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MAJOR ION CHEMISTRY OF ASAN RIVERCATCHMENT OF DEHRADUN DISTRICT (IMPACT ASSESSMENT OF ANTHROPOGENIC SOURCES)

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Abstract: Major ion chemistry of Asan river catchment were studied to find the out the impact of anthropogenic activities on water quality. Surface and groundwater samples were collected from Asan Catchment, surface water samples were collected from Asan river while ground water samples were collected from tube wells and hand pumps. The parameters *i.e.* pH , EC, TDS, SO^{2-}_4, Cl^-, NO^-_3, $PO^{2-}_4SO_4$, HCO^-_3, total hardness, Ca^{2+}, Mg^{2+}, Na^+, K^+ were analyzed for studying major ion chemistry of surface and groundwater of Asan river catchment. Total 38 samples were collected from surface and subsurface water. The physical parameter like temperature, conductivity and pH, DO were measured in the field while for the analysis of remaining parameters, samples were brought in laboratory and analyzed by using standard methods of APHA for water and waste water analysis. Ion- chromatography were used for the analysis of cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and anions (SO^{2-}_4, Cl^-, NO^-_3, PO^{2-}_4, F^-).The ions i.eCa, Na, and HCO_3 were found to be dominant ions in surface and groundwater. 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 is the primary source of major ions to these water. Study result shows that water is slightly acidic to basic in nature. The EC were ranged from 54.2 to 1353 micro Siemens/, TDS ranged from 91 mg/l to 553 mg/l, HCO_3 were ranged from 21.0 mg/l to 366 mg/l and pH were ranged from 6.0 to 8.7. All cations and anions were compared with WHO and BIS Standard of drinking water quality in order to ascertain its suitability for drinking purpose.

Keywords: Asan Catchment; Ion chemistry; Water quality.

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INTRODUCTION

Water is one of the most important natural resource for the survival of all living organism. The chemistry of surface water is governed by supply of various elements from natural (chemical weathering and rain) and anthropogenic source sewage, industrial effluent, mining and municipal solid waste) (Semwal 2009). The quality of surface and groundwater is severely deteriorating due to increased urbanization, industrialization and application of chemical fertilizers for agricultural lands. River has always been the most important fresh water resources. Since ancient times river has been used for various sectors i.e industry, transportation, agricultural and public water supply (Shiddamallayya, 2008). Presently large amount of waste *i.e.* industrial waste, domestic waste and sewage is discharged into the river.

The concentration of nitrate and chloride is increased in surface and ground water due percolation of sewage effluents, industrial waste and agricultural waste (Hern and Feltz , 1998, Hao Change, 2002). Hydrochemistry of the ground water is changed due to rock - water interaction and oxidation reduction during percolation of water through aquifers (Krishna Kumar *et al.* 2009). The ionic composition in glacial melt stream which are located in Bhagirathi river were studied separately to observe contribution of ions in the river. The cations composition in River Bhagirithi was Ca>Mg > Na > K> NH4 and anions composition HCO_3> SO_4>Cl> NO_3. (Semwal 2009). The hydrochemistry of the Himalayan river is predominantly governed by lithology of the basin and less commonly by anthropogenic sources. (Sarin 2005, Semwal 2009). The weathering of carbonate rocks, calcsilicatesandalbite by carbonic and sulphuric acid dominated in Himalayan river basin (Semwal 2006). The dominance of carbonate rock weathering were found in the Himalayan river (Singh AK 1992, 1998). The study of major anions (HCO_3, Cl, SO_4, PO_4, NO_3, F) and cations (Ca, Mg, Na, K) play a significant role in classifying water quality. An estimation of poor water quality gives real pictures for adopting management strategies for remediation. (Jotimani 2012). The deterioration of water quality due to industrialization and urbanization of Dehradun district were studied by many authors (Dudeja 2010, Bahukhandi 2012, 2011, 2010, 2009, Jain 2002). The study on the deterioration of water quality in Asan and Tons river due to anthropogenic sources and industrial sources was carried by Khan 2013 and found that abiotic factors have directly affected diversity of the plankton and resulted decreased planktonic diversity. The Asan river and its catchment is contaminating day by day due discharge of waste *i.e.* sewage waste, solid waste, agricultural runoff i.e. application of chemical fertilizer and pesticides in agricultural land and discharge of industrial effluent s (due to improper treatment methods) and improper disposal of hazardous waste. Maximum part of the Asan river flows through rural area, semi urban area or slums area and these communities are using surface and ground water (shallow hand pump and deep hand pump) for drinking and irrigation purposes. Increased urbanization in Dehradun district has posed on immense pressure on all the resources including water resources. Contamination of water resources not only linked with deterioration of water quality but causes with depletion of water resources and if present trend continue, there may be water scarcity in near future. The drinking water supplied directly from tube well to the villagers without any drinking water treatment process and further it is affecting human health and children are more susceptible to diseases. Apart from urbanization, the industrial development in Asan Catchment is also one of the major sources of surface and ground water pollution. Keeping in this view it has been purposed to conduct a study on assessment of anthropogenic activities on surface and ground water of Asan river catchment under the following objectives; study of major ion chemistry of Asan river catchment and imapct assessment of anthropogenic sources on surface and ground water.

The study area lies in Asan catchment in Dehradun district of Uttarakhand (Figure 1). Dehradun or Doon Valley is the capital city of the State of Uttarakhand in North India. It is surrounded by the Himalayas in the north, Siwalik Hills in the south, the River Ganges in the east and the River Yamuna in the west. It is located between 29 ° 58 'and 31 ° 2' 30 "north latitude and 77 ° 34 '45" and 78° 18' 30 "east longitude. The Tons River is one of the most important and largest tributary of the Yamuna River and flows south-southwest. The River Asan is another important tributary of River Yamuna flowing northwest of Doon valley and latter joins the Yamuna River.

EXPERIMENTAL

The present study is conducted on Assan river catchment which covers a stretch of approximately 20 km from upstream to

downstream (Figure 2). The origin point of this river is from Chandrbani (spring water) in Dehradun district and joined Yamuna river in Vikasnager. Total 38 surface and groundwater samples were collected from Asan Catchment in the year 2008. Surface water samples were collected from Asanriverand ground water samples were collected from tubewell, handpump and shallow handpump. All surface and ground water samples were collected in summer season (Apri- May), winter season (December - Jan) and post monsoon season (September - October). Sample were collected in polythene container, precleaned with 10% reagent grade nitric acid, followed by rinsing deionized water. The parameter *i.e* pH, Temperature, DO, EC and TDS weremeasured in the field with the help of Multiparameter monitoring Kit and bicarbonate were measured immediately after collecting the samples with acid- base titration method using methyl orange and phenopthelene indicator (APHA, 1998). Na and K were determined with a Flame photometer and while silica with the help of spectrophotometer. The remaining anions and cations were measured by Ion Chromatography.

Figure 2. Asan river map, Sources (Google)

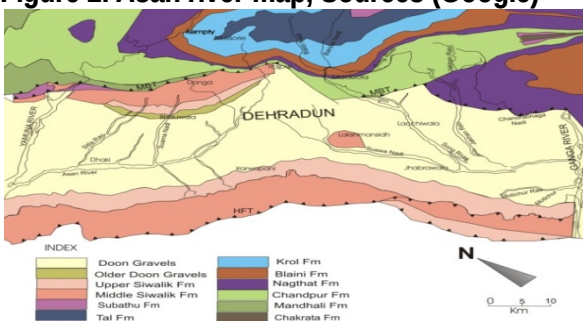

Figure 3. Geological / Drainage Map of Doon valley, (Valdiya, 1980; Joshi, 2003, Dudeja 2010)

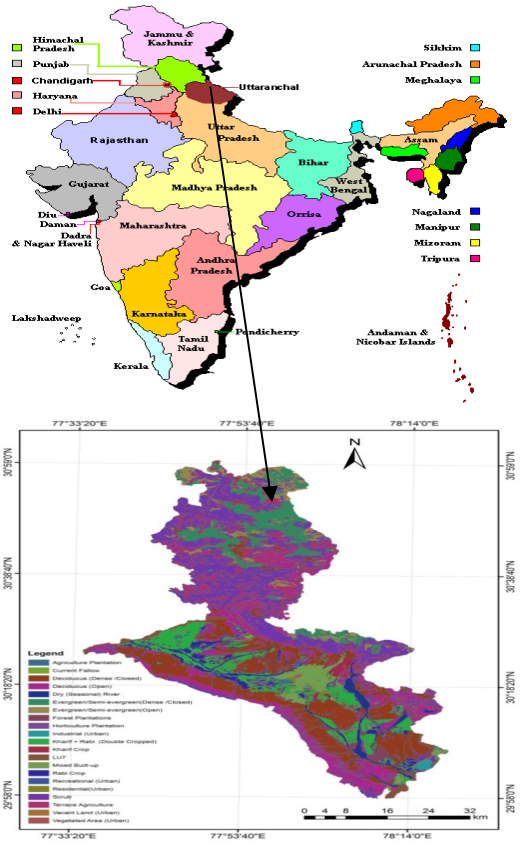

Figure 1. Location Map of the Study Area, ***Source : Bahukhandi Kanchan 2012***

RESULT AND DISCUSSION

The TDS concentration were ranged from 91 mg/l to 553 mg/l with an average concentration of 254 mg/l while pH value ranged from 6 to 8.7 with an average concentration of 6.8 indicating acidic nature of the water in Assan Catchment of Dehradun district. The concentration of various ions (max, minimum and average value) (Table 1) and their comparison with BIS standards for drinking water quality were shown in (Table 2.). Overall cations and anions concentration shows following trend in the study area.

Overall cations and anions concentration shows following trend in the study area. HCO_3>Ca>SO_4>Cl> NO_3>Mg>Na >Si > K >PO_4>F. The order of abundance of major anions are HCO_3 (64%)>SO_4(23 %)>Cl(6.2%)>NO_3 (4.7 %)>F(1.3%)>PO_4 (0.01 %) and for major cations in Ca (61 %) > Mg (23%) > Na (13%) > K (3.0%) in Assan catchment of Dehradun. HCO_3 and SO_4 are major anions which together contribute 87 % of total anions while Ca and Mg are major cations, together they account for 84% of cations in surface and ground water of Asan Cathcment. The coefficient of correlations between cations and anions was 0.98, indicating almost all the anions are balanced by caitons (Figure 4).

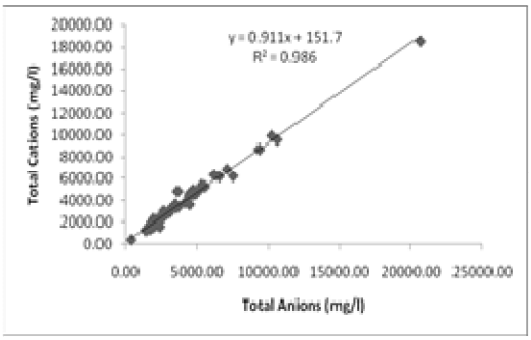

Figure 4. Equivalent ratio between anions and cations

The bicarbonate constitutes ~71% of the anions and calcium and magnesium constitute respectively 70% and 20% of cations. 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. Highratio of Na:Cl (2.5) in water of Asan river suggest less significant contribution of Na from other than marine source. The ratio of Na+K: TZ+ is 0.08 indicating the contribution from silicate weathering is limited to 8%. This indicates possibility of Na from anthropogenic source.

Table 1.Physio-chemicalcharacteristic of Asan Catchment

SL	Tem.	pH	TDS (mg/l)	EC µs/cm	DO mg/l	HCO3 mg/l	F mg/l	Cl mg/l	NO3 mg/l	mO4	SO4 mg/l	Na mg/l	K mg/l	Mg mg/l	Ca mg/l	Si mg/l	TH mg/l
D16	23.4	7.4	384.0	595.0	11.0	144.0	0.5	7.5	14.3	0.0	35.1	12.0	2.5	22.0	21.2	2.3	141.1
D17	22.0	7.2	390.0	595.0	8.0	203.0	1.4	5.7	4.1	0.0	0.01	12.0	2.5	20.0	23.6	21.0	138.6
D18	15.0	7.6	159.0	234.0	12.0	153.0	0.6	4.0	0.0	0.0	0.01	18.0	3.6	6.2	32.0	5.4	102.2
D19	23.4	6.9	366.0	446.0	5.0	203.0	0.9	3.9	6.3	0.0	26.0	11.2	2.4	14.3	41.0	5.3	157.0
D20	17.4	7.3	440.0	684.0	12.5	134.0	0.8	14.1	13.9	0.0	77.0	10.0	2.3	13.6	39.6	5.6	150.8
D21	23.5	6.5	214.0	323.0	6.5	116.0	0.5	8.2	21.4	0.0	30.0	7.3	2.1	11.5	32.0	6.7	124.0
D22	24.6	6.4	125.0	179.0	4.0	61.0	0.3	1.7	8.4	0.0	21.0	6.3	1.1	4.5	20.5	4.9	67.7
D23	23.3	6.5	219.0	340.0	5.3	78.0	1.0	6.0	19.2	0.0	31.0	10.0	1.5	3.0	29.0	5.0	81.9
D24	22.0	7.4	133.0	195.0	5.0	73.0	0.6	1.8	5.6	0.0	26.3	9.1	3.1	4.1	29.0	7.0	86.4
D25	25.1	6.8	114.0	168.0	4.4	73.0	0.8	2.0	0.2	0.0	22.0	9.1	4.4	4.2	21.5	9.1	68.8
D26	23.8	6.2	116.0	171.0	4.4	67.0	0.5	3.6	17.0	0.0	12.6	12.5	0.9	3.4	18.2	7.8	57.6
D27	17.8	7.6	553.0	903.0	11.0	366.0	0.1	22.1	29.3	0.3	168.5	14.2	7.5	34.2	118.8	8.8	425.3
D28	17.0	7.6	366.0	466.0	10.0	346.0	0.1	21.8	31.4	0.0	164.5	14.0	2.1	31.0	134.0	13.7	448.7
D29	17.4	7.3	440.0	684.0	12.5	241.0	0.8	14.1	13.9	0.0	77.0	19.5	4.2	26.1	64.0	5.6	260.6
D30	20.0	7.2	310.0	446.0	2.3	256.0	0.8	3.6	0.1	0.0	49.0	10.0	3.0	15.0	70.0	7.5	229.5

D31	18.7	6.5	307.0	441.0	3.1	158.0	0.6	15.2	24.4	0.0	57.0	12.0	10.2	12.0	61.3	5.9	196.3
D32	18.8	7.9	405.0	589.0	7.8	305.0	0.6	7.5	13.5	0.0	77.4	8.4	2.4	19.8	95.4	10.4	310.1
D33	21.8	7.0	323.0	466.0	3.1	195.0	0.6	5.1	8.1	0.0	0.01	9.0	2.1	15.2	38.7	13.1	155.2
D34	23.2	6.2	157.0	222.0	2.5	138.0	2.5	1.3	2.1	0.0	0.01	9.0	1.6	6.0	30.0	6.7	96.6
D35	16.4	6.2	251.0	358.0	2.4	176.0	0.5	0.3	0.1	0.0	0.01	4.5	0.9	4.9	43.0	15.2	123.3
D36	20.5	7.7	311.0	449.0	6.6	177.0	0.1	4.8	9.6	0.0	61.2	8.1	2.0	12.3	64.9	12.0	206.2
D37	23.1	6.3	165.0	232.0	3.7	115.0	0.1	0.3	1.9	0.0	0.01	4.5	0.6	2.5	28.0	17.0	77.5
D38	23.4	6.7	195.0	275.0	4.2	145.0	0.1	0.2	0.1	0.0	0.01	5.0	6.7	3.5	18.0	18.0	57.6
D39	21.6	6.7	159.0	221.0	4.3	105.0	0.1	1.9	3.6	0.0	0.01	5.6	0.8	2.6	23.5	21.0	67.1
D40	24.3	6.1	323.0	471.0	2.9	165.0	0.1	3.4	7.2	0.0	32.8	9.5	1.5	8.0	44.0	14.4	138.4
D41	24.3	6.1	323.0	471.0	2.9	176.0	0.1	41.0	41.0	0.0	29.0	33.5	16.0	9.0	55.0	9.1	168.9
D42	23.3	6.0	136.0	190.0	3.4	61.0	0.1	8.6	33.1	0.0	0.01	11.5	2.0	2.6	18.0	15.9	53.9
D43	17.3	7.1	549.0	840.0	2.0	158.0	0.1	57.8	25.5	0.0	44.5	39.5	4.9	9.0	53.3	14.1	164.8
D44	19.9	6.3	296.0	429.0	3.5	68.0	0.1	34.9	33.4	0.0	22.0	15.5	2.5	6.5	34.2	14.3	108.7
D45	22.7	6.3	117.0	165.0	5.7	65.0	0.1	3.2	12.7	0.2	18.1	5.4	0.1	2.0	20.4	17.6	57.2
D46	23.2	6.6	115.0	164.0	4.5	63.0	0.5	2.5	6.5	0.0	20.1	4.4	0.8	3.6	20.4	14.0	63.8
D47	23.7	6.3	99.0	137.0	4.5	58.0	0.1	3.7	0.8	0.0	15.0	4.7	0.7	2.8	16.0	17.6	49.9
D48	23.4	6.1	141.0	195.0	4.3	61.0	2.1	10.7	10.0	0.0	18.0	6.8	0.8	2.2	21.6	18.2	60.9
D49	24.2	6.5	128.0	178.0	4.5	67.0	0.7	2.1	3.0	0.0	30.0	5.1	1.4	1.7	25.2	15.0	67.5
D50	19.5	6.7	91.0	131.0	5.3	49.0	4.1	1.7	2.2	0.0	37.0	5.7	2.4	2.2	22.4	17.1	62.8
D51	17.6	6.4	336.0	451.0	4.7	21.0	0.8	1.8	0.0	0.0	0.9	3.4	0.9	0.5	3.6	16.0	10.7
D52	15.7	8.7	185.0	133.0	6.6	69.0	0.6	5.0	0.3	0.0	2.4	5.9	1.6	1.9	16.5	7.5	47.4
D53	23.8	6.9	247.0	358.0	3.4	63.0	0.9	24.0	6.0	0.0	6.9	4.5	1.0	2.9	29.8	7.6	83.4
Max	**25.1**	**8.7**	**553.0**	**903.0**	**12.5**	**366.0**	**4.1**	**57.8**	**41.0**	**0.3**	**168.5**	**39.5**	**16.0**	**34.2**	**134.0**	**21.0**	**448.7**
Min	16.4	6.0	91.0	131.0	2.0	21.0	0.1	1.7	0.0	0.0	0.01	3.4	0.1	0.5	3.6	2.3	10.7
Average	20.9	6.8	254.9	368.3	5.5	136.1	0.7	9.4	11.3	0.0	31.9	10.4	2.8	9.1	38.9	11.4	130.7

SL: Sampling Locations

The pH concentration was found less than 6.5 in almost 13 sampling location indicating acidic nature of the water. The pH beyond the range of 6.5 to 8.5 affects mucus membrane as per IS standard (10500, 1992, 1993). The increase acidic water is possibly attributed to higher concentration of NO_3, K, Cl from anthropogenic sources mainly due to improper disposal of solid waste, addition of chemical fertilizer due to surface runoff and discharge of industrial effluent into nearby stream or lands. These chemicals contaminate shallow aquifers as well as deep aquifers due to industrial effluent. Higher concentration of fluoride above (1.5 mg/l) can cause flourisis (Wee *et al*, 2000, Subba Rao and Naveda, 2003) The floridеconcentration has crossed maximum permissible limit of BIS standards of drinking water quality in two sampling location *i.e.* surface water (Asan River) D 48 (2.1 mg/L) and in ground water (boring water) , near industrial area Sidcul, D 50 (4.1 mg/l) which may be attributed to discharge of industrial effluent in nearby river or stream. The determination of TDS concentration is also very important to find out its suitability for irrigation and drinking purposes (Davis and De wiest 1966, Fatters , 1990. Higher concentration of TDS were found at the sampling location of D16 - Badowala (384 mg/l), D19 - Karbari (366 mg/l), D 27 –Chandrabani Spring (553 mg/l), (mg/l), D- 32 (405 mg/l), D 43 – Redapur(549 mg/l). Two samples have crossed the maximum permissible limit (500 mg/l) of BIS standards of drinking water quality. High concentration of TDS causes gastro-intentional irritation.

Table 2. Comparison of Ions with BIS standards for drinking water quality

#	Parameter	Max	Min	Average 172	BIS (IS 10500 : 1991) (Desirable Limit)	BIS(IS 10500 : 1991 (Permissible Limit)
1	Temp.	25.1	16.4	20.5	-	
2	pH	8.7	6.0	6.80	6.5 – 8.5	No relaxation
3	TDS	553	91	254	500 mg/l	2000 mg/l
4	EC (µcs/cm)	903	131	368	-	2250
5	DO	12.5	2.02	5.5		
6	Alkalinity (HCO_3)	366	21	136	200 mg/l	600 mg/l
7	F	4.1	0.1	0.7	0.6 mg/l 1.2 mg/l	1.5 mg /l
8	Cl	1.7	57.8	9.4	250 mg/l	1000 mg/l
9	NO_3	41	0.001	11.3	45 mg /l	100 mg/l
10	PO_4	0.3	0.01	0.01		0.3 mg/l (WHO)
11	SO_4	0.01	168	31.9	200 mg/l	400 mg/l
12	Na	39.50	3.4	10.4		
13	K	16	0.1	2.8		50 mg/l (WHO)
14	Mg	34.2	0.5	9.1	30 mg/l	100 mg/l
15	Ca	134	3.6	38.9	75 mg/l	200 mg/l
16	Si	21	2.3	11.4		
17	Hardness	448	10.6	130.7	300 mg/l	600 mg/l

All cations and anions were compared with BIS standards of water quality. Majority of the physical and chemical parameter were found to be under permissible limit of BIS standards for drinking water quality (Figure 5-12) however few parameters *i.e*. F, SO_4, TDS, pH, Ca and Hardness crossed the maximum permissible limit of Bureau of Indian Standard (BIS) for drinking water quality at few sampling locations. The SO_4 concentration in study area varies from 0.01 mg/l to 168 mg/l with an average value of 31.9 mg/l in winter season. The higher concentration of sulphate were found in Assan Catchment possibly due to weathering of gypsum bearing carbonate rock of Krol formation present in northern part of Doon valley. 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 Sodium Absorption Ratio (SAR) and Permeability Index (PI) etc. The water of the study area was found to be moderate to no problem category for irrigation purposes.

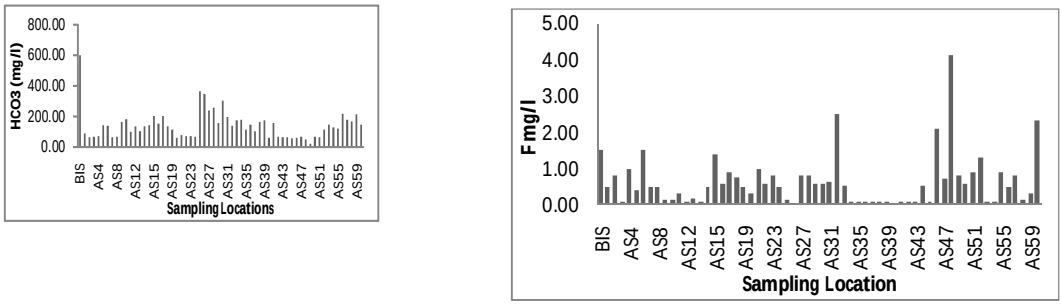

Figure 5. Comparison of HCO3 anf F with BIS standards for drinking water quality.

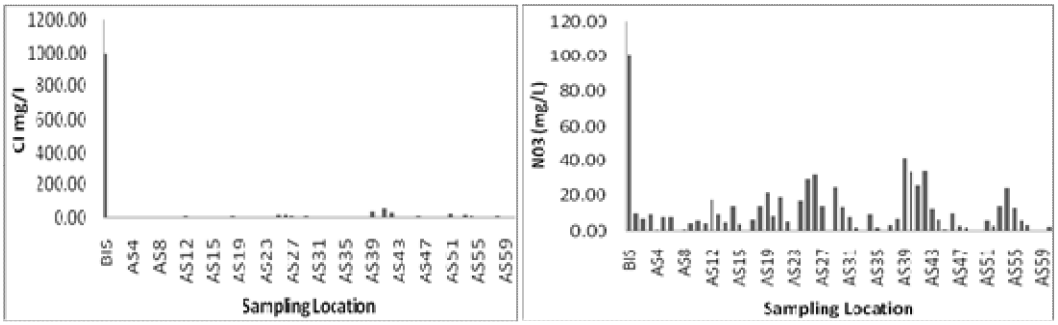

Figure 6. Comparison of Cl and $NO_3$with BIS standards for drinking water quality.

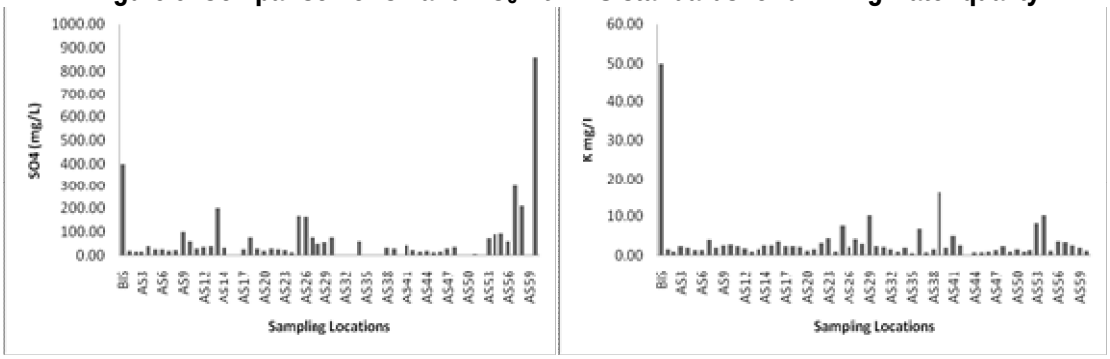

Figure 7. Comparison of $SO_4$and K with BIS standards for drinking water quality.

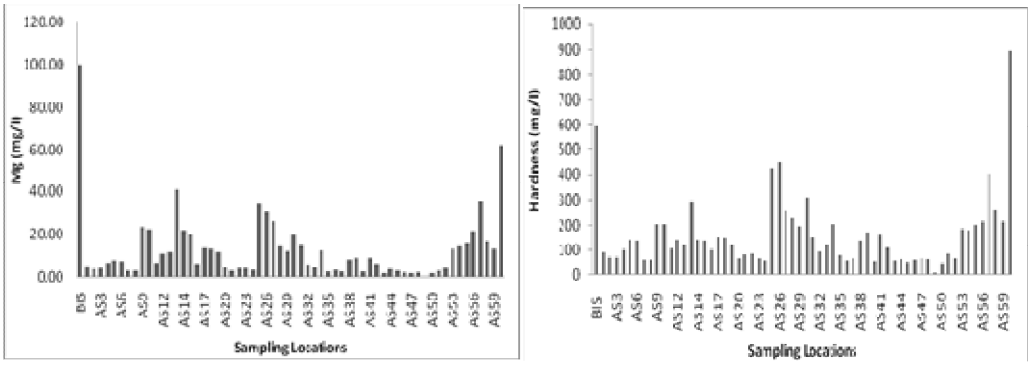

Figure 8. Comparison of Mg and Hardness with BIS standards for drinking water quality.

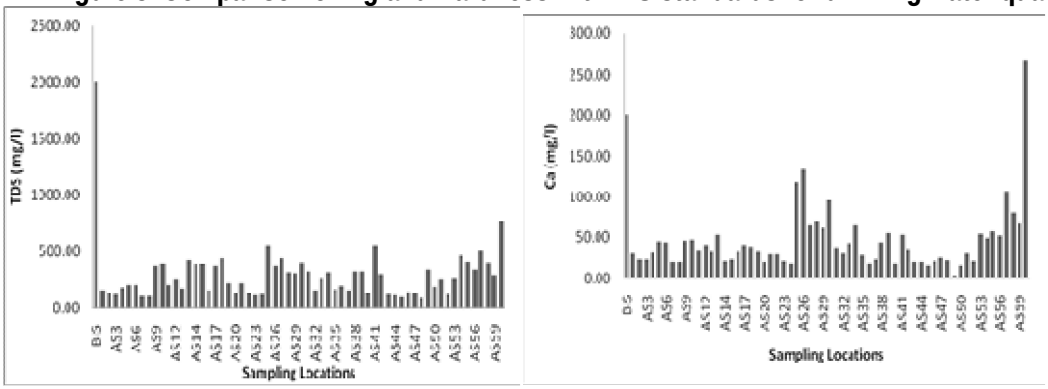

Figure 9. Comparison of TDS and Ca with BIS standards for drinking water quality.

The scatter diagram of (Ca+Mg) verses bicarbonate (Figure 10) shows that almost all of the Ca+Mg in Asan catchment are balanced by bicarbonate. This suggests that the chemistry of Asan catchment 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.

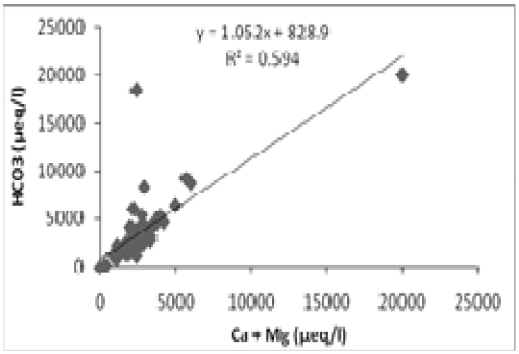

Figure 10. Equivalnet ration between HCO3 and (Ca +Mg).

The Ternary cations plot between (Ca +Mg), Na and K (Figure 11) indicated most of the cations data falls towards (Ca+Mg) vertex and on a Ternary anions plots that HCO_3, SO_4 and (Cl+ NO_3+F +PO_4) (Figure 12), most of the data falls towards the HCO_3vertex while few samples falls towards the (Cl+SO_4+NO_3+F) suggested the chemistry of the Asan Catchment is dominant by carbonate weathering but anthropogenic sources also affecting water chemistry of the region possibly due to improper disposal of waste in Dehradun city (Bahukhandi, 2012). The SiO_2 concentration ranges from 79.3µmole/l to 236.05µmole/l with a mean value of 166µmole/l.

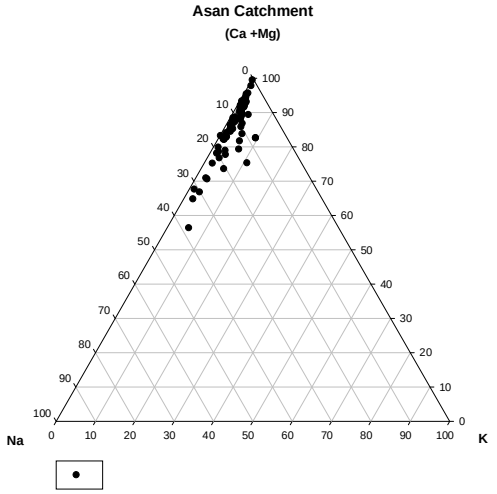

Figure 11. Ternary diagram between (Ca + Mg), Na and K (Cl +PO_4 +NO_3+F)

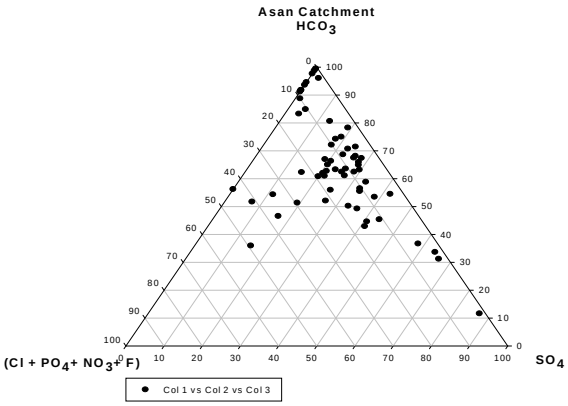

Figure 12. Ternary diagram between HCO_3, SO_4 and (Cl +PO_4 +NO_3+F)

CONCLUSION

The average (Ca+Mg)/HCO_3 equivalent ratio of 1.43, HCO3/TZ- ratio of 0.6, relatively high contribution of calcium and magnesium to the total cations TZ + and high 7 ratio of (Ca+Mg) /(Na+K) indicate that the carbonate weathering is primary source of major ions Asan Catchment of Dehradun district. 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, NO3 and SO4 crossed permissible limit of BIS standards for drinking water quality at few locations of Asan Catchment. The surface and ground water of the Asan Catchment area were found to be good category for irrigations purposes.

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