Wet Deposition and Long-range Transport of Major Ions Related to Snow at Northwestern Himalayas (India)

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ABSTRACT

The present study was carried out to understand the snow chemistry with special emphasis on the estimation of wet deposition fluxes and transportation of ionic species to the Himalayan regions from December 2015 to March 2017. All the snow samples were collected from three different sites of two locations, Jammu & Kashmir and Himachal Pradesh. In Jammu and Kashmir we have selected two sites, (an urban area Leh and other one was semi-urban area Beerwah). In Himachal Pradesh, we selected a site at Nirmand village which was a rural area. At Leh and Nirmand village, samples were showing higher alkalinity than at Beerwah site. The pH values of snow at Leh and Nirmand were recorded above 5.6 except one sample of both the sites. However, at Beerwah site almost 60% of the samples were found acidic (below 5.6) in nature. All these three sites showed three different means of neutralization and pH control. The study revealed that the high pH value of snowfall at Leh site could be due to the presence very high value of Ca^{2+} whereas the moderate pH at Nirmand village may be due to moderate concentration of Ca^{2+} and high NH_4^+ . In contrast at Beerwah site, low pH is probably due to very low concentrations of all the major cations. This study also suggested that non-sea salt sources contributed a significant fraction of SO_4^{2-} , K^+ , Ca^{2+} , and Mg^{2+} . However, on average, a significant amount of HCO_3^- was measured at all the three sites, indicating a substantial role of crustal sources in the study sites. Results of this study showed that these ionic species are contributed by local as well as long-distance sources in the region. Backward air mass trajectory analysis revealed that the ionic species were contributed by the air masses coming from North Atlantic Ocean, Africa, Europe, Middle East, and Mediterranean region to all these sites through long-range transport (LRT).

Keywords: Snow; pH; Ionic chemistry; Wet deposition flux; Back trajectory analysis.

INTRODUCTION

Increasing emissions of atmospheric aerosols significantly affect air quality (Allen *et al.*, 2016). The IPCC (2014) report warns of severe consequences on global and regional atmospheric processes due to increasing aerosol particles. Deposition of anthropogenic constituents via wet and dry removal processes from the atmosphere has adverse impacts on terrestrial and aquatic ecosystems (Seinfeld and Pandis, 2006). Snowfall is considered as one of the most active wet removal processes for air pollutants at high altitude sites. It deposits significant amounts of bio geochemically important trace chemical species on various surfaces on Earth. Water-soluble ionic species present in the Himalayan snow is substantially affected by air pollutants from long-range transport of various anthropogenic sources (Kulshrestha and Kumar, 2014). Previous studies on snow chemistry reveals that the combustion of fossil fuel and biomass burning were

dominantly responsible for air pollution (Zhang *et al.*, 2013; Kumar *et al.*, 2015, 2016). In general, snow composition shows spatial variation which largely depends upon the sources, characteristics of sampling site, elevation from the sea level, atmospheric conditions, sampling procedure and the transport of air pollutants, etc., (Marinoni *et al.*, 2001). Air mass trajectories combined with snow chemistry data provide valuable information about the origin of air pollutants (Fleming *et al.*, 2012; Kulshrestha and Kumar, 2014) and their impact on various ecosystems through deposition processes.

Therefore, extensive study has been undertaken on snow composition in the western countries (Reynolds, 1983; Jenkins *et al.*, 1987; Gunz and Hoffman, 1990; Marinoni *et al.*, 2001; Toom-Saunty and Barrie, 2002; Rohrbough *et al.*, 2003; Walker *et al.*, 2003; Niu *et al.*, 2013; Xu *et al.*, 2013; Zhang *et al.*, 2013). The Himalayas are remotely located from industrialized urban centers; and they provide ideal locations not only to study the evolution of atmospheric constituents but also in monitoring the tropospheric chemistry (Cunningham and Zoller, 1981). The Himalayas are considered as the most sensitive ecosystem as far as the atmospheric deposition is concerned (Kuylenstierna *et al.*, 2001; Zhang *et al.*, 2012; Tiwari *et al.*, 2012; Liu *et al.*, 2013; Balestrini *et al.*, 2014;

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Bisht *et al.*, 2017). It is adversely affected by local and long-range transport of pollutants (Tiwari *et al.*, 2012; Kulshrestha and Kumar, 2014; Roy *et al.*, 2016; Bisht *et al.*, 2017). Tourist activities, transportation, and other human activities are some of the local factors that significantly affect snow chemistry and adversely impact the aquatic and terrestrial ecosystems. In spite of its sensitivity, annual and seasonal depositions of various chemical species are poorly understood. There are very few studies reported on aerosols, rainwater and snow geochemistry in the Himalayan region (Ahmad and Hasnain *et al.*, 2001; Gajananda *et al.*, 2005; Tiwari *et al.*, 2012; Kuniyal *et al.*, 2013; Roy *et al.*, 2016; Bisht *et al.*, 2017). Similarly, in the western Himalayan region of India very few studies were done on fresh snowfall chemistry (Kapoor and Paul, 1980; Naik *et al.*, 1995; Lone and Khan, 2007; Kulshrestha and Kumar, 2014; Kumar *et al.*, 2015, 2016). Comparatively low concentration of air pollutants have been reported in the Himalayas on fresh snow chemistry (Marinoni *et al.*, 2001; Shrestha *et al.*, 2002; Kang *et al.*, 2004; Lone and Khan, 2007; Huang *et al.*, 2012; Kumar *et al.*, 2015, 2016; Bisht *et al.*, 2017). Thus, it represents the remotest part of India and could be considered as a reference for further studies. Hence, the main objective of this study was to investigate fresh snow chemistry in the Himalayas, ascertaining the local and long-range sources using NOAA HYSPLIT trajectories. The secondary objective was to investigate the marine and non-marine contributions in snow and discuss their environmental implications.

METHODOLOGY

Sampling Sites

Three sites from the Western part of the Himalayan region, which are having different land use land cover pattern (<http://bhuvan.nrsc.gov.in>) (Fig. 1), sources and population

densities were selected for the study. Among which two sites were Leh and Beerwah located in the state of Jammu and Kashmir while the third one was Nirmand village in Himachal Pradesh, India. The location of all sites has been shown in Fig. 1. Jammu & Kashmir state is divided into three regions- Ladakh, the Jammu division and the Kashmir Valley division. Each site has been separately described in subsequent sections.

Leh

Leh is one of the districts of the Ladakh division which represents India's northern boundary adjacent with Pakistan and China, covers approximately 52.6% area of Jammu & Kashmir. The geographical coordinates of Leh are 34.15°N and 77.57°E and 2.3 km to 5 km above mean sea level (amsl). The Topography of Leh is quite uneven and covered mostly with mountains. Ladakh, Karakoram, and Zaskar are three parallel ranges of the Himalayas. Ladakh lies in the rain shadow region of the Himalayas. The arctic type of climate prevails in the Ladakh region. Thus, Ladakh is considered as 'cold desert' which is located on the western end of the Himalayas with sparse vegetation. At Leh, the recorded minimum temperature in winters is -28°C whereas maximum temperature in summers is 35°C. Average annual rainfall in Leh is about 115 mm. The adverse climatic conditions and inaccessibility of the region are reflected in the limited population of around 150000 in Leh district. The Ladakh region is mainly comprised of Palaeozoic to Cretaceous sediments, meta-sediments, granitic intrusions and the Ladakh batholith. The latter is an intermediate rock which is located to the north of the Indus River (Dortch *et al.*, 2008).

Beerwah

Beerwah is a sub-district of Central Kashmir which is a part of the Budgam district of Jammu & Kashmir. The Beerwah

Fig. 1. Map showing the sampling sites.

lies between 74.59°E and 34.01°N at an elevation of 1.7 km amsl. Karewas, plateau-like terraces kind of agricultural landscape are predominantly present there. Agriculture is the main occupation of the people in this area. It is located about 30 km from Srinagar city in South-West direction. The main sources of pollution are automobiles and brick kilns, which are situated about 3–4 km from the main town. Panjal traps forming hilly and mountainous terrain of the district with hard formations of igneous and metamorphic rocks. The Karewa formation and alluvium of Quaternary and Tertiary age (Plio-Pleistocene) underlie the valley area and consists of alternate bands of sand, silt, gravel & clay, interspersed at two to three levels locally by glacial boulder beds. This formation of Plio-Pleistocene age lies dis-conformably over the older rocks ranging in age from Cambrian to Triassic.

Nirmand

Kullu is a broad open valley which is sandwiched between the Lower Himalayan, Pir Panjal and Great Himalayan Ranges. Nirmand village (the study area) is located in Kullu district of Himachal Pradesh, India (31.43°N and 77.65°E). Nirmand village is situated on the border of Kullu and Shimla district, and is often called as Kashi of the Himalayas. It is situated nearly 87 km away in South from the Kullu District headquarters and about 150 km north from Shimla. Their climate is characterized by the cold and dry condition which over the year consists of three seasons. The summer season in Kullu which is from March to June has maximum temperature reaching 30°C during the day with nights retaining a bit of chill. Winters are characterized by snowfall and heavy frosts from December to January with the possibility of early snowfalls occurring in November also. The geological structure of this region is mainly formed by granites (unclassified) formations and it has Udalfs (20) type of soil cover which is high base status of humid regions. The region is without vegetation cover. Fresh snow samples were collected using the snow collector at three sites in Western Himalayan region of India: (1) Leh (the main city of Ladakh): represents urban site having lots of tourist activities (2) Beerwah: this is semi-urban site (3) Nirmand: this site in the Kullu valley represent rural site away from the urban site Shimla, considered as a green belt area due to less or no tourist activity. Total 40 snow samples were collected during the sampling period-13 from Leh, 11 from Beerwah and 16 from Nirmand. Sample collector (a plastic tray having ~30cm diameter) was placed about ~2 m above the ground level usually on rooftops or at elevated places. Samples were collected on an event by-event basis from December 2015 to January 2017. Sampling was done according to the methodology adopted by Kumar *et al.* (2015). The collector was thoroughly washed with Milli-Q and air dried before, and after each time the sample was collected. The collector was kept on the rooftop during the snowfall event and removed immediately after the collection. Fresh snowfall samples deposited on the collector was immediately transferred into pre-cleaned polypropylene bottles. Biological degradation of the samples was avoided by adding Thymol (< 5 mg) to each batch. Ambient conditions of the samples were preserved by storing them in a refrigerator. Samples were brought in the

laboratory within 15 days from their collection and preserved for further analysis. Measurements of pH and EC of snow samples were done immediately so that the samples could be processed further for major cations and anions. Field blanks were also collected and analyzed using procedures similar to the snow sample.

Chemical Analysis and Quality Control

The major water-soluble ionic species such as cations (Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+}) and anions (Cl^- , F^- , SO_4^{2-} , NO_3^- , HCO_3^-) were quantitatively determined by Ion Chromatograph (Metrohm 883Basic IC Plus). Metrosep C4-100/4.0 column and an eluent of 1.7 mmol L⁻¹ nitric acid and 0.7 mmol L⁻¹ Dipicolinic acid at a flow rate of 0.9 without suppressor was used for determination of cations. While Metrosep A SUPP 4, 250/4.0 column and an eluent of 1.8 mmol L⁻¹ Na_2CO_3 and 1.7 mmol L⁻¹ NaHCO_3 at a flow rate of 1.0 with Metrohm suppressor technique were used for determination of anions. HCO_3^- was determined by using 0.0025 NH_2SO_4 . The details of the chemical analysis procedure are discussed elsewhere (Singh *et al.*, 2014).

The Data Quality Control

Ion balance technique was used to check the quality of analytical data of water-soluble ionic species for all sites (WMO, 1994). The mean ionic ratio helps us to know the reliability of the analytical results. If all the major anions and cations are analyzed, the ratio is expected to the present study, the ratio was found to be 1.08 ± 0.16 , 1.4 ± 0.13 and 1.04 ± 0.14 for Leh, Beerwah, and Nirmand, respectively. The higher significant correlation coefficients between Σ^- and Σ^+ were observed over all the sites. The ratio was found to be close to unity over Leh and Nirmand site suggesting the completeness and correctness of the analytical measurements. However, the ratio over Beerwah shows significant deviation from unity, suggesting the acidic nature of snow where acidic component is not completely neutralized by basic cation.

Wet Deposition fluxes through Snowfall Deposition

Wet deposition flux (F) of all ionic species was calculated during the winter season of 2015–2017 by using the formula

$$F = (C \times V)/A \quad (1)$$

here:

F = Deposition Flux in meq m⁻²

C = Average concentration of Ionic components in $\mu\text{eq L}^{-1}$

V = Volume of snow (36.98 L for Beerwah and Nirmand site, and 16.86L for Leh),

A = Area of the tray (314 cm²).

The Contribution of Ionic Species Through Different Sources

We have used the following methodology to identify the source of contributed ionic species:

Marine Contribution

Equivalent ratio and enrichment factor (EF) of measured ions viz. Cl^- , SO_4^{2-} , Mg^{2+} , K^+ , Ca^{2+} were calculated in order

to determine the marine and non-marine contributions in snow. Sodium was taken as the reference element in above calculations assuming all sodium coming from marine sources (Keene *et al.*, 1986). The sea salt fraction (ssf) and non-sea salt fraction (nssf) were assessed by using the formula given below (Kumar *et al.*, 2015).

$$\%ssf = 100/EF_{sea\ water} \quad (2)$$

$$\text{here } EF_{sea\ water} = \frac{\left[\frac{X}{Na^+} \right]_{show\ melt}}{\left[\frac{X}{Na^+} \right]_{sea\ water}}$$

where [X] is the concentration of desired ionic species ($\mu\text{eq L}^{-1}$).

$$\%nssf = 100 - \%ssf \quad (3)$$

The $EF > 1$, suggested significant influences of other sources instead of marine sources. Norman *et al.* (2001) reported non-marine fraction by the entrainment of atmospheric particulate matters in precipitation occurring along the air mass trajectories.

Non-marine Contribution

Non-marine sources can be categorized into two major categories i.e., crustal and anthropogenic sources. Out of these two, anthropogenic sources mostly enhance the acidity of precipitation while crustal sources decrease the acidity by buffering of the acidifying species (Rodhe *et al.*, 2002; Kulshrestha, 2013). Due to opposite characteristics in controlling acidity of precipitation, it is essential to quantify separately the non-marine fraction into crustal associated fractions and anthropogenic fractions. We have termed crustal associated fractions which has fractions of acidic components (SO_4^{2-} , NO_3^-) present as salt of calcium i.e., CaSO_4 or $\text{Ca}(\text{NO}_3)_2$. We have followed the approach of Kulshrestha *et al.* (1997) and Jain *et al.* (2000) to calculate the contribution of crustal associated fraction and anthropogenic fraction of ionic species. For the calculation of the crustal associated fraction (CF) of major ionic components, nssCa^{2+} was considered as reference element in snowfall samples (Kulshrestha *et al.*, 2003). The presence of crustal components in the form of nssCa^{2+} has been reported in precipitation globally (Rahn, 1976; Rodhe *et al.*, 2002; Kulshrestha *et al.*, 2003; Budhavant *et al.*, 2014). Percent crustal fraction (CF) was calculated as follows

$$\%CF = 100/EF_{Soil} \quad (4)$$

$$EF_{Soil} = \left[\frac{y}{\text{nssCa}^{2+}} \right]_{snowfall} / \left[\frac{y}{\text{nssCa}^{2+}} \right]_{soil}$$

here:

y = nss concentration of ionic species (nssSO_4^{2-} , nssCa^{2+} , nssK^+ , nssMg^{2+} , NO_3^- , NH_4^+ and F^-) in $\mu\text{eq L}^{-1}$; (y/nssCa^{2+}) Soil is taken as standard ratio of local soils.

Then, the percent Anthropogenic (Anthro) fractions of each component were calculated as follows

$$\% \text{Anthro}_x = \% \text{nss}_x - \% \text{CF}_x \quad (5)$$

Average contribution of different sources: The average contribution of different sources viz. marine, crustal and anthropogenic was calculated by the following formula:

$$\text{Average marine \%} = \frac{\sum X_{ssf}}{\sum X_{Total}} \times 100 \quad (6)$$

here $\sum X_{ssf}$ = Sum of concentration of all ssf values in each air mass cluster in $\mu\text{eq L}^{-1}$.

$\sum X_{Total}$ = Sum of concentration of all components in each air mass cluster in $\mu\text{eq L}^{-1}$.

$$\text{Average crustal \%} = \frac{\sum X_{CF}}{\sum X_{Total}} \times 100 \quad (7)$$

here $\sum X_{CF}$ = Sum of concentration of all Crustal Fraction values in each air mass cluster in $\mu\text{eq L}^{-1}$.

$$\text{Average Anthropogenic \%} = 100 - \text{Average marine\%} - \text{Average crustal\%} \quad (8)$$

Back Trajectory Analysis

Three-days back trajectory analysis was also performed (Figs. 6(a)–6(c)) for the confirmation of the possible sources of pollutants over the Himalayan region. Backward air mass trajectories for 72 h of 2000 m above ground level were calculated using the geographic information system (GIS) based software, TrajStat for all snowfall samples (Wang *et al.*, 2009).

The Neutralization Factor of the Ionic Species

Kaya and Tuncel (1997) reported that the acidification potential of wet precipitation is mainly determined by the presence of HNO_3 , H_2SO_4 , and organic acids, whereas alkaline (basic) substances such as NH_3 , MgCO_3 and CaCO_3 are primarily responsible for their neutralization. Hence, the relative abundance of these acidic and alkaline species greatly determines the pH of precipitation. Cations such as (Ca^{2+} , Mg^{2+} , and NH_4^+) react with acids (H_2SO_4 and HNO_3) to form NO_3^- and SO_4^{2-} salts in the atmosphere.

The neutralization factor of these species were calculated by the following formula

$$NF_{Xi} = \frac{[X_i]}{[\text{NO}_3^- + \text{nssSO}_4^{2-}]} \quad (9)$$

where $[X_i]$ = The concentration of desired ionic species i.e., nssCa^{2+} , nssMg^{2+} and NH_4^+ in $\mu\text{eq L}^{-1}$.

RESULTS AND DISCUSSION

pH of Snow

The pH of snow samples at Leh site ranged from 7.02 to 8.11 with an average of 7.48 ± 0.38 , at Nirmand site varies

from 5.30 to 7.09 with an average 6.39 ± 0.48 (Fig. 2), a similar range of pH at Mukteshwar site, Nainital and Kullu, in the north western Himalayan region have been reported by Tiwari *et al.* (2012), Kumar *et al.* (2015) and Bisht *et al.* (2017), respectively. As alkaline precipitation is considered to be a typical feature of the Indian region, the snow samples were observed with > 5.6 pH due to its enrichment of suspended atmospheric dust with calcium carbonates (Kulshrestha *et al.*, 2003). Influence of natural dust particles in the rainwater chemistry has been reported over India (Delhi) by Kulshrestha *et al.* (1996, 2003); Jain *et al.* (2000). The pH of precipitation is usually measured at 5.6 in a clean atmosphere owing to the equilibration with atmospheric CO_2 (Charlson and Rodhe, 1982). The enrichment of natural particles with carbonate and bicarbonates of calcium that eventually neutralize the resulting acidity. At Beerwah site, the pH was found to be slightly acidic and vary from 5.18 to 6.47 with the mean 5.77 ± 0.37 . Kumar *et al.* (2016) have also reported an almost similar range of pH at Gulmarg site. Of this, about 45% of total snow samples were found to be acidic (below 5.6) at this site. Many co-workers have been also found the similar range of pH in precipitation at different sites of Himalayan region (Valsecchi *et al.*, 1999; Liu *et al.*, 2013; Kulshrestha and Kumar, 2014; Roy *et al.*, 2016).

Deposition of Major Ions in Snow

The average concentration of ionic species at three sites (Leh, Beerwah, and Nirmand) over Western Himalayan regions of India along with the minimum and maximum concentrations in snow collected during the winter season of 2015–2016 and 2016–2017 is presented in Table 1. The pH and conductivity of snow samples have also been shown in

Table 1. At Leh site the mean concentration ($\mu\text{eq L}^{-1}$) of cations in snow samples were found in the following order $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+ > \text{Na}^+ > \text{K}^+$ whereas the abundance of anions were as follow $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{F}^-$. At Beerwah site the mean concentration ($\mu\text{eq L}^{-1}$) of cations were found in the following order $\text{Ca}^{2+} > \text{NH}_4^+ > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ whereas the anions were found as follow $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{F}^-$. At Nirmand site the mean concentration of were like $\text{NH}_4^+ > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{Mg}^{2+}$ for cations and $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-} > \text{NO}_3^- > \text{F}^-$ for the anions. Their percentage contribution in the snow samples has been calculated and depicted in Fig. 3 for all the sites.

At the Leh and Beerwah site, the Ca^{2+} ions were the most dominant whereas at Nirmand site it was much lower. At Leh site, the average concentration of Ca^{2+} accounts for approximately 18% of all ions and 42% among all cations, whereas at Beerwah site it accounts approximately 12% of all ions and 33% among all cations. It was observed that the average concentration of Ca^{2+} at Beerwah site was lower than Gulmarg (Kumar *et al.*, 2016) (Fig. 4). The highest concentration of Ca^{2+} in precipitation mainly contributed by local and transported dust (Satyanarayana *et al.*, 2010; Budhavan *et al.*, 2011; Balestrini *et al.*, 2014; Bisht *et al.*, 2017; Khan *et al.*, 2018), from the suspended soil (Rahn *et al.*, 1976; Kulshrestha and Kumar *et al.*, 2014) and from vehicular emission, cement factory etc. (Sanusi *et al.*, 1996).

In the present study, we observed high concentration of both Ca^{2+} and HCO_3^- at Leh and Beerwah site. It was mainly due to the influence of natural dust particles enriched with carbonate and bicarbonates of calcium (Kulshrestha *et al.*, 1996; Cong *et al.*, 2007; Li *et al.*, 2007). Similar results were also reported in various studies in the Himalayan region

Fig. 2. Monthly average pH variation of snow at different sites of Himalayas. Note Red line indicates the neutral cloud water pH.

Table 1. Average concentrations ($\mu\text{eq L}^{-1}$) of measured ionic species, pH and conductivity in snow sample at three different locations (Leh, Beerwah and Nirmand) in Western Himalaya of India along with minimum (Min.) and maximum (Max.) during 2015–2017.

	Leh			Beerwah			Nirmand		
	Min	Avg	Max	Min	Avg	Max	Min	Avg	Max
pH	7.02	7.48	8.11	5.18	5.80	6.47	5.30	6.39	7.09
EC	7.78	44.40	109.20	0.25	9.01	25.00	2.04	96.24	530.00
Na^+	0.48	24.14	73.91	1.01	17.80	57.83	1.66	35.36	372.23
NH_4^+	6.27	28.77	96.67	9.04	26.36	63.33	0.24	112.44	614.37
K^+	0.15	17.40	53.85	0.53	15.64	53.59	0.35	27.15	113.36
Ca^{2+}	17.66	74.34	220.16	5.57	40.66	131.50	34.50	53.05	84.00
Mg^{2+}	7.14	33.49	70.61	0.66	21.17	90.53	0.19	12.62	51.03
F^-	0.07	2.74	21.05	0.09	1.93	10.00	1.58	8.24	39.47
Cl^-	2.13	23.72	49.15	2.54	20.39	50.85	0.80	67.71	343.75
NO_3^-	0.22	14.62	25.48	0.31	11.36	27.41	0.11	7.02	27.42
SO_4^{2-}	0.80	19.70	40.63	0.37	15.40	33.33	0.90	16.71	36.25
HCO_3^-	32.79	179.07	524.59	32.79	157.97	393.44	32.79	163.93	262.30

Fig. 3. The percentage contribution of individual cations and anions in snow samples at all sites.

Fig. 4. Distributions of analyzed water-soluble ionic species at the three sampling sites in Himalayan region. The box plots along with box normal distribution indicate the mean (solid rectangular box within box) and median (solid line within box) distributions and the 90th, 75th, 25th, and 10th percentiles.

(Huang et al., 2012; Zhang et al., 2012; Balestrini et al., 2014; Kumar et al., 2015). After Ca^{2+} and Mg^{2+} , NH_4^+ ion has been the most abundant at Leh and Beerwah site, whereas at Nirmand site the average concentration of NH_4^+ was highest among all the cations (Fig. 4). A high concentration

of NH_4^+ amongst major cations at Nirmand site suggested a significant influence of anthropogenic sources such as livestock, agricultural activities, human and animal excreta, (Galloway, 1995; Singh and Kulshrestha, 2012; Khan et al., 2018). Khan et al. (2018) suggested the nearby vegetation

and agriculture farming may contribute to the raised concentration of biogenic NH_4^+ . Other sources such as increased tourist activities could also be considered as a significant source for NH_4^+ in this region nowadays. Among all the anions, HCO_3^- and Cl^- was highest at all three sites. Similar results were observed at high altitude Himalayan stations (Kumar *et al.*, 2015; Roy *et al.*, 2016; Bisht *et al.*, 2017). We have found the average SO_4^{2-} concentration was higher than the NO_3^- concentration at all the three sites (Fig. 4). Similar results were reported by (Zhang *et al.*, 2012; Tiwari *et al.*, 2012; Liu *et al.*, 2013; Balestrini *et al.*, 2014; Roy *et al.*, 2016; Bisht *et al.*, 2017) over Himalayan region. The high concentration of SO_4^{2-} could be attributed to the anthropogenic sources which emit SO_2 . Since industrial activities were found to be lacking at all these sites, the maximum contribution to SO_4^{2-} from the LRT and trans-boundary transport of other regions as well as the local influence of diesel driven vehicular emissions cannot be ruled out. NO_3^- concentrations were very low at all the three sites. In snow samples, high concentrations of NO_3^- could be attributed to their primary emissions as NO_x from the increased vehicular activities that are eventually transformed to water-soluble NO_3^- species in the atmosphere (Finlayson-Pitts and Pitts, 1986). Other than vehicular emissions, biomass burning by locals to produce heat during winters could be another regional factor (Singh *et al.*, 2014). Apart from regional emissions, long-range transport of $\text{NO}_x/\text{NO}_3^-$ by various air masses approaching the sampling sites could be attributed to a high concentration of NO_3^- . At all the three sites concentration of carbonate was found to be very high in snow samples due to the contribution of soil dust comprising high fractions of CaCO_3 , MgCO_3 , and MgSO_4 .

Wet Deposition Fluxes Through Snow Fall Deposition

Table 2 represents the average wet deposition fluxes for all the samples collected during the winter and spring seasons. From the table, it is very clear that the average wet deposition fluxes at Leh was in the order like- $\text{HCO}_3^- > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+ > \text{Na}^+ = \text{Cl}^- > \text{SO}_4^{2-} > \text{K}^+ > \text{NO}_3^- > \text{F}^-$ and at Beerwah followed the order- $\text{HCO}_3^- > \text{Ca}^{2+} > \text{NH}_4^+ > \text{Mg}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{K}^+ > \text{SO}_4^{2-} > \text{NO}_3^- > \text{F}^-$ while at Nirmand site it is like $\text{HCO}_3^- > \text{NH}_4^+ > \text{Cl}^- > \text{Ca}^{2+} > \text{Na}^+ > \text{K}^+ > \text{SO}_4^{2-} > \text{Mg}^{2+} > \text{F}^- > \text{NO}_3^-$. At Leh and Beerwah, the highest value of wet deposition fluxes was recorded for HCO_3^- and Ca^{2+} which may

Table 2. Average wet deposition fluxes during winter and spring seasons (meq m^{-2}).

Ions	Leh	Beerwah	Nirmand
Na^+	13	21	42
NH_4^+	15	31	132
K^+	9	18	32
Ca^{2+}	40	48	62
Mg^{2+}	18	25	15
F^-	1	2	10
Cl^-	13	24	80
NO_3^-	8	13	8
SO_4^{2-}	11	18	20
HCO_3^-	96	186	193

be due to crustal influence (Jain *et al.*, 2000; Kulshrestha *et al.*, 2003). Whereas at Nirmand site maximum wet deposition fluxes were recorded for HCO_3^- and for NH_4^+ suggested anthropogenic activity in this region. Elevated deposition fluxes for Na^+ and Cl^- might be due to marine aerosols deposited at all sites. Acidic species like SO_4^{2-} and NO_3^- are lesser in comparison to Ca^{2+} suggesting alkaline nature of precipitation, which is very common in the Indian region.

Source Apportionment

For assessing the role of source categories and their percentage contribution, the results were further evaluated with marine and non-marine fractions. Non marine fractions were estimated for their crustal and anthropogenic fractions using the approach reported by Kulshrestha *et al.* (1997).

Marine Contribution

The sea salt fraction(ssf) and non-sea salt fractions (nssf) of viz. Cl^- , SO_4^{2-} , K^+ , Mg^{2+} , and Ca^{2+} were calculated and presented in Table 3. At Leh and Beerwah sites, the ratios of SO_4^{2-} , K^+ , Ca^{2+} , Mg^{2+} were found to be higher than that of seawater. Similar results were also found by Kumar and co-workers (2015) at Mukhteshwar site of Kullu District. However, at Nirmand site, the ratios of Cl^- , SO_4^{2-} , K^+ , and Ca^{2+} were found to be more than that of seawater, which indicates that crustal (soil dust) and anthropogenic influence of these ions are in the snow over the western Himalayas in India. At all the sites, the results showed that Cl^-/Na^+ ratio was very close to seawater ratios representing its major contribution from marine sources. In Indian region, higher ratios of $\text{SO}_4^{2-}/\text{Na}^+$, K^+/Na^+ , and $\text{Ca}^{2+}/\text{Na}^+$ in precipitation have been reported at various sites (Kulshrestha *et al.*, 2003; Safai *et al.*, 2004; Tiwari *et al.*, 2007; Bisht *et al.*, 2015). Ali *et al.* (2004) revealed that the compounds containing Ca^{2+} , Mg^{2+} , and K^+ are incorporated into the atmosphere by the erosion of soil in the form of their carbonate salts. The nssf of SO_4^{2-} , K^+ , Mg^{2+} , and Ca^{2+} confirms the dominance of crustal and anthropogenic sources of Ca^{2+} , K^+ , Mg^{2+} , and SO_4^{2-} . The similar results have also been reported by various studies on the snow chemistry (Keene *et al.*, 1986; Naik *et al.*, 1995; Zhu *et al.*, 2012; Niu *et al.*, 2013; Kumar *et al.*, 2015).

Non-marine Contribution

Table 4 shows the percent contribution of crustal fractions (CF) and anthropogenic fractions (Anthro) of each ionic species of snowfall species. As shown in Table 4, all the three sites have maximum Ca^{2+} contribution, which is associated with the crustal fraction. A similar result was found at a different site of the Himalayan region by Kumar *et al.* (2015, 2016). Some researchers have suggested that nss Ca^{2+} in snow samples is due to transported dust at Himalaya and Tibetan Plateau (Mayewski *et al.*, 1983; Kumar *et al.*, 2015, 2016).

The percent contribution of NO_3^- and NH_4^+ were found to be higher in anthropogenic in comparison to crustal fraction. At all the three sites, very high fraction of anthropogenic NO_3^- was observed. Previous studies also reported NO_3^- is mostly of anthropogenic in nature (Das *et al.*, 2005; Singh *et al.*, 2007; Budhavant *et al.*, 2009; Tiwari *et al.*, 2012; Bisht *et al.*, 2015; Roy *et al.*, 2016; Bisht *et al.*, 2017). In

Table 3. Equivalent concentration ratios of ionic components with respect to Sodium.

Site	Ions	Sea Water*	Snow Melt	EF	ssf%	nssf%
Leh	Cl ⁻	1.16	0.98	0.85	118.05	0.00
	SO ₄ ²⁻	0.13	0.82	6.53	15.32	84.68
	K ⁺	0.02	0.72	32.76	3.05	96.95
	Ca ²⁺	0.04	3.08	69.99	1.43	98.57
	Mg ²⁺	0.23	1.39	6.31	15.86	84.14
Beerwah	Cl ⁻	1.16	1.09	0.94	106.15	0.00
	SO ₄ ²⁻	0.13	0.87	6.93	14.44	85.56
	K ⁺	0.02	0.88	39.94	2.50	97.50
	Ca ²⁺	0.04	2.29	51.96	1.92	98.08
	Mg ²⁺	0.23	1.19	5.41	18.50	81.50
Nirmand	Cl ⁻	1.16	1.92	1.65	60.56	39.44
	SO ₄ ²⁻	0.13	0.47	3.78	26.45	73.55
	K ⁺	0.02	0.77	34.90	2.87	97.13
	Ca ²⁺	0.04	1.50	34.10	2.93	97.07
	Mg ²⁺	0.23	0.36	1.62	61.63	38.37

Table 4. The percent contribution of marine fractions, crustal fractions (CF) and anthropogenic fractions (Anthro) of each ionic species.

Ions	LEH			BEERWAH			NIRMAND		
	ssf	nssf		ssf	nssf		ssf	nssf	
	Marine	CF	Anthropogenic	Marine	CF	Anthropogenic	Marine	CF	Anthropogenic
Cl ⁻	100	0	0	100	0	0	61	39	0
F ⁻	0	1	99	0	2	98	0	1	99
NO ₃ ⁻	0	31	69	0	22	78	0	29	71
SO ₄ ²⁻	15	66	19	15	45	40	26	74	0
K ⁺	3	97	0	3	72	25	3	43	54
Ca ²⁺	1	99	0	2	98	0	3	97	0
Mg ²⁺	16	68	16	19	81	0	62	38	0
Na ⁺	100	0	0	100	0	0	100	0	0
NH ₄ ⁺	0	7	93	0	4	96	0	2	98

global precipitation, NO₃⁻ has also been reported in air mass trajectories due to long-range transport (Avila and Alacron, 1999; Satyanarayana *et al.*, 2010).

The nssSO₄²⁻ at Beerwah and Leh site showed the higher percentage contribution of Anthropogenic SO₄²⁻. This might be due to fossil fuel combustion at the origin of air masses as well as during the transport of air masses before reaching the site. Apart from LTR, the contribution from local sources such as the use of generators which are mostly operated on diesel cannot be ruled out. The presence of anthropogenic SO₄²⁻ in the form of (NH₄)₂SO₄ and NH₄HSO₄ has been reported in precipitation worldwide (Finlayson-Pitts and Pitts, 1986; Kulshrestha *et al.*, 2003). At Leh and Nirmand site the crustal fraction of SO₄²⁻ was very high than that of anthropogenic form. This high crustal SO₄²⁻ at both the sites may be due to SO₂ adsorption onto Ca²⁺ rich dust particles as it scavenges acidic precursor (Kulshrestha *et al.*, 2003b; Kulshrestha, 2013), which is very common in India. The maximum percentage fraction of nssK⁺ is contributed by crustal sources at Leh and Beerwah sites. Sometimes local soils contain a very high level of potassium (Jain *et al.*, 2000). But at Nirmand site nssK⁺ mainly contributed by anthropogenic sources. At this rural site biomass burning is the main reason for high nssK⁺ by anthropogenic sources.

Apart from biomass burning, nssK⁺ due to crustal sources have been reported in precipitation (Zhang *et al.*, 2007). Besides marine origin, Mg²⁺ is also contributed by crustal sources at all three sites. Mg²⁺ has been reported in snow samples due to a significant contribution from crustal sources (Kang *et al.*, 2004).

The average percent contribution of marine, crustal, and anthropogenic sources was calculated and showed in Fig. 5. The order of dominance followed the sequence- at Leh: Crustal (56%) > Marine (24%) > Anthropogenic (20%), at Beerwah: Crustal (46%) > Marine (27%) = Anthropogenic (27%). The dominant contribution of crustal fraction in snow samples due to local as well as long range transport has been suggested by Shrestha *et al.* (2002) and Zhang *et al.* (2013). After crustal, the contribution of the marine fraction is dominated over anthropogenic. A similar result was observed by Kumar and co-workers in snow at different sites of Himalayas (Kumar *et al.*, 2015, 2016). The pH of snow samples at both sites also suggested a significant contribution of crustal components, i.e., alkaline species over anthropogenic components, i.e., acidic species whereas seasalt fraction does not play an important role in controlling the pH of precipitation samples. At the Nirmand site the contribution from sources followed the sequence- Anthropogenic (40%) > Crustal (33%) > Marine

Fig. 5. Marine, crustal and anthropogenic fraction at all sites.

(27%). At this mainly activities are biomass burning, agriculture, suggested pollution coming from this contribute to anthropogenic sources. The pH of this site and the results of ions suggested complete neutralization of (SO_4^{2-}) by NH_4^+ to form $(\text{NH}_4)_2\text{SO}_4$ & NH_4HSO_4 and CaCO_3 rich dust particles forming calcium sulphate.

Three-days back trajectory analysis was also performed (Figs. 6(a)–6(c)) for the confirmation of the possible sources of pollutants over the Himalayan region. Backward air mass trajectories for 72 h of 2000 m above ground level were calculated using the geographic information system (GIS) based software, TrajStat for all snowfall samples (Wang *et al.*, 2009).

Mostly westerly air masses prevailed during the study. The air mass trajectories at Leh site show that the North Atlantic Ocean, Africa, Europe, Middle East, China, and Mediterranean region are the sources which contribute through the long-range transport of pollutants (Fig. 6(a)). At Beerwah site, the air masses arrived from Africa, Europe, Pakistan, Kazakhstan, Afghanistan and Middle-East along with Punjab, Haryana, Delhi, Uttar Pradesh (Fig. 6(b)). Both the LRT and the local sources are responsible for deposition of pollutants in snow at this site. At the Nirmand site, the air masses mainly approached from Africa, China, Pakistan, Uzbekistan, Tazakistan along with Punjab, Haryana, Delhi, Uttar Pradesh, Madhya- Pradesh, Maharastra (Fig. 6(c)).

Statistical Approach for Source Identification

Statistical analysis is also used to identify the relationship between major ions in snow samples and their possible sources. For, the estimates of correlation coefficients, the graph were plotted between the water-soluble ions in snow samples in Figs. 7(a)–7(c) for the respective sites. A good correlation between SO_4^{2-} and NO_3^- in snow samples at all the site suggesting the origin of these ions from the similar sources such as combustion of fossil fuel in which SO_2 and NO_x are emitted that eventually get oxidised into SO_4^{2-} and NO_3^- (Kulshrestha *et al.*, 2005; Kumar *et al.*, 2016). A strong correlation between major sea salt components such as Na^+ and Cl^- at all the sites indicative of their origin from marine source. Similarly, a good correlation is observed between ions such as Ca^{2+} and SO_4^{2-} at all sites, Ca^{2+} and Mg^{2+} at

Beerwah and Nirmand site, Mg^{2+} and SO_4^{2-} at Beerwah site. It might be due to the chemical interactions between crustal components rich in Ca^{2+} and Mg^{2+} with the acids such as H_2SO_4 and HNO_3 in precipitation. These reactions enhance the alkalinity of precipitation and decrease the acidity of snow samples interestingly SO_4^{2-} and NO_3^- showed good correlation with NH_4^+ derived from anthropogenic activities as well as with crustal components such as Ca^{2+} and Mg^{2+} . The strong correlation suggested the chemical reaction between these ion said in the stoichiometric neutralization of the acidic moieties present in the snow melt. The formation of NH_4 , SO_4 , $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 in precipitation samples have been reported due to reaction of ammonia in the atmosphere with H_2SO_4 and HNO_3 (Kulshrestha *et al.*, 2005; Seinfeld and Pandis, 2006).

Source Identification of Ions Using Principal Component Analysis

The principal component analysis (PCA) was attempted using snow chemistry data to identify the processes and emission sources of water-soluble ions in snow. Table 5 presents PCA results with varimax rotation. At Leh site, PC the total variance and showed high loading for F^- , Na^+ , Ca^{2+} and Mg^{2+} clearly reflecting their origin from crustal sources. PC2 explains 22.38% of variance had a high loading of Na^+ and NH_4^+ . Na^+ mainly comes from sea salt and also derived from soil, whereas NH_4^+ , indicating its unique anthropogenic source from volatilization of animal manure, human excreta and agricultural activities. The PC3 contained K^+ with 15.32% of the total variance, may be linked with biomass burning. PC4 explains 11.76% of the total variance and due to high loading of NO_3^- , could be vehicular emissions.

At Beerwah site, three components that were extracted may be attributed to three different sources. PC1 explained the 40.33% of the total variance and was found to be loaded with NH_4^+ , Na^+ , K^+ , Cl^- , NO_3^- and SO_4^{2-} indicating the influence of secondary inorganic aerosol from the anthropogenic sources. This factor can be attributed to regional pollution arising from coal-burning activities (Na^+ , K^+ , Cl^- , SO_4^{2-}) and agricultural practices (NH_4^+). PC2 was loaded with Ca^{2+} and Mg^{2+} and explained the 18.38% of the total variance. Loading of these variables in second factor suggests the influence of

Fig. 6. Airmass back trajectory at Leh, Beerwah and Nirmand respectively.

Fig. 7(a). Correlation matrix and frequency distribution graphs of water soluble ions in snowmelt at Leh site.

crustal and windblown soil dust. PC3 explained 14.02% of the variance and found to be loaded with K^+ and F^- . Presence of K^+ , and F^- variables indicate the influence of biomass burning sources over the studied area.

At Nirmand site, PC 1 showed high loading of NH_4^+ , K^+ , Na^+ and Cl^- with total variance of 34.91%. Na^+ and Cl^- suggested the contribution from salty soil profile in the region and longrange transport of sea winds. K^+ and NH_4^+ are tracer of biomass burning which includes domestic burning of firewood and agricultural residues. This PC represents a combination of coal and biomass burning. PC2 showed high loading of NH_4^+ , NO_3^- , and SO_4^{2-} with a total variance of 26.14%. These ions are secondary in origin and formed by chemical reactions in the atmosphere of ammonium sulfate and ammonium nitrate. PC3 showed high loading of Mg^{2+} and Ca^{2+} with a total variance of 17.48%. These ions are typically associated with crustal materials in windblown dust, resuspended dust, and dust from paved and unpaved roads.

Therefore, the overall conclusion could be inferred from both the statistical approach viz. correlation matrix and PCA that at Leh site Ca^{2+} and Mg^{2+} have strong correlation and PCA suggested they have common sources mainly coming

from crustal sources. At Beerwah Na^+ , K^+ , Cl^- , SO_4^{2-} and NH_4^+ are major source of pollution suggested local burning, agriculture activities are dominant in this region. At Nirmand site correlation table shows NH_4^+ , K^+ , NO_3^- , SO_4^{2-} have good correlation and PCA suggested they all are coming from anthropogenic sources.

Acidification and Neutralization Potentials

At Leh, the neutralization factor (NF) values of Ca^{2+} , NH_4^+ , and Mg^{2+} were estimated and found to be 2.34, 0.92, and 0.90, respectively (Fig. 8). Beerwah site also showed a pattern of NF where the NF value of Ca^{2+} , NH_4^+ , and Mg^{2+} was estimated and found to be 1.62, 1.07, and 0.70, respectively. These results suggested that at both sites, maximum neutralization occurred by Ca^{2+} and NH_4^+ in snow. Similar results were also observed by Kumar and co-workers in the snow at other sites of India, showing maximum neutralizing capacity for Ca^{2+} is about 1.65 at Mukhteshwar (Kumar *et al.*, 2015) and 1.17 at Gulmarg (Kumar *et al.*, 2016). The maximum neutralization by Ca^{2+} and NH_4^+ in precipitation has been reported by other workers worldwide (Kulshrestha *et al.*, 2003; Zhang *et al.*, 2007; Satyanarayana *et al.*, 2010; Roy *et al.*, 2017).

Fig. 7(b). Correlation matrix and frequency distribution graphs of soluble ions in snow at Beerwah site.

Kulshrestha *et al.* (1995) have suggested that neutralization by Ca²⁺ and Mg²⁺ done through a below-cloud process, whereas by NH₄⁺ done via an in-cloud process. Further, coarse mode aerosols predominantly contain Ca²⁺ and Mg²⁺ ions, and fine mode aerosols contain NH₄⁺ ion. Jain *et al.* (2000) suggested in, calcite-rich suspended dust neutralizes acidic component present in precipitation in India. At Nirmand site the NF values of NH₄⁺, Ca²⁺, and Mg²⁺ were estimated and found to be 5.15, 2.35 and 0.22 respectively, showing that NH₄⁺ neutralization dominant over Ca²⁺ at this site. The high concentration of NH₄⁺ was consistent with more NH₃ sources found at this site, mainly emitted from biomass burning, fertilizer, and animal breeding (Bouwman *et al.*, 1997). The higher NF of NH₄⁺ than Ca²⁺ was also observed over a rural station near Bhubaneswar on the east coast of Bay of Bengal (Das *et al.*, 2005; Das *et al.*, 2010). Roy *et al.* (2017) also reported the same results at high altitude Himalayan stations in eastern India.

CONCLUSION

The mean pH of snow at Leh, Beerwah and Nirmand was

74 ± 0.38, 5.77 ± 0.35 and 6.46 ± 0.39 respectively well above 5.60, which is the reference pH of snow and ranged between 5.18 and 8.11. During the study period, almost 60% of snow-water samples were found to be acidic in nature at Beerwah. Maximum pH was observed at Leh site, and the minimum was observed at Beerwah site. The average pH was higher at Leh (urban) and Nirmand (rural) than at Beerwah (semi-urban) due to the dominance of soil-derived particles. Overall the study revealed that basic ions largely control pH and acidity of snow water over the Himalayan region. The acidity in the snow is largely neutralized by Ca²⁺ at Leh and Beerwah site, whereas at Nirmand site it was neutralized by NH₄⁺. The order of measured major cations Ca²⁺ > Mg²⁺ > NH₄⁺ at Leh and Beerwah, but at Nirmand NH₄⁺ > Ca²⁺ > Na⁺. The dominant anion was HCO₃⁻ at all the sites. The major acidifying ion in snow was sulfate (SO₄²⁻), which was influenced by the long-range transport from the North Atlantic Ocean, Africa, Europe, the Middle East, and Mediterranean region. The high concentrations of cations were associated with depressions rich in calcite. Among the cations, Ca²⁺ makes the highest contribution at Leh and Beerwah sites, indicating the incorporation of soil

Fig. 7(c). Correlation matrix and frequency distribution graphs of soluble ions in snow at Nirmand site.

Table 5. Factor loading from PCA in snow at three sites.

Species	Leh				Beerwah			Nirmand		
	1	2	3	4	1	2	3	1	2	3
F ⁻	0.68	0.51	-0.21	0.02	-0.53	-0.21	0.51	-0.33	0.29	0.44
Cl ⁻	-0.76	0.28	0.44	-0.19	0.69	-0.25	-0.55	0.98	0.00	-0.15
NO ₃ ⁻	-0.38	0.29	0.21	0.75	0.88	-0.04	0.25	0.20	0.58	0.63
SO ₄ ²⁺	0.29	0.37	0.45	-0.59	0.83	0.28	0.22	0.31	0.80	0.42
Na ⁺	0.63	0.52	0.37	0.29	0.66	-0.38	-0.23	0.54	-0.70	0.12
NH ₄ ⁺	0.67	0.60	0.05	0.04	0.75	0.09	0.10	0.75	0.52	-0.26
K ⁺	0.32	-0.50	0.75	0.05	0.51	0.30	0.64	0.98	-0.02	-0.14
Ca ²⁺	0.57	-0.66	0.31	0.15	-0.35	0.79	-0.16	0.24	-0.51	0.64
Mg ²⁺	0.81	-0.39	-0.32	-0.01	0.23	0.78	-0.31	0.28	-0.53	0.53
Variance %	35.46	22.38	15.32	11.76	40.33	18.38	14.02	34.91	26.14	17.48

dust into the snow samples, which reflects a major crustal influence, whereas at Nirmand site NH₄⁺ contribution was highest, due to more agricultural or anthropogenic activity in this region. As the results suggested high concentrations of ions at the Leh site than Beerwah and Nirmand site, their limited deposition pathways at Leh reflected signatures of climate change over the upper Himalayan ranges and lesser

transboundary sources during the advections from the west. This study also reveals the LTR of air pollutants being transported more to the lower regions than the upper region. The neutralizing factor analysis highlighting the influence of anthropogenic as well as crustal sources. The results of this study have indicated that soil dust, sea salts, burning of biomass and coal are the major contributor of atmospheric deposition.

Fig. 8. Neutralization factor of nssCa^{2+} , nssMg^{2+} , NH_4^+ at (a) Leh, (b) Beerwah and (c) Nirmand sites (the axis break on Y-axis has given from 0.3 to 1.8).

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