

Hydrochemistry and stable isotopes study of the precipitation at Haraz Basin, north of Iran

Abdollah Shamsi^{1*}, Gholam Hossein Karami¹, Azizollah Taheri¹, Daniel Hunkeler²

¹ Faculty of Earth Sciences, Shahrood University of Technology, Shahrood, Iran

² Faculty of Sciences, Center for Hydrogeology and Geothermics (CHYN), University of Neuchatel, Neuchatel, Switzerland

*Corresponding author, e-mail: a.shamsi@shahroodut.ac.ir

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Abstract

Stable isotopes (Deuterium and Oxygen-18) have a broad application in many of water related sciences. Precipitation is the most important input to the water cycle which shows considerable spatial and temporal variability in its isotope content. To study the precipitation isotope content, 51 samples from August 2015 to July 2016 have been collected mainly on a monthly basis with few events based samples at five stations in Haraz basin, north of Iran. A local meteoric water line (LMWL) of the Haraz basin is expressed by the equation $\delta D = 7.66\delta^{18}O - 8.48\text{‰}$. Both slope and interception of LMWL are lower than corresponding values for the Global Meteoric Water Line (GMWL). The isotope composition of precipitation generally shows a seasonal fluctuations and it has been influenced by rainfall amount and ambient air temperature. Considering the precipitation chemistry at Haraz basin shows that the Ca^{2+} and HCO_3^- are the main ionic species accounting for 70.8% of total ionic concentration. Total ionic concentration shows a seasonal trend of lower values in wet and higher concentrations at the dry months. The absence of strong correlation between ion species, suggests that precipitation's chemistry affected by crustal elements, marine salt and anthropogenic activities.

Keywords: Haraz; Stable Isotopes; LMWL; Precipitation Chemistry

Introduction

Stable isotopes Deuterium (δ^2H) and Oxygen-18 ($\delta^{18}O$) are valuable natural tracers that have a broad application in hydrogeology, geology, hydrology, climatology, ecology and pollution monitoring (Clark & Fritz, 1997; Sidle, 1998; Thomas & Rose, 2003; Aggarwal *et al.*, 2005; Herczeg & Leaney, 2011; Sanford *et al.*, 2011; Soderberg *et al.*, 2013; Somaratne *et al.*, 2016). Precipitation is major component of the water cycle so that many researchers devoted to evaluate its stable isotopes content in different regions (e.g. Harvey & Welker, 2000; Stump *et al.*, 2014; Hager & Foelsche, 2015; Kazemi, *et al.*, 2015; Tappa *et al.*, 2016). Similarly, other researchers investigated the affecting parameters on isotope signature of the precipitation (e.g. Peng *et al.*, 2004; Pang *et al.*, 2012; Hussain *et al.*, 2015; Crawford *et al.*, 2017; Zhu *et al.*, 2016; Wang *et al.*, 2016). Moreover, stable isotopes used to estimation of evaporation from water surface (e.g. Gibson *et al.*, 1993; Williams *et al.*, 2004; Gibson & Ried 2010; Skrzypek *et al.*, 2015). Furthermore, researchers studied the temporal and spatial variations of stable isotopes in rivers (Liu *et al.*, 2005; Miljević *et al.*, 2008; Wang *et al.*, 2014). Additionally, surface water and groundwater interactions have been investigated by application of stable isotopes (Adomako *et al.*, 2015).

Precipitation is the primary and main source of the input to the water cycle (Kattan, 1997; Harvey & Welker, 2000). Therefore, its stable isotope and hydrochemistry characteristics are basics for studies in related field (Kattan, 1997; Xiao *et al.*, 2013; Shamsi & Kazemi, 2014; Préndez *et al.*, 2014). Global Meteoric Water Line (GMWL) refers to the average ratio of the δD vs. $\delta^{18}O$ is approximate compositions of rain and snow on the global scale (Craig, 1961; Dansgaard, 1964). Since stable isotopes are spatially variable, it would be more valuable to use Local Meteoric Water Line (LMWL) for different locations (Harvey & Welker, 2000; Peng *et al.*, 2004; Sturm *et al.*, 2005; Kazemi *et al.*, 2015).

Because of importance role of precipitation in the water cycle, its chemistry is important to study and allows tracing the spatial and temporal assessment of anthropogenic activities and climate change effects on hydrology and ecosystem (Balestrini *et al.*, 2000; Ladouche *et al.*, 2009; Greilinger *et al.*, 2016; Rogora *et al.*, 2016). Moreover, fossil fuels and other air pollutants could produce a signature, such as $H_2SO_4^{2-}$ and HNO_3^- (Xiao *et al.*, 2013) that could be traced by investigating of the precipitation chemistry.

This research is intended to evaluate the hydrochemistry and stable isotopic contents of the

precipitations in the Haraz Basin through a hydrologic year and evaluate their spatial and temporal variations in five sampling stations. In addition, it is aimed to develop the LMWL for the central part of the Alborz Mountain in the north of Iran.

Study Area

The study area is located in the mountainous part of the Haraz Basin ($51^{\circ}36'$ to $52^{\circ}26'$ N and $35^{\circ}45'$ to $36^{\circ}08'$ E) at the northern part of Iran in the central Alborz Mountain, 85 km northeast of Tehran (Figure 1). This region is characterized by an altitude drop from almost 5671 m above sea level (a.s.l) at Damavand summit to 850 m a.s.l. at the outlet of the mountainous part of the basin in Panjab area. The entire catchment has relatively steep topography with an average slope of 45° .

Data of 20 years' shows that the mean annual amount of precipitation varies from 624 mm at Polour to 140 mm in Panjab station (Figure 2a). The annual precipitation amount is higher in the elevated parts (Khalili, 1973) and shows about 5 mm raise for every 100 m increase in elevation. Precipitation amounts are largest during winter (mainly December to February) and lowest during

summer month (Khalili, 1973; Alijani & Harman, 1989). Snow is dominant form of precipitation from October to May (wet season) while rain is the dominate type of precipitation from June to September (dry period). The hydrologic cycle of these high-altitude watersheds is characterized by snowpack accumulation during late autumn, winter, and early spring which is followed by a snowmelt runoff period during middle spring to early summer.

Air temperature ranges from -20 to 30°C and -15 to 28°C at Polour and Baladeh stations respectively (Figure 2b). Air temperature is cooler with higher range of variability in the southern part of the study area and becomes warmer and less variable to the north (Figure 2b).

The annual average potential evaporation (pan evaporation) is 1270 and 1000 mm at Polour and Baladeh stations respectively (Figure 2c) and it shows higher annual amounts and more variability at Polour in comparison to the Baladeh station (Regional Water Company of Mazandaran 2017). Likewise, the values of relative humidity show higher variability and wider range at Polour station in comparison to the Baladeh station (Figure 2d).

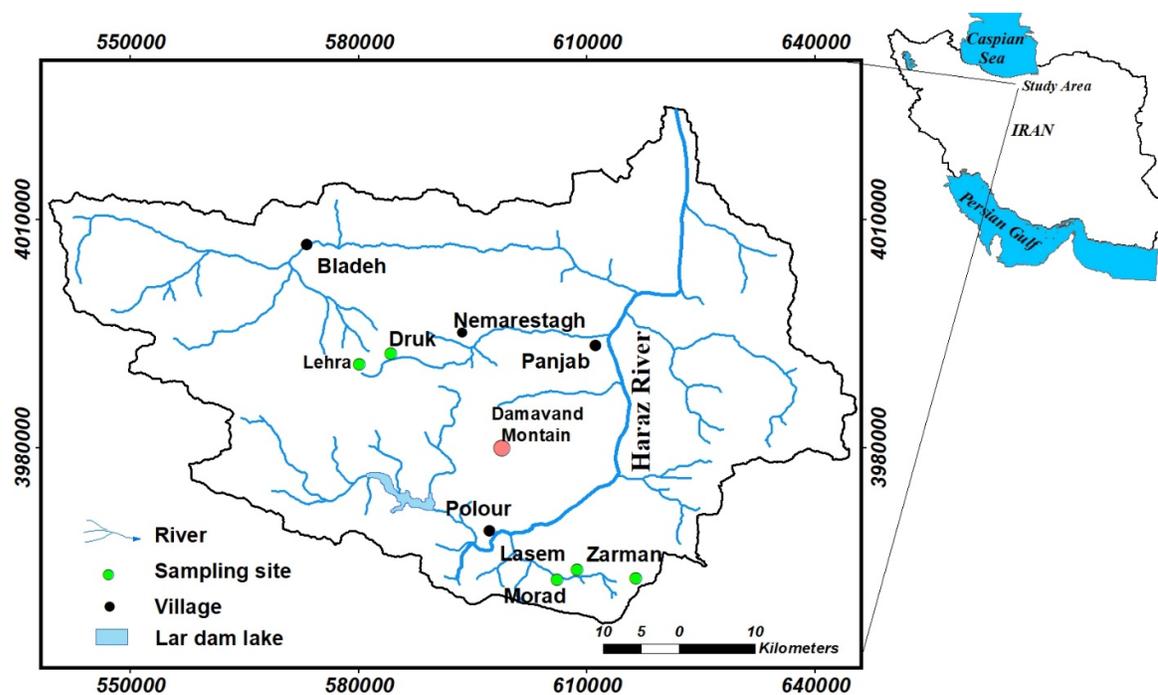


Figure 1. Geographical locations of the study area and 5 sampling sites at Haraz basin (Distance of Druk and Lehra sampling points from Baladeh climatology station are 26.1 and 24.2 kilometers; distance of Morad, Lasem and Zarman sampling points from Polour climatology station are 12.4, 15.7 and 22 kilometers respectively).

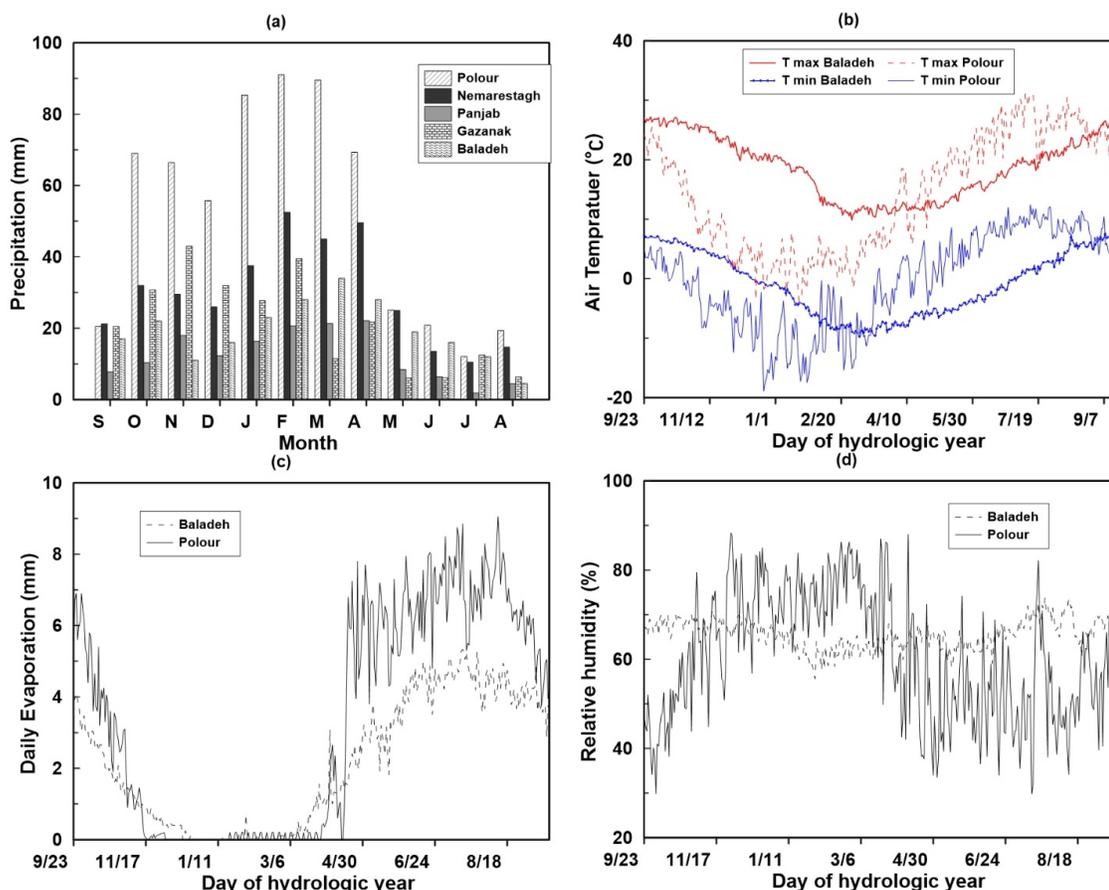


Figure 2. Climatological parameters of Haraz Basin, (a): monthly average of precipitation data distribution at six monitoring stations, (b): average daily minimum and maximum temperatures, (c): average pan evaporation and (d) relative humidity at Baladeh and Polour climatology stations.

Materials and Methods

Totally 51 samples of the precipitations collected at the five stations (snow/rain) from August 2015 to July 2016 on monthly basis (Table 1) with few exceptions due to malfunctioning of the system or destroying by wild animals. Few event based samples (Fresh snow and rain) were collected immediately after the occurrence of each events. To avoid the evaporation effects and wild animal disturbances rain collectors buried 30 cm below the ground surface which connected via a tube to funnel at ground surface. A film of paraffin oil used in the rain container. For the monthly basis rain samples, each month the collector replaced with new one to avoid the disturbances by mixing. In the case of snow, sampling was carried out from the whole column of the snow that deposited after the previous sampling that has been separated by a plastic cover at the bottom of snow pits. To minimize the evaporation effects on the snow column, the selected stations chosen at places to be

covered by natural shadow without a direct sunlight in the snowing periods. It should be noted fine grains size of snowpack samples confirms negligible subjection to sublimation (Feng *et al.* 2002). The snow samples were collected in clean polyethylene 2.5 liter bottles. After naturally melting at room temperature (14°C) samples were filtered through 0.4 µm pore size filters and a 70-mL of each transferred into a dark brown polyethylene bottle with waterproof seals. For chemistry analysis, 50 ml of samples stored in polyethylene bottle for measuring anions and the same volume was acidified with nitric acid to pH lower than 2 for measuring cations in sampling time. Samples stored in a dark and cool place (4.5°C) for the chemical and isotope analyses. Isotope analysis has been carried out in cooperation with International Atomic Energy Agency (IAEA) in Vienna. Hydrochemical analysis carried out in Center for the Hydrogeology and Geothermic (CHYN) at the University of Neuchatel.

Table 1. Isotopic composition of precipitation samples collected from the Harza basin at 5 stations from August 2015 to July 2016.

Sample ID	Altitude (m a.s.l)	Precipitation type	Date	P (mm)	δD ‰	δO ‰	T (°C)	D-excess ‰
Morad-2015/01	2675	Rain	9/18/2015	23.0	-6.00	-0.47	14.00	-2.24
Morad-2015/02	2130	Rain	10/19/2015	15.6	7.36	0.36	12.70	4.48
Morad-2015/04	2600	Snowpack	12/3/2015	48.0	-79.68	-11.55	-7.18	12.72
Morad-2016/05	2550	Snowpack	1/17/2016	78.0	-88.06	-11.86	-6.54	6.82
Morad2016/06	2550	Snowpack	2/13/2016	41.0	-49.19	-8.38	-2.91	17.85
Morad-2016/07	2550	Snowpack	3/8/2016	40.0	-80.48	-11.21	3.58	9.20
Morad-2016/08	2293	^a Fresh snow	4/7/2016	4.2	-144.09	-19.39	8.20	11.03
Morad-2016/09	2500	Rain	5/9/2016	70.0	-6.58	-2.92	12.06	16.78
Morad-2016/10	2500	Rain	6/16/2016	34.0	-19.81	-3.77	17.56	10.35
Morad-2016/11	2500	Rain	7/21/2016	11.0	-2.30	-0.11	19.00	-1.42
Druk-2015/01	2670	Rain	9/17/2015	23.0	8.12	-0.62	15.00	13.08
Druk-2015/02	2670	Rain	10/18/2015	15.6	-25.82	-3.55	12.70	2.58
Druk-2015/03	2850	Snowpack	11/8/2015	50.2	-54.89	-8.45	-2.79	12.71
Druk-2015/04	2830	^a Fresh snow	12/1/2015	53.5	-109.88	-15.06	-7.18	10.60
Druk-2016/05	2667	Snowpack	1/16/2016	80.0	-54.07	-8.72	-6.54	15.69
Druk-2016/05	2670	Snowpack	4/6/2016	105.0	-37.67	-6.63	-2.91	15.37
Druk -2016/06	2667	Snowpack	2/12/2016	45.0	-73.38	-10.98	-3.00	14.46
Druk-2016/07	2667	Snowpack	3/7/2016	46.0	-79.00	-11.70	8.20	14.60
Druk -2016/08	2667	^a Fresh snow	4/6/2016	4.8	-110.37	-14.93	12.06	9.05
Druk-2016 /09	2670	^b Rain	5/10/2016	76.0	-19.82	-3.86	17.56	11.06
Lasem-2015/01	2700	^b Rain	9/18/2015	23.0	-2.85	-0.76	12.14	3.23
Lasem-2015/02	2670	Rain	10/19/2015	18.0	-49.13	-5.83	12.70	-2.49
Lasem-2016/05	2600	^a Fresh snow	12/3/2015	50.0	-133.08	-17.31	-7.18	5.40
Lasem-2015/04	2600	^a Fresh snow	1/17/2016	83.0	-110.03	-14.82	-6.54	8.53
Lasem-2016/06	2670	Snowpack	2/13/2016	43.0	-56.44	-9.00	-2.91	15.56
Lasem-2016/07	2600	Snowpack	3/8/2016	42.0	-64.87	-9.65	3.58	12.33
Lasem-2016/08	2724	Snowpack	4/7/2016	5.0	-68.58	-9.91	8.20	10.70
Lasem-2016/09	2670	^b Rain	5/9/2016	75.0	-33.24	-5.93	12.06	14.20
Lasem-2016/10	2670	^b Rain	6/16/2016	36.0	-14.65	-2.73	17.56	7.19
Lehra-2015/02	2950	Rain	10/18/2015	15.6	-20.45	-2.08	12.70	-3.81
Lehra-2015/03	3000	Snowpack	11/8/2015	53.0	-55.98	-9.00	-2.79	16.02
Lehra-2015/04	3000	^a Fresh snow	12/1/2015	55.3	-115.50	-15.90	-7.18	11.70
Lehra-2016/05	3000	Snowpack	1/16/2016	82.0	-44.32	-7.80	-6.54	18.08
Lehra2016/06	3000	Snowpack	2/12/2016	48.0	-48.05	-8.12	-2.91	16.91
Lehra-2016/07	3000	Snowpack	3/7/2016	48.0	-93.44	-12.49	3.58	6.48
Lehra-2016/08	2900	Snowpack	4/6/2016	112.0	-36.72	-6.22	8.20	13.04
Lehra-2016 /09	2950	^b Rain	5/10/2016	79.0	-28.84	-4.94	12.06	10.68
Lehra-2016/10	2950	^b Rain	6/15/2016	35.0	-35.83	-6.24	17.56	14.09
Zarman-2015/01	2948	Rain	9/18/2015	15.6	-44.80	-6.44	12.70	6.72
Zarman-2015/02-1	3270	^a Fresh snow	9/18/2015	19.0	-100.07	-13.65	-2.79	9.13
Zarman-2015/02	3114	Snowpack	10/19/2015	18.0	-52.44	-7.24	12.14	5.48
Zarman-2015/03	2700	^a Fresh snow	11/9/2015	53.0	-156.00	-21.43	-2.79	15.44
Zarman-2015/04	2724	Snowpack	12/3/2015	55.0	-50.61	-8.88	-7.18	20.43
Zarman2015/05	2948	Snowpack	1/17/2016	90.0	-23.76	-4.16	-6.54	9.52
Zarman2016/06	2980	Snowpack	2/13/2016	50.0	-35.76	-7.10	-2.91	21.04
Zarman-2016/07	2980	Snowpack	3/8/2016	48.0	-58.08	-9.15	3.58	15.12
Zarman-2016/08	2948	Snowpack	4/7/2016	110.0	-42.16	-7.30	8.20	16.24
Zarman-2016/09	2948	Rain	5/9/2016	78.0	-21.41	-4.25	12.06	12.59
Zarman-2016/10	2948	Rain	6/16/2016	36.0	-31.47	-6.41	17.56	19.81
Zarman2016/11	2948	Rain	7/21/2016	13.0	-3.09	-0.87	17.56	3.87
Zarman-2015/01	2948	Rain	9/18/2015	15.6	-44.80	-6.44	12.70	6.72

a, event based fresh snow; b, event based rain sample

The cations (NH_4^+ , Na^+ , K^+ , Mg^{2+} , Ca^{2+}) were analyzed by ion chromatography Dionex DX-120 and anions (Cl^- , NO_3^- , SO_4^{2-}) were measured within Dionex ICS-1600 ion chromatograph with a detection limit of 0.1 mg L^{-1} . Bicarbonate were measured by Titrino plus 848 working with HCl 0.1 M for titration.

Results of stable isotopes Oxygen-18 and D

The result of isotope analysis at the five monitoring sites are summarized in Table 1. The isotope ratios ranges from -21.43 to 0.36 ‰ and -156 to 8.12 ‰ , for $\delta^{18}\text{O}$ and δD , respectively (Table 1). Local meteoric water line (LMWL) for the Haraz Basin constructed based on the stable isotope (δD and $\delta^{18}\text{O}$) ratios of 51 samples of five sites (Figure 3a). Most sample lies very close to the Global Meteoric Water Line (GMWL) with exception for a few samples of late spring and summer that show more deviations. LMWL of Haraz Basin follows the regression of $\delta\text{D} = 7.66\delta^{18}\text{O} - 8.46\text{‰}$, with significant linear correlation ($R^2 = 0.98$). Based on the type of the precipitation including Fresh snow, snowpack and rain samples dominantly lies on lower left, middle and upper right part respectively (Figure 3a). Generally, snow samples (snowpack and fresh snow) have more depleted isotope signature whereas the rain samples are more enriched.

Deuterium excess (D-excess) of the samples calculated using the defined formula by Dansgaard

(1964) as $\text{d-excess (‰)} = \delta\text{D (‰)} - 8 * \delta^{18}\text{O (‰)}$. D-excess values at Haraz Basin range from -3.81‰ to 21.04‰ , with an average of 10.93‰ (Table 1). Generally, d-excess of higher elevated stations have a wider range of the variability than lower elevated stations. D-excess content of wet season samples shows higher variability in comparison to the dry season samples (Figure 3b).

Seasonal variations

Figure 4 presents a seasonal trend of the $\delta^{18}\text{O}$ and δD at five sampling sites over the sampling period. There is a significant systematic seasonal variation in isotope composition of precipitation corresponding to the general trends of the air temperature and amount of precipitation. Samples of dry period (late spring, summer, and early autumn) are more enriched while the samples of wet period (the late autumn, winter, and early spring) shows more depleted (Figure 4). As can be seen in Figure 4 the samples from five sites shows temporal and special variations. The most enriched samples found at the Morad station while the most depleted sample observed at Zarman station. Samples of the Zarman station shows more range of variability in comparison to the other stations. Lehra and Zarman, which are situated in higher elevation, showing similarity in isotope signature fluctuations. Morad, Druk and Lasem have similar annual trends.

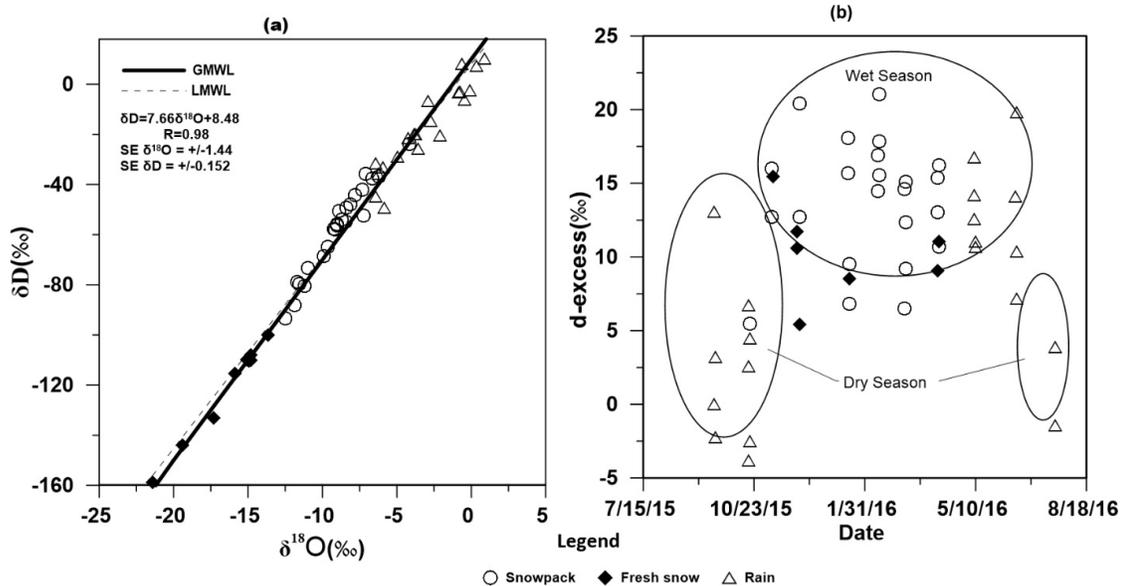


Figure 3. (a): $\delta^2\text{H}-\delta^{18}\text{O}$ relationship for the all collected precipitation samples at 5 sampling sites in Haraz Basin ($n=51$), (b): and temporal variation of d-excess.

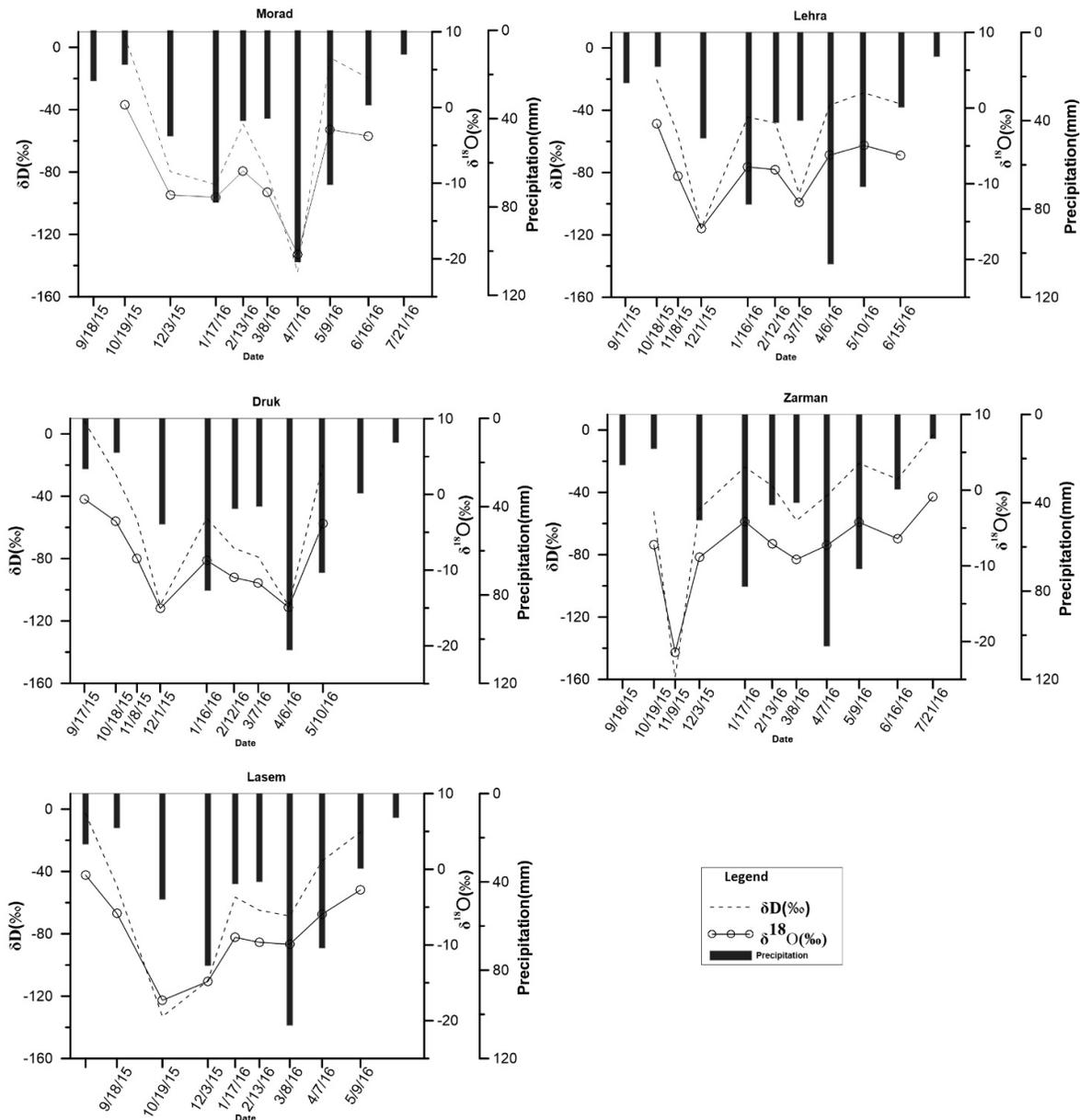


Figure 4. Seasonal variation of the isotope content at 5 sampling sites.

Temperature Effect

The values of temperature have not been measured at the monitoring sites but based on available meteorological daily data, the mean ambient air temperature has been calculated based on the average value of several years daily records at Polour station. As can be seen in Figure 5a, by increasing the air temperature, the isotope content becomes heavier with correlation coefficient of 0.61 ($P < 0.0001$) for δD and 0.65 ($P < 0.0001$) for $\delta^{18}O$. Precipitations of warm season in the form of the rain, have heavier isotope content in comparison to

the snow samples which deposits in the cold season. Considering the d-excess versus the temperature shows that the lower the ambient air temperature the higher the value of d-excess (Figure 5b). Snow samples have higher values of d-excess with limited range of variability while the rain samples show lower values with a wider range of variation.

Altitude Effect

Generally, there is no linear relation between elevation and $\delta^{18}O$ ($R^2 \square 0.0008$ and $P\text{-Value} \square 0.99$). However, considering samples based on the form of

precipitation (fresh snow, snowpack and rain) shows three general trends with elevation (Figure 6a). Rain samples show a negative trend with elevation and by increasing the elevation the isotope content becomes lighter, but the fresh snow and snowpack samples show positive trend as by increasing the elevation the isotope content becomes heavier (Figure 6a). Event based rain and

fresh snow samples shows normal relation with elevation and becomes depleted by increasing the altitude (Figure 6b). Precipitations of the dry season (rain) are more sensitive to the elevation than winter time precipitations (snow). Depletion of the $\delta^{18}\text{O}$ in dry season event base precipitation is 0.9‰ for 100 m raise of elevation while it is 0.4‰ for wet season samples.

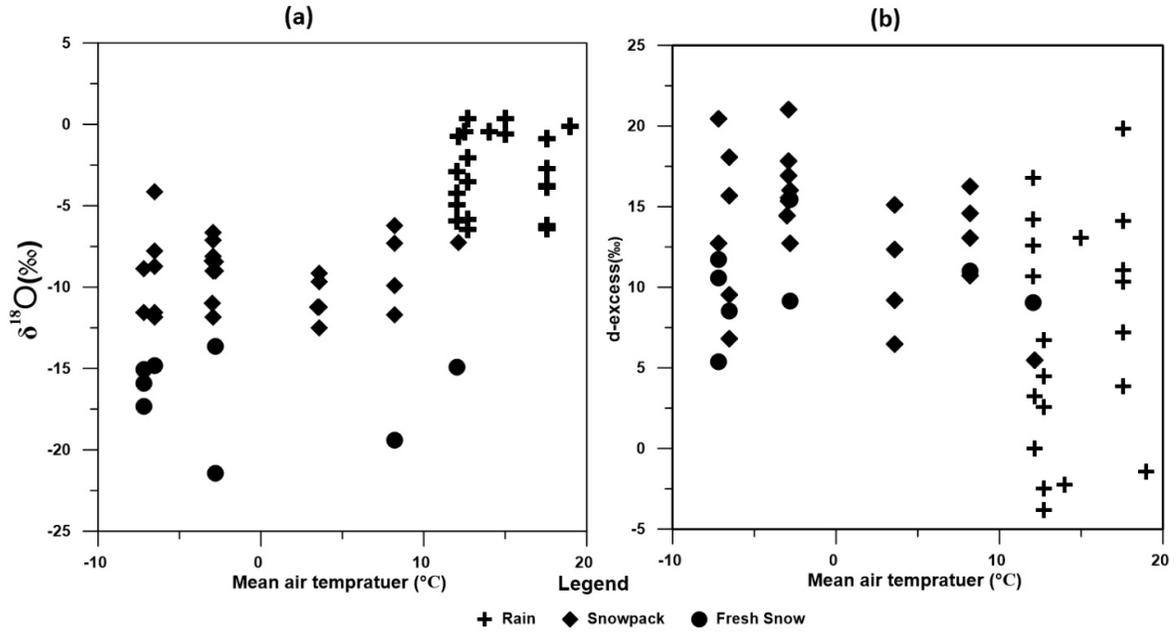


Figure 5. (a): Temperature effects on the $\delta^{18}\text{O}$ ratio of the precipitations (b): Relation between ambient air temperature and d-excess.

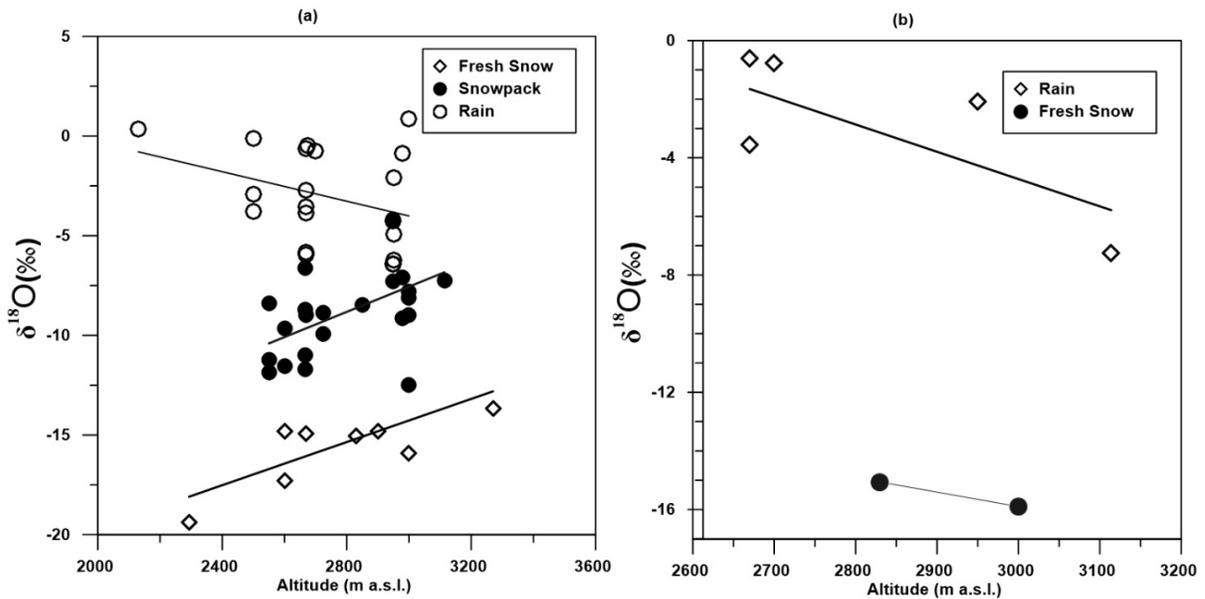


Figure 6. Altitude effects on the isotope composition of the precipitations; (a) $\delta^{18}\text{O}$ relations with altitude of integral samples (b): event base samples with elevation

Results of precipitation chemistry

Chemical of precipitation

Table 2 illustrates the volume weighted chemical composition of precipitations at five sampling sites. Ionic balance below 10, good correlation between total anions versus cations ($R^2=0.99$) and measured Electrical Conductivity (EC) alongside calculated EC of the samples (Figure 7a, b, c) confirms the satisfactory quality of the results (e.g. Galloway & Likens, 1987). Similarly, high correlation of alkalinity and cations ($R^2=0.94$) confirms the reliability of analyzed results (Figure 7d). The pH of the samples ranged from 4.5 to 9 with an average of 7.3 the lower value observed in the rain samples and the higher value in the snow samples. Electrical

conductivity of the samples ranges from 548 to 18 $\mu\text{S}/\text{cm}$ with an average of 102 $\mu\text{S}/\text{cm}$. As shown in Figure 8 Ca^{2+} and HCO_3^- are the dominant cation and anion respectively and together accounted for 70.8% of total ionic concentration in all samples. The ionic abundance in descending order were SO_4^{2-} , Na^+ , NO_3^- , Cl^- , NH_4^+ , Mg^{2+} and K^+ . The maximum concentration of the HCO_3^- , SO_4^{2-} , NH_4^+ and K^+ were found at the Zarman sampling site whereas the minimum concentration of HCO_3^- , Ca^{2+} , Mg^{2+} and Cl^- observed at the Lehra. In the winter, all of the constituents have the lowest amount while in the late spring, summer and early autumn samples had the highest concentrations.

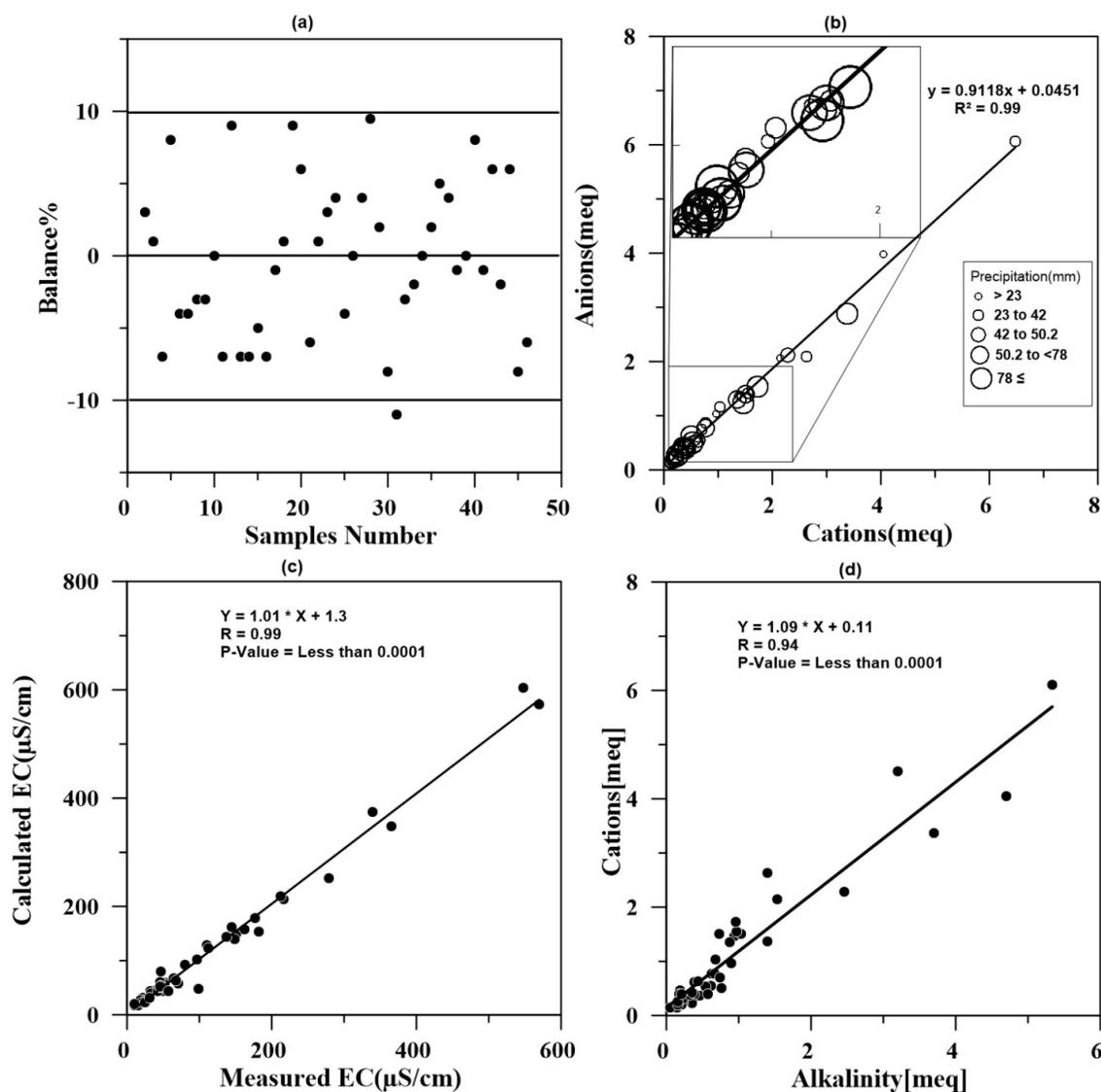


Figure 7. Quality control of the samples chemical analysis for (a): the ionic balance, (b): cations vs anions (c): the calculated conductivity vs the measured electrical conductivity (d): Cations vs alkalinity.

Table 2. Annual volume weighted mean ions concentration in (meq/L), EC, pH and TDS at five sampling stations

	Zarman	Lasem	Abmorad	Lehra	Druk
EC($\mu\text{S}/\text{cm}$)	92.5	118.2	93.7	144	137
pH	7.66	7.23	7.39	7.23	7.38
TDS	45.3	63.6	51.5	59.9	81.5
Alkalinity	0.71	0.93	0.70	0.76	1.55
Ca^{2+}	0.69	0.72	0.70	0.40	0.61
Mg^{2+}	0.04	0.04	0.05	0.03	0.05
Na^+	0.07	0.07	0.09	0.08	0.10
K^+	0.05	0.02	0.01	0.02	0.04
NH_4^+	0.21	0.02	0.01	0.05	0.10
HCO_3^-	0.51	0.80	0.59	0.48	1.21
Cl^-	0.08	0.09	0.06	0.03	0.05
SO_4^{2-}	0.14	0.10	0.12	0.07	0.08
NO_3^-	0.09	0.03	0.10	0.06	0.12

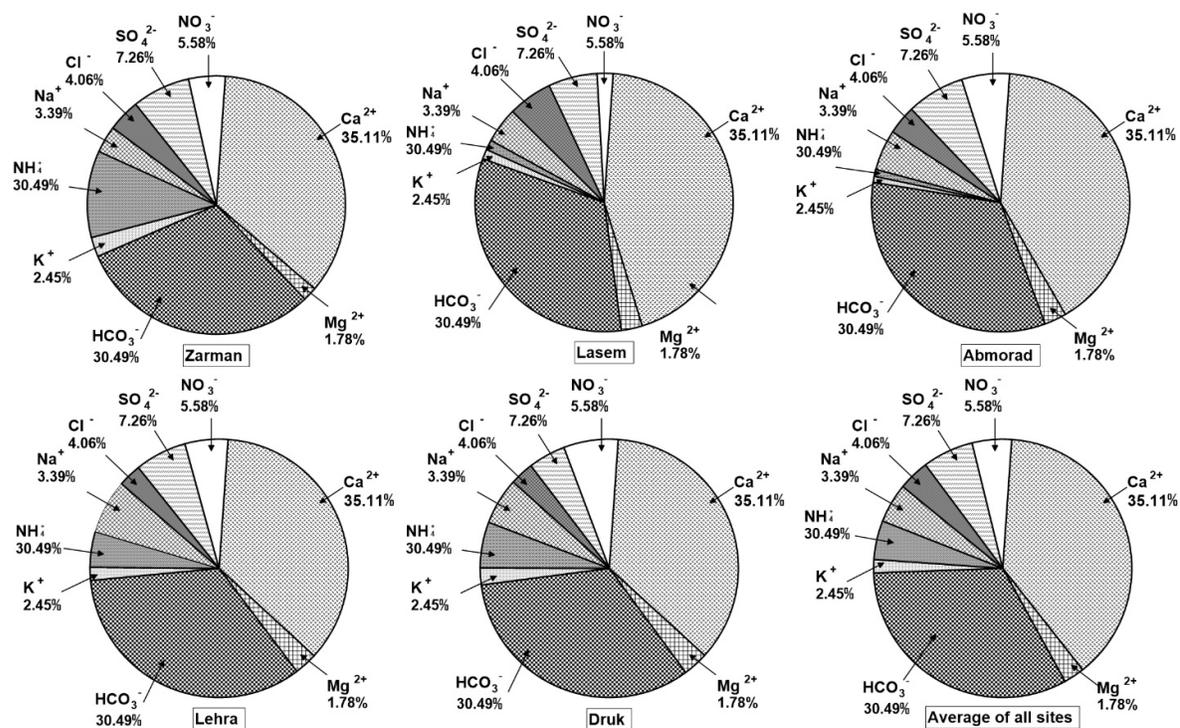


Figure 8. Annual percentage of chemical species in precipitation at 5 sampling sites and average of all sites (meq/l).

Temporal variability of the precipitation chemistry

The ion concentration of Haraz Basin varied largely around the volume-weighted values (Table 2). Temporally, wide ranges of variability in precipitation chemistry were observed in the Haraz basin (Figure 9). Nevertheless, the concentrations of the major ions (i.e., Ca^{2+} , HCO_3^- , Mg^{2+} , SO_4^{2-} , Na^+ ,

Cl^- , K^+ , and NO_3^-) show similar seasonal variations, increasing in summer and decreasing in winter. End summer samples show the highest value of the ion concentrations. It should be mentioned that few irregular values observed in the middle of the wet season (Figure 9).

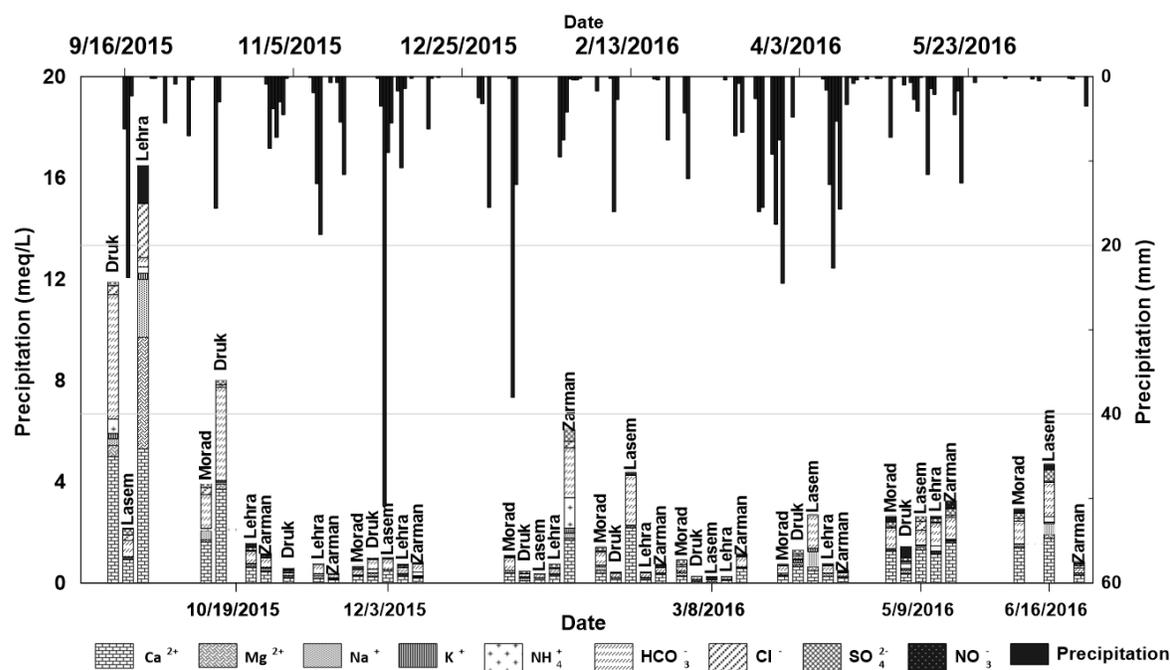


Figure 9. Temporal trends of major ion concentrations in precipitations (meq/l).

Correlation and Principal Component Analysis (PCA) of ion species

To find out the association between the ions in precipitation and likely sources of the pollutants, the correlation among the ions calculated and summarized in Table 3. Among the statistically significant correlations, Ca^{2+} was strongly correlated with HCO_3^- (0.96) and Mg^{2+} (0.86) and K^+ is correlated with NH_4^+ (0.74), HCO_3^- (0.7), Cl^- (0.66) and SO_4^{2-} (0.55).

The PCA was applied to identify the sources of chemical ion in precipitation and associate their possible sources (Lee *et al.*, 2000; Facchini-Cerqueira *et al.*, 2014; Li *et al.*, 2016). The PCA analysis was conducted using SPSS 23.0 to find out the relationship between the chemical species measured in precipitation. The principal components with eigenvalues >1 were selected and factor loadings that higher than 0.5 were considered to be significant (Migliavacca *et al.*, 2005; Sakihama *et al.*, 2008; Facchini-Cerqueira *et al.*, 2014). Table 4 shows the varimax-rotated principal component patterns for all the precipitation at five stations. Three extracted factors accounted in total for 85.22% of the variance. The first factor (F1) accounts for 56.4% of total variance, that characterized by high loading of all the ions with exception of NO_3^- and Na^+ . Factor 2 with a variation of 16.7%, only presents a significant

loading for HCO_3^- . Factor 3 accounts for 12.8% of the total variance with high loading factor for NO_3^- . Plotting the F_1 against F_2 indicates three distinct clusters of variables (Figure 10).

Enrichment factor of the chemical composition

Enrichment factor (EF) of the constituent ions in precipitation have been applied to identify the origin of the constituents (Zhang *et al.*, 2007; Ma *et al.*, 2012; Kazemi *et al.*, 2015; Li *et al.*, 2016). EF calculation is based on the ratio of ions concentration in precipitation in comparison to the reference materials. Usually, Na^+ considered as a reference for sea salts and it is assumed that originated from the marine sources and Ca^{2+} used as a reference for the elements originated from the terrestrial sources, EF values were computed by following equations;

$$\text{EF}_{\text{seawater}} = [\text{X}/\text{Na}^+]_{\text{precipitation}} / [\text{X}/\text{Na}^+]_{\text{seawater}}$$

$$\text{EF}_{\text{soil}} = [\text{X}/\text{Ca}^{2+}]_{\text{precipitation}} / [\text{X}/\text{Ca}^{2+}]_{\text{soil}}$$

Where X is the desired ion concentration and $[\text{X}/\text{Na}^+]_{\text{seawater}}$ is the ratio based on seawater composition (Keene *et al.*, 1986) and $[\text{X}/\text{Ca}^{2+}]_{\text{soil}}$ of the soil is the ratio of crustal composition (Taylor, 1964). Constituents are expressed in $\mu\text{eq/L}$ and ppm for EF calculation of sea salts and soil components, respectively.

Table 3. Correlation matrix of chemical species in precipitation.

	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	HCO_3^-	Cl^-	SO_4^{2-}	NO_3^-
Ca^{2+}	1								
Mg^{2+}	0.85**	1							
Na^+	0.32	0.55**	1						
K^+	0.60**	0.72**	0.52**	1					
NH_4^+	0.40**	0.50**	0.30	0.88**	1				
HCO_3^-	0.95**	0.85**	0.40**	0.52**	0.31	1			
Cl^-	0.44**	0.53**	0.24	0.84**	0.87**	0.27	1		
SO_4^{2-}	0.52**	0.50**	0.36	0.75**	0.77**	0.36	0.74**	1	
NO_3^-	0.01	-0.09	-0.01	-0.08	-0.11	-0.09	-0.14	0.16	1

**Correlation is significant at the 0.01 level.

Table 4. Factor loading, Eigenvalues (EV), Variance and cumulative variance for 3 Factors with EV above 1 of chemical constituents in precipitation.

	F ₁	F ₂	F ₃
Ca^{2+}	0.81	0.49	0.08
Mg^{2+}	0.87	0.39	-0.05
Na^+	0.55	0.20	0.07
K^+	0.93	-0.23	-0.04
NH_4^+	0.82	-0.51	-0.07
HCO_3^-	0.74	0.63	-0.05
Cl^-	0.80	-0.50	-0.11
SO_4^{2-}	0.80	-0.35	0.29
NO_3^-	-0.08	0.00	0.99
Eigenvalues	5.07	1.51	1.08
Variance %	56.4	16.7	12.08
Cumulative %	56.4	73.21	85.22

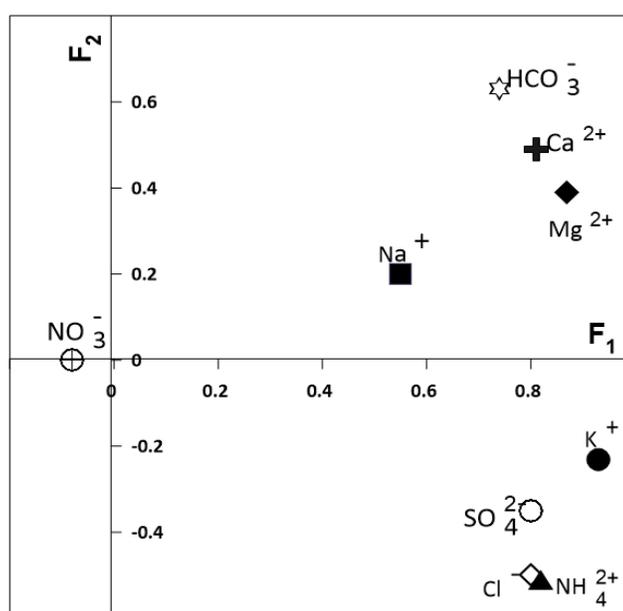


Figure 10. The loadings for the first and second factors with Varimax normalized rotation.

Values much more than 1 and much less than 1 is considered to be enriched and diluted, respectively (Zhang *et al.*, 2007; Ma *et al.*, 2012). The value of EF for the sea salt and soil components based on volume average concentrations are summarized in Table 5. The EF of the all five stations are following the same trends. The $EF_{seawater}$ values of Ca^{2+} , Mg^{2+} and Na^+ are higher for sea salt while the EF_{soil} values of crustal components are higher for SO_4^{2-} and Cl^- . The average $EF_{seawater}$ of Ca^{2+} is 173.48 indicating the dominance of the crustal

sources. The average EF values of K^+ with respect to the marine and crustal sources are 18.43 and 3.15, respectively. EF values of Mg^{2+} is higher for the sea salts than crustal components and its average were 2.48 and 0.08, respectively. EF_{soil} and $EF_{seawater}$ values of SO_4^{2-} are high with average of 2.72 and 9.76 for soil and sea salts. NO_3^- show an irregular spatial distribution with average EF_{soil} of enrichment in comparison to the soil sources.

Table 5. Enrichment factors of precipitation relative to the soil and seawater

Sampling sites	EF	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	NO_3^-
Morad	EF_{soil}	-	0.08	4.37	1.57	65.73	21.83	27.94
	$EF_{seawater}$	152.41	2.02	-	8.54	0.66	9.49	-
Druk	EF_{soil}	-	0.09	4.33	4.24	38.64	10.82	7.31
	$EF_{seawater}$	245.83	3.77	-	23.26	0.63	7.59	-
Lasem	EF_{soil}	-	0.08	6.50	2.97	60.73	18.54	24.32
	$EF_{seawater}$	129.14	1.84	-	10.85	0.52	6.83	-
Lehra	EF_{soil}	-	0.10	4.23	4.23	169.11	28.64	15.03
	$EF_{seawater}$	133.12	2.39	-	23.74	1.49	10.88	-
Zarman	EF_{soil}	-	0.07	2.54	2.76	66.09	23.78	24.11
	$EF_{seawater}$	206.67	2.40	-	25.77	0.91	14.02	-
Average	EF_{soil}	-	0.08	4.39	3.15	80.06	20.72	19.74
	$EF_{seawater}$	173.43	2.48	-	18.43	0.84	9.76	-

Discussion

Stable isotopes of precipitations (rain/snow) in Haraz Basin follows the general regression of $\delta D = 7.66\delta^{18}O - 8.46\text{‰}$ with significant correlation ($R^2=0.98$). Both slope (7.66) and intercept (8.46) of the LMWL are slightly smaller than corresponding values for GMWL and similar to those in the mountainous region (Sinclair & Marshall, 2009; Affolter *et al.*, 2015; Meredith *et al.*, 2015; Crawford *et al.*, 2017). The isotope content of rain samples is more enriched while the fresh snow samples are more depleted. Slightly lower slope and intercept of LMWL indicating the higher evaporation effect on the samples of late spring and summer in comparison to the other seasons (Affolter *et al.*, 2015; Wu *et al.*, 2015).

Precipitations fall in the form of rain in higher temperature conditions are more enriched in comparison to the cold season precipitations (Figure 5a). Roughly estimation of temperature effects on the isotope content of $\delta^{18}O$ is about (~ 0.6 to 0.7‰ $\delta^{18}O/^\circ C$) (Dansgaard, 1964), but it could be 3-10 %

for precipitations originating from the Pacific Ocean (Vachon *et al.*, 2010). In the study area, no strong linear correlation observed in between $\delta^{18}O$ and ambient air temperature. However, rain samples which commonly occur at higher than $10^\circ C$ are more enriched than fresh snow samples that occur at lower temperatures. This could be the result of either sub cloud evaporation effect (Hager *et al.*, 2015; Wu *et al.*, 2015; Zhu *et al.*, 2016) or higher condensation temperature of the rain samples at dry season or both process.

Noticeable differences between the isotope content and d-excess values of fresh snow and snowpack indicating possibility of post-depositional modification of the isotopic signatures of snowpack. Later precipitations on snow (particularly rainfall), evaporation, fractionation through melting, condensation of air-water vapor and air ventilation into the snow column are among the most important process that change the isotope composition of snow (Earman *et al.* 2006). Air ventilation through the snow column is among the most important post depositional process that could

alters the stable isotope content of snow (Town *et al.*, 2008). Fresh snow has low density and highly porous environment (Gjessing, 1977; Zermatten *et al.*, 2014) so small change in the surface pressure (less than three Pascals), temperature gradient (Sturm & Johnson, 1991) and strong winds is sufficient for air flow through the snow (Albert & Hardy, 1995) and replace 20-30 percent of the air in the snow column continuously (Gjessing, 1977). Air ventilation through the snowpack results in the mass exchange between the saturated vapor in the snow column and undersaturated air mass (Neumann *et al.*, 2005), that exchange will cause enrichment of the $\delta^{18}\text{O}$ and δD values in the snowpack (Cooper *et al.*, 1993; Nikolayev & Mikhalev, 1995; Stichler *et al.*, 2001; Earman *et al.*, 2006). Low ambient air temperature and high reflectance of snow minimizes the evaporation effect on snowpack which confirmed by snowpack isotope ratios that do not follow the evaporation line. So that, it is proposed ventilation of air mass through the snowpack results in moisture recycling through the snowpack that alters its isotope content. Moisture recycling occurs by ventilation of dry air mass with relatively heavier isotope content, results in deposition of heavier isotopes in the solid phase and alters the snowpack isotope content. The stable isotopes distribution of precipitation at the Haraz Basin has been influenced by both rainfall amount and temperature. The difference between the dry and wet seasons d-excess could be ascribed to the different sources of the moisture. This explanation is alongside with the results of back trajectory analysis by Heydarizad *et al.*, (2019). They concluded that lower d-excess relates to the lower latitude water sources such as Persian Gulf and Arabian Sea while higher d- excess precipitation originates from higher latitude water body such as Mediterranean Sea which dominates the precipitations of north of Iran. The wet season precipitation almost associated with Mediterranean air mass (Khalili, 1973; Alijani & Harman, 1989, Heydarizad *et al.*, 2019) which are characterized by higher d-excess (Tian *et al.*, 2007). In contrast, the dry season precipitation containing lower d- excess most probably originated from a mixture of southwestern air mass (Farajzadeh *et al.*, 2007; Roozitalab *et al.*, 2018) and evapotranspired water over the continent (Constanze *et al.*, 2002). Higher d-excess values in snowpack samples in comparison to the fresh snow indicating the negligible effect of evaporation and pointing to the

process such as moisture recycling that increase the d-excess values (Froehlich *et al.*, 2008). Indeed, the early spring rain samples have similar d-excess values to the snow samples this confirms their same origin of moisture from Mediterranean air masses.

Precipitations isotope content becomes depleted by increasing elevation due to losing water content by increasing the elevation (Dansgaard, 1964; Rozanski *et al.*, 1993). Likewise, cooling of the air mass results in the saturation, condensation and rainout, fractionation during condensation lead to the isotope depletion of precipitation at higher elevation (Moran *et al.*, 2007). The global altitudinal gradient of $\delta^{18}\text{O}$ is -0.1 to -0.6‰/100 meters and -1.5 to -4‰/100 meters for deuterium. Precipitations isotope content of Haraz Basin shows no liner correlation with elevation for the entire of the samples. However, considering the samples based on type of precipitation (Figure 6a); shows positive and negative correlation for snow and rain samples, respectively. Depletion of the $\delta^{18}\text{O}$ in event based rain samples is 0.9‰ for 100 m raise of elevation while it is 0.4‰ for fresh snow samples. Such irregularity in snowpack and fresh snow samples probably related to the post deposition processes mainly moisture recycling.

Regarding the chemistry of precipitation, Ca^{2+} and HCO_3^- are dominant cation and anion respectively those accounts for more than 70.8% of total ionic concentration (Figure 8). Precipitation chemistry varied widely through the hydrologic year (Figure 9) similar to the results of studies on precipitation chemistry (e.g. Sakihama *et al.*, 2008; Wu *et al.*, 2016). Higher precipitation amounts connect to lower ion concentrations and vice versa (Figure 9), pointing to the increasing of the atmosphere pollutant accumulation in the absence of the precipitation (Xiao *et al.*, 2013). Few slightly high ion concentration observed in the middle of the wet season is possibly associated to the reworking of dust over the snowpack due to early snow melt in south facing slope.

Based on results of factor analysis three factors accounted in total for 85.22% of the variance. The first factor (F1) that characterized by high loading of all the ions (56.4%) with exception of NO_3^- and Na^+ suggesting a mixed sources of crustal, sea salt and anthropogenic origins (Al-Khashman, 2009; Zhao *et al.*, 2013). Significant loading of HCO_3^- in factor 2 with a variation of 16.7% and high loading of HCO_3^- in factor 1 could be explained by the crustal components and dissolution of atmospheric

CO₂ in precipitation. Total variance of factor 3 is 12.8% with high loading factor for NO₃⁻ resulting from anthropogenic activities. Plot of the F1 against F2 indicates three distinct clusters of variables (Figure 10). As can be seen from Figure 10 HCO₃⁻, Ca²⁺, Mg²⁺ and Na⁺ involved in the same group representing their crustal sources. Clustering of SO₄²⁻, NH₄²⁺, K⁺ and Cl⁻ in the same domain signifying their main origins are the same (most probably marine and anthropogenic). NO₃⁻ is pointed in left part proposing its anthropogenic activity source.

Regarding the origin of ions in precipitation high values of EF_{seawater} indicating their major terrestrial/anthropogenic origins (Kazemi *et al.*, 2015). Similarly, the high values of EF_{seawater} over EF_{soil} for Ca²⁺, Mg²⁺, K⁺ and Na⁺ points to their main crustal origin while the higher values of EF_{soil} over EF_{seawater} Cl⁻ points to its marine origin and negligible crustal origin (Zhang *et al.*, 2007; Li *et al.*, 2016). The elevated EF of SO₄²⁻ values for sea salt and soil sources indicates presence of anthropogenic effects in addition to these sources (Ma *et al.*, 2012). Negligible marine source of NO₃⁻ suggesting that nitrate commonly originated from anthropogenic sources as well as the atmospheric source (Ma *et al.*, 2012).

Conclusions

In this research, stable isotopes (δ¹⁸O and δD) and chemistry of precipitation at the five stations in Haraz Basin from August 2015 to July 2016 on monthly basis were analyzed and evaluated. Based on the stable isotope results, LMWL of the Haraz is following δD = 7.66δ¹⁸O - 8.48‰ with significant correlation (R²=0.98). These values are slightly lower than corresponding values of the GMWL, which could be ascribed to sub cloud evaporation effect on precipitation. The seasonal trends of stable

isotopes in precipitation are following the precipitation amount and wet season precipitations are more depleted than dry season samples. D-excess values are higher for the wet season and lower for dry season samples indicating the different moisture sources.

Wet deposits chemistry of Haraz Basin dominated by the Ca²⁺ and HCO₃⁻ ionic species accounting for 70.8% of total ionic concentration. Overall ions concentrations show relatively similar trends and have a low concentration in wet seasons and high concentration at the dry months.

The high values of EF_{seawater} over the EF_{soil} for Ca²⁺, Mg²⁺, K⁺ and Na⁺ indicates that these ions have major terrestrial/anthropogenic origins. The higher values of EF_{soil} over EF_{seawater} of Cl⁻ points to its negligible crustal origin and its conservative behavior. Factor analysis results indicating three groups of the ion clusters that approves the crustal, marine salts, and anthropogenic sources which lead to an irregular correlation relation between ion species. The findings and data of this study have practical implications for those are going to use stable isotope in water related sciences in the nearby area e.g. studying surface, groundwater and comprising process mainly for recharge and developing more reliable water management strategies. The results of precipitations chemistry may be beneficial those are interested in the field on ecological effects of precipitation and anthropogenic pollutants.

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