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ISOTOPIC AND CHEMICAL CHARACTERIZATION OF SHAHASTRADHARA SPRING, DEHRADUN

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Abstract— **The increasing water demand has led to heavy exploitation of groundwater resources in many parts of the country, particularly in the hilly regions. The water resources available in the hilly regions and are restricted to groundwater sources due to higher slopes. The major source surface water bodies such as rivers, lakes, springs etc is rainfall and minor is glaciers. The study shows that isotopic composition of precipitation shows depleted nature during monsoon period due to moisture source from the oceanic region and enriched isotopic composition during non-monsoon period due to moisture source from westerlies and local evaporation. The study also represents that the temperature shows expected positive and negative relationship with individual locations. Studies conducted worldwide during last few decades have established that stable oxygen and hydrogen isotope ratios provide useful tools for hydrological. In case of groundwater, stable isotopes have been used to estimate recharge rates and to identify the recharge zones, to determine the affect of evaporation on groundwater system, to estimate diffusion rates in unsaturated zones, to study the groundwater surface water interaction and to identify source of salinity (Bhattacharya et al., 1985, Navada et al., 1986; Deshpande et al., 2003).The stable isotopic characteristics of Himalayan River namely, Ganga, Yamuna and Indus.**

Keywords : **Isotopes, Absorption Spectrophotometry, Mass Spectrometer, global meteoric water line (GMWL), Salinization.**

I. INTRODUCTION

The ground water in mountainous region emerges out in the form of springs, locally called as Dhara. These springs are the major source of drinking and other domestic requirements in the hilly terrain. Mountainous region hydrology become more complex due to high variability of climatic conditions, physiographical conditions and variable geological set-up which leads to significant differences and variations in hydrological behavior of mountain catchments. Further complexities are also added due to presence of snow, glaciers at high altitude region and distribution forest cover in different part of the catchment. Therefore, an advance technology such as isotopic techniques, remote sensing technique. Where isotope play major role to explore the hydrological fact of river catchment, lakes, springs and reservoir located in mountainous area. Thus isotopic technique is the best alternative method is to know the hydrological processes of hilly region.

II. STUDY AREA

The district is bordered by the Himalayas in the north, the Shivalik Hills to the south, the river Ganges to the east, and the river Yamuna to the west. It lies on 30°387'N latitude and 78°132'E longitude. The main area of study is Shahastradhara and its surroundings for its isotopic and chemical characterization.

Sahastradhara meaning "thousand fold spring" is one of the most popular tourist destinations in the Uttarakhand state and is located in Dehradun place. It is a sulfur water spring of very low temperature and remarkable medicinal value. The aesthetic beauty of the site is exaggerated by the Baldi River and the caves. The place has an ecstatic beauty of nature where water drips from limestone stalactites, making the water sulphur abundant and thus the place is also called as sulphur springs. It is sulphur water spring of relatively lower temperature than its surroundings.

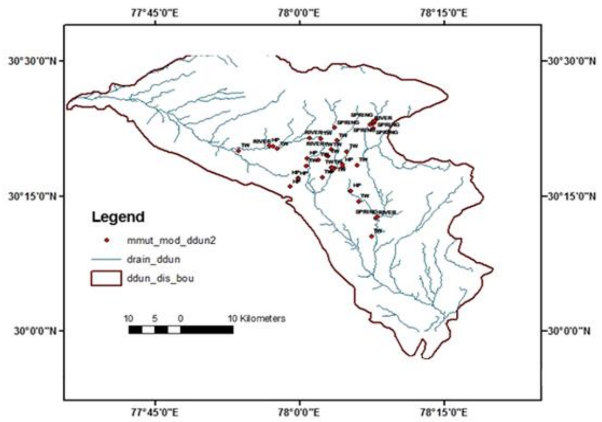

Fig: 1.2 Map of Dehradun with sample locations

III. METHODOLOGY

A. Sampling and Analysis

To identify the isotopic signatures of ground water Forty (40) samples comprising groundwater (8 springs, 5 rivers, 19 tube wells and 8 hand pumps) have been collected (Table 1), of the study area during 2015 and have been analysed for $\delta^{18}O$ and δD. The altitude of sampling locations were measured with an altimeter and cross-verified with GPS. For stable isotopes measurements, samples were collected in pre-cleaned 60 ml and 1500 ml Polypropylene bottles (Tarsons make). These were rinsed profusely at site with sample water and filled with water samples, tightly capped (to prevent evaporation and exchange with the atmospheric moisture) as shown in fig 1 and brought to the laboratory for chemical and isotope analysis. Field parameters such as, pH and electrical conductivity (EC) are measured using Hanna portable pH/EC meters. Accuracy are ± 0.1 for pH and ± 1% for EC. Anion composition of groundwater is determined by volumetric analysis for and Cl^- (± 0.5 mg/L), and by molecular absorption spectrophotometry for NO_3^- , SO_4^{2-} (1 to 2% accuracy) in the Laboratory of water chemistry, National institute of Hydrology, Roorkee.

Fig: 1 Sampling of River and Spring water.

Stable isotopes ratios ($\delta^{18}O$ and δD) were carried out with a laser-based Automated LGR's Isotopic Water Analyzer (model IWA - 35EP) in the Nuclear Hydrology Laboratory of National Institute of Hydrology, Roorkee, India. Isotopes ratio values are reported in delta per mil notation (δ‰) relative to Vienna Standard Mean Ocean Water (VSMOW). The $\delta^{18}O$ and δD measurements were done by using Dual Inlet Isotope Ratio Mass Spectrometer (DI-IRMS). For oxygen and hydrogen isotopes, 400µL water samples were taken and hokobeads were used as catalyst. With which each batch of samples, secondary standards developed with reference to primary standards (i.e., V-SMOW) were also measured and the final δ-values were calculated using a triple point calibration equation. The overall precision, based on 10 points repeated measurements of each sample was with the ±0.1‰for $\delta^{18}O$ and ±1‰ for δD.

$$\delta\ (‰) = \left[\frac{R_{sample} - R_{VSMOW}}{R_{VSMOW}}\right] \times 1000$$

R_{Sample} and R_{VSMOW} are the ratio of the less abundant heavier isotope of interest to the most abundant isotope either $^{18}O/^{16}O$ or D/H of the sample and standard respectively. Analytical precisions are 0.20 ‰ for δD and 0.03 ‰ $\delta^{18}O$. The d-excess defined as (δD – 8*$\delta^{18}O$), is used to get more valuable information related to the hydrological cycle and the interaction of water in its different state, with different environmental system.

B. Isotope composition of water samples

Isotope's ratio displays great amplitude in rainfall data. Deuterium, Oxygen -18 and d-excess values range respectively from -53.2 to -36.8‰; -8.17 to -5.41‰ and 6.12 to 17.0‰. The minimum value of d-excess of 8.17 ‰ for the ground water sources is the single negative value and represent the first sample collected at Dehradun in the month of April-May. Whereas for Shahstradhara springs minimum value of d-excess is 10.99 ‰. Ground water sources have the same range of isotope composition rainfall amount of 2865 mm in the month of June. Ground water sources have the same range of isotope composition. In comparison to rainfall, they have amplitude which are two times lower for δ^{18}O and almost 12 times lower for δD. Isotope composition of ground water sources are very similar with average values of – 46.87 ‰ for δ D and -7.23 ‰ for δ^{18}O. These values are lower than average composition of rain water that is δ D = –1.17‰ and δ^{18}O = – 1.34 ‰. It is also seen from Table 1 that isotope ratios and d-excess in rain water are very heterogeneous with high C.V (coefficient of variation) in opposition of ratios and d-excess in groundwater where values of C.V are lower than 25%. However, the mean values of d-excess in rain water and Shahstradhara springs are very similar around 12.54 ‰. The average value of d-excess in Shahstradhara springs is only lower with one unit.

Table 1

S. No.	Source (gw /river /spring)	Location with Block, district DDN	Ph	EC (µmho)	Altitude (m)	Lat (north)	Long (east)	Cl⁻ (ppm)	SO_4^{2-} (ppm)	NO_3^- (ppm)	δ^{18}O (‰)	δD (‰)	d-excess
1	SPRING	SHAHASTRADHARA	7.85	929	785	30.382	78.122	0.00	105.00	2.20	-7.92	-50.8	12.576
2	SPRING	SHAHASTRADHARA	7.81	929	795	30.375	78.128	0.00	179.00	1.76	-7.86	-50.2	12.699
3	SPRING	SHAHASTRADHARA	7.77	938	860	30.385	78.129	0.00	180.00	1.32	-7.65	-48.9	12.267
4	SPRING	SHAHASTRADHARA	7.85	838	781	30.388	78.128	0.00	58.00	3.52	-7.69	-49.8	11.769
5	SPRING	SHAHASTRADHARA	7.57	412	856	30.391	78.131	0.00	188.00	3.96	-8.03	-53.2	10.985
6	SPRING	SHAHASTRADHARA	8.33	393	790	30.389	78.13	0.00	69.00	1.32	-8.17	-51.6	13.733
7	SPRING	ROBBER'S CAVE, GUCHHUPANI	8.0	520	701.5	30.376	78.06	1.80	261.00	±15.84	-7.63	-51.1	9.895
8	SPRING	SPRING, LACHIWALA	7.89	659	488	30.211	78.135	1.00	124.00	5.72	-7.78	-48.5	13.74
9	RIVER	SHAHASTRADHARA(RIVER SONG)	7.69	958	680	30.384	78.124	0.00	166.00	2.20	-7.61	-47.6	13.298
10	RIVER	PREM NAGAR	7.74	525	537.9	30.341	77.954	1.60	155.00	2.20	-7.49	-51.4	8.579
11	RIVER	TANSA RIVER,BIRPUR	8.37	775	639.6	30.357	78.017	6.40	140.00	1.32	-7.15	-49.6	7.64
12	RIVER	TAPKESHWAR TEMPLE	8.09	755	630	30.357	78.917	3.20	85.00	3.96	-7.02	-49.3	6.916
13	RIVER	REHAN RIVER, LACHIWALA	8.06	589	485	30.209	78.132	0.00	95.00	9.68	-7.51	-48.5	11.59
14	TW	M.P.SPORTS CLG,RAIPUR	7.68	837	604	30.331	78.082	3.00	290.00	3.52	-7.68	-47.7	13.701
15	TW	MARUTIVIHAR, RAIPUR	7.63	600	615	30.307	78.099	2.20	140.00	3.08	-7.43	-46.3	13.199
16	TW	UPPER NATHANPUR	7.52	519	619	30.303	78.075	10.20	35.00	6.60	-6.78	-41.5	12.663
17	TW	RAJIV NAGAR, NEHRU COLONY	7.52	605	614	30.300	78.061	10.60	58.00	7.48	-7.01	-42.3	13.82
18	TW	OLD NEHRU COLONY, DDN	7.59	700	620	30.303	78.055	11.40	68.00	9.68	-7.02	-45.6	10.583
19	TW	SURVEY CHOWK, RACE COURSE	7.49	665	682	30.324	78.05	9.20	164.00	10.56	-7.21	-46.4	11.225
20	TW	SHAHPUR SANTORE	7.19	526	588.9	30.337	77.962	51.60	120.00	4.84	-7.79	-51.6	10.782
21	TW	FOREST RESEARCH CENTRE	7.12	728	604	30.316	78.032	55.40	98.00	3.96	-5.65	-37.1	8.052
22	TW	EAST HOPETOWN	7.54	535	504.1	30.333	77.895	4.00	75.00	3.52	-7.24	-49.2	8.736
23	TW	SEWALA KALAN MAJRA,(NAVIN MANDI)	7.11	997	583.7	30.305	78.012	4.40	232.00	0.44	-6.81	-43.3	11.164
24	TW	BALUPUR INTERSECTION	7.23	775	644	30.302	78.056	6.80	165.00	10.56	-7.10	-47.2	9.532
25	TW	MINI MASSORIE, GARHI CANTT	7.01	666	689	30.355	78.037	3.00	173.00	7.48	-7.88	-51.6	11.395
26	TW	HATHIBARKALA ESTATE	7.63	959	719	30.352	78.064	1.80	240.00	1.76	-7.51	-49.1	10.955
27	TW	JALKAL, KARANPUR	7.9	387	657	30.335	78.055	0.00	237.00	3.52	-7.84	-51.7	11.045
28	TW	JALKAL, KARANPUR	7.9	897	657	30.335	78.055	1.40	272.00	2.64	-8.07	-51.7	12.933
29	TW	BOHRA HOSPITAL, PRAGATI VIHAR, AJABPUR	7.09	726	629	30.296	78.055	3.20	208.00	9.68	-7.28	-41.3	17.008
30	TW	DOIWALA	7.35	559	455	30.176	78.124	0.00	98.00	2.64	-7.44	-46.2	13.352
31	TW	MOTHRWALA,TEHRINAGAR	7.32	486	457	30.284	78.039	3.00	179.00	5.28	-7.13	-45.4	11.630
32	TW	KUWANWALA	7.78	511	456	30.24	78.102	3.60	44.20	3.52	-7.46	-49.0	10.759
33	HP	UPPER NATHANPUR	7.44	500	612	30.307	78.074	6.00	25.00	4.84	-6.92	-42.2	13.167
34	HP	PARED GROUND,RACE COURSE	7.73	526	631	30.325	78.047	1.80	130.00	10.56	-7.39	-49.6	9.491
35	HP	KERI GAUN, PREM NAGAR	7.48	839	527.7	30.343	77.947	12.38	110.00	3.52	-5.45	-36.8	6.842
36	HP	ASHIMA VIHAR,SUBBHASH NAGAR	7.19	688	575	30.283	77.998	39.80	84.00	10.56	-5.72	-37.2	8.547
37	HP	ASHIMA VIHAR,SUBBHASH NAGAR	7.2	525	574.8	30.282	77.997	13.00	95.00	4.84	-5.41	-37.2	6.123
38	HP	SHAKTI ENCLAVE, KAONLI,GMS ROAD	7.1	896	604.8	30.319	78.013	24.60	225.00	11.88	-6.91	-47.3	7.986
39	HP	RTO ASHARORI	6.93	282	643	30.267	77.984	0.00	143.00	3.28	-6.70	-46.3	7.238
40	HP	MAYAWALA CHOWK, HARRAWALA	6.58	462	555	30.259	78.089	1.80	139.00	6.16	-7.14	-43.4	13.767

IV. 4SOURCES OF RAINFALL

Using precipitation worldwide, Craig (1961) defined the relation between δD and δ^{18}O called Global Meteoric Water Line (GMWL) with slope equal to 8 and an intercept of 10. The best fit regression line obtained for rain water is $\delta D = 7.2 * \delta^{18}O + 7.8$ (R^2 = 0.92) (fig 2). This Local Meteoric Water Line LMWL obtained has a lower slope and lower intercept due to the effect of local climate conditions and moisture trajectory on original isotopic composition of oceanic vapor. The slope of the regression lines yields an altitude effect of -0.24‰ per 100 m in δ^{18}O. The altitude effect in δ^{18}O in groundwater is close to the altitude effect observed in precipitation. However, the slight depleted δ^{18}O in groundwater at particular altitude corresponding to the δ^{18}O value of precipitation indicates that there is a horizontal mixing of groundwater generated at higher altitude. But they are lower than average values obtained in the Himalayan Region of India between latitude 30°20' and 30°35'N and longitude 78° 0'E and 78° 9'E. As climatic conditions in these area are comparable with those in our study area, this regional trends is conform to the NE direction of India monsoon moisture and could be attributed to continental effect.

Although, samples collection was limited to summer season period, amount effect on isotope composition of rain events were observed among isotope data at some extent (fig 2). This graph shows that the source of shahastradhara spring is precipitation, whereas the samples of Hand pumps located at Ashima Vihar and Shakti Enclave and Tube well at FRI have been evaporated. The value of d-excess represents the actual source of Reservior which for precipitation ranges between 8-12‰ (±1‰).

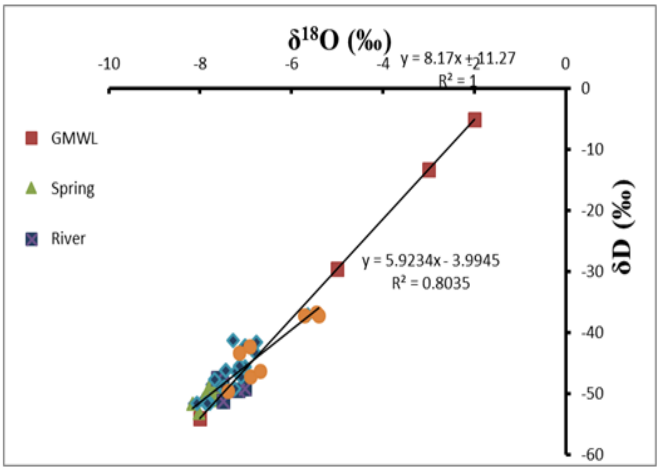

Fig 2: Graph between δ^{18}O and δD.

The values below 8‰ i.e on left side of dotted line as shown in fig. 3 represents mixing of ground water with snow/glacier's water or they got evaporated. Two rivers i.e. River Tansa and River Dulhani source is glacier because their origin is at higher altitude. Whereas the hand pumps at Keri gaun, Ashima vihar, Shakti Enclave and RTO Asharori are got evaporated.

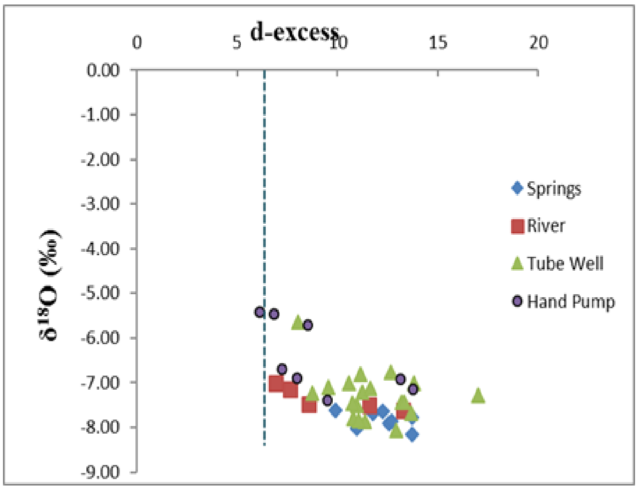

Fig 3: Graph between δ^{18}O and **d-excess.**

A. Groundwater mineralisation

The fact that electrical conductivity in groundwater is relatively higher than common values of EC in rainwater in Dehradun lets keeping that the recharge processes command mainly the dilution of native groundwater. Actually, in the area where infiltration takes place rapidly, native ground water is highly diluted and gets depleted in heavy isotope. In figure 4, particular trends such as increasing EC with increasing isotope composition could not be underline. Consequently, mineralisation process by evaporation is accessory before water/soil and water/rock interaction. All the samples having EC values above permissible limit (200 mg/l). To underline salinization processes, binaries plots, δ^{18}O vs Cl^- and δ^{18}O vs $SO4^{2-}$ are used (Fig 5 and 6). When salinization come from leaching of salts, concentration of these ions increase without significant variation of isotope ratios. When mixing of infiltrating water is source of salinization, Cl^- and SO_4^{2-} ions concentrations are almost uniform with significant variation in stable isotope composition. Fig 5 and 6 show that most of points range in the mixing domain. Some points underline leaching processes

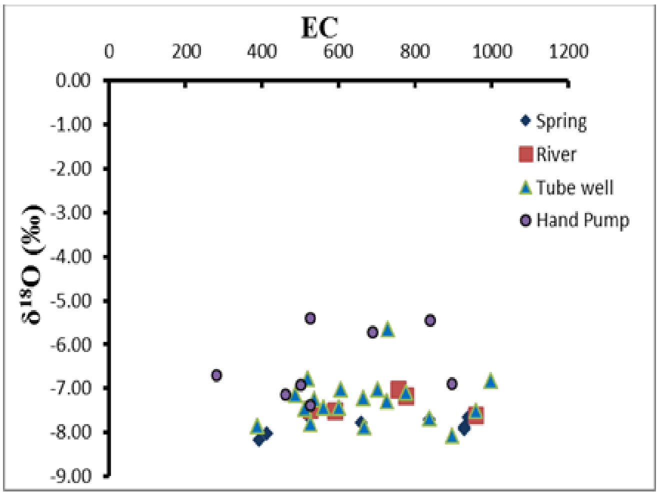

Fig 4: Graph between **EC** and **δ^{18}O.**

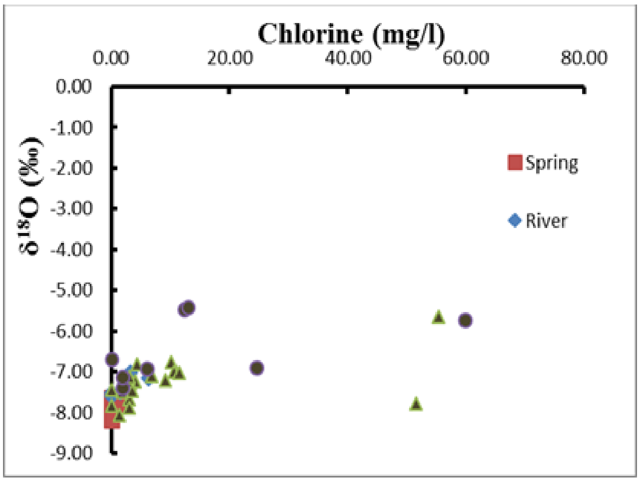

Fig 5: Graph between **Cl^-** and **δ^{18}O**

Dissolution and re-precipitation of mineral, silicate weathering and direct exchange between water and mineral crystal lattice allow isotopic enrichment of δ^{18}O in groundwater. As the graph (Fig 5) represents the locations ranging beyond 50 mg/l are Shahpur Santore (TW), Forest Research Centre (TW) and Asharori (HP) shows the salinization of the reservoirs.

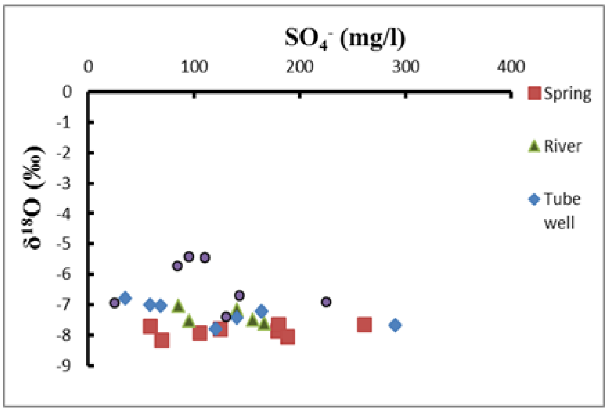

Fig 6: Graph between **SO_4^-** and **δ^{18}O**

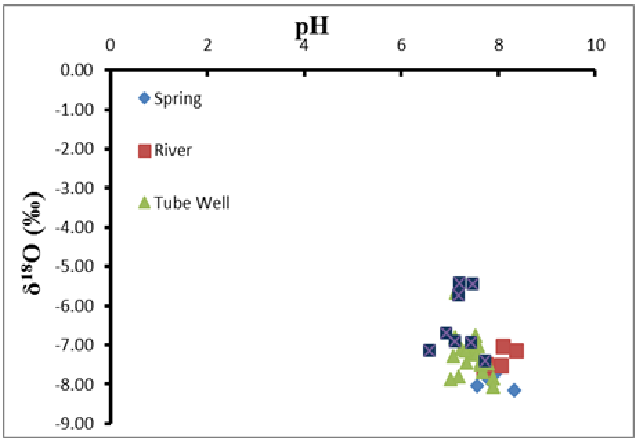

Fig 7: Graph between **pH** and **δ^{18}O**

The graph (Fig 6) shows the Sulphate values, the values exceeding 200 mg/l shows the salinization of those reservoirs i.e. Robber's cave spring, M.P. Sport college's tube well and Shakti Enclave's hand pump.

pH describes the acidty nd alkalinity of water. Prescribed limit for natural water sources ranges from 6.5 to 8.5. In the above graph (Fig 7) represents that all the locations have pH value in desirable range.

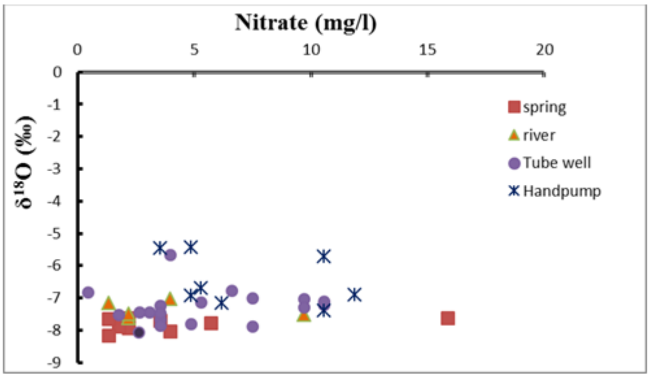

Fig 8: Graph between NO_3^- and $\delta^{18}O$

There are some isolated cases where the concentration of nitrate-nitrogen down gradient of large volume on-site wastewater disposal sites, septic/solids disposal, and landfills which may exceed the drinking water limit. Areas of intense farming contains the nitrate-nitrogen concentration high. That exceeds the EPA(Environmental Protection Act) drinking water limit of 10 mg/L (fig 8). From the graph reservoir exceeding the permissible limit are Robber's cave (Spring), Survey Chowk (TW),Balupur Intersection (TW), Pared Ground (HP), Ashima Vihar (HP) and Shakti Enclave (HP).

V. CONCLUSION

Results obtained from this study show that isotope ratios in rainfall display a great amplitude and are well scattered along GMWL. The best fit regression line for rain water is $\delta D = 7.2*\delta^{18}O + 7.8$ ($R^2 = 0.92$) and defines a Local Meteoric Water Line (LMWL) for the study area. Low slope and low intercept are due to secondary evaporation from the falling raindrops. Wide range of d-excess values suggests precipitation originating from mixing of oceanic and recycled continental air masses. These precipitation are subjected to amount effect. Isotopic composition of groundwater is very homogenous (CV<25%) and points are scattered along GMWL and LMWL. This indicates meteoric origin of groundwater. The best fit regression line for groundwater is $\delta D = 4.1*\delta^{18}O - 1.3$ ($R^2 = 0.86$). Binaries diagrams of electrical conductivity and main anions vs $\delta^{18}O$ evidenced water/rock interaction and anthropogenic influences as dominant sources of mineralisation. Salinization from leaching of soil salts are accessories. Isotope exchange between water and aquifer matrix and high dilution of native groundwater induced significant change in isotope composition in some sample. Although, the presence of some natural purging capacity in aquifers, point sources contamination are significant.

The $\delta^{18}O$ -δD relationship for groundwater samples yields a slope of 8.21 that is similar to Local Meteoric Water Line of Dehradun's reservoir basin. It reveals that isotopic composition of precipitation is well preserved in groundwater of the study area and evaporation during infiltration, if any, is minor. The distinct $\delta^{18}O$ in groundwater at each sites reveals that groundwater in the area originates through only precipitation. The close similarity in altitude effect of groundwater and precipitation confirms that the source of recharge is precipitation. This study reveals that isotopic composition of precipitation and groundwater will be useful in identifying the source of recharge of groundwater/springs in a Himalayan catchment.

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