493	319	3.19	45	104.5	171.2	3.627299	1.60286	46.77795	111	112.8	2.312
RH130	7.37	462	293	2.93	8.6	69	222.48	6.726983	1.559801	36.93061	105	107.15	3.63
RH131	7.15	466	296	2.96	2.5	109.22	124.16	3.363886	0.707764	71.23611	346	346.93	2.509

7.6   MICROBIOLOGICAL ANALYSIS

Total 94 samples of surface and groundwater were collected from Dehradun and Haridwar district for microbiological analysis. Two test mainly *total coliform*(TC) and *E.coli* (EC - Faecal colifrom) were carried out. During winter season ~ 50% samples (46 samples) showed presence of TC and ~ 28% (23 samples) showed presence of *E.coli* (Faecal coliform) (Table 7.11).

Microbiological analyses are summarized in Table 7.11 in which MPN value of Total coliform and E.coli in surface and groundwater are given and their spatial distribution is shown in Fig 7.25, 7.26, 7.27. Among surface water of Dehradun district, 24 samples showed positive result to *total coliform* (TC) and MPN count of *E.coli* were present in 13 samples.

The tributary of song river namely; Rispana, Suswa and Bindal river shows presence of TC and E.coli in lower reaches passing through urban area of Dehradun. The TC in winter season varies form 123 MPN/100ml to 238 MPN/100ml along Rispana river, 109 MPN/100ml to 638 MPN/100ml along Bindal and 128/100ml to 143 MPN/100ml along Suswa river. The TC value in Suswa river increased substantially (> 15 times) in summer season but were reduced in post monsoon season possibly due to dilution in monsoon month when more surface runoff is available in rivers. In spite of presence of *total coliform*, *E.coli* are absent in Suswa river except at Raigarh (RH 63) where *E.coli* (172 MPN/100ml) are present possibly due to concentrated sewage discharge from local source.

In Rispana river, TC varies from 124 MPN to > 238 MPN and *E.coli* from 2 to 148 MPN in winter season except in Nalapani area near Sahastradhara bypass road (RH 113) where TC and *E.Coli* exceeded 2400 MPN/100ml. In this area, in absence of natural surface runoff, the river is receiving municipal sewage water. In absence of significant samples it is not possible to observe seasonal variation except in lower reaches at Daudwala (RH 67) where significant increase in TC (1011 MPN/100ml) and *E.coli* (791 MPN/100ml) has been

observed in post monsoon season. This could be because of mixing of domestic sewage from adjacent areas in monsoon time with surface runoff.

In Bindal river, TC varies from 109 MPN / 100 ml at Patel Nagar to 639 MPN/100 ml (at Bahamanwala). No increasing trend has been observed in downstream. The one sample collected at Patelnager (RH 126) shows increase in TC and E.coli in summer season as compared to winter and post monsoon season. This is because in absence of surface runoff, the river receives only domestic and sewage waste.

In the Asan river, which originate from a spring near Chandrabani and flows through the western Doon valley, TC and *E. coli* does not show much concentration (TC ~ 1 to 11 MPN/100ml and *E.coli* – 1MPN/100ml) during winter season and are absent in post monsoon season. However in summer season, the two samples Chandrabani spring (RH -74) and Asan river at Bhudhpur (RH 79) show very high total colifrom (1011 MPN/100ml) and 3.1 and 272 MPN/100ml counts of *E.coli* in RH 79 and RH 74 respectively. The increase in bacterial count during summer reflect the importance of runoff component in river water as in absence of sufficient natural discharge in river, polluted water dominate the total discharge of the river.

The increase in bacteriological count in summer season is because the flow of river is predominantly maintained by domestic and sewage waste. In absence of adequate natural surface runoff, river loses its self purification capacity and the ecology of the river is adversely affected which is evident from the growth of hyacinth at several places along the bank of Asan river. The presence of bacteria in Chandrabani spring indicates recharge of the springs by the domestic and sewage water from its surrounding area.

The presence of bacteria were also recorded in hadpumps, dugwells and tubewell lying close to lower reaches of Suswa, Bindal and Rispana river indicating pollution of shallow aquifers. The *total coliform* in handpumps varies from 3.1 MPN to > 2419 MPN/100ml at Mothronwala (RH 70) and Defense colony (RH 130). *E. coli* varies from 2 MPN to > 2419 MPN/100ml

at Daudwala (RH 69) in summer season. These handpumps are located on the river terraces or old flood plain deposits and are recharged by infiltration of river water during post monsoon and by irrigation and domestic sewage waste. This sewage waste infiltrates down and recharges the shallow aquifers and thus polluting the shallow aquifers lying along the rivers. This pollution is also evidenced by the higher nitrate concentration at these locations. The presence of bacteria in shallow aquifers also indicates the survival of bacteria up to a depth of about 20-25 m.

The bacteria counts in shallow groundwater (handpumps and tubewell) also show seasonal variation. Although number of infected handpumps are more (34%) of the analyzed sample) in winter season in comparison to summer (28%) and (17 %) in post monsoon, the concentrations of TC and EC are high in summer season indicating increased effect of faulty municipal waste disposal system.

In Haridwar district, the bacteriological analysis was carried out in Ganga river in upstream and downstream of Ram Jhula, at Rishikesh, upstream and downstream of Har Ki Pairi at Haridwar and a local stream in Roshnabad industrial area of Haridwar district. Few samples from shallow handpump and tubewell were also analyzed to assess impact on shallow aquifer. The *total coliform* and *E.coli* both are absent in Ganga river/channel in winter season except in Ganga channel before Har Ki Pairi. This is because a local stream carrying urban waste joins the Ganga channel before Har Ki Pairi. Although I are present in summer season in Ganga channel at Har Ki Pair of Haridwar (408 to 2420 MPN/100ml), in Rishikesh (2420 MPN/100ml) and in the local stream of Roshnabad area (2420 MPN/100ml), *E.coli* are absent in summer season but present in post monsoon (263 to 756 MPN/100ml) at Har Ki Pairi and Rishikesh (RH 36, RH 40) (Fig. 7.25 and 7.26).

The presence of *E.coli* and *total coliform* in significant number in summer and postmonsoon season also indicate enhanced tourist activity during these seasons and mixing of sewage waste during monsoon with surface runoff into Ganga channel. The local stream which drains through urban area is carrying

waste and disposing it in Ganga channel before Har Ki Pairi. The high *total coliform* during summer and high *E coli.* during post monsoon season in Ganga river at Laxman Jhula and Triveni Ghat of Rishikesh indicate local source of sewage waste in the Ganga river. The handpump at Muni Ki Rati and tubewell (infiltration well) at Risikesh (RH 38) extracting subsurface water from shallow aquifers also show presence of *total coliform and E.coli* and during post monsoon season. Since the aquifer in this area are of unconfined nature and consists of coarse sand, they receive contamination from local sources during post monsoon season along with recharge.
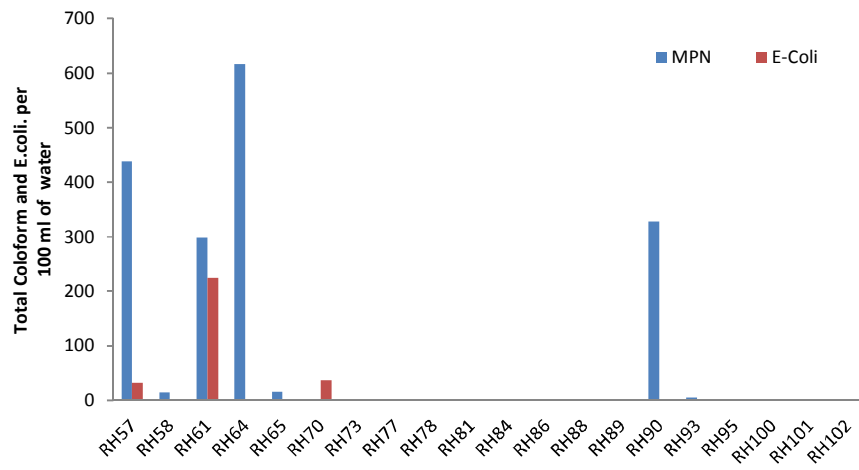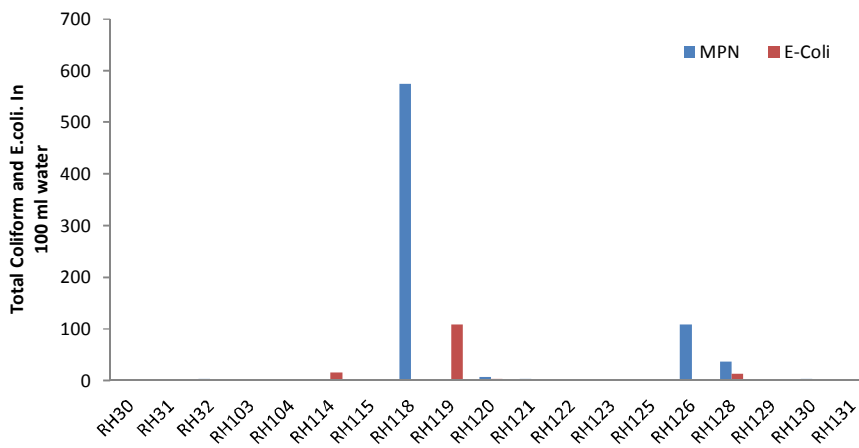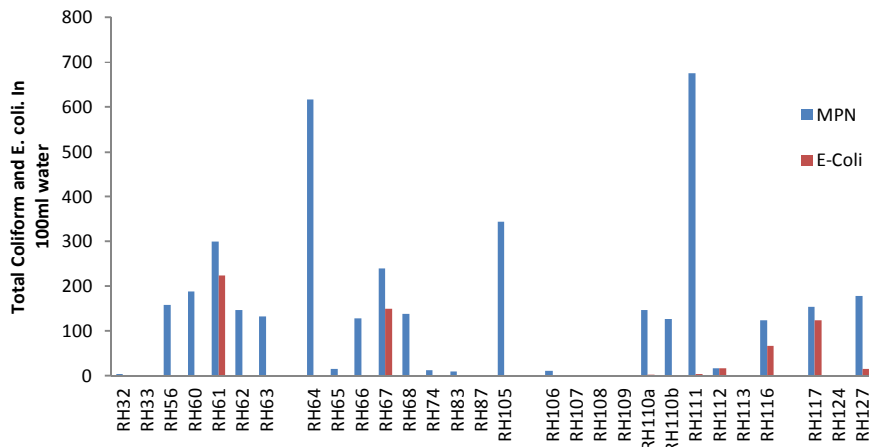
Fig. 7.23: MPN and E.coli in surface and ground water of Dehradun and Haridwar district
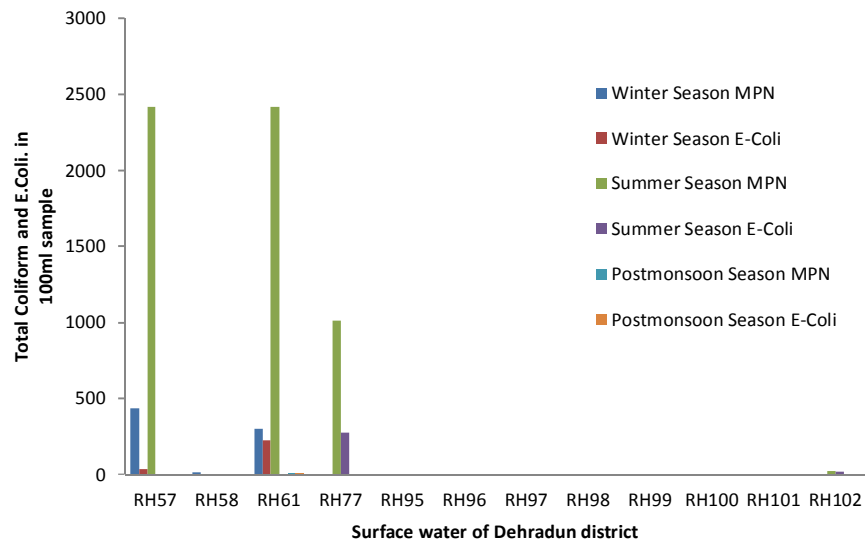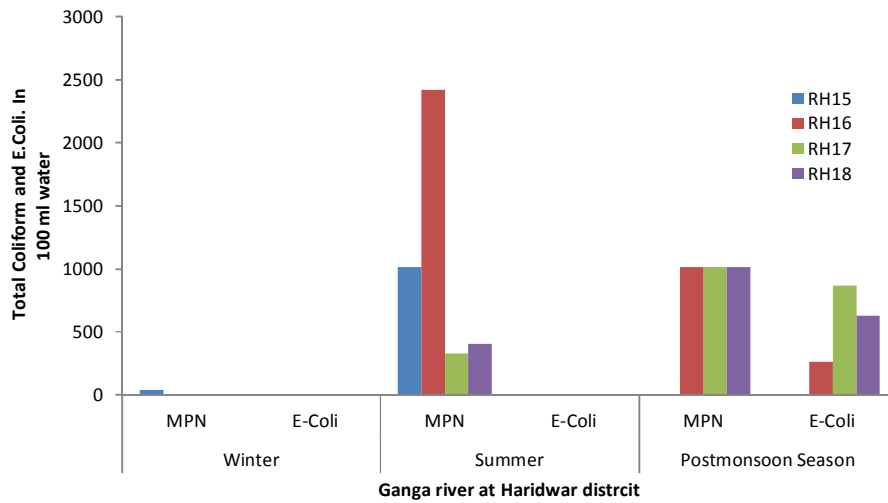
Fig. 7.24: Seasonal Variation of E.coli. and MPN in Surface and Ground water of Dehradun district
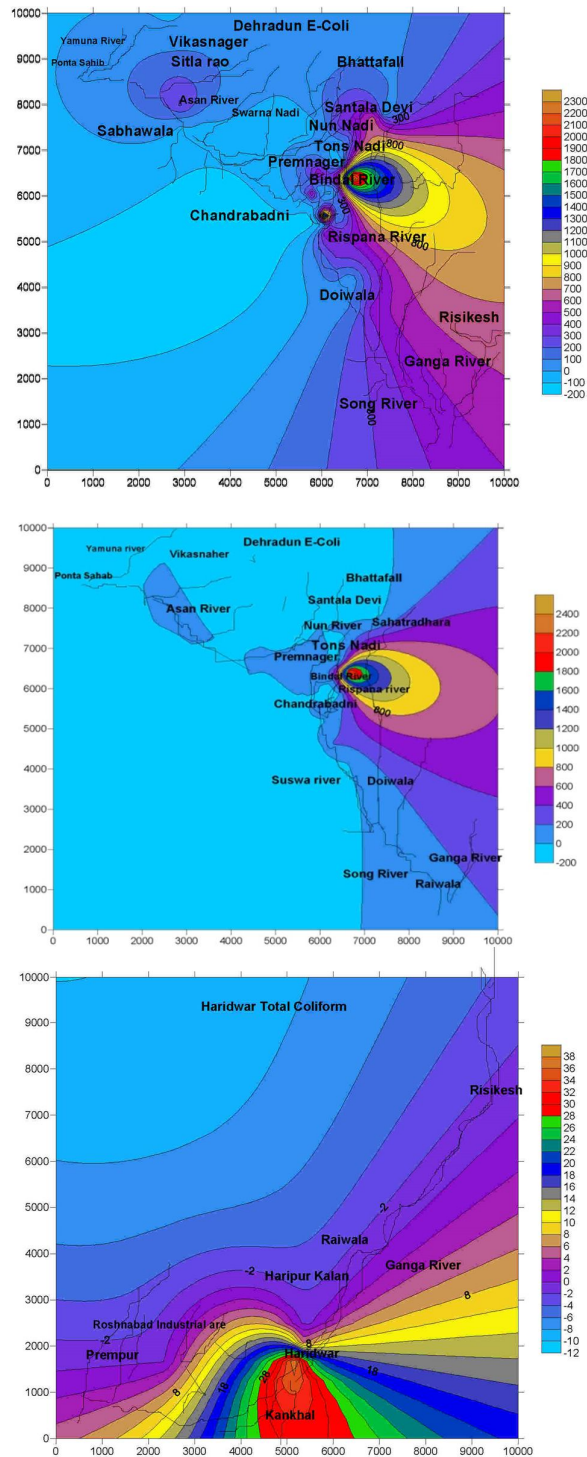
Fig. 7.25: Spatial variation of total coliform and E.coli in surface and groundwater of Dehradun and Haridwar districts in winter season
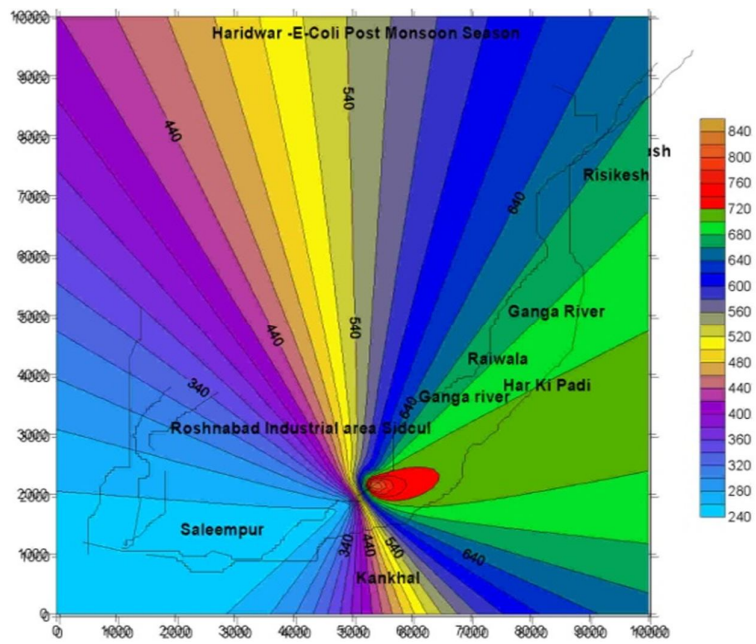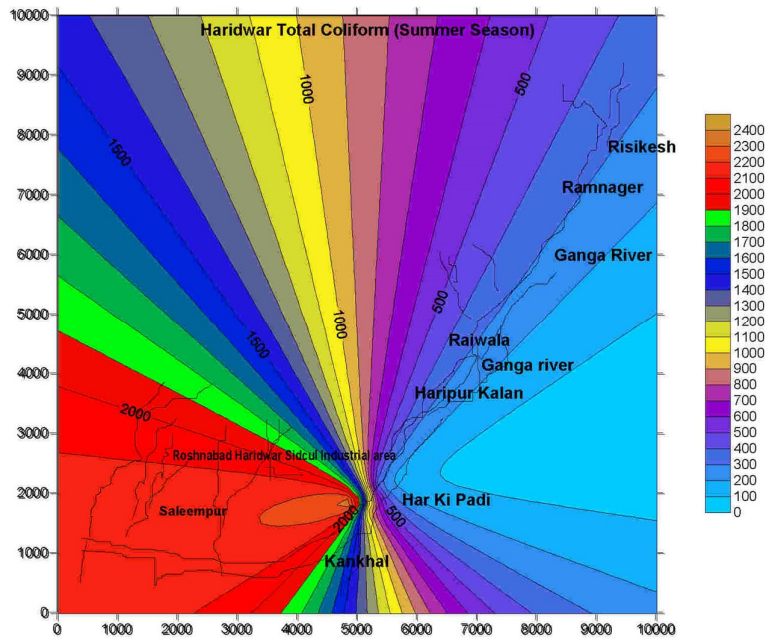
Fig. 7.26: Spatial variation of total coliform and E.coli in surface water at Haridwar during summer and post monsoon season.

Table 7.11: Microbiological analysis (MPN and E.Coli.) result in winter, summer and post monsoon season in Dehradun and Haridwar district.

S.No.		Winter season		Summer monsoon		Post monsoon	
		MPN	E.Coli	MPN	E.Coli	MPN	E.Coli
1	RH6			>2419.6			
2	RH7						
2	RH9	0	0				
3	RH15	38	0	1011.5	0		
4	RH16	0	0	2419.6	0	1011	263.1
5	RH17	0	0	328.2	1	1011.2	870.4
6	RH18	0	0	408		1011.2	629.4
7	RH27	3	0				
7	RH30			1011.2	1011.2		
8	RH32	3	0				
9	RH33	0	0				
10	RH34						
10	RH36	0	0	2419.6	0	1011.2	755.6
11	RH37	0	0	0	0		
12	RH38			0	0	1011.2	2
13	RH39					1011.2	403.4
14	RH40	0	0	>2416	0	1011	158.6
15	RH41						
15	RH56	138	0				
16	RH57	437.4	31.5	2419	0		
17	RH58	13.5	0	0	0		
18	RH59						
19	RH60	166	0				
20	RH61	298.7	224	2419	0	2	1
21	RH62	143	0	2419	0	0	0
22	RH63	128.4	0	>2419	27.5	1011.2	172.3
23	RH64	616.7	0				
24	RH65	14.8	0				
25	RH66	128.4	0				
26	RH67	238.2	148	72.3	16.8	1011.2	791.5
27	RH68	137.9	0				
28	RH69	148.3	2	>2416	2419.6		
29	RH70	>2419	37				
30	RH71	10.9	0				
31	RH72	638.6					
32	RH73	0	0				
33	RH74	11	0	791.5	601.5		
34	RH77			1011.2	272.3		
35	RH78	0	0				
36	RH79	1	1	1011.2	3.1		
37	RH80						
38	RH81	0	0				
39	RH83	8.6	1				
40	RH84	0	2				
41	RH86	0	0				
42	RH87	0	0				
43	RH88	0	0				
44	RH89	0	0				
45	RH90	328.2	2				

S.No.		Winter season		Summer monsoon		Post monsoon	
		MPN	E.Coli	MPN	E.Coli	MPN	E.Coli
60	RH93	5.2	0				
61	RH95	0	0	0	0		
62	RH100	0	0	0	0	0	0
63	RH101						
64	RH102			20.1	17.3		
65	RH103			0	0	0	0
66	RH104			3.1	<1	4	
67	RH105	328	21.3				
					1012	0	0
68	RH106	9.8	0	1011	0	721.5	228.2
69	RH107	1	1	1011	0		
70	RH108						
71	RH109			>2419.6	0		
72	RH110a	135	2				
73	RH110b	26.2	0				
74	RH111	30.5	3				
75	RH112	17.3	16				
76	RH113	>2419	>2419				
77	RH114	33.2	15.6	0	0		
78	RH115			0	0		
79	RH116	123.9	66.7				
		18					
80	RH117	148.3	123				
81	RH118	575	0				
82	RH119	198.9	88				
83	RH120	6.3	3.1				
84	RH121	3.1	0			23.3	3.1
85	RH122	0	0				
86	RH123	0	0				
87	RH124	0	0	1011.2	72.5	1011	1668
88	RH125	0	0	72.3	14.8	9	3
89	RH126	109.2	0	207.5	86.2	33.6	18.3
90	RH127	178.9	14	1011.2	376.2		
91	RH128	36.9	14	38.9	20.3		
92	RH129	<1	0				
93	RH130	3.1	1.5				
94	RH131	4.1/5.2	0	4.1	2	0	

7.7   TEMPORAL CHANGES IN WATER QUALITY

Till now no systematic assessment of industrialization and urbanization carried out in Dehradun and Haridwar district. The studies carried out by Jain(1996-1997), Jain (2002), Divya (2007)), Central Ground Water Board-report of (2001, 2002, 2003, 2004, 2005, Pandey (1999), GJ Chakrapani (2005), Kumar Abhay 1998 etc. Haridwar Jal Sansthan report (2005, 2006) are limited to few parameter only and have not taken into consideration the land use parameter.

 To study the temporal changes due to urbanisation and industrialization the result are compared with data of (Jain 2001).

The data presented in table (7.12, 7.13 and 7.14) shows that the anions viz HCO_3, Cl, NO_3 and cations viz. Ca, Mg, Na and K are tend to increase in the year 2008 in comparison to 2001 data of Jain (2002) per and post monsoon season possibly indicating of urbanisation and industrialization (Table 7.12, 7.13).

The other ions such as HCO_3, NO_3, and PO_4 has also increased   in groundwater of Haridwar district which points out that due to phenomenonal growth of urban and industrial had deteriorated centers over a decade after the formation of Uttarakhand had deteriorated the quality of surface and groundwater. the quality of surface and ground water.

A comparison of the data of the present study (2008) of the Haridwar area (Ganga river and groundwater) with previous data of Jain 1988 showed significant increase in TDS and EC.

Table 7.12: Comparison of Data (Jain2002) in Premonsoon Season in Dehradun district

	Year	pH	EC	TDS	HCO$_3$	F	Cl	NO$_3$	PO$_4$	SO$_4$	Na	K	Mg	Ca
Max	2002	7.9	1914	1225	240	1.16	28	25	0.24	640	28	5.2	79	251
	2007	7.68	920	481	425	0.28	60.8	242	4.28	174	26	21.7	45.6	115
Min	2002	6.4	83	53	23		0.7	0.7	0.01	1	1.4	0.1	2.1	7.1
	2007	6.11	116	81.2	94.08	0.055	1.21	0.75	0	11	2.2	0.2	5.8	26
Average	2002	7.46	490	314	123	0.38	4.1	8.5	0.08	72	6	1.7	20	50
	2007	6.94	445.7	266.5	207.3	0.128	14.72	23.1	0.199	59	10.3	5.57	21.5	53.2

Table 7.13: Comparison of Data (Jain2002) in Post Monsoon Season in Dehradun district

		pH	EC	TDS	HCO$_3$	F	Cl	NO$_3$	PO$_4$	SO$_4$	Na	K	Mg	Ca
Max	2002	7.8	2210	1414	249		38	51	0.1	685	34	6.8	94	272
	2007	8.07	925	483	337	0	42.7	35.8	0.002	156	18	12	34	94
Min	2002	6.6	107	68	30		0.2	0.4	0.01	2	0.2	0.1	2.6	9.6
	2007	6	124	79	61	0	1.14	0.3	0	0.2	1.8	0.4	1.9	13
Average	2002	6.9	525	335	130		4.2	8.5	0.04	79	6	0.9	22	54
	2007	7.11	478.8	270.8	147.3	0.5225	9.858	14.2	0.04	52	7.29	3.55	16.7	40.7

Table 7.14: Comparison of Data (Jain 2002) in Post Monsoon Season in Haridwar district

Haridwar -1999		Tem	pH	TDS	EC	DO	HCO$_3$	F	Cl	NO$_3$	PO$_4$	SO$_4$	Na	K	Ca	Mg
Canal water	Cwa	22.5	7.8	85	133	8.5	58		72	1.3	0.3	24	34	5.4	23	3.9
	CWb	15	8.2	130	205	9.8	220		4	0.4	0.07	27.5	33	5.9	72	6.8
River water	Rwa	22	7.8	85	131	8.9	58		41	1.4	0.3	24.1	33	5	24	3.9
	RWb	14	7.9	120	200	10	30		75	0.5	0.07	29	37	5.1	35	6
Ground water - 50 feet (pre)		25.5	7.9	341	560	1.1	290		8.2	5.5	0.21	39.9	40	10	73	22
Ground water - 50 feet (post)		17.1	7.8	345	577	1.2	281		8.9	5.4	0.2	40	39	10	73	22
Ground water - 100 feet (pre)		25	7.6	320	510	1.5	250		6.1	5	0.15	35	35	9.2	69	20
Ground water - 100 feet (post)		18	7.5	319	500	1.1	240		6	5.1	0.15	35.8	35	9	69	20
Ground water <100 feet (pre)		24	7.6	307	480	1	230		5	4.2	0.14	32.5	30	7	62	19
Ground water <100 feet (post)		19	7.4	172	269	1	116		7	1.2	0.18	27.5	31	4	36	7.8
	Average	20.21	7.8	222	357	4.4	177.3		23	3	0.18	31.5	35	7.1	54	13
	Average	22.98	7.3	398	614	9.2	248.3	0	14	26	0.35	20.6	10	2.9	71	10

Cwa = Canal water, Rwa = River water

CHAPTER VIII

SUMMARY AND CONCLUSION

The rapid industrialization and urbanization has led to overexploitation and pollution of water resources. After the formation of Uttarakhand state pace of urbanization, growth of population centers, industrial growth has increased manifold in Uttarakhand region. Pollutants are increasingly added to the surface and groundwater system through various human activities and natural degradation process. The evaluation of the impact of industrialization and urbanization on water resources is an integral part of development and management strategy of water resources development programme.

Therefore a detailed study of surface and groundwater quality of Dehradun (Doon valley) and Haridwar district of Uttarakhand has been undertaken to assess their suitability for drinking, domestic and irrigation purposes. The impact of industrialization, urbanisation and agricultural practices on surface and groundwater quality is also evaluated. In addition to water quality assessment, major ion chemistry of these waters is studied to understand chemical weathering process and to assess ionic sources.

The synclinal trough-shaped Doon Valley in Dehradun district bounded by the Precambrian rocks of the Lesser Himalayan formations in the north and Tertiary Siwalik in the south forms a part of the submontane region of the Garhwal Himalaya (Fig.3). Geological structure of the Doon valley is characterized by two major faults, along which rock slabs of mountain mass have been uplifted and moved southward. The Doon valley and Siwalik range are principally composed of the rocks classified into the Lower, the Middle and the upper Siwaliks. The Asan and Song rivers tributaries of Yamuna and

Ganga river, mainly drain the Doon Valley. The tributaries of Asan are Saurna, Nimi and Tons, and those of Song are Rispana, Bindal and Suswa. Although surface runoff is high, a significant amount of rainfall infiltrates through the highly porous Doon Gravels and recharges the groundwater. Geohydrological, the structurally controlled intermontane Doon Valley is divisible into three zones (Bartarya, 1995).

1. The Lesser Himalayan zone;
2. The Synclinal Central zone; and
3. The Siwalik zone.

The steeply sloping *Lesser Himalayan Zone* consisting of rocks of the Lesser Himalayan formations (phyllites and quartzite, shales, sandstone, greywackes, slates, dolomite and limestone of Jaunsar, Blaini-Krol-Tal sequence) has secondary porosity and permeability, and is characterized by springs and seepages. *The Synclinal Central Zone* a synclinal depression between Lesser Himalaya and Siwalik is occupied by Doon Gravel. The Doon gravels have primary porosity and permeability and forms the main aquifer in the area. The groundwater is present in multilayered aquifers under unconfined and semiconfined conditions. The subsurface geohydrology indicates that the horizons comprising boulders and gravels set in a coarse sandy matrix are the main water-bearing horizons. The discharge from the tubewells varies from 600 to 3000 l/min through a tapped horizon of 30 to 50 m with a depression of 2 to 7 m.

The Siwalik zone consists of rocks of Middle (friable, medium grained, grey-coloured massive sandstone and mudstone) and Upper Siwalik (alternate polymictic conglomerate and subordinate grey micaceous sandstone). Groundwater is present under semi-confined and confined conditions and the water table is relatively deep. Although, the conglomerate unit of the Upper Siwalik is highly porous and permeable, water quickly leaves the area as surface runoff.

The study area in **Haridwar district** is a part of Indogangetic plain and Siwalik hills. The Indogangetic plain is composed of Pleistocene to recent alluvium material brought down by river from the Himalayan regions. The alluvium is made of sand, silt, clay, kankar and gravel. Geologically the area can be divided into following four major regions; *the Siwalik Range* (the outermost range of Himalayas, extending over a altitude rage of 500 - 900m), *the Bhabhar* (foot hill or Piedmont Alluvial Plain), *the Tarai* (the spring line or seepage zone) and *the Indogangetic plain* (the alluvial plain). Two types of aquifers have been reported from the Haridwar (Singh et al 1979). The upper one is the shallow unconfined aquifer which generally extends to the depth around 25 m. The deeper one is confined to semi confined in nature. Water table contour in the area indicate south ward trend of groundwater flow. The Roshnabad industrial, area south of Siwalik foothills, is located in piedmont zone. It consists of alluvial material deposited by the stream descending down from the Siwalik range. This predominant unit possesses a series of wide fans, developed into the fan terrace. Water table is relatively deep and much of the ground water recharged by rainfall though percolation to deep aquifers. The Haridwar and Risikesh area are characterized by palaeo- channels.

Surface and ground water samples from Dehradun and Haridwar districts were collected during January, April and September in the year 2008 representing the winter season, summer season and post monsoon season. The ground water samples from tubewells and handpumps were collected from three broad landuse categories i.e agricultural, urban and industrial areas of Dehradun and Haridwar districts. The surface water samples were also collected from Bindal, Rispana, Song, Suswa, Asan, Nun, Nimi Nadi and Yamuna River in Dehradun and Ganga river in Haridwar and Risikesh area to study the impact of urbanization and industrialization. These samples were analyzed for dissolve major ions (HCO^-_3, SO^-_4, Cl^-, NO_3^- PO^-_4 F^- Na^+, K^+, Mg^{2+}, Ca^{2+}, SiO_2) and for trace metals such as As, Cd, Mn, Co, Cu, Cr, Ni, Fe, Zn, Pb, Ba, and Sr in selected samples. The variation in chemical constituents of surface and ground waters of these three landuse categories and their seasonal variations are studied.

The temperature in study area ranges from 6.35^0C to 29.6^0C with an average of 21^0C winter season, during summer season it varies from 19^0C to 29^0C with an average of 25^0C and in post monsoon it varies from 8^0C to 34^0C with an average of 26^0C. The results shows that the water are slightly alkaline (pH value range from 6 to 8.5 with an average of 7.2) possibly due to dominance of carbonate lithology in the study area.

The average pH in groundwater of industrial area of Dehradun district does not show much variation and varies from 6.7, 6.4 and 7.2 respectively in summer, post and winter season except that of Selaqui Industrial area which become slightly acidic in post monsoon possibly due to leaching of acids from soil into groundwater. Similar variation was observed in agricultural area of Dehradun ad Haridwar district. In urban area pH tend to be alkaline in nature with an average pH varies from 8 and 7.6 during summer and post monsoon season and does not show much changes in winter season possibly due to higher dissolution of carbonate rocks during post monsoon season. The relatively high concentration of DO in winter season in comparison to summer season data is related to its temperature sensitive solubility in water being higher in cold water than warm water.

The TDS content in study area vary from 91mg/l to 796mg/l with an average of 351mg/l in winter season, in summer season 325mg/l and relatively low value 276mg/l during post monsoon season. The TDS in tubewell (groundwater) of Dehradun varies from 377mg/l to 510mg/l with an average of 423.7mg/l while in handpump it varies from 99mg/l to 761mg/l with an average of 340mg/l. The TDS concentration in tubewell water of Haridwar area ranges from 175mg/l to 740mg/l with an average of 365mg/l and in handpump it varies from 288mg/l to 796mg/l with an average of 470.8mg/l. The ions like SO_4, Cl and PO_4 tend to increase in handpump as compared to tubewell water of Dehradun.

The average TDS in surface water (Ganga river) of Haridwar district varies from 143mg/l in summer season, 169mg/l in winter season and 214mg/l in postmonsoon season. The average TDS concentration is high (430mg/l) in

surface water in comparison to groundwater (307mg/l) of Dehradun district. All ions HCO_3, F, NO_3, Cl, SO_4, Na, K, Mg and Ca tend to decrease in ground water in comparison to surface water of Dehradun district.

Over all, the seasonal variation in TDS and EC shows that the ionic concentration is high in winter and low in post monsoon season in surface and groundwater of Dehradun and Haridwar district. The seasonal variation in groundwater shows higher ionic concentration in summer season in comparison to winter and postmonsoon season while in surface water of Dehradun minimum ionic concentration in summer season. This indicate dilution of surface and groundwater due to recharge during monsoon season. The increased flow velocity during monsoon does not allow water to remain in contact with host soil-rock mass for longer time. The dilution of water due to recharge during monsoon season possibly lower the ionic concentration while evaporation during summer and winter season and enhanced rock water interaction increases ionic concentration which in turn increases TDS and EC concentration in winter and summer season in comparison to post monsoon season.

Among anions bicarbonate is the most dominant ion (65%) followed by sulphate (23.3%), chloride (6.4%) and nitrate (4.9%), fluoride (0.4%), phosphate (0.3%) in winter season. The total alkalinity in study area is represented by bicarbonate concentration as carbonate (CO_3^-) is absent in water of the Dehradun and Haridwar district. Its concentration varies from 21mg/l to 708mg/l with an average of 259mg/l. The bicarbonate also shows seasonal variation being highest in winter season and lowest in post monsoon season. The major source of HCO_3^- in the study area is from carbonate and silicate weathering of rocks.

Among cations, calcium is most dominant ion, contributing about 63% followed by Mg (24%), Na (10.7%) and K (2.3%) in winter season. The order of abundance remains same in summer and post monsoon season. The Ca and Mg together account for 87% of the total cation and Mg:Ca ratio is 16.6. Similarly bicarbonate and sulphate together contribute ~88% of the total

anions and $SO_4 : Cl$ ratio is 16.9. These observations lead to the conclusion that chemistry of surface and ground water of Dehradun and Haridwar district is dominated by weathering of carbonate rock. The influence of carbonate lithology on water chemistry is also evident from the high $(Ca^{2+} + Mg^{2+})/HCO_3$ ratio (1.4) and good correlation of bicarbonate with both Ca and Mg ($r^2 \sim 0.8$), Further, when sulphate is taken into account, the ratio of $(Ca^{2+}+Mg^{2+})/ (HCO^-_3 +SO_4)$ becomes 0.95 indicating importance of sulphate in ionic equilibrium of chemistry of the waters of the study area.

The (Ca+Mg)/(Na+K) ratio ranges 1.2 to 43.9 with an average of 9.1 in study area of Dehradun and Haridwar. The ratio of Ca:Na varies from 2.7 to 496 with an average value of 59, the excess Ca over sodium indicate carbonate and gypsum source for calcium. The average (Ca+Mg) : HCO_3 equivalent ratio of 1.4, relatively high contribution of (Ca+Mg) to the total cations (TZ+) and high (Ca+Mg): (Na+K) equivalent ratio of 9.1 indicate that carbonate weathering could be primary source of major ions to these water. It is estimated that about 90% (average) bicarbonate comes from carbonate weathering and $\sim 9\%$ from silicate weathering in the study area.

The major ions chemistry of surface water of Dehradun (Bindal, Rispana, Asan, Nun and river Yamuna) show that calcium and magnesium are major cations, together they account for 56 to 99% of cations. The Mg :Ca equivalent ratios varies from 1.6 to 1.4 with an average of 0.40 in winter season, 0.7 in summer season and 0.5 during post monsoon season. The contribution of sodium and potassium to the total cation is relatively high in summer incomparison to post monsoon season.

In Ganga river at Haridwar the Ca+Mg constitute >90% among cation and HCO_3 account for about 73% of the anions. The contribution of Na and K from silicate weathering, estimated from (Na*+K): TZ+ ratio, is limited to 9 % in winter season and 7 % in summer and post monsoon season. The low abundance of SiO_2 (73μmole/l to 136μmole/l with an average value of 110μmole/l) and low $SiO_2:HCO_3$ molar ratio 0.06 also indicates a relatively

low contribution of ions from silicate weathering. The molar ratios Na^+ and Cl^- indicate their contribution either from rainfall or from anthropogenic sources.

The surface and groundwater of study area belongs to Ca-Mg-HCO$_3$ and Ca-Mg-SO$_4$ Hydrochemical facies. On a ternary diagram relating HCO$_3$, SO$_4$, (NO$_3$+Cl) most of the data cluster towards the alkalinity apex with secondary trend towards sulphate suggesting carbonate -- evaporate -- pyrite weathering in basin. Similarly cations plots (Ca, Mg and Na+K) shows that most of the samples falls in Ca apex and towards the central of the field indicating carbonate weathering as source of major ions in waters of the study area. The ionic ratios and relative concentration of ions suggests that the major source of ions in water of the study areas remains rock weathering, although anthropogenic activities have influenced the ionic composition.

Flouride concentration does not show much variation and found to be almost same ~ 0.4mg/l in all three season. The average concentration of chloride in study area is 14mg/l, 10.3mg/l, 12.5mg/l respectively in summer post and winter season. However higher concentration (>44mg/l) of chloride was present at few sampling locations in Dehradun (Bindal river at Bharuwala, Patel Nagar are, Rispana river at Nalapani area and in handpumps in Gandhigram area located in adjacent flood plain area of these rivers) and Haridwar districts (seasonal streams and handpump in village Revala Mehdood and Saleempur village area). The increase is possibly due to direct discharge of domestic/ sewage waste and industrial effluent directly in soil layer and river water. The silica also shows seasonal variation being higher in winter and lowest in summer season.

The nitrate concentration in water of the study area varies from 0.004mg/l to 263 mg/l with an average of 16.3mg/l in winter season. It also showed seasonal variation and average concentration varies from 20.3mg/l and 10.4mg/l during summer and post monsoon season respectively. Lower concentration in post monsoon season is due to recharge during monsoon. Nitrate has shown positive relationship (r^2= 0.7) with chloride during winter and summer season indicating same sources during these season. However

poor relationship in postmonsoon season is possibly due to dilution and atmospheric contribution of chloride during monsoon.

At few locations in surface and groundwater of Dehradun (for example Rispana river at Nalapani, Bharuwala (RH 67, RH 113), Bindal river at Patel Nagar, Bharuwala (RH 117, RH 67, RH 68) and handpumps and tubewells located adjacent to these river (RH 55, RH 58, RH 121, RH 125) and in ground water of Haridwar district (for example Ravala Mehdood RH7, RH8) the nitrate concentration is approaching desirable or has exceeded drinking water limit of BIS (1991) and WHO standard. Drinking of water with high nitrate concentration may cause methemoglobinemia (a blue baby syndrome) particularly in infant. The discharge of sewage and municipal waste directly into these rivers in Dehradun district and leakage from sewage pits and untreated discharge of effluent in subsurface water system from industrial area of Roshnabad, Haridwar district are the possible source of excess nitrate in water of study area. Application of fertilizer in agricultural field is another source of NO_3 in these waters.

In majority of the samples, phosphate was not detected in study area except in few handpumps of the Haridwar district, and in lower reaches of Rispana (8.2mg/l), Bindal (17mg/l), and Suswa (1.1mg/L) river in Dehradun district. PO_4 tend to increase in handpumps water in comparison to Tubewell water of Haridwar in down slope direction of Sidcul industrial area indicating contamination of shallow aquifers possibly due to leaching of industrial effluent directly discharged from industrial area and discharge of domestic and sewage waste in upper soil layer.

Phosphate has also shown positive relationship with potassium indicating potash rich fertilizer as their possible source. The phosphate at these locations has also exceeded permissible limit of WHO standards for drinking water quality at these locations.

The sulphate is next abundant anions after bicarbonate and its concentration varies from 0.01 mg/l to 861mg/l in winter season. Average sulpahte

concentration does not show much variation in winter (71mg/l) and summer season (72mg/l). However relatively depleted concentration (average 52mg/l) were observed in post monsoon season due to dilution effect during monsoon. At few locations in surface water of Dehradun such as Nun river (RH106, RH107), Rispana river (RH110, RH113) Sahastradhara stream (RH111, RH112), Bhattafall stream (RH109), in lower reaches of Song and Suswa river and in ground water of Revala Mehmood area of Roshnabad in Haridwar district, relatively higher concentration of sulphate (>90mg/l) as compared to average are observed. Among them the sulphate concentration exceeds drinking water desirable limit of (ISI 1991) of 200mg/l at few places. The higher concentration of SO_4 at these locations is related with weathering of gypsum and pyrite mineral present in limestone and dolomite rocks of Krol formation present in upper catchment of these streams /rivers. SO_4 has also shown positive relationship between Mg ($R^2=0.8$). The excess (>200mg/l) concentration of sulphate causes gastrointestinal irritation, if Mg and Na are also present in higher amount.

Ca is the dominant cations in waters of the study area constituting about 63% of the total cations and its concentration varies from 3.6mg/l to 267mg/l with an average of 59mg/l in winter season. The Ca shows seasonal variation being maximum 64mg/l (average) in summer season to lowest 49mg/l (average) in postmonsoon season indicating dilution effect during monsoon. Excess concentration, than average of 59mg/l of winter season were also observed in summer season in surface water of Suswa river, lower reaches of Rispana, Bindal, Nun, Asan and Song river, and Sahastradhara stream in Dehradun district, and in seasonal streams of Roshnabad area in Haridwar district. The ground water of certain pockets in Dehradun (handpump and tubewell present in lower catchment of Suswa river, Rispana and Bindal river of Kurkawala, Doodhli, Bharuwala, Bhamanwala) and parts of Haridwar district, (handpumps and tubewell present in Roshnabad area) also show excess than average concentration. The desirable drinking water limit for Ca is 75mg/l and maximum permissible limit is 200mg/l according to WHO and BIS standard for drinking water quality.

The Mg is the second dominant cations, constituting about 24% of total cations, after Ca in waters of the study area and its concentration varies from 0.5mg/l to 62mg/l with an average of 15mg/l in winter season. Although magnesium does show variation between postmonsoon (15.9mg/l) and summer season (21.6mg/l) being enriched in summer but its winter concentration is similar to postmonsoon season. Mg show overall positive relationship with Ca ($r^2 = 0.7$) and SO_4 ($r^2 = 0.8$) indicating similar carbonate source of these ions. The carbonate rocks in the form of dolomite and limestone of Krol formation are present in northern part of the Doon valley. Mg concentration is less in water of Haridwar district in comparison to Dehradun district possibly due to lithological difference in the catchments of both areas. Mg concentration at all sampling location is under the permissible limit of BIS and WHO standards for drinking water quality.

The higher concentration (20mg/l to 74mg/l) of potassium in Bindal river at Haridwar bypass road, Bhamanwala (RH 72), Patelnager (RH 117), in Rispana near Nalapani (RH 113), Kedarpurum (RH 127) and in Handpump at Bharuwala (RH 126) in Dehradun district indicate deterioration in surface and groundwater quality because of Urbanization. Further, relatively higher concentrations of potassium in handpumps of Sidcul area (RH6 and RH8) also indicate effect of industrial effluent discharge in soil.

All the ions HCO_3, F, NO_3, Cl, SO_4, Na, K, Mg and Ca tend to decrease in groundwater of Dehradun when compared with surface water. The seasonal data shows minimum concentration of the ions in post monsoon, and a maximum concentration during winter season. Most of the ion concentration in surface water of Dehradun and Haridwar districts is high in summer season as compared to post monsoon period indicating the effect of elevated temperature, increased evaporation and absence of recharge during the low water level period of the pre monsoon season. However, ions such as HCO_3, F, Cl, PO_4, SO_4 and Mg are tend to decrease in post monsoon season when compared with summer season due to less contribution of soil salt during post monsoon season. Further in agriculture and industrial area of Haridwar

district, where groundwater is withdrawn from shallow aquifers through handpumps and dugwells, ions such as Cl, NO_3, PO_4, K and Na are tend to increase in surface and shallow groundwater (handpumps) of agriculture and industrial area when compared with urban area indicating the deterioration of water quality of shallow aquifers in agriculture area. This indicates leaching of ions in shallow groundwater from artificial fertizers, animal waste and from sewage pits.

The TDS concentration appears to be useful indicator of impact assessment of industrialization and urbanization in the study area. A higher TDS in urban area (436mg/l) and surface water (420mg/l) in comparison to agricultural (420mg/l) and industrial area (149mg/l) corroborate the observation of deterioration in surface and groundwater quality from the anthropogenic sources and reflect the impact of urbanization on water chemistry in Dehradun district.

In Haridwar district, the higher TDS in groundwater of agriculture (481mg/l) and industrial area (408mg/l) in comparison to urban area (318mg/l) and surface water (103mg/l) indicate impact of agriculture and industrial activities. The direct discharge of industrial waste in soil zones finds its way to shallow aquifers of village area located in down slope direction. Direct disposal of domestic, sewage and animal waste though shallow soak pits in upper vadose zone increases the ionic concentration (Cl, NO_3, PO_4 and K) in shallow aquifers in industrial and agriculture area.

The hardness in study area varies from 203mg/l and samples falls under moderately (<120mg/l) hard (<180mg/l) and very hard category (>180mg/l). However, in Dehradun, few samples of Bindal river in lower reaches (RH 72, RH 126), of handpumps (RH 123) in Bhamanwala and tubewell (RH 115) in Karanpur area and those of Bhattafall, Sahastradhara stream has crossed the permissible drinking water limit of Hardness of BIS standards of drinking water quality. The surface water (Ganga river) of Haridwar falls under moderately hard category. Therefore, the groundwater of industrial and agriculture area falls under very hard category in comparison to urban area

while majority of the samples falls under moderately hard category. In general surface water is harder than groundwater.

The higher electric conductivity of waters at Bhattafall (1353µs/cm), Sahastradhara (1392µs/cm), Tapkeshwar (776µs/cm) and Chandrabadni (903µs/cm) in Dehradun district is attributed to their ionic source in limestone and dolomite rocks.

The drinking water quality of the study area was also assessed by microbiological analysis comprising two test – the *Total Coliform* and *E.coli*. The total coliform bacteria count varies from 3.1 to >2400 MPN/100ml and E.coli from 1 to 225/100ml with the exception of Rispana river. Of the total 94 samples collected in winter season from surface and ground water from Haridwar and Dehradun district, ~ 50% samples (46 samples) showed presence of *Total coliform* and 28% showed presence of *E.coli* in the vicinity of urban population. The percentage of positive result of *Total coliform* has increased to 73% and 70% and of *E.coli* to 36% and 47% respectively, during post monsoon indicating higher bacteriological pollution during summer and post monsoon season.

Its sequence of dominance was observed as summer > postmonsoon > winter. This suggests presence of thermotolerant and disease causing group of bacterial population in surface and shallow groundwater of the study area. This also indicate the growth of many pathogenic and non-pathogenic bacteria for health hazards in water of urban area due to contamination from sewage and runoff discharge in aquatic ecosystem within the vicinity of dense population centers.

The water of Bindal, Rispana and Suswa river in their lower reaches and handpumps and borewell lying close to these river shows presence of *Total coliform* and *E.coli*. This together higher nitrate concentration indicate pollution of river water due to untreated disposal of municipal waste in these river. Presence of bacteria in handpumps and borewells suggest faecal contamination of shallow aquifers recharged by these rivers.

The majority of physio-chemical parameters, such as pH, EC, TDS, Hardness, chloride, sulphate, carbonate, bicarbonate, nitrate, sodium, sodium, potassium, magnesium SAR and PI, which decide the suitability of water for irrigation are under moderate to no problem category of irrigation use.

The physical and chemical parameters of water quality of the study area, when compared with BIS and WHO standards of drinking water quality, were found to be under permissible limit of BIS and WHO standards except F, Cl, SO_4, NO_3, PO_4 and K at few sampling locations of surface and groundwater of Dehradun and Haridwar district. For example in industrial area of Haridwar, three samples of F and NO_3 have exceeded the maximum permissible limit of drinking water quality of WHO and BIS standards. Similarly surface and shallow groundwater at few locations is polluted from faecal contamination.

For trace metal viz Fe, Pb, Cd, Hg, Pb, Cr, Co, Sr, As, Cu, Ni,B, Fe and Mn analyzed in selected samples and were found to be under permissible limit of BIS and WHO standards of drinking water quality except the Cu concentration at few sampling location in urban area of Haridwar district where it exceeded the desirable limit of 50ppb of BIS standard but remained under maximum permissible limit of BIS standards of drinking water quality in all three season viz. winter, summer and postmonsoon season.

A comparison of physicochemical parameters of present study with previous data (Jain, 1998 and 2002) indicates increase in EC, TDS, HCO_3, NO_3, and PO_4. This further corroborates impact of population growth and urbanization on water quality of surface and groundwater after the formation of Uttarakhand.

Industrial area of Haridwar Sidcul - RH-1

Sidcul – RHII

RH- Sidcul – Tubewell

Sidcul Borewell : RH

Sidcul Effluent (Haridwar)

Haridwar – Village area

Haridwar- Chauhan Mohalla

Haridwar : Teen Dhara

Ganga River – Dhobhi Ghaat

Ganga River Dhobhi Ghaat

Har ki Padi –Upstream

Har Ki Padi – Downstream

Yamuna Upstream   **Yamuna Downstream**

Robberse Cave

Bhattafall

Nun River

Bindal River

Suswa River

Rispana River Kedarpuram

Chandrabani spring

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