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Assessment of surface and ground water Quality of Haridwar district of Uttarakhand

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Abstract : An analytical study of major cations and anions of surface and ground water of Haridwar district has been carried out to assess the spatial and seasonal variation of water quality. The impact of industrialization, urbanization and agricultural practices on surface and groundwater quality had been evaluated. Major ion chemistry of these waters has been studied to understand chemical weathering process, factors controlling on ionic chemistry and to assess ionic sources.

Surface and groundwater samples were collected during January, May and October representing the winter season, summer and post monsoon season. The groundwater samples from tubewells and handpumps were collected from three broad land use categories i.e. industrial, agricultural and urban. These samples were analyzed for dissolve major ions (HCO_3^- , SO_4^{2-} , Cl^- , NO_3^- , PO_4^- , F^- , Na^+ , K^+ , Mg^{2+} , Ca^{2+} and SiO_2). Among anions HCO_3^- was the most dominant (73%) followed by SO_4^{2-} (15.4%), Cl^- (6.6%), NO_3^- (4.8%), F^- (0.6%) and PO_4^- (0.3%) and among cations, Ca^{2+} is the most dominant (71%) followed by Mg^{2+} (19%), Na^+ (7.7%), and K^+ (2%). Most of the samples were of Ca- HCO_3 type followed by Ca- HCO_3 - SO_4 and Ca-Mg- HCO_3 - SO_4 types.

The seasonal variation in groundwater shows higher ionic concentration in summer season in comparison to winter and post -monsoon season. 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. The surface and ground water were found to be under moderate to no problem category for irrigation purposes.

Key Words : Hydrochemistry, Water quality, Industrialization, Urbanization, Water Pollution, Seasonal variation.

1. Introduction

Urbanization, industrialization and agricultural development are the major causes for the variation in ionic chemistry of surface and groundwater. 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 Haridwar district of Uttarakhand has been undertaken to assess the spatial, temporal and seasonal variation in water quality and its suitability for drinking, domestic and irrigation purposes. The study on understanding weathering and geochemical process in

major river of the India and world has been carried out by (Bartarya SK 1993; Handa B.K 1972; Pandey S.K 1993; Raymahasay, 1970; Hu et al., 1982; Abbas and Subramaniam 1984; Sarin and Krishnaswami, 1984, 1999; Sarin et al. 1989; 1999; 1990; Hang et al. 1990; 1995; Chakrapani et al. 1995; Chakrapani 2005; Bhatt and Saklani 1996; Suresh 1989) and internationally (Stallard H.K et al. 1982; Hasnain et al. 1989; Dalai et al. 2002; Berner 1987, 1983; Stallard 1983). Hydrochemistry of surface and groundwater studied by (Stallard and Edmond 1983; Drever 1988; Edmond & Huch 1997; Harris et al. 1998; Gaillardet et al. 1999; Millet et al. 2002; Das 2003; Dhimon 2003; Dupre et al. 2003; West et al. 2005; Bhatt et al. 2007; Anderson et al. 1997 and Divya et al. 2011). The water quality of study area and ionic composition of the rivers studied by (Livingstone 1963; Meybeck 1976; Turekian 1969; 1971). It has been estimated that 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).

As per (Gibbs 1970) more than 90% river are rock dominant type. The remaining rivers are rain dominant types or evaporation crystallization types containing SO_4 , Na^{++} , Cl^- ions dominant (Gibbs 1970; Feth, 1971). (Ramesh et al.1995) conducted study on migration and contamination of major and trace element in groundwater in Madras city. (Parekh and Patel 2007) conducted geochemical assessment of Meghal Tidal Regulation of Saurashtra region indicated high concentration of TDS and particularly of Ca^{2+} , Na^+ , Cl^- , Mg and SO_4^- due to industrial development.

The deterioration of water quality and hydro chemical process due to heavy metals were studied by (Pandey et al. 2007; Kumar et al. 2007; Malarkodi and Krishnaswamy 2007). (Chakrapani 2002) studied Himalayan lake in Kumaun region namely: Nainital, Bhimtal, Sattal and Naukchial 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 and observed that the water of the Ganga river 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. The impact assessment of anthropogenic contamination due to point sources and non point sources in water quality have been studied by (Baig et al., Bu et al.; Rani et al. 2011; Shetty et al. 2013).

Numbers of research had been carried out on impact assessment of industrial and urban effluent on water quality and suitability of water for irrigation and drinking purposes (Upadhyay 1988; Chankrapani and Subramanian 1990; 1993; Das et al. 1997; Nanda and Tiwari 2001; Radhakrishna 2001; Nayak et al.; 2002; Das 2003; Sundary et al.; 2005; 2006; 2009) in Mahanadi river and other part of India and (Shanmugasundharam A, 2015) studied suitability of ground water quality for drinking purposes. However effects of industrialization and urbanization on surface and groundwater quality particularly in Haridwar have been poorly understood. After the formation of Uttarakhand in 2009, the rate of industrialization and urbanization has increased which caused contamination of water due to industrial waste, agricultural waste and urban waste. The objective of this study is to evaluate the major ion chemistry of surface and groundwater in terms of chemical weathering and to identify ionic sources and to understand factors controlling the water chemistry of the region.

1.1. Location of the Study Area

Haridwar district, covering an area of about 2360 km², is in the southwestern part of Uttarakhand state of India Figure 1. Haridwar is situated at an altitude of about 250 meters 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' N to 30° 15' N and latitude range 77° 45' to 78° 10' E. The climate of the Haridwar District is relatively hot and humid with an average annual rainfall of about 1127.2 mm.

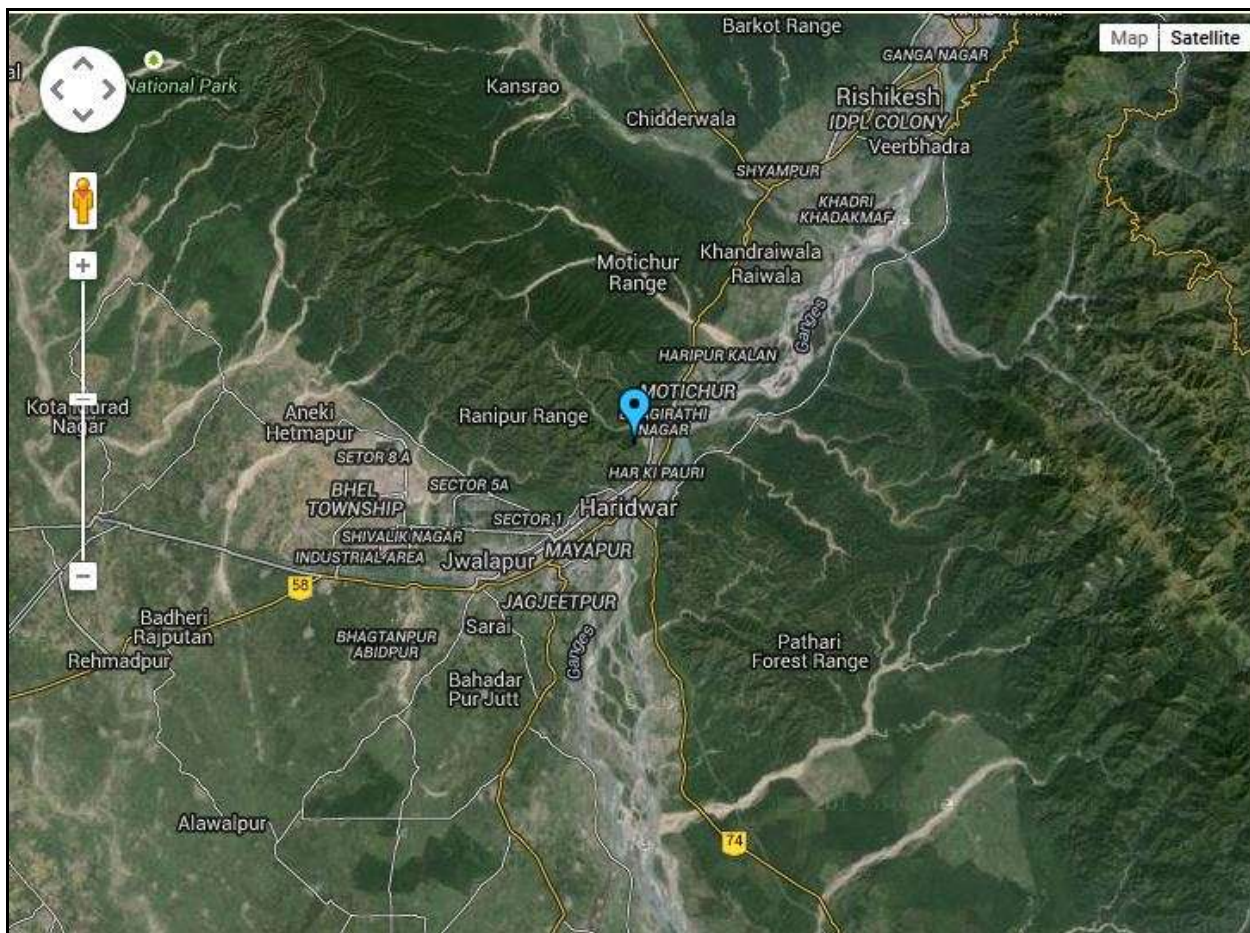


Fig.1. Location Map of the Study area

2. Material and Methods

Total 36 samples were collected from surface water (river and stream) and groundwater (Tubewell and Handpump) in winter season and 23 samples during summer season and post monsoon season from the catchment of Ganga river, urban and industrial area of Haridwar district Table 1. The water 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 urban area), agricultural area and industrial area of the Haridwar districts. The sampling sites are shown in Fig. 2, and the relevant details of samples location are given in Table 1. 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 deionized (18-2 mega ohm water form milli pore water purification system). 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 by using American Public Health Association (APHA 1995; Eaton et al. 2005) and (BIS 1991 : 2005) standards of water quality and suitably modified for the wide range of concentration encountered. The parameter i.e pH, temperature, total dissolved solid (TDS), dissolved oxygen (DO) and electric conductivity (EC) were analyzed in the field. All the major ions Na, K, Ca, Mg, F, Cl, NO₃, PO₄ and SO₄ were analyzed by ion chromatography using Ion Chromatograph Model D X-500 (DIONEX, USA). Heavy metals i.e Ni, Cd, Cr and Cu were measured by using Inductive Couples Plazma (ICP). 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, 1998).

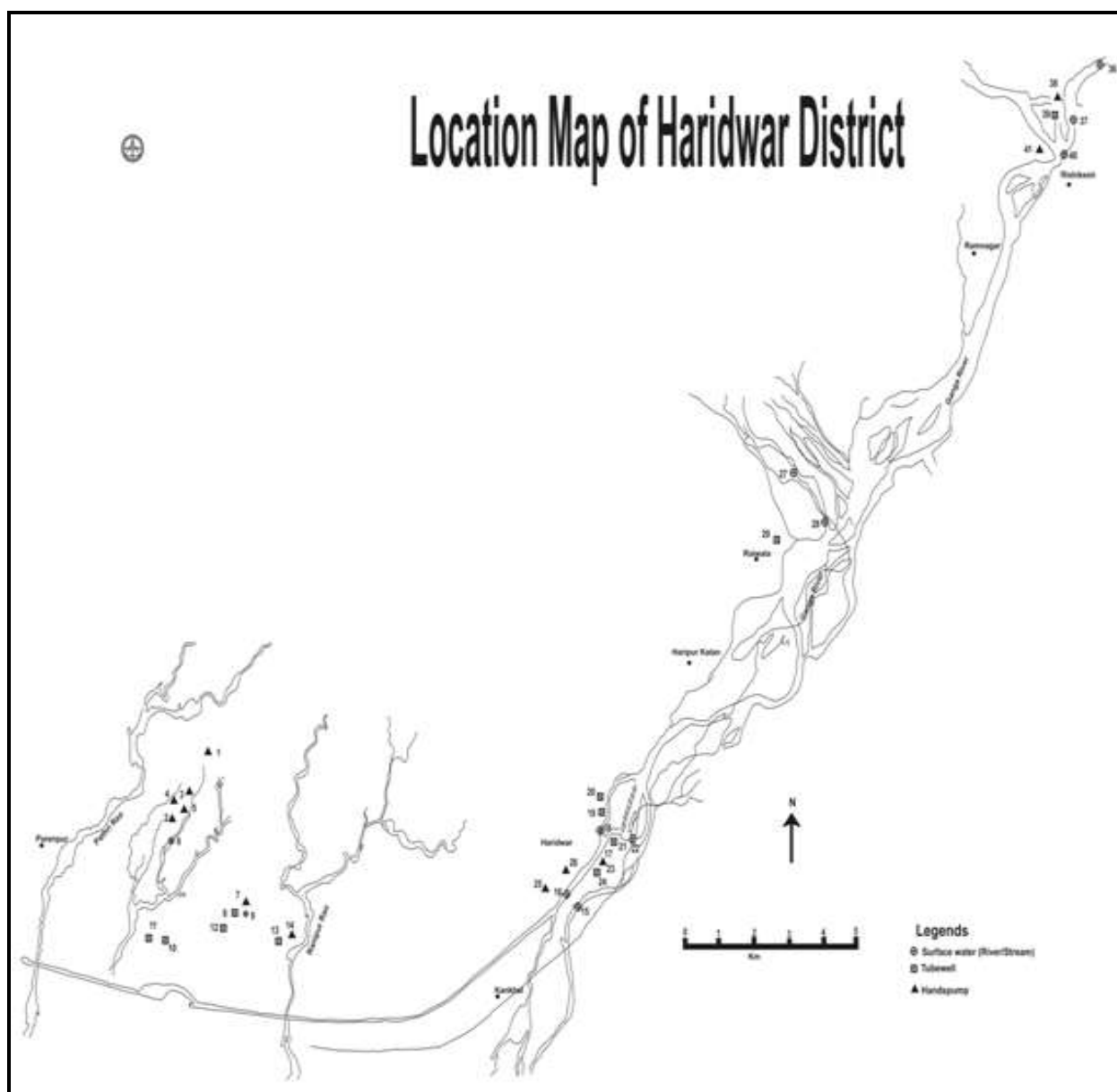


Fig.2 Sampling locations in Haridwar district , Kanchan (2011)

Table 1 Sampling Locations of study area

S.N.	Sample	Location	Surface Water	Ground water
1	RH1	Roshnabad Haridwar, Residential Complex,		TubeWell
2	RH2	Roshnabad Reserve Police Line		Tubewell
3	RH3	Sidcul Water Supply Satation		
4	RH4	Sidcul Tubewell -4		Tubewell
5	RH5	SAB Industries, Sidcul Tubewell 3		Tubewell
6	RH 6	Seasonal, Sidcul Stream	Surface	
7	RH7	Ravala Mehdood		Tubewell
8	RH8	Ravala Mehdood, Chauhan Mohlla		Handpump shallow
9	RH9	Surface stream near Saleempur	Surface	
10	RH10	Saleempur		Handpump shallow

S.N.	Sample	Location	Surface Water	Ground water
11	RH11	Saleempur, Dandipur, Handpump		Shallow Handpump
12	RH12	Ravala Mehdood		Handpump
13	RH13	Rampur		
14	RH14	Ranipur		Tubewell
15	RH15	Ganga river, upstream Neel Dhara	Surface	
16	RH16	Ganga river, channel from Har ki padi below bridge	Surface	
17	RH17	Down Stream, Har ki Padi	Surface	
18	RH18	Har ki Padi, Upstream	Surface	
19	RH19	Haridwar Jal Sansthan		Infiltration Well
20	RH20	Infiltration well 18, Haridwar		
21	RH21	Parmarth Ashram near Shri Gurucharan Asharam		
22	RH22	Ganga river	Surface	
23	RH23	Rodi Belwala, Tubewell No-7		Infiltration Well
24	RH24	Alaknanda Nalkoop , Shakti Chowk		Infiltration Well
25	RH25	Tubewell 7,		Tubewell
26	RH26	Ngarpalika office Jal Sansthan Haridwar		Tubewell
27	RH27	Song River at Raiwala below bridge	Surface	
28	RH28	Ganga river at Gohri Mafi village afterconfluence of Song river	Surface	
29	RH29	Gohri Mafi Raiwala		Handpump
30	RH36	Laxman Jhula, Risikesh	Surface	
31	RH37	Ramjula, Risikesh	Surface	
32	RH38	Jal Nigam Office, Muni Ki Rati, Risikesh	Surface	
33	RH 39	Muni ke Rati, Risikesh		Handpump
34	RH40	Triveni Ghaat, Risikesh	Surface	
35	RH41	Railway Station, Jalkar Compound, Risikesh		Tubewell
36	RH42	Pump No-5, Bharat Sanchar Limited Nigam Limited, Risikesh Deharadun Road		Tubewell

The statistical analysis was carried out using SPSS 17 to identify the correlation between physicochemical water quality. Ternary diagram have been plotted with the software Sigma Plot 2001. Piper diagram, were developed using Aqua Chem Software version 2011.1. Spatial variation of various parameter were carried out by using Surfer 8 software. The parameter such as Na %, sodium absorption ratio (SAR), permeability index (PI), Wilcox diagram & US Salinity Laboratory classification were used in order to assess the water for suitability of irrigation purposes.

3. Result & Discussion

3.1 Ionic Variation

Water temperature in study area varies from 14.4°C to 21.4°C. The pH of surface water varies from 7.4 to 8.3 with an average value of 7.9 and in groundwater it varies from 6.85 to 8.54 with an average of 7.2 during winter season in Haridwar district Table 3. Among the anions bicarbonate is the most dominant (73%) followed by sulphate (15.4%), chloride (5.6%) and nitrate (4.8%), fluoride (0.6 %), phosphate (0.09%) in winter season. Calcium and Magnesium are major cations together they account for 90% of total cations. Calcium constitute 71% of total cation followed Mg (19%), Na (7.7%) and K (1.9%). Overall cation and anions concentration shows following trend in the study area in all three seasons.

$\text{HCO}_3 > \text{SO}_4 > \text{NO}_3 > \text{Ca} > \text{Cl} > \text{Mg} > \text{Na} > \text{Si} > \text{K} > \text{PO}_4 > \text{F}$

The concentration of HCO₃ 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. In Haridwar district, the HCO₃ 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 HCO₃ concentration is 283 mg/l in winter, 307 mg/l in summer and 268 mg/l in post monsoon season Table3. In urban area the average HCO₃ concentration varies from 178 mg/l in winter, 179 mg/l in summer and 124mg/l in post monsoon season. 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 ground water chloride concentration were ranged from 9.7 mg/l to 54 mg/l in all three seasons Table 3.

Table.3. Max, minimum and mean value of ions in urban, agricultural area in surface and ground water of Haridwar district (mg/l).

Parameter	Industrial area (mg/l)			Agricultural area (mg/l)			Urban area (mg/l)			Surface water (mg/l)		
	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

Nd= Not detectible

In Haridwar district the fluoride 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. The ions i.e. F, NO₃ and K exceeded the maximum permissible limit of WHO and BIS standards for drinking purpose at few sampling locations of Haridwar district indicating increased impact of anthropogenic activities. Figure 16. Trace metals for various parameter i.e Ni, Cd, Cr and Cu were given in table 4 and were found to be under permissible limit of BIS standards of drinking water quality.

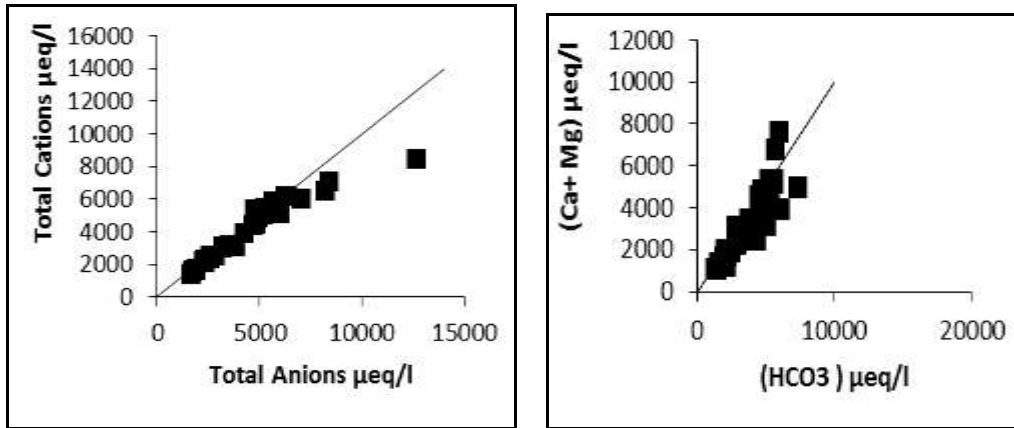


Fig. 3 Equivalent ratio between total cations and anions & between (Ca+Mg) & HCO₃

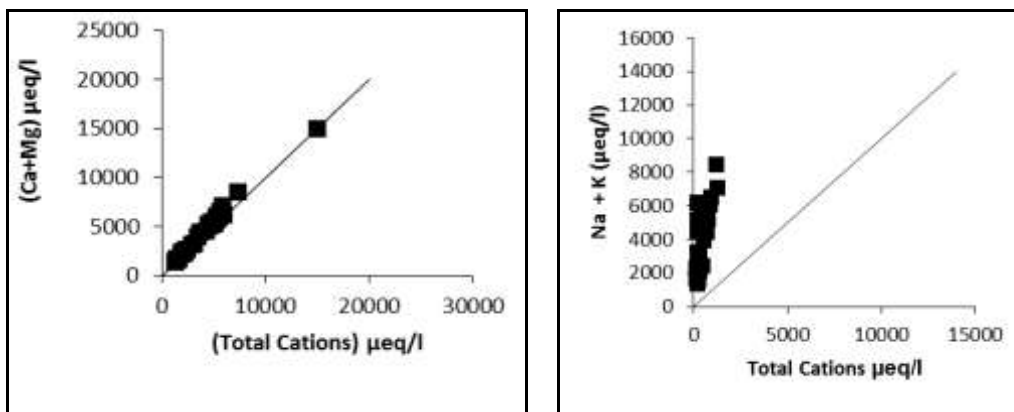
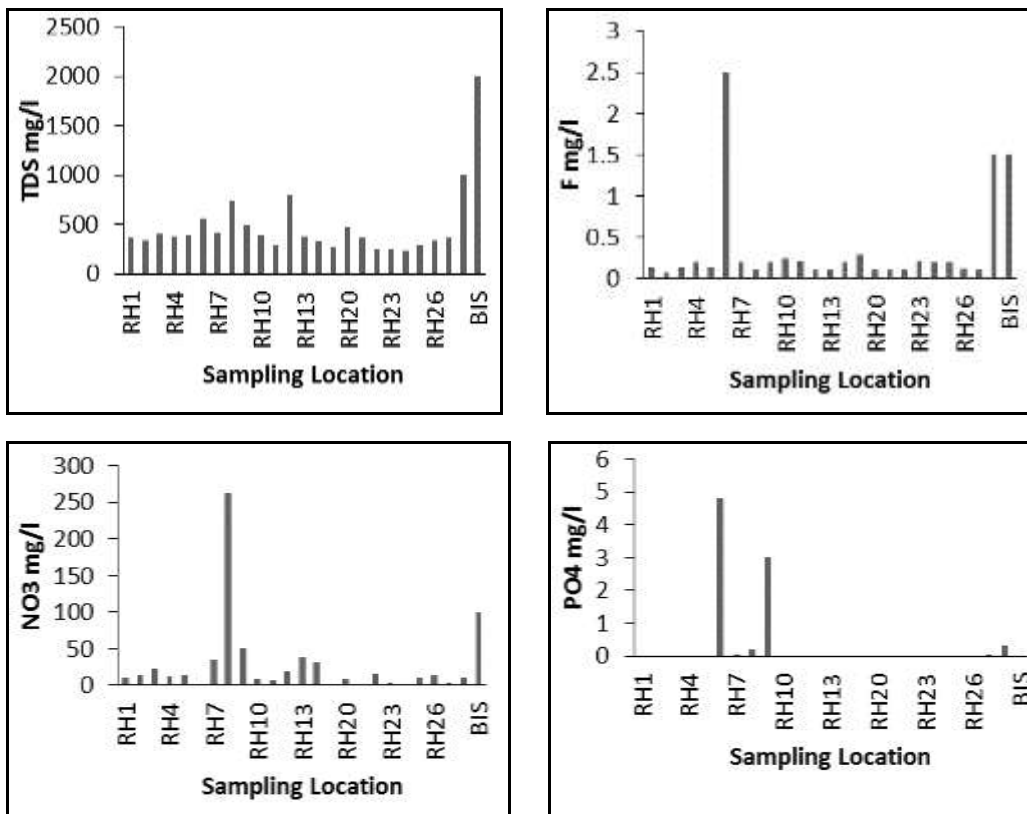


Fig. 4 Equivalent ratio between (Ca + Mg) : Total Cations (TZ+) & between (Na+K) : TZ+



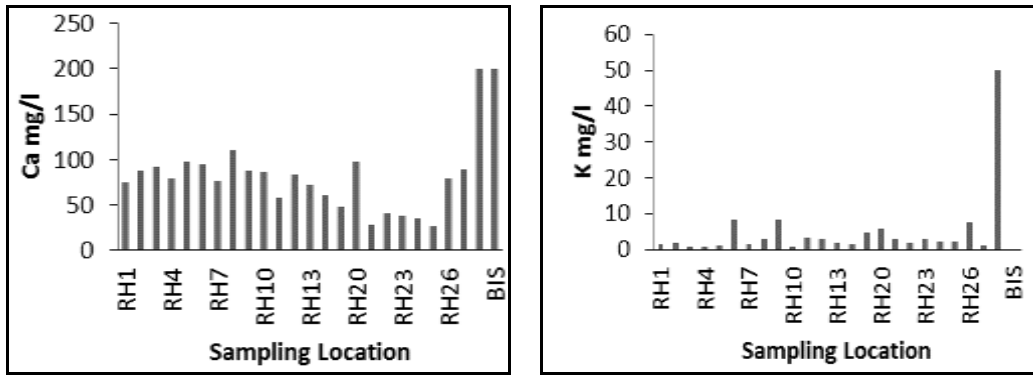


Fig. 16. Comparison of ions with BIS standards of drinking water quality.

Table 4. Seasonal variation in the concentration (ppb) of trace metals.

Sample Code	Ni			Cd			Cr			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

<DL= Below detectible limit

3.2 Sources of Ions

The dissolved concentrations of ions in river water were derived from various sources including rock weathering, rainfall, glacial melt water, wind-blown dust but among all these sources, rock weathering is major source of ions in water composition of study area as per the (Gibb’s schemes; 1970;) (Fig.5). Major ions chemistry of the water can be modified by anthropogenic sources i.e. sewage waste, improper disposal of waste, industrial effluents and chemical fertilizer from agricultural runoff, (Semwal N and Jangwan J.S. 2009)

The TDS has shown positive relationship with HCO₃ (r² = 0.822), Na (r² = 0.7), Mg(r² =0.8), Ca (r²= 0.7) , Cl (r²= 0.5), NO₃ (r²=0.5), and PO₄(r²=0.3) Table 2 indicating high concentration of HCO₃, Ca, Mg, NO₃ and PO₄ ions in water bodies. The spatial variation of Ca follows a pattern similar to that of Mg and show good positive relationship (r² =0.7) indicating same source of Ca and Mg. The mean ratio of Ca+ Mg : Na + K in entire study area is ~ 11.2 which is greater than worlds average of ~ 2.2 indicating that weathering of carbonate lithology is a major source of ions in water. Excess of Na over Cl and higher Na/Cl molar ratio ranging from 1.2 to 11.6 (mean 2.7) suggest that a much of the Na and K has a source other than precipitation

possibly through rock weathering. High equivalent ratio of Na : Cl (2.7) suggesting that Na and K could be derived from silicate weathering apart from precipitation (Stallard & Edmond 1983).

Table 2. Coefficient of correlation between various ions

	TDS	EC	HCO ₃	Cl	NO ₃	PO ₄	SO ₄	Na	K	Mg	Ca
TDS	1	0.90	0.82	0.5	0.5	0.3	0.1	0.7	0.2	0.8	0.7
EC	0.90	1	0.90	0.6	0.5	0.3	-0	0.9	0.2	0.7	0.8
HCO ₃	0.82	0.90	1	0.4	0.3	0.4	0.2	0.7	0.2	0.5	0.9
Cl	0.54	0.61	0.45	1	0.7	0.3	0.0	0.6	0.2	0.4	0.5
NO ₃	0.49	0.51	0.45	0.7	1	0.0	0.2	0.6	0.0	0.4	0.4
PO ₄	0.30	0.32	0.40	0.3	0.0	1	0.2	0.3	0.6	0.1	0.3
SO ₄	0.1	0.03	-0.19	0.0	0.2	-0.2	1	0.2	0.1	0.5	0.2
Na	0.79	0.90	0.76	0.0	0.6	0.3	0.2	1	0.1	0.5	0.6
K	0.23	0.24	0.28	0.1	0.0	0.5	0.1	0.2	1	0.0	0.1
Mg	0.81	0.70	0.58	0.2	0.4	0	0.5	0.5	-0	1	0.6
Ca	0.75	0.76	0.90	0.5	0.4	0.3	0.3	0.6	0.1	0.6	1

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

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

$$\text{Alkalinity}_{\text{silicate}} = \text{Alka}_{\text{total}} - \text{Ala. Carb. weathering}$$

It is estimated that on an average 79% of bicarbonate came from carbonate weathering and ~ 20.5% bicarbonate comes from silicate weathering, based on Ca, Mg and total bicarbonate concentration, by using (Raymahasay 1986) in Haridwar district. (Chakrapani 2004) reported that about 5-12% of HCO₃ is derived from silicate lithology implying carbonate weathering account for major amount of HCO₃. 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). As per (Gibbs 1970) the plot between TDS and Na⁺ / Na⁺ + Ca⁺² indicated the chemical composition of ions dominance by rock weathering (Fig.5).

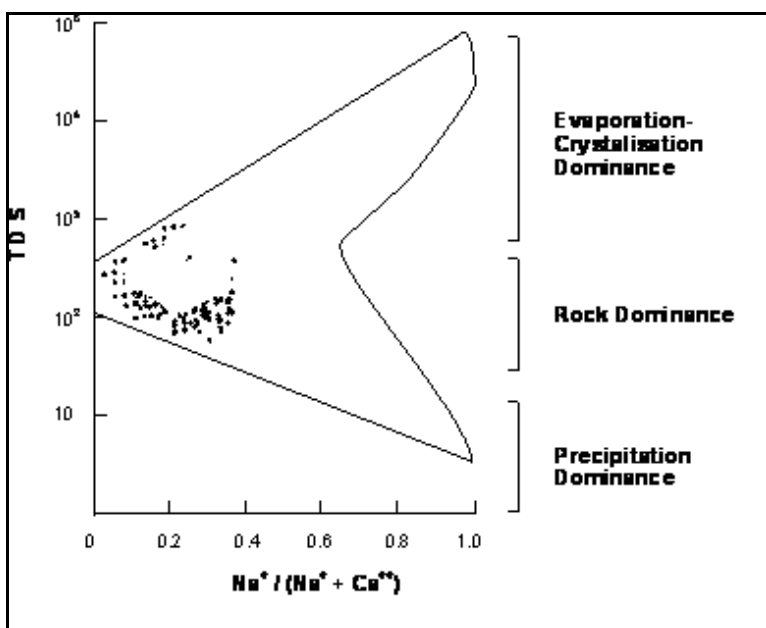
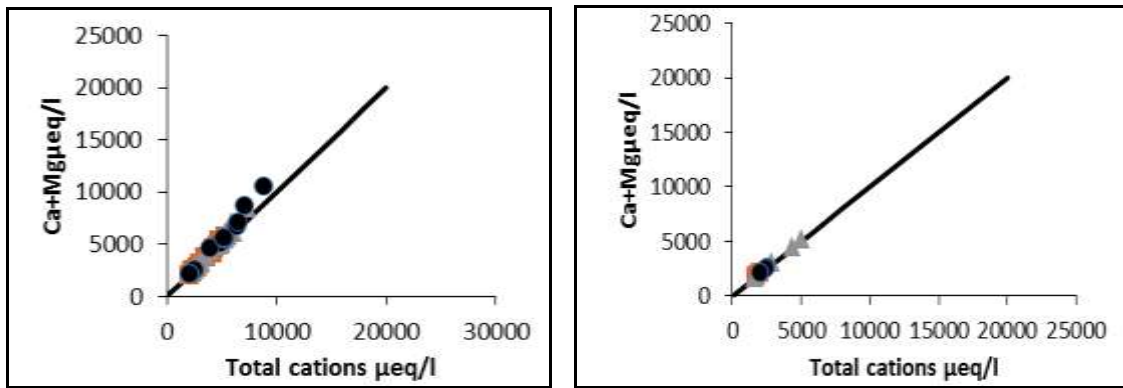


Fig.5 Plot of TDS vs Na / Na + Ca (Gibbs 1970)

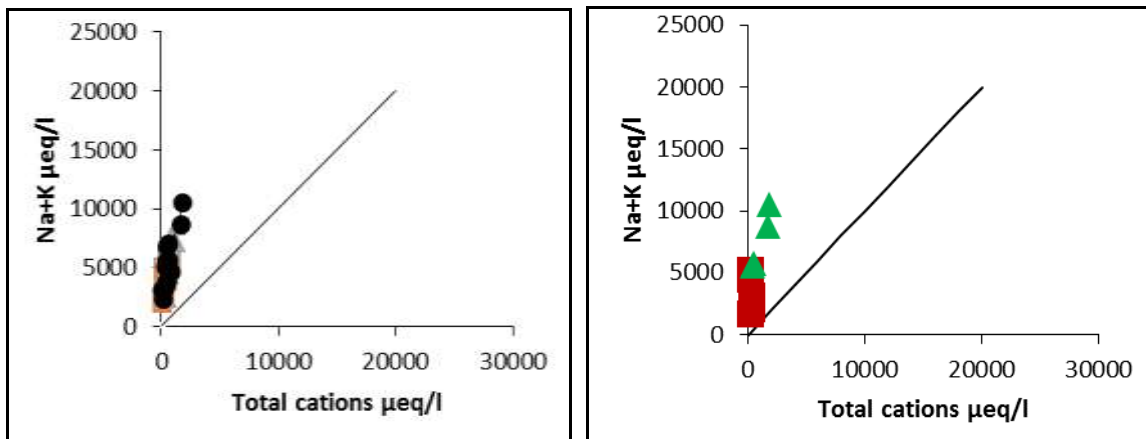
■ Winter Season ● Post Monsoon Season ▲ Summer Season



a) Haridwar Groundwater

Fig. 6 Scatter diagram between (Ca+Mg) and total cations in groundwater & in Ganga river during winter, summer and post monsoon season.

■ Winter Season ● Post Monsoon Season ▲ Summer Season

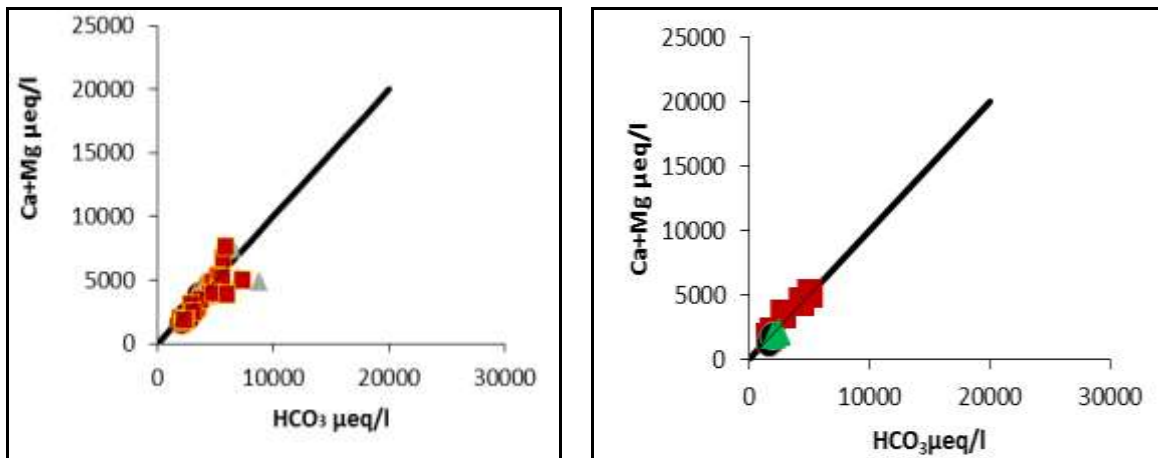


a) Groundwater of Haridwar

b) Surface Water of Haridwar

Fig. 7 Scatter diagram of (Na+K) and total cations in the ground water of during winter, summer and monsoon season.

■ Winter Season ● Post Monsoon Season ▲ Summer Season



a) Groundwater of Haridwar

b) Surface water of Haridwar

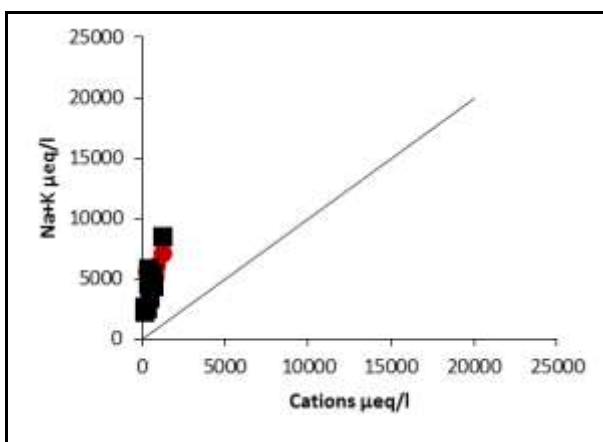
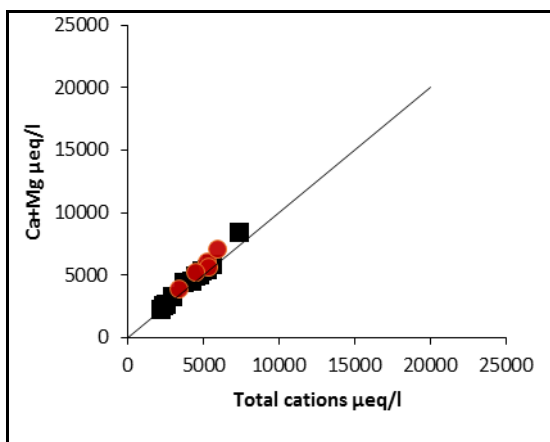
Fig.8 Equivalent ratio of Ca+Mg and (HCO₃) groundwater of Haridwar district.

A plot of (Ca +Mg) vs HCO₃ Fig 8 shows that in most of the samples the (Ca+Mg) content is slightly in excess of HCO₃ suggesting that the excess of (Ca+Mg) in these water should be balanced by SO₄²⁻, NO₃⁻ and Cl (Fig 6). The (Ca+Mg) vs TZ+ plot Fig.8 shows that most of the point approach equiline i.e. 1:1 trend with

an average equivalent ratio of 0.9. The contribution of cations through silicate weathering is obtained using the (Na*+K):TZ ratios (Na signifies sodium corrected for chloride) as an index of silicate weathering which indicated the sodium and potassium derived from silicate weathering is accounting about 9 % in all three seasons viz. summer, winter and post monsoon season. The Na+K : TZ+ ratio varies from 0.7 to 0.9 in all three seasons. The low abundance concentration of SiO₂, 73 μmole/l to 136 μmole/l with a mean value of 110 μmole/l and low SiO₂ : HCO₃ molar ratios (0.044 to 0.09 with a mean value of 0.06) also indicate the contribution of ions from silicate weathering is very less in Ganga basin. The molar ratio of Na/Cl of Ganga water at Haridwar varies from 0.3 to 1.4 with a mean value of 1.05 indicating either rainfall or halite dissolution as a major source (Ahmad *et al.* 1998). The surface and ground water of the study area were classified as various chemical types on a Piper diagram (Piper 1944), which were represented on the basis of effects of land use pattern in surface and ground water quality of Haridwar district. The surface and ground water was classified as Ca-HCO₃, Ca-Mg-HCO₃, Ca-Mg-HCO₃- SO₄ hydrochemical facies types in most of the sampling locations of the study area (Fig.12). In a few locations it was also of Ca-HCO₃-Cl and Ca-HCO₃-NO₃ hydrochemical facies types which were mainly due to contamination of water due to urban municipal solid waste, sewage waste and untreated industrial effluent which is directly discharged into the river and near by streams. As per the ternary diagram anion plot (Fig.10) relating HCO₃, SO₄ and (Cl+NO₃+PO₄) most of the data falls close to the HCO₃ vertex and on a cation diagram of Ca, Mg and (Na+K), most of the data falls close to the Ca vertex and towards the center of the field indicating dominance of carbonate weathering in the study area (Fig.11). The equivalent ratio of (Ca+Mg) : (Na + K) increases considerably during the summer season (19.6) in comparison to the winter season (6.7) and post monsoon season (13.5). The ratio of SO₄ : Cl (8.8) during the summer season and (10.8) and (9.7) were found respectively during the winter and post monsoon seasons and thus indicate that the Ca & SO₄ ions tend to increase in the summer season whereas the ions like Cl, NO₃, Mg, Na tend to increase in the post monsoon season in comparison to the summer season. High coefficients of correlations relations between SO₄ and Ca ($r^2 = 0.85$) indicated the sources of these ions were originated were mainly due to weathering of gypsum, pyrite and calcium rich feldspar in the basin which showed dominance of carbonate weathering in surface water of the study area (Dudeja *et al.* 2011).

Handpump ■

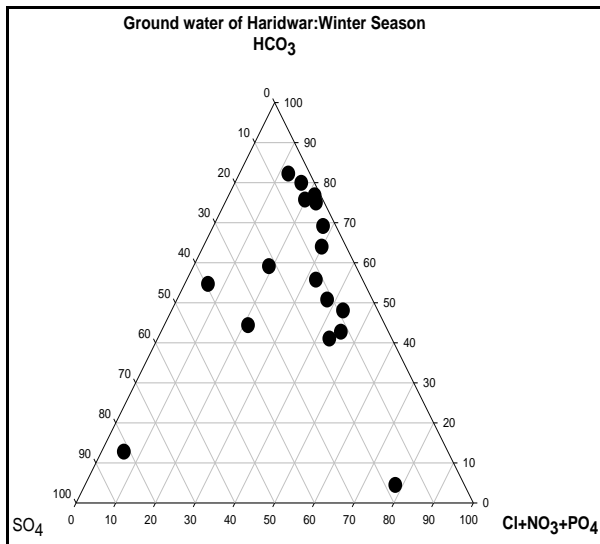
Tubewell ●



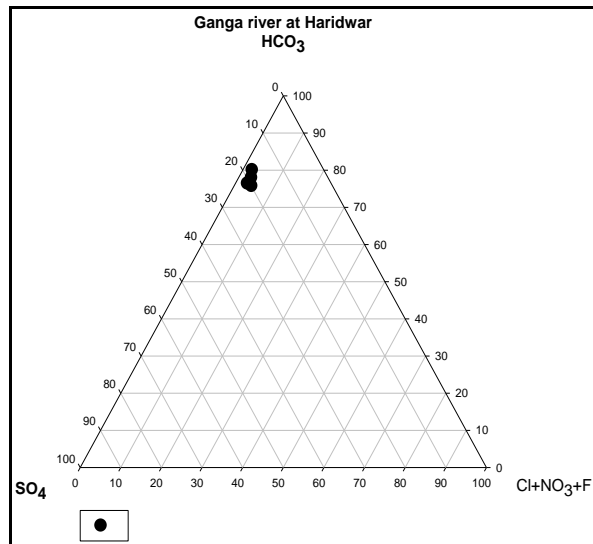
a) Ca+Mg : TZ+

b) Na + K : TZ

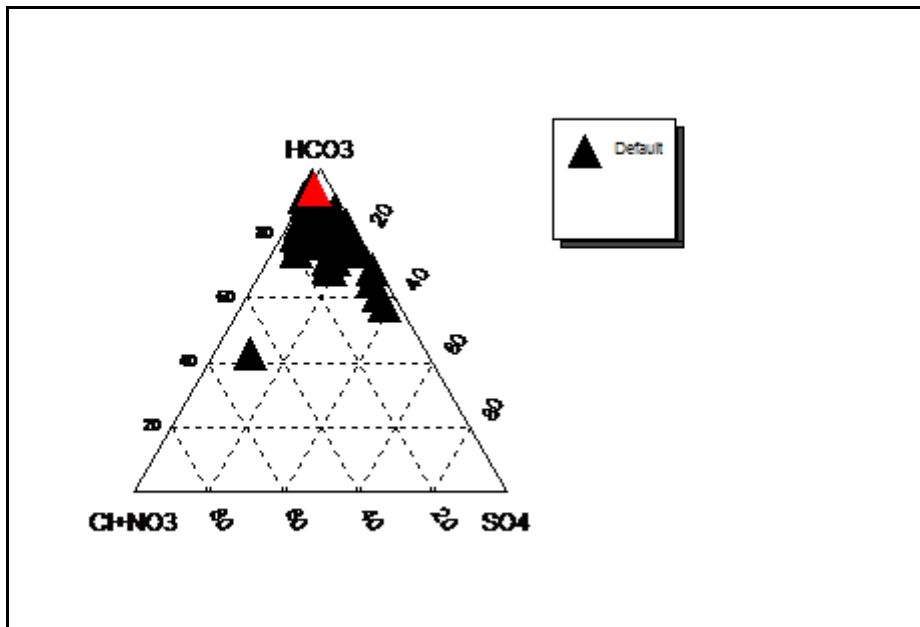
Fig.9 Equivalent ratio between (Ca+Mg) and Total cations in Tubewell & Handpump



a) Ground Water

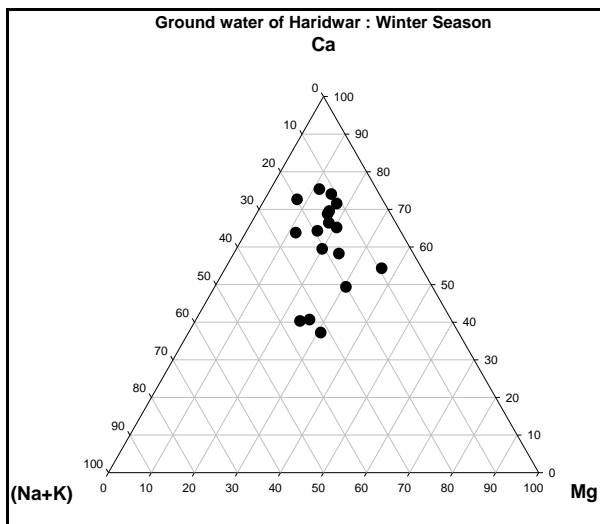


b) Surface Water

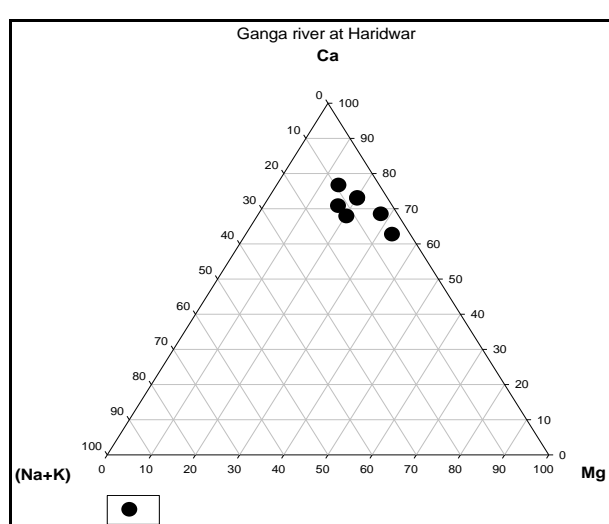


c) Surface and ground water

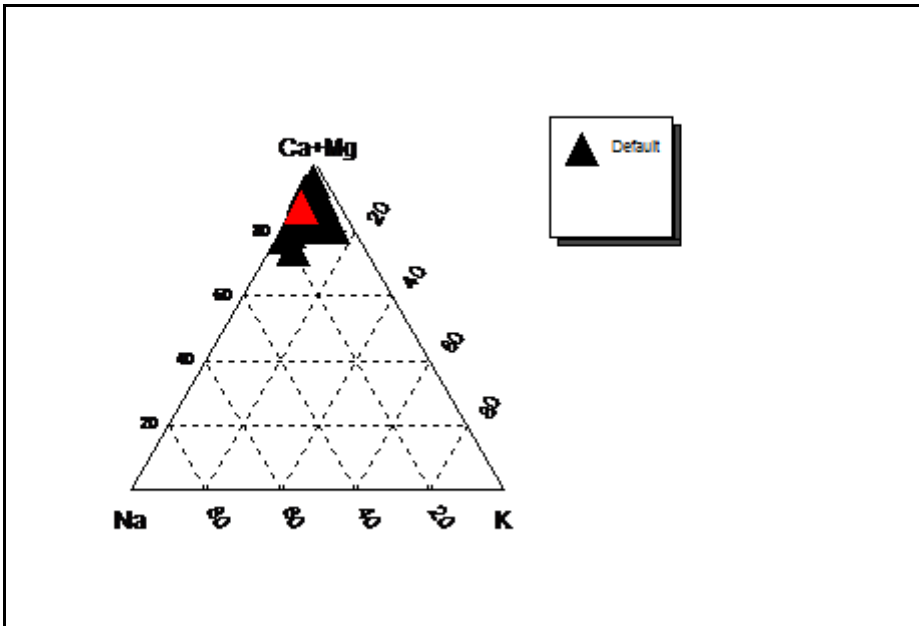
Fig. 10 Ternary diagram showing relationship between Anions : SO_4 , HCO_3 and $(\text{Cl} + \text{NO}_3 + \text{PO}_4)$ a) Ground water b) Surface water c) Surface and ground water



a) Ground Water



b) Surface Water



b) Ternary diagram of surface and ground water
 Fig: 11 Ternary diagram showing relationship between Cations : Ca, Mg and (Na+K) a) Ground water
 b) Surface Water c) Ground and Surface Water

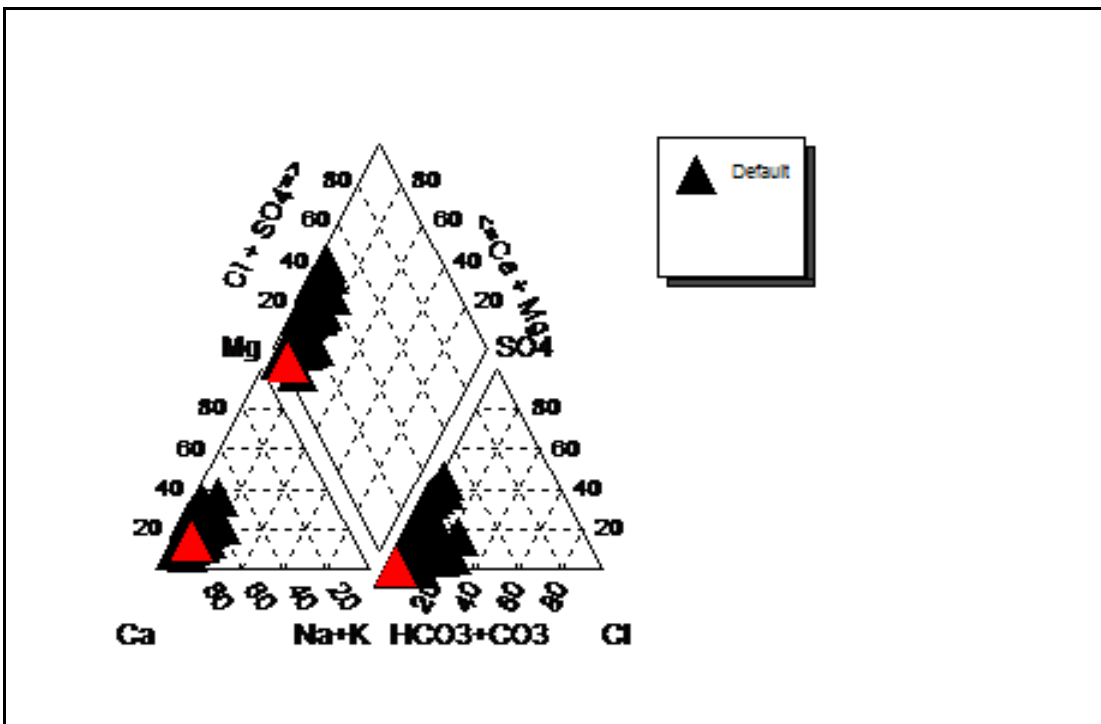


Fig. 12 Piper Diagram showing various chemical types in surface and ground water.

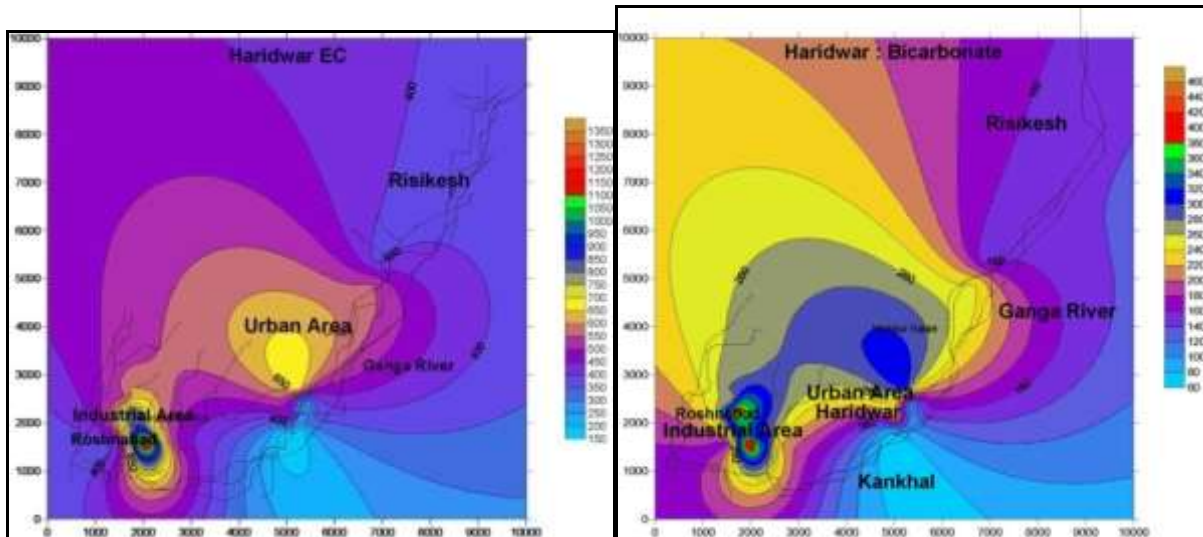


Fig.13 Spatial variation of EC and HCO₃ mg/l in Haridwar District

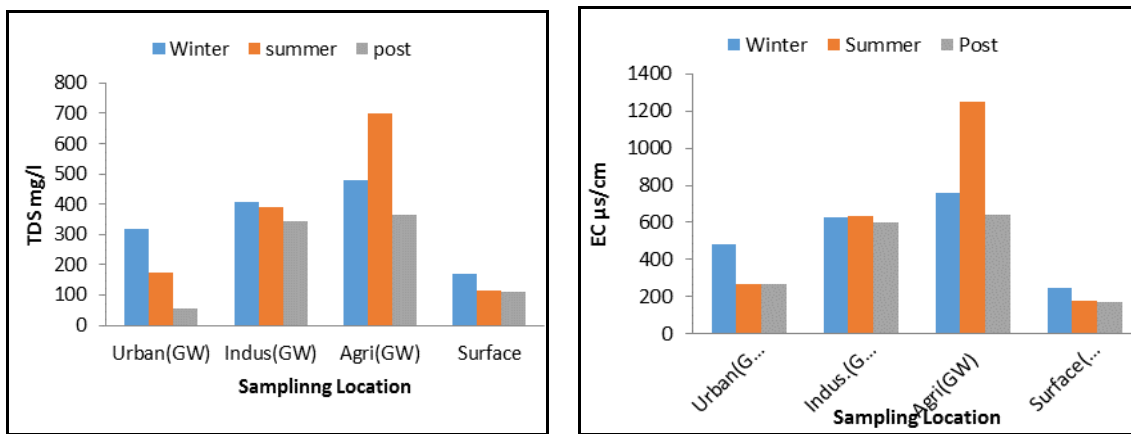


Fig. 14 Season variation of TDS and EC in Urban , industrial, agricultural and in surface water (Ganga river)

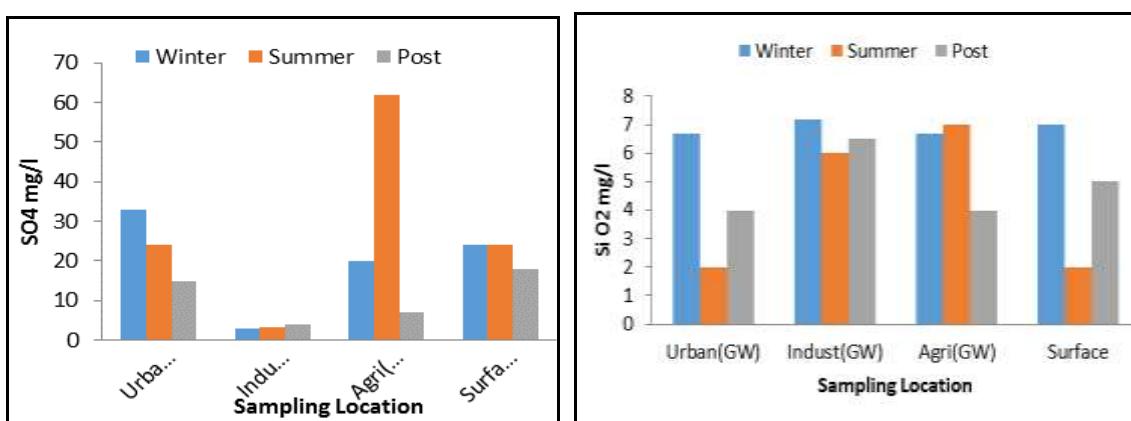


Fig. 15 Season variation of SO₄ and SiO₂ in Urban , industrial, agricultural area of groundwater (GW) and in surface water (Ganga river)

3.3 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 in ground water. The pH vary from 6.8 to 8.5 with a mean value of 7.3 in winter season, 6 to 8 with a mean value of 7 during summer season and in post monsoon it vary from 6 to 8.7 with an average of 7. The HCO₃ concentration is highest 4071µEq/l in winter season, found moderate

3159 $\mu\text{Eq/l}$ in summer season and lowest 2348 $\mu\text{Eq/l}$ in post monsoon season. 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%). The ions like Cl, NO_3 , SO_4 , K and Mg are tend to increase in post monsoon season in comparison to pre-monsoon season which may be attributed due to dissolution of ions attached with clay minerals.

The TDS value in tube well varies from 175mg/l to 740mg/l with an average of 365mg/l and in hand pump it varies from 288mg/l to 796mg/l with an average of 471mg/l. The ions (F, Cl, PO_4 , Na, K, Mg and Ca) in waters of hand pump (shallow aquifers) of Haridwar tend to increase in comparison to water of tubewell (deep aquifers). In Haridwar district the hand pumps are generally drilled to a depth of 40m and draw water from shallow aquifers in comparison to tube wells 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. The increase in ionic concentration in water of hand pumps in comparison to tube wells 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 hand pumps in village area which is discharged in open drainage and in soil without any treatment.

The abundance of anions and cations in tube wells and hand pumps 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%)

The high ratio (Ca+Mg) : (Na+K) \sim 10 (in micro equivalent) and equivalent ratio of (Ca+Mg) : $\text{HCO}_3 \sim$ 1 and relatively high concentration of (Ca+Mg) to total cations (Ca+Mg : TZ+ = 0.8) indicate influence of carbonate lithology (Chakrapani 2005).

3.4 Surface Water

In Ganga water of Haridwar the among anions the bicarbonate constitute 73% followed by Cl (24%), SO_4 (22%) and NO_3 (1%) and among cations Ca constitute 71% followed by Mg (19%), Na (6%) and K (4%). The (Ca+Mg) account for more than 90% of the cation and HCO_3 constitute about 73% of the anions. The 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). The seasonal variation in TDS and EC shows that the ionic concentration is maximum in winter and minimum in post monsoon season in surface water Haridwar district. The dilution of water during monsoon season, possibly lower the ionic concentration in post monsoon season while evaporation during summer season increase ionic concentration during pre-monsoon season. On a ternary cation diagram of Ca, Mg and Na+K Fig.11b most of the data fall either close to Ca vertex or towards the center of the field and also on the ternary anions diagram of HCO_3 , SO_4 and (Cl+ NO_3) Fig. 10, 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 1984; 1992a; 1992b) also substantiate the present observations.

3.5. Suitability of Water for Irrigation Purposes

The suitability of river water for irrigation were carried out on the basis of analyzing pH, EC, TDS, hardness, chloride, sulphate, carbonate, bicarbonate, nitrate, sodium, potassium, calcium magnesium, silica and iron. The pH value ranged 6.2 to 8.4 and indicated moderate to no problem category for irrigation purposes Table 5. 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). Irrigation using river water with high TDS can add salt concentration to the soil. According to (Langenegger 1990), the EC is its measure of salinity. 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). Based on EC concentration 7 samples were found to be in excellent category and 20 samples are categorized under good category and 2 samples are categorized under permissible category, thus all samples are found under excellent to permissible category of irrigation water quality as per (BIS guidelines 1991) . As per TDS measurement all samples were under good to permissible limit for irrigation purposes (Table 5). The most common toxicity in the irrigation water is from Chloride. If the chloride concentration in the leaves exceed the tolerance of crop, injury symptoms develop such as leaf burn or drying of leaf tissue (Sundaray et al. 2009). The chloride concentration in all sampling location of the study area was less than 4meq/l (BIS 1991) indicating its suitability for irrigation purposes Table 6. As per (Ayers and Westcot 1994) all samples are in no problem class for irrigation purposes with respect to chloride content (Table 5).

Table 5. 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	6.5-8.54, 5.1- 6.4 and 8.5 to 9.5, 0-5.0 and 9.5	6.4 – 8.54	7.6	No problem Moderate Severe
2. EC $\mu\text{s/cm}$ (Salinity hazard)	<250 250- 750 750 – 2250 2250- 5000	166- 1330	370	Excellent Good Permissible Unsuitable
3. TDS Mg/l	200- 500 500 – 1,500 1,500 – 3,000	103 – 796	330	Good Permissible Unsuitable
4. Cl Meq/l	< 4 4 – 10 >10	0.001 – 1.7	0.3	No Problem Moderate Severe
5. $\text{NO}_3\text{-N}$ (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	60- 354	177	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	7 - 33	18.00	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	0.07 –15.6	5.2	Soft Permissible Unsuitable
10. PI	Class I >75% Class II 50-75% Class iii < 25%	5.7%-28.9 %	14.7	Excellent Good Unsuitable

Table 6. Irrigation water quality parameter

Sample	pH	EC μ s/cm	TDS(mg/l)	Cl meq/l	NO ₃ (mg/l)	SO ₄ mg/l	Hardness mg/l	Na%	RSC	PI %	CAI I	CAI S	SAR %
RH1	7.24	558	369	3.69	11.3	3.02	215.2	9.88	1.45	47.7	87.8	93	7.017
RH2	7.24	523	346	3.46	13.68	7.3	234.7	10.4	0.20	44.8	121	125	7.69
RH3	7.1	618	405	4.05	22.5	3.04	250.3	6.204	0.57	50.7	176	178	4.68
RH4	7	582	380	3.8	11.6	1.3	226.5	7.558	1.61	45.4	93.1	96.9	5.51
RH5	7.12	605	395	3.95	13.9	0.9	267.1	6.732	1.07	51.5	36.3	45.0	5.14
RH6	7.7	862	555	5.55	0	0.01	274.4	13.47	2.89	49.6	1099	1100	9.25
RH7	7.2	645	423	4.23	35	9.3	231.5	7.877	1.84	40	377	377.92	5.71
RH8	6.93	1225	740	7.4	263	66.4	354.1	14.27	1.15	50	1985	1985.81	4.2
RH9	7.44	753	493	4.93	50	13.78	253.6	13.97	1.67	42.4	519	520.32	9.23
RH10	6.85	603	396	3.96	8.5	18.2	257.1	5.84	0.89	54.7	1117	1117	4.52
RH11	7.1	414	288	2.88	7.7	14.32	165.4	13.29	0.40	55.4	1001	1001.27	9.92
RH12	6.9	1330	796	7.96	20	5.8	286.9	17.28	5.17	51.3	289	293.22	16.3
RH13	7.1	590	381	3.81	38	17.4	218.1	13.89	1.13	57.45	393	394.77	10.6
RH14	7	500	332	3.32	31.4	15.1	180.8	15.87	1.10	71.03	354	355.83	11.4
RH15	7.7	185	129	1.29	1.3	21.8	79.07	6.72	0.36	73.95	33.5	36.6	1.87
RH16	7.8	192	136	1.36	1.3	21.5	76.74	6.89	0.42	68.67	30.4	33.78	5.189
RH17	8.3	227	157	1.57	1.8	27.8	93.18	11.83	0.56	68.64	36.2	42.19	7.4.02
RH18	8.3	205	143	1.43	1.9	28	92.37	12.27	0.39	64.29	42.4	47.83	3.4.20
RH19	7.4	415	280	2.8	1	21.7	137.34	9.22	1.15	45.08	160	161.84	3.33
RH20	7.2	700	470	4.7	9	24.3	270.894	9.81	1.00	76.49	487	488.19	6.42
RH21	7.2	558	370	3.7	1.92	23	96.11	19.1	1.12	53.4	20	33.66	5.9.63
RH22	8.54	377	254	2.54	16	20	150.1	5.62	1.40	58.4	273	273.57	2.75
RH23	8.54	377	254	2.54	2.84	24.5	117.2	6.82	0.43	61.4	62.1	64	2.155
RH24	7.9	166	236	2.36	1.8	25.6	105.3	5.94	0.37	63.5	39.1	42.25	2.1.77
RH25	7.4	286	419	4.19	9.8	27.6	112.1	11.5	1.40	44.1	187	188	5.70
RH26	7.33	517	346	3.46	13.73	29.14	236.4	8.66	0.96	38.5	309	310.2	4.00
RH27	8.1	385	615	6.15	6.6	98.7	209.9	4.09	1.11	37.6	111	112.8	2.48
RH28	8.24	494	329	3.29	6.2	93.2	243	3.74	1.05	34.7	96.8	98.7	2.33
RH29	7.6	555	370	3.7	4.3	101.6	291.44	3.10	0.91	66.6	73.6	76	2.23

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 IS	SAR %
RH30	6.4	232	155	1.55	10	20	93.87	11.3	0.38	74.3	131	132	5.04
RH31	6.31	181	125	1.25	7.2	17	70.37	12.6	0.21	72.6	140	141	5.20

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

The sodium adsorption ratio (SAR) measure of alkali/sodium hazard to crop, high sodium concentration lead to development of an alkaline soil. 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) Fig. 18. The SAR value were founds less than 10 Table 5 in all the sampling location except one samples RH 14 (12.63) thus belong to good to excellent category for irrigation purposes. When the concentration of carbonate increases above the total amount of calcium and magnesium, the water quality may be deteriorated, this excess carbonate combined with calcium and magnesium to form solid material(scale) and deteriorate water quality for irrigation purposes. Negative RSC at some locations indicate incomplete precipitation of calcium and magnesium (Tiwari and Manzoor 1988b). 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: $RSC = (CO_3 + HCO_3) - (Ca + Mg)$

As per (Ayres and Westcot 1994) most of the crop relatively unaffected until nitrogen exceeds 30 mg/l but sensitive crops may be affected by nitrogen concentration goes above 5 mg/l. The nitrate concentration in study area range from 1 mg/l to 263 mg/l, total 11 samples are categorized under no problem category with the concentration of less then 5 mg/l, 15 samples are categorized under moderate category with range of 5 mg/l to 30 mg/l and 3 samples are categorized under severe category with above 30 mg/l Table 6. The sodium toxicity cause leaf burn and dead tissue along the outside edges of leaves in contrast to symptoms of chloride toxicity which normally occur initially at the extreme leaf tip (Sundaray 2009). Sodium percentage in study area is calculated as per the following formula where all the ionic concentration are express in µeq/L (Wilcox 1948) found that the Na% in all sampling location of is less then 40% indicated excellent to good category of water for irrigation purposes Table 5, Fig.17.

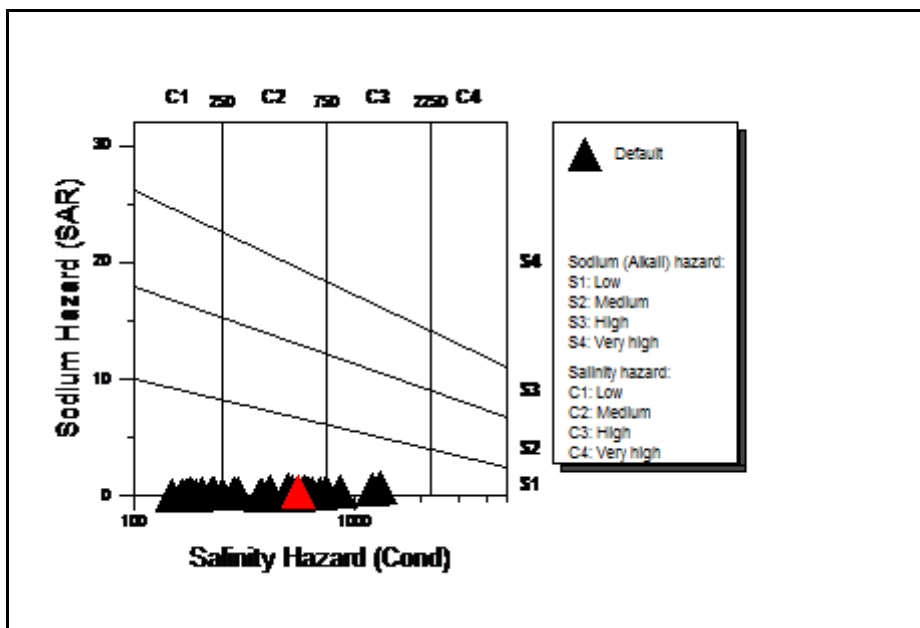


Figure 17 : Wilcox Diagram for classification of surface and ground water.

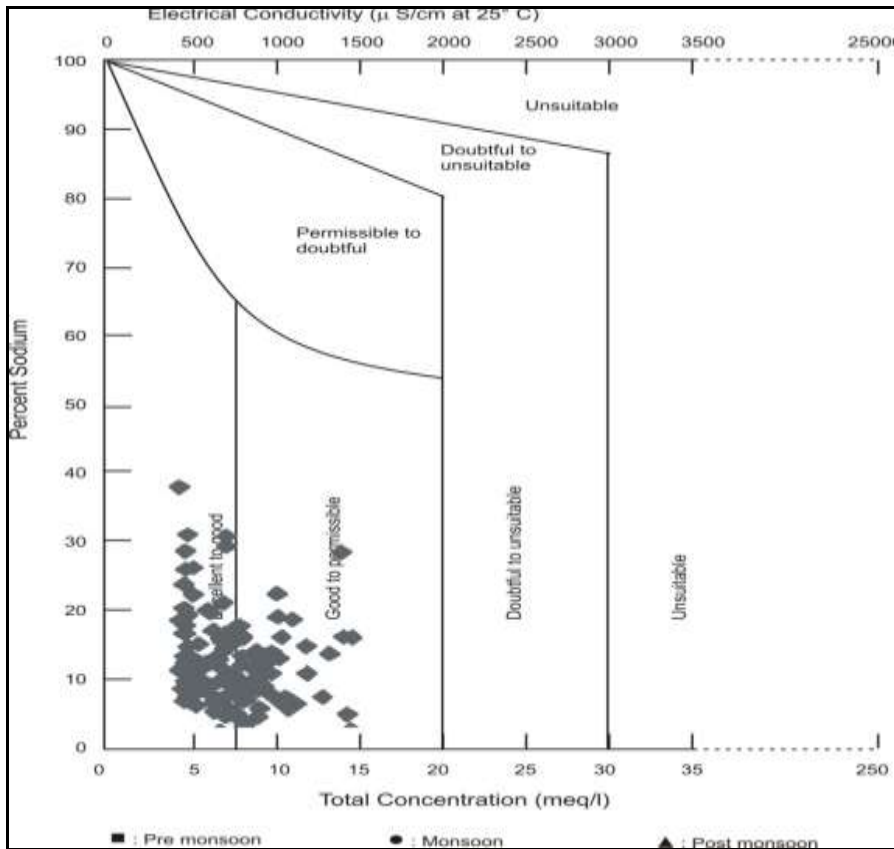


Fig. 18. US Salinity Laboratory classification of Surface and Ground water of Haridwar districts.

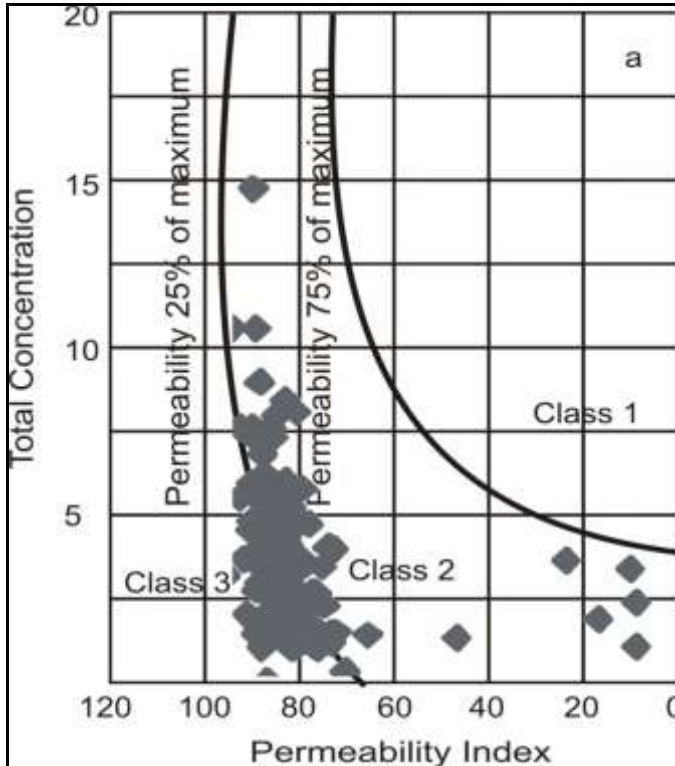


Fig. 19. Permeability Index Diagram for classification of Surface and Ground water of in Haridwar districts.

Based on RSC value in surface and ground water of Haridwar district 22 samples of in the industrial area were falls under unsuitable category (1.25 – 2.50) and 9 samples falls under permissible category (> 1.25)

Table (5). 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 $\mu\text{eq./L}$.

The PI values at all the sampling locations in Haridwar district were found in between 25%- 100% indicating good to excellent category for irrigation purposes Fig. 19. 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 (CAI) developed by (Schollar 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 Haridwar the ratio of CAI – I and CAI – II was found to be positive in 3 sampling locations in industrial area, 1 sampling location in urban area and in surface water ratio was 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.

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 Haridwar district were plotted in the graphical diagram (Fig 18) of irrigation water (US Salinity Laboratory 1954) and found that most of the samples were falls into C1S1 (low salinity with low sodium) and C2S2 (medium salinity with medium sodium) categories. The Na% was plotted against conductivity, which was designated as a Wilcox diagram (Wilcox 1955). According to Wilcox diagram (almost all the samples of Haridwar district falls into “Excellent to Good” category.

3.6 Microbiological Analysis

Coliform group of bacteria are indicator of pathogenic organism and presence of coliform in water in an indicator of contamination of human and animal faecal waste (Seth et al. 2014). The water contaminated with *Escherichia coli* (E-coli) and total coliform is associated with health risk and spread various diseases i.e Campbacteriosis, Shigellosis, Cholera, typhoid, diarrhea and cholera (Gabow 1996). Presence of E-coli indicate water is contaminated by fecal waste (Khazael et al. 2004). According to BIS, the the coliform count should be less < 10 colonies/100 ml and E-Coli should be zero colonies / 100 ml. Total 10 samples of surface and groundwater were collected from Haridwar district for microbiological analysis. Two test mainly *total coliform*(TC) and *E.coli* (*Escherichia coli*) were carried out. Total coliform and E-coli were absent during winter season except two sampling location (RH 15 – 38 per 100 ml, RH32 – 3 per /100 ml). The Total Coliform (TC) varied form 3 MPN/100ml to 38 MPN/100ml during winter season (Fig. 20). The TC value ranged from 408 MPN /100 ml to 24196 MPN /100 ml in pre-monsoon season and during post-monsoon season it ranged from 1011 MPN/100 ml in all samples (4 samples) . The TC value decreased in post monsoon in comparison with pre-monsoon season which possibly due to dilution in monsoon month when more surface runoff is available in rivers. E –coli was absent during winter season , in summer season E coliform were found only in two samples (RH 17 – 1 MPN/100, RH 30 -1011 MPN/100 ml) and during post monsoon E Coli were found in all samples. The E-coli value vary from 263 MPN/100 ml to 870 MPN/100 ml during post monsoon season. The increased concentration in Ecoli and total coliform is discharged to municipal waste and sewage discharged into 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. The presence of *E.coli* and *total coliform* in significant number in summer and post-monsoon season indicated enhanced tourist activity during these seasons and mixing of sewage waste during monsoon with surface runoff into Ganga channel. 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.

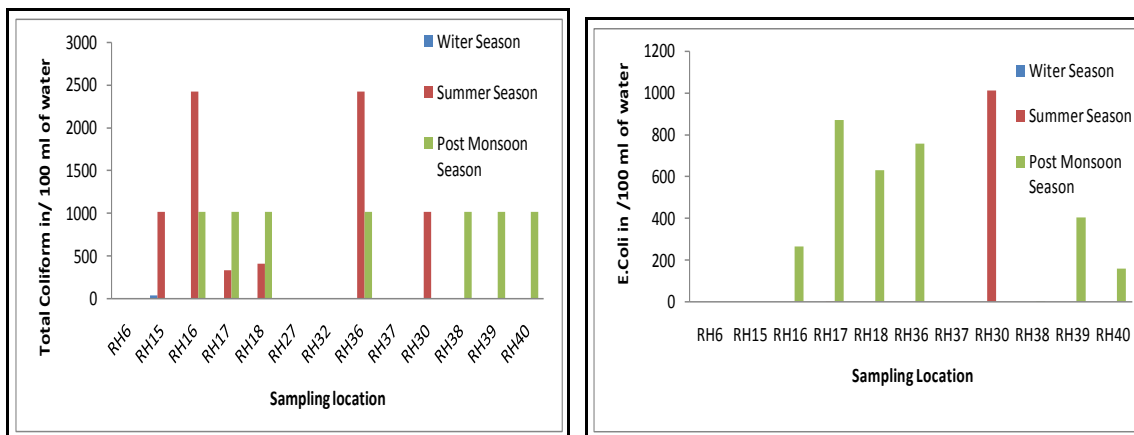


Fig. 20 Seasonal Variation of Total Coliform & E-coli in Surface and Ground water.

3.7. Temporal Change in Water Quality

The study carried out by (Jain 1996-1997), 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 urbanization and industrialization the result were compared with data of (Jain 2001, Jain 1996-1997) that the ions i.e. HCO_3^- , NO_3^- , K, and PO_4^{3-} has also increased in groundwater of Haridwar district which indicated phenomenal growth of urban and industrial centers over a decade after the formation of Uttarakhand and thus deteriorated the quality of surface and groundwater. the quality of surface and ground water.

Conclusion

Weathering of carbonate became the major source of ions in the hydrochemistry of surface and groundwater. The high equivalent ratio between $\text{Ca}^{2+} + \text{Mg}^{2+} / \text{HCO}_3^-$ (~1.2), $\text{Ca} / \text{HCO}_3^-$ (~1.09) and high $\text{Ca} + \text{Mg} / \text{Na} + \text{K}$ (~11.2) and correlation of bicarbonate with Ca (0.9) and Mg (0.6) indicated influence of carbonate lithology. 90% of bicarbonate came from carbonate weathering and 9 % bicarbonate comes from silicate weathering. The seasonal variation in TDS and EC shows that the ionic concentration is maximum in summer season in comparison to post monsoon season in surface water of Haridwar district. The decrease of the ions in post monsoon season is attribute to increased recharged during monsoon lowered the ionic concentration, while evaporation during premonsoon season increased the ions concentration in summer season. In ground water the ions concentration high in post monsoon season as compare to premonsoon 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, hence reducing the ions concentration in post monsoon season. The Total coliform and E.coli has been increased in summer season and post monsoon season indicating higher bacteriological pollution in Ganga river due to enhanced tourist activities in these season.

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