Chapter 3

Stable Isotopes in the Yamuna River System

3.1 INTRODUCTION

Stable isotopes of oxygen and hydrogen being the constituents of water molecules serve as "ideal conservative" tracers to study hydrological processes. Variations in the isotopic ratios ($^{2}H/^{1}H$ and $^{18}O/^{16}O$) in water are brought about in response to processes such as mixing of water from different sources, condensation of water vapour and evaporation of water. The variations in stable isotope ratios in waters are used to characterize these hydrological processes operating in surface and groundwater systems and to trace their sources.

Rivers receive waters from various sources: precipitation, snow/glacial melt and groundwater influx. The relative contributions of these sources vary with time of the year depending on the locations of the river catchment. The water budget of a river is controlled by processes such as mixing of its tributaries, evaporation during its transit and its interaction with the groundwater regime. Rivers which receive waters mainly from precipitation at a certain period of the year (e.g. monsoon period in India), respond to changes in the isotopic composition of the precipitation, the time of response being dependent on factors such as the size of the river, gradient of the river bed and vegetation in the catchment. Measurement of stable isotopic composition in the rivers can have many applications. These include identification of the sources of water, assessment of the mixing proportions among them and the estimation of evaporation losses (Ingraham, 1998). In addition, comparison of stable isotope data of river waters with those of precipitation and ground waters from the same region can be used to evaluate infiltration of river water to subsurface aquifers and the role of evapotranspiration in water budget of precipitation (Payne, 1983; Gat and Matsui, 1991; Krishnamurthy and Bhattacharya, 1991; Ingraham, 1998). More recently, Lambs (2000), using $\delta^{18}O$ and conductivity and their mixing relation in stream waters of the Bhagirathi river near Gangotri in the Himalaya, quantified the relative contributions of glacier and snow melt to its water budget.

This chapter presents δD-$\delta^{18}O$ systematics of the Yamuna River System (YRS). The comprehensive stable isotope data acquired in this study in conjunction with those available for New Delhi precipitation (IAEA, 1998), help to infer the sources of water to the YRS and assess the role of processes such as recycling of moisture via evaporation of rainwater and river water, mixing of rain and snow melt, rainout from the cloud mass and the catchment

topography in controlling the isotopic composition of the YRS. The altitudinal variations in the river water isotopic composition, an aspect discussed in some detail in this study, has important implications to (i) tracking the source of water recharging at different elevations and (ii) reconstruction of paleoelevation in the Himalayan region (Chamberlain and Poage, 2000; Garzione et al., 2000a, b).

Prior to this work, $\delta^{18}O$ and δD measurements in the headwaters of the Ganga and the Indus draining the Himalaya have been used to derive information on source(s) of water to these rivers and 'altitude effect' of precipitation in the catchment area as imprinted in the rivers (Ramesh and Sarin, 1992; Bartarya et al., 1995; Pande et al., 2000). Garzione et al. (2000a,b) studied the variation of $\delta^{18}O$ with altitude in the tributaries of the Seti River and the Kali Gandaki in the Nepal Himalaya and used these data in conjunction with $\delta^{18}O$ of carbonates to estimate paleoelevation of Tibet.

The results of the present study have been integrated and compared with those from the Ganga and the Indus headwaters (Ramesh and Sarin, 1992; Pande et al., 2000) and the Gaula catchment (Bartarya et al., 1995) to better understand the variability in the stable isotope composition of the rivers draining the southern slopes of the Himalaya and their implications to paleoaltitude estimation.

3.2 RESULTS AND DISCUSSION

The $\delta^{18}O$ and δD values of the Yamuna mainstream and its tributaries for the three sampling periods are presented in the Table 3.1. They range from -6.2 to -10.3‰ and -41.7 to -72.0‰ for $\delta^{18}O$ and δD respectively, corresponding to the altitude range of ~500 to ~2400 m. In general, the isotopic composition of the streams are more depleted during monsoon and in samples from higher altitude. The isotopic composition of the Yamuna waters are slightly enriched in ^{18}O and D compared to the Ganga headwaters ($\delta^{18}O$: -7.8 to -14.4‰ and δD: -51 to -103‰, Ramesh and Sarin, 1992) and depleted relative to streams of the Gaula river catchment in the Lesser Himalaya (-5.2 to -9.0‰ and -37 to -63‰; altitude ~550-1700 m, Bartarya et al., 1995). These differences most likely result from altitude and seasonal effects. Among the Ganga headwater samples, those from the Bhagirathi (at Gangotri) and Kedarganga collected at ~3000 m altitude, close to their glacial melt source have the most depleted isotopic composition (Ramesh and Sarin, 1992). The ranges in isotopic composition for the remaining Ganga headwaters are within those observed for the (Table 3.1). In addition

to altitude, some variability in the isotopic composition of these two river systems can arise from seasonal effects (see following section) as the Ganga samples were collected during April whereas those from Yamuna were sampled in June, September and October.

Table 3.1 δD, $\delta^{18}O$, deuterium excess and ΣCat^* data of the Yamuna and its tributaries in the Himalaya.

Code	River	Altitude (m)	Season[a)]	$\delta^{18}O$ (‰)	δD (‰)	d[b)] (‰)	$\Sigma Cat^{*c)}$ (µEq)
Yamuna mainstream							
RW98-16	Yamuna	2350	PM	-10.3	-67.1	15.3	1069
RW99-13	Yamuna	2350	S	-9.4	-62.1	13.1	1056
RW98-20	Yamuna		PM	-9.9	-63.7	15.5	1101
RW98-25	Yamuna	1465	PM	-9.2	-58.1	15.5	1188
RW99-19	Yamuna	1465	S	-8.6	-56.2	12.6	1269
RW98-22	Yamuna		PM	-9.0	-57.9	14.1	1226
RW99-17	Yamuna	1737	S	-9.0	-59.3	12.7	1196
RW99-18	Yamuna	1234	S	-8.6	-55.5	13.3	1454
RW98-15	Yamuna		PM	-9.0	-58.5	13.5	1480
RW98-14	Yamuna		PM	-8.7	-57.9	11.7	1581
RW98-12	Yamuna		PM	-8.7	-57.0	12.6	1467
RW99-11	Yamuna	1219	S	-8.1	-55.9	8.9	1686
RW98-9	Yamuna		PM	-8.7	-57.5	12.1	1959
RW99-51	Yamuna		M	-9.9	-72.0	7.2	903
RW98-6	Yamuna	768	PM	-8.5	-57.2	10.8	2060
RW99-30	Yamuna	768	S	-8.0	-53.1	10.9	2536
RW99-64	Yamuna	768	M	-8.7	-57.5	12.1	1675
RW99-31	Yamuna	500	S	-7.9	-52.7	10.5	2204
RW99-53	Yamuna	500	M	-9.9	-70.0	9.2	1007
RW98-1	Yamuna	628	PM	-9.1	-61.7	11.1	1432
RW99-2	Yamuna	628	S	-8.6	-59.2	9.6	2167
RW99-58	Yamuna	628	M	-9.9	-67.3	11.9	1274
RW98-4	Yamuna	601	PM	-7.9	-53.5	9.7	3279
RW99-5	Yamuna	601	S	-7.4	-51.0	8.2	3538
RW99-55	Yamuna	601	M	-7.8	-53.8	8.6	2785
RW98-33	Yamuna	484	PM	-10.3	-68.5	13.9	2973
RW99-7	Yamuna	484	S	-7.8	-54.4	8.0	3063
RW99-54	Yamuna	484	M	-9.5	-65.5	10.5	1495
Tributaries							
RW98-17	Jharjhar Gad		PM	-9.0	-57.6	14.4	544
RW98-18	Didar Gad		PM	-9.2	-60.6	13.0	290
RW99-14	Didar Gad		S	-8.6	-55.6	13.2	319
RW98-19	Pali Gad	1851	PM	-8.3	-52.7	13.7	1127
RW99-16	Pali Gad	1851	S	-7.6	-48.7	12.1	1621
RW98-13	Barni Gad		PM	-8.4	-55.8	11.4	2533
RW99-12	Barni Gad		S	-7.4	-53.0	6.2	3839
RW98-21	Purola	1443	PM	-8.1	-52.4	12.4	1746
RW99-20	Purola	1443	S	-7.5	-51.6	8.4	3161
RW99-15	Bajri Gad	2060	S	-7.3	-52.1	6.3	472
RW98-23	Oli Gad		PM	-8.3	-54.1	12.3	1912
RW98-24	Gamra Gad		PM	-8.6	-56.1	12.7	1835

RW98-26	Godu Gad		PM	-8.2	-51.8	13.8	[illegible]
RW99-21	Godu Gad		S	-7.8	-54.6	7.8	895
RW98-27	Tons	1419	PM	-10.2	-66.9	14.7	524
RW99-22	Tons	1419	S	-9.8	-61.1	17.3	472
RW98-28	Tons		PM	-10.2	-65.4	16.2	551
RW99-26	Tons	1217	S	-9.2	-59.4	14.2	409
RW99-27	Pabar	1224	S	-8.5	-58.6	9.4	697
RW98-29	Tons		PM	-10.1			642
RW99-28	Tons		S	-9.0	-58.3	13.7	536
RW99-25	Tons		S	-9.3	-61.7	12.7	701
RW98-31	Shej Khad	1004	PM	-9.3			2074
RW99-23	Shej Khad	1004	S	-8.3	-57.4	9.0	3073
RW98-30	Tons	1004	PM	-9.7	-62.5	15.1	1297
RW99-24	Tons	1004	S	-8.6	-58.7	10.1	2550
RW98-5	Amlawa		PM	-7.9	-53.3	9.9	2106
RW99-62	Amlawa		M	-8.1	-53.8	11.0	2174
RW98-32	Tons	770	PM	-9.0	-59.3	12.7	2614
RW99-29	Tons	770	S	-8.3	-55.6	10.8	2603
RW99-63	Tons	770	M	-9.8	-65.6	12.8	1856
RW98-8	Aglar	948	PM	-8.3	-54.8	11.6	4255
RW99-10	Aglar	948	S	-7.7	-53.7	7.9	9152
RW99-52	Aglar	948	M	-8.3	-61.1	5.3	4177
RW98-2	Giri		PM	-7.3	-50.7	7.7	5707
RW99-3	Giri		S	-6.8	-48.1	6.3	7156
RW99-57	Giri		M	-7.2	-50.7	6.9	4540
RW98-3	Bata	615	PM	-7.6	-47.8	13.0	3069
RW99-4	Bata	615	S	-6.4	-44.2	7.0	4047
RW99-56	Bata	615	M	-7.1	-48.2	8.6	3276
RW98-10	Tons		PM	-7.3	-46.7	11.7	5122
RW99-65	Tons		M	-6.5	-41.7	10.3	4291
RW98-11	Asan		PM	-6.8	-45.3	9.1	6098
RW99-1	Asan		S	-6.2	-44.4	5.2	5531
RW99-61	Asan		M	-6.6	-44.0	8.8	5872
Springs							
RW98-7	Kemti Fall		PM	-8.6	-57.4	11.4	9142
RW99-60	Shahashradhara		M	-6.9	-44.7	10.5	34950

[a]S = summer, M = monsoon, PM = post-monsoon, [b]d =$\delta D-8\delta^{18}O$. [c]$\Sigma Cat^* = Na^*+K+Ca+Mg$, Na^* is sodium corrected for cyclic contributions using Cl as an index (Data from table 4.1).

3.2.1 Seasonal variation

In regions, such as the YRS basin, experiencing monsoon precipitation, there is heavy downpour during three months, July, August and September of every year. The local rainfall in the YRS basin, is largely governed by tropical storms and depressions forming over the Bay of Bengal and Arabian Sea which enter into the region from southeast and southwest direction (Devi, 1992). Such intense rainfall during monsoon is characterized by lighter stable isotopic composition, compared to those during the non-monsoon months, as monsoon

rains are derived from cloud mass which become isotopically lighter by progressive rainouts during their movement (Rozanski et al., 1993; Araguas et al., 1998).

The $\delta^{18}O$ and δD values of the YRS samples, indeed, show clear seasonal variations (Table 3.1), samples from the monsoon season (September) being more depleted in ^{18}O and D compared to those collected during summer (June, Fig. 3.1, Table 3.1). This trend, as

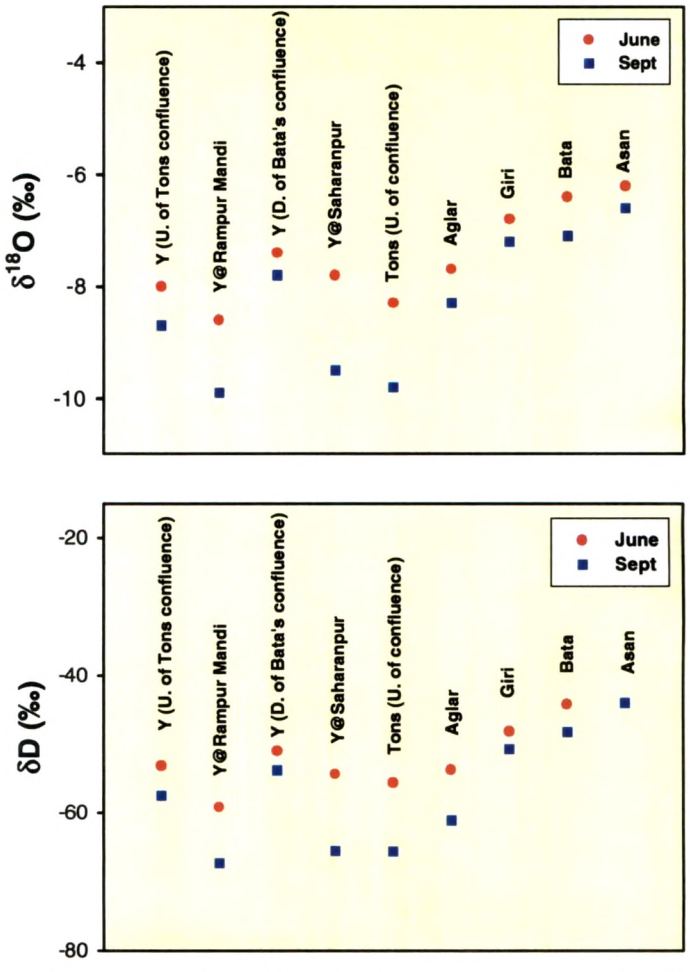

Fig. 3.1 Seasonal variation of $\delta^{18}O$ and δD in the YRS. June samples are enriched in ^{18}O and D compared to September samples. Y: Yamuna, D: downstream, U: upstream

already discussed, can be explained in terms of heavy rainfall during monsoon, commonly known as "amount effect". In north India, air-masses carrying large amount of moisture move from the source region during monsoon season and shed a significant fraction of their moisture during their transit in spells of heavy rainfall events. Such rainouts continuously

deplete the heavy isotopes from the onward moving clouds. As a result, vapor clouds farther away from source, such as those reaching the Himalayan region, are isotopically depleted and precipitation from such clouds are characterized by lower δ-values. The isotopic composition of precipitation at any given location, therefore, would depend, in addition to the the initial isotopic composition of the cloud vapour and temperature of condensation, on the fraction of moisture removed from the cloud by condensation prior to reaching the location. This fraction is likely to vary with season, with more rain out during the monsoon thus making its impact more pronounced in September as it is a month with more rainfall than June. Thus, the oxygen isotopic ratios in September samples are expected to be depleted relative to those in June. This is consistent with the results (Fig. 3.1) that $\delta^{18}O$ of September samples are 0.5-1.5‰ depleted compared to June samples. Rozanski et al. (1993) also observed a decrease in $\delta^{18}O$ of precipitation at New Delhi with an increase in the amount of precipitation during the period of May to September. Heavy monsoonal precipitation undergoes little post condensation exchange with the water vapor and evaporation compared to the light rainfall thus enhancing the amount effect (Hoffmann and Heimann, 1997). During monsoon season, lower temperature, higher humidity and rapid downpour does not allow evaporation of rains and their significant exchange with water vapour after their condensation, whereas rainfall during June, being less in amount, is likely to undergo appreciable exchange when the temperature is relatively higher. Hence heavier isotopic composition of the YRS waters during June can also be due to possible evaporation of the waters during their flow or as a result of partial evaporation of rain which contribute water to the YRS during this month (see later sections).

3.2.2 The $\delta^{18}O$-δD relationship

The isotopic composition of the river waters, usually, is related to that of local precipitation. In small drainage systems, $\delta^{18}O$ and δD of runoff is identical to that of local precipitation whereas in large river systems, the rivers carry an "average" signature of the precipitation in the drainage basin.

Regression line drawn in a $\delta^{18}O$-δD space for the global precipitation defines the Global Meteoric Water Line (GMWL) and that for the precipitation in a region is named the Local Meteoric Water Line (LMWL). The slope of the GMWL is ~8 (Craig, 1961; Rozanski et al., 1993). The regional precipitation, if not influenced by processes such as evaporation,

defines a LMWL with a slope close to 8. This slope becomes <8, if the raindrops undergo evaporation during their fall. Hence relation between $\delta^{18}O$ and δD in rain and surface waters helps to assess the role of evaporation in altering their isotopic composition. $\delta^{18}O$-δD relations in river waters when compared with those of GWML and LWML, provide information on the isotopic composition of the source. In addition, it also yields information on the preservation/alteration of stable isotopic composition of precipitation contributing to the streams and evaporation of stream waters during their transit.

(a) Monsoon:

Fig. 3.2 presents the $\delta^{18}O$-δD plot for the monsoon (September) samples. Regression analysis of the data (Williamson, 1968) gives the best fit line (BFL):

$$\delta D = (7.71\pm0.27)\delta^{18}O + (7.13\pm2.3), \quad (n = 14, r = 0.98, p< 0.005, \text{Table 3.2}) \qquad (1)$$

The slope of the BFL for the monsoon period (Fig. 3.2) is marginally lower than that of the global meteoric water line (GMWL; Rozanski et al. 1993):

$$\delta D = (8.17\pm0.06)\delta^{18}O + (10.35\pm0.65) \qquad (2)$$

but similar to that derived for precipitation at New Delhi for the monsoon period, July, August and September for the years 1961-95 (IAEA, 1998):

$$\delta D = (7.80\pm0.05)\delta^{18}O + (7.2\pm0.4) \quad (n = 79, r = 0.99) \qquad (3)$$

The eqn. 3 can be considered as the local meteoric water line (LMWL). The similarity in the slopes of rain waters at Delhi (eqn. 3) and the September river water samples, with values of 7.7±0.3 to 7.8±0.1, suggests that evaporation of raindrops during the interval between their condensation and fall, and that of the river water during its flow, if any, is only minor and that the isotopic composition of precipitation is well preserved in stream waters of monsoon season. Further, the observation that the value of the slope in the September samples (Fig. 3.2) is not significantly different from 8, suggests that the rainfall in this region during monsoon occurs essentially under equilibrium condition obeying Rayleigh condensation. These two sets of data taken together (equations 1 and 3) suggest that the monsoon meteoric water line (MMWL) in this part of the Himalaya can be characterized by a slope of ~7.8 and an intercept ~7.

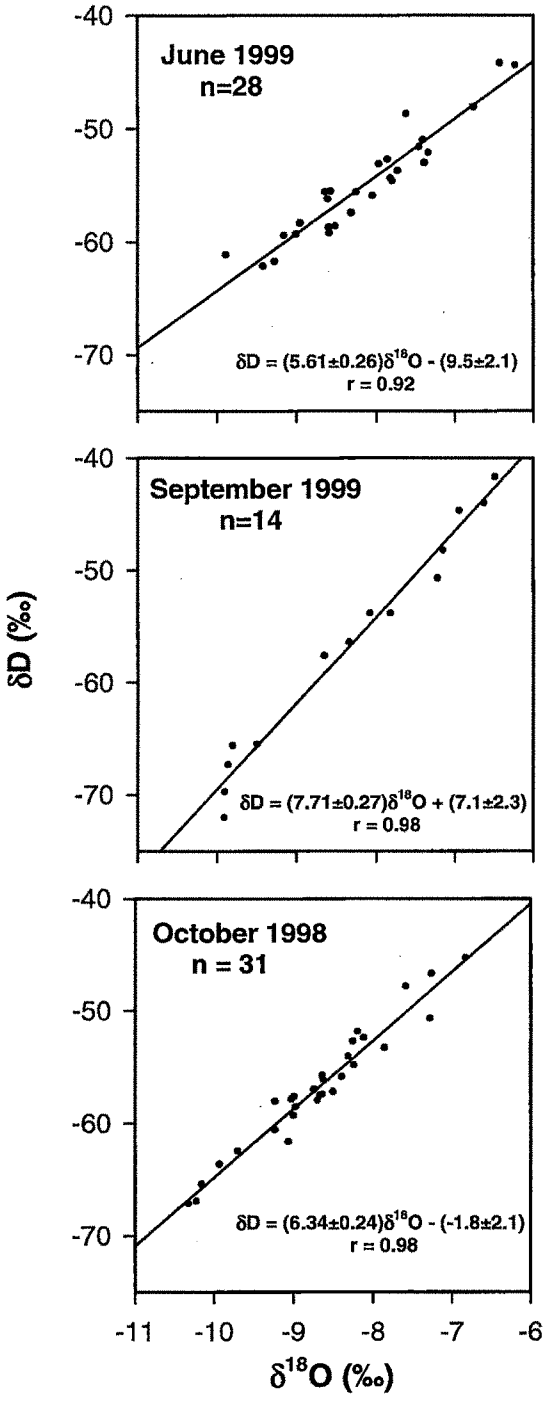

Fig. 3.2 $\delta^{18}O$-δD co-variation plots for samples from the Yamuna and its tributaries during three different sampling periods. The number of samples and the regression equations [calculated using Williamson (1968)] are also given. The errors are ±1σ.

***(b) Summer and post-monsoon*:**

The Yamuna waters collected during June (summer) and October (post-monsoon) show the following relations:

$$\delta D = (5.61\pm0.26)\delta^{18}O - (9.5\pm2.1) \quad (n = 28, r = 0.92, p < 0.005) \qquad (4)$$

and $$\delta D = (6.34\pm0.24)\delta^{18}O - (-1.8\pm2.1) \quad (n = 31, r = 0.98, p < 0.005) \qquad (5)$$

respectively. The slopes of the BFLs of these periods (Table 3.2) are less than those of the monsoon BFL and the GMWL (Table 3.2), indicating that evaporation of waters at some stage has taken place. This could be from the falling raindrops contributing to these streams and/or from the stream waters during their flow. Statistical analysis of available $\delta^{18}O$ and δD data in rainwaters from New Delhi (IAEA) during June yields the relation:

$$\delta D = (6.26\pm0.07)\delta^{18}O + (2.83\pm0.2) \quad (n = 29, r = 0.95, p < 0.005) \qquad (6)$$

The slope of this line (eqn. 6) is significantly lower than that of GMWL and is marginally higher than that for the June waters (eqn. 4) but similar to that for the October collection (eqn. 5). The lower value of rainwater slope than that of GMWL suggests that the isotopic composition of streams in this region during summer is controlled predominantly by the composition of rainwater which themselves have undergone evaporative enrichment. The marginally lower slope in rivers during June, if validated by more data, can be because of some amount of evaporation during their flow. The slightly higher value of the slope during October, compared to that during June, can be due to differences in the source and/or evaporation. It must, however, be mentioned that as waters of the YRS represent a composite of melt water from glaciers and several previous rains, the agreement in slope values among the various δD-$\delta^{18}O$ plots (eqns. 1-6) allows only to draw broad inferences. It is difficult, for example, to discern quantitatively from these slopes and associated errors, the relative significance of evaporation of rain drops during their fall vis-a-vis during their flow in the streams though the latter seems to be of minor importance in the samples analyzed.

***(c) Comparison with the Ganga headwaters and Gaula catchment*:**

As mentioned earlier, Ramesh and Sarin (1992) and Bartarya et al. (1995) have reported δD-$\delta^{18}O$ measurements in the streams of the Ganga headwaters and the Gaula catchment in the Himalaya. The slope and intercept of the BFL for the Ganga headwaters (Ramesh and Sarin, 1992) are same, within errors, as those for the Yamuna samples during monsoon (Table 3.2):

$$\delta D=(7.45\pm0.23)\delta^{18}O + (8.0\pm2.0) \quad (n = 23, r = 0.98, p<0.01) \qquad (7)$$

This is intriguing considering that the Ganga samples were collected in April when the dominant source of water to the rivers is snow and glacier melt. The results of Bartarya et al. (1995) on snow and rain water samples from the Gaula catchment area in the Lesser Himalaya, south-east of the amuna and the Ganga headwaters, show that they cover a wide range, 0.1 to -13.7‰ and -3 to -106‰ for $\delta^{18}O$ and δD respectively. The $\delta^{18}O$ - δD plot, for these snow and rain samples, shows significant scatter with a slope and intercept of 7.13 and 14.97 respectively. The lower value of slope relative to GMWL has been interpreted in terms of evaporation of rain drops during their fall (Bartarya et al., 1995). Interestingly, the springs and streams in the Gaula catchment have a higher slope of ~8.36 and intercept 10.7 but the line is less well defined as the data points have less spread.

Table 3.2 δD-$\delta^{18}O$ relation and deuterium excess in the Yamuna, Ganga and Indus headwaters in the Himalaya and New Delhi rainwater

Samples	Month	No. of samples	Slope[a)]	Intercept[a)]	r	d (‰)[b)] range	d (‰)[b)] mean
YRS	Sept.	14	7.71±0.27	7.1±2.3	0.98	5.3-12.8	9.6±2.2
N. Delhi Rain	July-Sept.	79	7.80±0.05	7.2±0.4	0.99	0.2-19.5	8.8±4.0
YRS	June	28	5.61±0.26	-9.5±2.1	0.92	5.2-17.3	9.9±3.1
YRS	Oct.	31	6.34±0.24	-1.8±2.1	0.98	7.7-16.2	12.7±2.0
N. Delhi Rain	June	29	6.26±0.07	2.8±0.2	0.95	-22.3-14.6	1.9±9.5
Ganga[c)]	April	23	7.45±0.23	8.0±2.0	0.98	6.2-21.0	13.7±3.1
Gaula[d)]	Feb.-Oct.	20	8.36±0.59	10.7±5.2	0.86	2.2-21.6	9.6±4.8
Indus[e)]	August	19	9.12±0.29	31.1±4.2	0.98	7.8-18.4	14.7±3.1

[a)]Slopes and intercepts are calculated based on Williamson (1968). Errors are ±1σ. r is correlation coefficient.
[b)]Deuterium excess values, range, mean and one standard deviation. [c)] Ramesh and Sarin (1992), [d)]Bartarya et al., (1995), [e)]Pande et al.(2000).

3.2.3 Deuterium excess:

The "deuterium excess" in a precipitation sample is defined as $d = \delta D - 8\delta^{18}O$ (Dansgaard, 1964). It results primarily due to non-equilibrium processes (Dansgaard, 1964) and is the difference between the measured δD value and the expected equilibrium value calculated based on the measured $\delta^{18}O$. The magnitude of d values is determined by conditions of the vapour source (e.g. relative humidity, temperature and wind speed over the evaporating surface) and moisture recycling in the area experiencing the precipitation

(Rozanski et al., 1993). The deuterium excess of the stream waters in the YRS, for the three periods of sampling, ranges from 5.2‰ to 17.3‰ with a mean of ~11‰ (Table 3.2), 2.5‰ higher than the long term annual average of 8.5‰ observed for precipitation at New Delhi (Araguas et al., 1998). The mean d values for the three seasons though overlap with each other within errors (Table 3.2); samples collected during June have relatively lower d values compared to those in September and October (Fig. 3.3). About half the number of June samples have d values less than 10‰ (Table 3.1), which is typical of continental precipitation events with moisture source from the oceans (Dansgaard, 1964). It is suggested (Araguas et al., 1998) that partial evaporation of raindrops below the cloud base, under conditions of low relative humidity and light rainfall, can substantially reduce the d values of rains collected at ground level. The relatively low d values in samples collected from the YRS during June are likely to be caused by contributions from partially evaporated rains. This is consistent, as already discussed, with the observed lower slopes of $\delta^{18}O$-δD regression lines for both the YRS waters and New Delhi precipitation during June (section 3.2.2). It can be seen in Table 3.2 that the New Delhi rains during June have mean d values lower than those for monsoon season. This attests to the idea that the rainwater undergoes evaporation during their fall during this month resulting in lower deuterium excess in them. Datta et al. (1991) attributed lower d values in rainfall at New Delhi during nonmonsoon periods to the partial evaporation of raindrops during their fall. Araguas et al. (1998) also observed that at New Delhi, during January to May, d values of rainfall gradually decrease with an increase in $\delta^{18}O$ which was explained in terms of enhanced evaporation of raindrops below the cloud base.

There is a significant inverse correlation between $\delta^{18}O$ and d values for the June and October samples (Fig. 3.4). In the upper reaches of the YRS, samples are depleted in ^{18}O and have higher d whereas the samples in the lower reaches have enriched ^{18}O and lower d values. This trend can result from different mixing proportions of water from two end members, i.e. snow/glacier melt water and precipitation. Snowmelt would give higher d and lower $\delta^{18}O$ values as kinetic fractionation involved during the formation of snow results in high d excess values (Cooper, 1998). This component would be more dominant at higher altitudes.

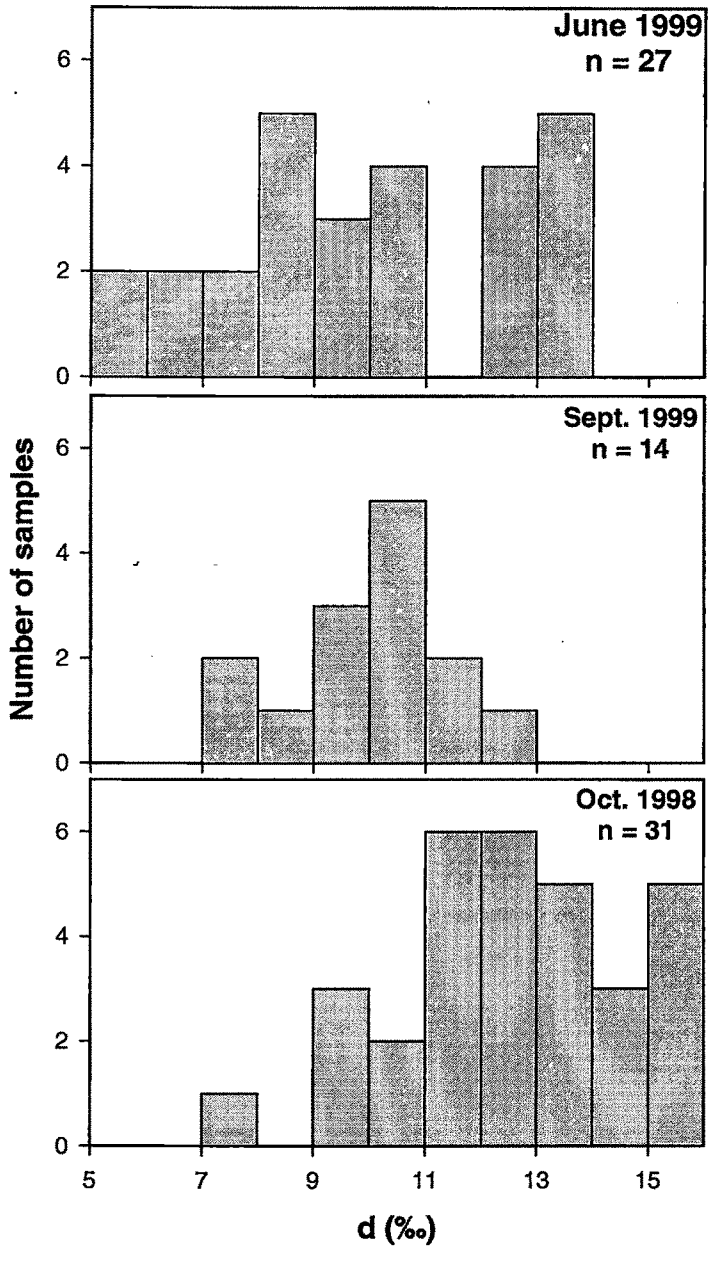

Fig. 3.3 Distribution of deuterium excess (d) in the YRS for three sampling periods. Samples collected in October have higher d values than those collected in June and September. RW99-22 not plotted

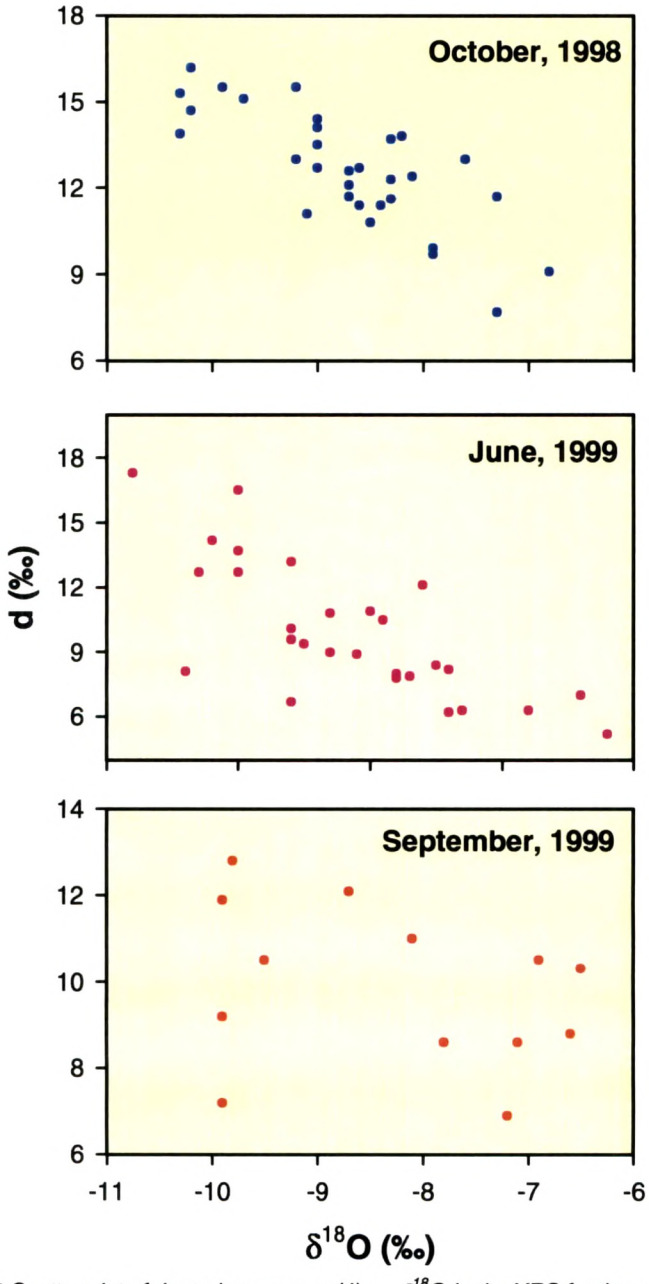

Fig. 3.4 Scatter plot of deuterium excess (d) vs. $\delta^{18}O$ in the YRS for three sampling periods. A negative correlation is evident for October and June whereas September data show more scatter.

It is also seen from the data (Fig. 3.3, Table 3.1) that in general, October d values are higher relative to those in June and September samples. October samples have an average d of 12.7 compared to 9.6 and 9.9 for September and June respectively [Considering that the numbers of samples analyzed were different during these periods, difference of mean test was performed to determine if the mean d values are indeed different. The results show that the mean d of October is different than that of June ($t = 4.69$) and September ($t = 4.78$) at 95 % confidence level]. About 90% of the samples collected during October have d values greater than 10 (Fig. 3.3). Deuterium excess in precipitation, as already mentioned, depends on the source vapour conditions as well as the moisture recycling in the area. The long term average d value for the New Delhi precipitation is about 8.5 (Araguas et al., 1998), however, it exhibits large scatter over the year. During October, many of the d values of New Delhi precipitation are >10. Hence it is likely that high d values observed in October samples of the YRS reflect the signature of the source, i.e. precipitation characterized by moisture recycling (cf. Krishnamurthy and Bhattacharya, 1991). Addition of re-evaporated moisture from continental basins as well as vegetation surface to the water vapour moving inland can also bring about high d values in the precipitation (Njitchoua et al., 1999). Hence higher d values for the October samples can result from enhanced contribution of recycled moisture to precipitation through evaporation and/or evapotranspiration during this period when there is a bloom in vegetation after the monsoon rainfall.

In September samples of the YRS, the d values are in between those of June and October (Fig. 3.3). Also, the plot of $\delta^{18}O$ vs. d shows considerable scatter during this period (Fig. 3.4). This can arise because the relative contribution of recycled moisture to rain during September is likely to be less. The rainfall in this region during September is generally much higher than that during October. For example at Dehradun located in the lower reaches of the YRS, the rainfall in September is about 8 to 10 times higher than that in October. Therefore, the relative contribution of the recycled moisture to the October rains (the retreating period of the monsoon) from post-monsoon vegetation bloom is likely to be more. This is supported by available data on rainfall and evapotranspiration at selected locations in the Yamuna catchment. During September, the rainfall far exceeds the evapotranspiration whereas in October, evapotranspiration is more than rainfall resulting in a net loss in the water budget of the region (Devi, 1992; Chapter 2, Fig. 2.7). Hence the influence of recycled moisture via

evapotranspiration is likely to be pronounced in the isotopic composition of the October rainfall. As a result, deuterium excess in October are higher than those during September. In addition, the fact that September samples were fewer in number and were collected primarily from lower altitudes may also contribute to lower d values.

Thus, in the waters of the Yamuna and its tributaries the variability in the deuterium excess seem to be controlled primarily by three processes, i.e. mixing of snowmelt and precipitation, partial evaporation of raindrops and recycling of moisture through evaporation of soil water and evapotranspiration from vegetation.

3.2.4 Altitude effect

It is well established (Yurtsever and Gat, 1981; Clark and Fritz, 1997) that the isotopic composition of precipitation varies with elevation of the sampling location. When air masses are orographically lifted, they cool and the ensuing precipitation is enriched preferentially in the heavier isotopes. As a result, the next phase of precipitation at still higher altitude is relatively depleted in heavy isotopes; this progressive depletion with height is known as "altitude effect". The altitude effect depends on factors such as the precipitation history, the topography and the precipitable moisture remaining in the cloud. The altitude effect on $\delta^{18}O$ in mid-latitude precipitation generally ranges between 0.15 to 0.30 ‰ for each 100 m of altitude gained (Schotterer et al., 1996). Both continental effect and altitude effect are manifestations of Rayleigh distillation: one operating on a large spatial scale due to cloud migration and the other operating in a given region due to continuous extraction of water from the rising cloud due to drop in temperature with height. Bhattacharya et al. (1985) and Krishnamurthy and Bhattacharya (1991) have observed continental effect in northern Indian precipitation and have modeled these data to determine the sources of water vapor to the cloud system. Since precipitation is the dominant source of water in streams, particularly during monsoon, their isotopic composition should also reflect the altitude effect associated with precipitation. However, as stream water at any given site represents a mixture of waters from various streamlets draining from higher altitudes up to the site, it is likely to be isotopically lighter relative to the local precipitation at that site. As a result, the altitude effect estimated in stream waters will be partially reduced from that of precipitation. The results for the Ganga head waters (Ramesh and Sarin, 1992) and streams from Gaula catchment area (Bartarya et al., 1995) showed that there is a decrease in $\delta^{18}O$ and δD values of waters with

increase in altitude of sampling locations. Studies of Garzione et al. (2000 a, b) in the Seti River and the Kali Gandaki watersheds in Nepal also show the altitude effect in $\delta^{18}O$ of the streams.

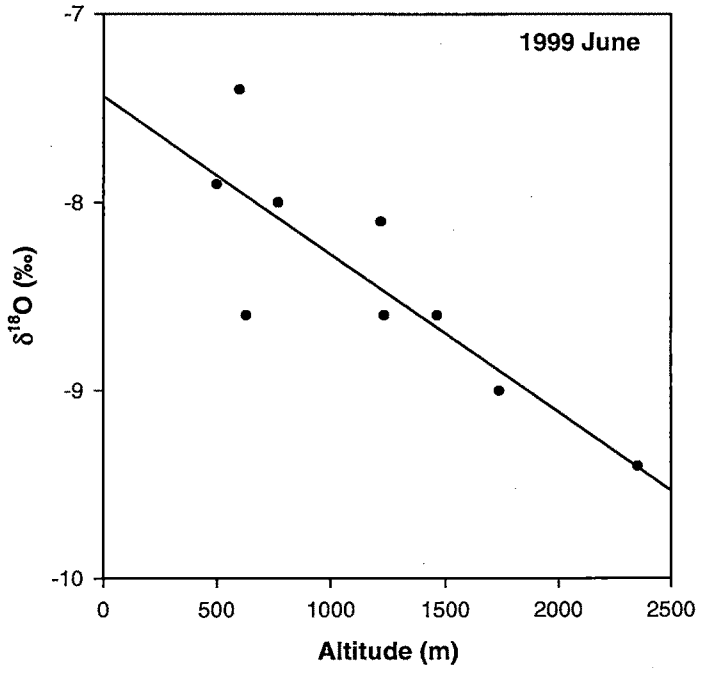

Fig. 3.5 $\delta^{18}O$-Altitude plot for the Yamuna samples collected in June. The slope of the regression line is a measure of the altitude effect (see Table 3.3 and text).

The altitude-$\delta^{18}O$ data for the Yamuna mainstream in the Himalaya (Fig. 3.5, Table 3.3) show that the altitude effect for the Yamuna during summer and post-monsoon are similar within errors with values of 0.09 and 0.11‰ per 100 m respectively. The calculation of altitude effect during monsoon was not done as only 6 samples of the Yamuna mainstream were collected covering an altitude range of only ~480 to 770 m. Considering that the range in isotopic composition together with the slope and intercept of the altitude-$\delta^{18}O$ plots are similar during summer and post-monsoon, these data were combined to derive an average altitude effect for the Yamuna (Table 3.3):

$$\delta^{18}O = (-0.107\pm0.005) \times 10^{-2} \text{ Altitude(m)} \ -7.33\pm0.06 \ (r = -0.85, p < 0.01) \quad (8)$$

The slope of the regression line gives an altitude effect of 0.11‰ per 100 m for $\delta^{18}O$. This compares with the values of 0.09-0.29 reported for various river systems in the Himalaya (Table 3.3). The altitude effect in the YRS is lower compared to 0.19‰ per 100 m for the

Ganga headwaters (Ramesh and Sarin, 1992) and 0.14‰ per 100 m for the streams in the Gaula catchment area (Bartarya et al., 1995), but very similar to 0.09‰ per 100 m for the Indus (Pande et al., 2000). Garzione et al. (2000 a, b) derived an altitude effect of 0.29‰ per 100 m for $\delta^{18}O$ in the tributaries of the Seti River and the Kali Gandaki in the western-central Nepal. Chamberlain and Poage (2000) estimated, from the available data set, a global average altitude effect of 0.21‰ per 100 m for $\delta^{18}O$ in the surface waters.

In order to compare the altitude effect estimated from springs and streams with that in precipitation, it is necessary to correct for the effect of integration of $\delta^{18}O$ signatures in rivers from higher altitudes to the sampling altitudes as was done by Ramesh and Sarin (1992). Their model, based on simplified assumptions, suggests that the altitude effect derived for river water data would be a factor of two lower than that in the precipitation. Application of Ramesh and Sarin (1992) model to the YRS data would yield a value of 0.22‰ per 100m for altitude effect for $\delta^{18}O$ in precipitation in the region. Simple modification of this model by including the effect of evaporation during stream flow does not change this value significantly. The integration effect in Seti River and Kali Gandaki data (Garzione et al., 2000a, b) is expected to be significantly less as they are based predominantly on $\delta^{18}O$ data on small tributaries. Therefore, in this case the measured altitude effect in rivers, 0.29‰ per 100m, is expected to be close to that in precipitation.

Table 3.3 Altitude-$\delta^{18}O$ relation in River Systems in the Himalaya

River	Month	No. of samples	Altitude effect[a)]	Intercept	r
Yamuna	June	10	-0.09±0.01	-7.4±0.1	-0.84
Yamuna	October	6	-0.11±0.01	-7.9±0.1	-0.86
Yamuna	June, Oct.	16	-0.11±0.01	-7.3±0.1	-0.85
Ganga[b)]	April	5	-0.19±0.01	-8.4±0.2	-0.98
Gaula[c)]	Feb, June, Oct	30	-0.14±0.01	-6.3±0.2	-0.69
Indus[d)]	August	6	-0.09±0.01	-12.1±0.4	-0.58
Seti[e)]	March, April	12	-0.29±0.03	-5.9±0.2	-0.96
Kali-Gandaki[e)]	Sept, Oct	38	-0.29±0.01	-6.8±0.3	-0.96

[a)] in ‰ $\delta^{18}O$ per 100m, calculated based on Williamson (1968). Errors are $\pm 1\sigma$.
[b)] Ramesh and Sarin (1992), [c)] Bartarya et al. (1995), [d)] Pande et al. (2000), [e)] Garzione et al. (2000a, b).

It is seen from the compilation in Table 3.3 that the measured altitude effects vary at least by a factor of two among various river systems draining the southern slopes of the Himalaya. The cause for such significant differences in the altitude effect in the major rivers needs to be better understood. A likely explanation for these differences is that they are caused by variable amount effect. The fraction of moisture being rained out in different catchment varies depending on local topography and temperature. Indeed, the role of amount effect has been invoked by Araguas et al. (1998) to explain the oxygen isotope composition of rainfall in the southern part of south-east Asia and by Rozanski et al. (1993) to account for the lack of correlation between $\delta^{18}O$-temperature in this region with surface temperature 20-30°C. Thus, if we accept the hypothesis that rainout is the dominant factor influencing the altitude effect, we can estimate the fraction of moisture removed in the Yamuna catchment as the cloud mass ascends in the Himalayan region. Based on $\delta^{18}O$ and δD values of the streams at the foothills of the Himalaya (Dehradun, RW98-10, Table 3.1) and at the highest sampling location (Hanuman Chatti, RW98-16, Table 3.1) and a simple Rayleigh distillation model we estimate that the cloud mass loses about 25% of its moisture by rainout during its ascent between these two locations (Appendix-3.1). Following a similar approach and using $\delta^{18}O$ and δD values of the Ganga at the foothills and at altitude ~2400 m, it is estimated that the cloud mass loses about 30% of its moisture in the Ganga catchment. Slightly higher estimated rainout in the Ganga cacthment is as expected and attests to the idea that amount effect predominantly governs the altitude effect in this region. It is to be noted that the amount of rainfall in the Himalaya shows a variation with the topographic set up (e.g. north vs. south facing slopes, Devi, 1992). Hence the amount effect, which influences the altitude effect in the region, is to some extent regulated by the local topography. Other factors which may also contribute to these variability are relative mixing proportions from various sources. The Yamuna samples were collected in June and October when summer monsoon is the major source of water, whereas the Ganga samples collected in April may have a dominant glacial melt component. In addition, there could be difference in the supply of moisture to the clouds through evaporation of soil water and evapotranspiration from vegetation.

Comparison of altitude effect in surface water of the Himalayan river systems shows that it varies by a factor of ~2 in catchments lying within a distance of a few hundred kilometers. Such variation may have implications to use of altitude effect in estimation of

paleoelevation in the region. Chamberlain and Poage (2000) compiled data on variations of $\delta^{18}O$ in surface waters with altitude all across the globe and derived an average lapse rate of $\delta^{18}O$ with altitude. They used this average lapse rate and $\delta^{18}O$ in authigenic minerals (kaolinite and smectite) to estimate the paleorelief of mountain ranges. Garzione et al. (2000a, b) estimated the paleoelevation of Tibet using the contemporary altitude effect in the Kali Gandaki and Seti River basins and $\delta^{18}O$ of Miocene-Pliocene carbonates from the southern Tibetan Plateau. Implicit in the above studies is the assumption that altitude effect in the past is the same as that of present day and that it is invariant over the spatial scale of paleoelevation reconstruction. Variations of altitude effects by a factor of ~2, as revealed in this study, in catchments only a few hundred kilometers apart points to the need to have careful scrutiny of the validity of the above assumptions.

3.2.5 Stable isotope-stream chemistry relationship

Stable isotope composition of river waters is determined by the source water isotope systematics, mixing and evaporation. Studies of river water properties such as temperature, chloride concentration and conductivity in conjunction with its stable isotope composition have provided useful information on their sources of water and their mixing proportions (Rodhe, 1998; Lambs, 2000). Lambs (2000) observed a negative correlation between conductivity and $\delta^{18}O$ in surface waters of the Bhagirathi which was attributed to a two component mixing between the isotopically depleted glacial melt with higher conductivity and isotopically enriched snowmelt with lower conductivity.

In this section, we examine the relation between ΣCat^* (the concentration of total cations, ΣCat, in river waters corrected for cyclic component estimated using chloride as an index, $\Sigma Cat^* = \Sigma Cat - Cl$ in equivalent units) and $\delta^{18}O$ in the Yamuna mainstream. The mainstream integrates the contributions of cations and water of various tributaries draining the catchment. At any point in the mainstream, its elemental and isotopic composition represent the "average" contribution of the whole catchment, from its source till that point. Hence downstream variation of cation contribution from the catchment lithology should be best reflected in the mainstream. The extent of chemical weathering (and hence ΣCat^*) in the river basins would depend upon factors such as lithology temperature and vegetation, among others. In the Yamuna basin in the Himalaya, the extent of chemical weathering near the

source is expected to be less intense due to lower temperature, sparse vegetation and dominance of crystalline rocks compared to that along its course downstream in the Lesser Himalaya characterized by warmer climate, more vegetation and more abundance of sedimentary rocks such as carbonates. Thus, as a result of all these, ΣCat* is expected to increase along the course of the Yamuna, consistent with the observation that it trebles from 1056 and 1069 μEq at Hanuman Chatti to 3063 and 2973 μEq at Saharanpur during June and October respectively (Table 3.1).

Fig. 3.6 is a plot of log(ΣCat*) vs. $\delta^{18}O$ for the Yamuna mainstream during the three seasons of sampling. The data shows a significant correlation that can be described by the relation:

$$\log(\Sigma Cat^*) = 0.19\delta^{18}O + 4.85 \quad (r = 0.89, n = 26) \tag{9}$$

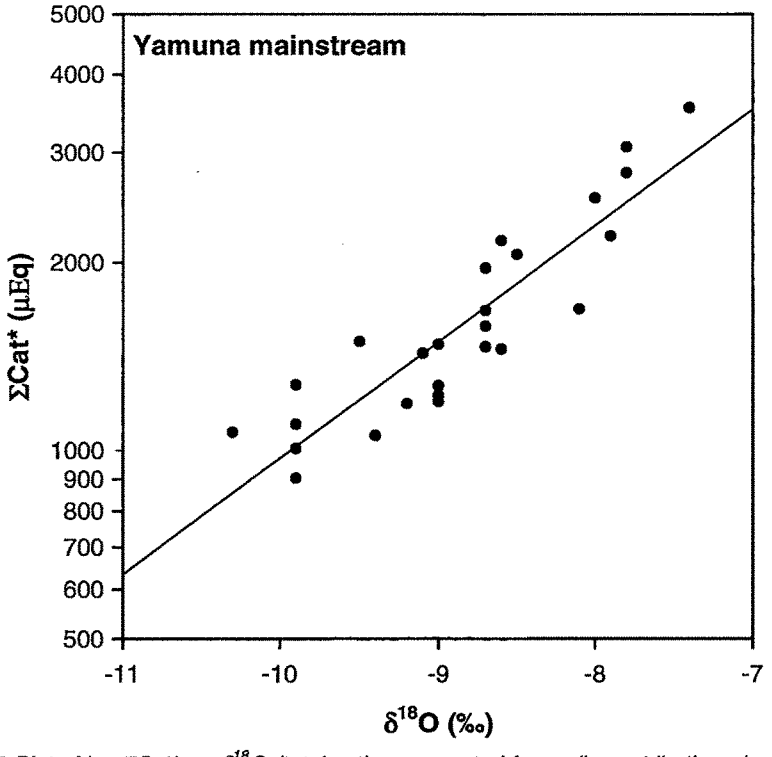

Fig. 3.6 Plot of log ΣCat vs. $\delta^{18}O$ (total cations corrected for cyclic contributions (see text) in the Yamuna mainstream waters. A tight correlation is evident (#RW98-33 not plotted).*

The above relation results because these properties, $\delta^{18}O$ and ΣCat* are both influenced by a common variable, altitude, and unlikely to be because of a causal link between them. The variations in $\delta^{18}O$ and ΣCat* along the course of the Yamuna are brought

about by independent processes, altitude effect and intensity of chemical weathering respectively. Chemical weathering of various rocks is influenced by factors such as lithology, temperature, vegetation and rainfall, whereas $\delta^{18}O$ of the river water is influenced by continentality, temperature and topography of the catchment. In the YRS basin, the temperature varies with altitude, at higher altitudes it is lower. At higher altitudes ΣCat* is lower because of lower temperature and less abundance of easily weatherable lithologies such as sedimentaries. $\delta^{18}O$ is more depleted because the source waters are derived from cloud which are expected to be depleted in ^{18}O because of rainout during its traverse. ΣCat* abundance, indeed, shows a negative correlation with altitude, but with larger scatter. However, considering that physical processes such as mixing and evaporation are likely to affect both ΣCat* and $\delta^{18}O$ similarly and that data on altitude are limited in this study we have used their interrelation to draw inferences on the altitude dependence of ΣCat*. Altitudinal variations in lithology and temperature contributes to ΣCat* variation in the YRS. If, however, weathering of "monolithologic" system (such as silicates) is considered, then it seems to depend mainly on temperature. This dependence is seen in the YRS silicate cations (Na* and Si) which has been used to deduce activation energy of silicate weathering in the catchment (Chpater 4, section 4.2.8).

Relation (9) suggests that ΣCat* would increase by a factor of ~1.5 for every 1‰ increase in $\delta^{18}O$. Considering that the $\delta^{18}O$ altitude effect is ~0.11 ‰/100m (Table 3.3), it can be inferred from the plot that ΣCat* would double as the Yamuna traverses downstream by ~1.4 km in altitude in the Himalaya. The Tons river results also show a correlation between ΣCat* and $\delta^{18}O$ for the two seasons, summer and postmonsoon for which data are available. However, pooling the data of the Yamuna and Tons exhibits a larger scatter ($r = 0.77$, $n = 37$). If the Tons and the Yamuna data are combined then the ΣCat* doubling would be per ~1.6 km decrease in altitude, a result similar to that obtained for the Yamuna mainstream but more representative of the Yamuna River System in the Himalaya.

3.3 CONCLUSIONS

The Yamuna and its tributaries in the Himalaya have been extensively sampled and analyzed for their oxygen and hydrogen stable isotope compositions. These measurements have led to the following observations and conclusions:

(i) δD values in the Yamuna and its tributaries range from -41.7 to -72.0‰ and $\delta^{18}O$ from -6.2 to -10.3‰, the most depleted values being in the monsoon and high altitude samples. The seasonal trends can be understood in terms of amount effect which is more pronounced during monsoon, a season characterized by heavy rainfall events, which deplete the heavy isotopes from the forward moving clouds.

(ii) The δD and $\delta^{18}O$ relation for the monsoon samples yield a slope of 7.71±0.27, quite similar to that for rainwater at New Delhi 7.80±0.05, suggesting that the isotopic signatures of rainfall are well preserved in the stream waters during this season. A similar conclusion is also borne out from samples collected in June, however, the slope of the δD-$\delta^{18}O$ plots for the YRS streams and the rain water at New Delhi during this season center around ~5.8, showing definite evidence of evaporative enrichment of rain during their fall. The deuterium excess in the YRS and New Delhi precipitation suggests that high d values in the YRS during October can be due to an inherent signature of a source with a significant component of recycled moisture.

(iii) The "altitude effect" in $\delta^{18}O$ in the YRS samples is derived to be 0.11‰ per 100m, about a factor of two less than that reported for the Ganga headwaters. This difference in the deduced altitude effects between the Yamuna and the Ganga headwaters is attributable primarily to the influence of amount effect on isotope fractionation. Such large variability in the altitude effect in the river catchments in the Himalaya suggests that reconstruction of paleoelevation in the Himalaya based on the present day altitude effect should be accompanied by proper assessment of altitude effect in the region.

(iv) The $\delta^{18}O$ and the major cation abundances (corrected for cyclic components) in the Yamuna mainstream show a strong positive correlation This relation may arise from a common variable influencing both of them, i.e. altitude. The correlation leads to the inference that the major cation abundance would double as the Yamuna flows about 1.4 km. downstream.

Appendix-3.1

The rainout process by which the raindrops are continuously removed from the cloud vapor by condensation occurs essentially under equilibrium condition. At any given time the isotopic composition in the rainfall is given by the Rayleigh condensation equation:

$$R_l = \alpha R_0 f^{\alpha-1} \qquad \text{(A1)}$$

where R_l is the ratio of the isotopes ($^{18}O/^{16}O$ or D/H) in the evolved liquid (rain), R_0 is the initial ratio in the vapour, f is the fraction of the vapor remaining and α is the temperature dependent isotope fractionation factor during the vapor-liquid transition.

Using the isotopic composition of the stream at the foothills in the catchment as αR_0 and that of the stream at the highest sampling location as R_l, the residual fraction of the vapor and hence the amount of rainout can be calculated using equation (A1).

Rainout calculated from $\delta^{18}O$

From equation (A5):

$f = \exp[\ln(R_l/\alpha R_0)/(\alpha-1)]$

since $\alpha R_0 = R_{\ell_o}$, we have $f = \exp[\ln(R_l/R_{\ell_o})/(\alpha-1)]$

or $f = \exp[\{\ln((\delta_l+1000)/(\delta_o+1000))\}/(\alpha-1)]$ (A2)

Taking δ_o = -7.3‰ (Tons at Dehradun, RW98-10) and δ_l = -10.3‰ (Yamuna at Hanuman Chatti, RW98-16), f varies between 72 to 76% (using the values of α from 1.0093 to 1.0112 in temperature range 25 to 5 °C, Clarke and Fritz, 1997), hence the rainout from the cloud during its movement between these two locations is 28 to 24%.

Rainout calculated from δD

Taking δ_o = -46.7‰ (Tons at Dehradun, RW98-10) and δ_l = -67.1‰ (Yamuna at Hanuman Chatti, RW98-16), f varies between 76 to 81% (using the values of α from 1.079 to 1.105 in temperature range 25 to 5 °C, Clark and Fritz, 1997), hence the rainout from the cloud during its movement between these two locations is 24 to 19%.