

Snow Chemistry at Mukteshwar in Central Himalayan Region of India

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Abstract

The present study reports snow chemistry and source apportionment at Mukteshwar in central Himalayan region of India during winter 2012-13. In this study, fresh snowfall samples were collected at Mukteshwar during winter season of 2012-13. The results showed that the pH of the snowmelt samples ranged from 5.47 to 7.95 with an average of 6.37 indicating alkaline nature of precipitation which is similar to the range reported. The concentration of ions followed the following order- $\text{Ca}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NH}_4^+ > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+ > \text{F}^-$. Very high concentration of Ca^{2+} indicated the dominance of crustal sources. Source fraction calculations revealed that crustal, marine and anthropogenic sources contributed 40%, 38% and 22% ionic components in snowmelt, respectively. Since, Mukteshwar is remote site as compared to Delhi, values of NO_3^- were compared with the NO_3^- reported in the precipitation (rain water) of Delhi as NO_3^- is an indicator of vehicular pollution in urban areas. Such comparison of NO_3^- values suggested that though Mukteshwar precipitation had 1/3 of NO_3^- in precipitation as compared to Delhi, but considering it as a small town, precipitation at Mukteshwar is significantly influenced vehicular sources possibly due to Long Range Transport (LRT) of pollution.

Keywords: Himalaya; Precipitation; Vehicular pollution; NO_3^- ; Crustal sources

Introduction

Air pollution is considered as one of the major environmental challenges. Huge amount of air pollutants is injected into the atmosphere due to rapid urban and industrial growth during past few decades. South East and South Asian are the major air pollution emitters due to rapidly increasing energy demand for their fast growing economy. Among south Asian countries, Indian emissions are significant. After China, India is the second biggest emitter of SO_2 in Asia [1]. However, the levels of gas like SO_2 are quenched by atmospheric dust in India resulting in very low ambient SO_2 [2,3]. Nevertheless, emissions of atmospheric aerosols and gaseous pollutants have caused the problems of acid deposition, ozone depletion, climate change and monsoon modification etc. [4-6]. Once emitted, most of these pollutants are scavenged by removal processes. Wet deposition is one of the most effective deposition processes of airborne pollutants.

Long term study of wet deposition can be used to notice the changes in oxides of N & S content thereby relating to coal & petroleum energy consumption patterns. Hence, rain and snow chemistry become very important to know the sources of pollution and their possible effects on ecosystems and environment. Precipitation chemistry in general, provides information about the deposition fluxes of various air pollutants to different ecosystems. Due to its significance, snowfall chemistry has been studied extensively throughout the world [7-14]. Fresh snow chemistry in Himalaya ranges had shown relatively low concentration of air borne pollutants are representative of remote site [9,11,15]. The ionic content in Himalayan snow is highly affected by the impact of long range transport of anthropogenic sources of air pollutants [16]. Snow chemistry at Shanghai in China suggested that fossil fuel combustion and biomass burning is the major source of air pollution [14].

Acid deposition, a serious threat to terrestrial, aquatic and marine ecosystem has been studied comprehensively at various places in North America, Europe, Japan and other countries of the world [2,17-19]. Acidic precipitation is determined primarily by the interaction of acidic and basic species in the atmosphere. Acidic species are dominated by SO_2 and NO_x which is precursor of H_2SO_4 and HNO_3 respectively which are mainly emitted by fossil fuel combustion. On the other

hand, alkaline species (Ca^{2+} , Mg^{2+} and NH_4^+) help in enhancing pH of precipitation. The main source of these species is atmospheric dust which is made up of carbonates and bicarbonates of Ca and Mg [2,3,20]. Unlike North America and Europe, it is interesting that higher pH of precipitation is reported in India even at higher SO_4^{2-} concentration which might be due to huge amount of dust in the atmosphere [3].

In India, several studies have been reported on rain chemistry mostly in urban areas [2,21-26] with few studies from rural sites [27-30]. The detailed and updated studies on fresh snowfall chemistry are even rare in rural areas of Himalayan region of India [16,31,32]. Hence, this study was carried out to fill this knowledge gap about the chemical characteristics of snow in central Himalaya by selecting Mukteshwar as a rural representative site. The present study also focuses on quantification of relative contributions of marine and non-marine sources during winter season. Further, non-marine fractions have been quantified into crustal associated and anthropogenic sources. An attempt has been also made to highlight the extent of influence of vehicular pollution in urban area like Delhi vs. remote area like Mukteshwar by considering NO_3^- concentration as an indicator of vehicular pollution.

Materials and Methods

Sampling site

Mukteshwar is located at 29.47°N 79.64°E in Nainital district of Uttarakhand state of India (Figure 1). It is situated in the Kumaon Hills of central Himalaya at an altitude of 2286 meters. It lies approx. 51 km NE of Nainital city, 51 km from Nainital, 72 km from Haldwani and 395 km from Delhi city. Mukteshwar is rich in scenic beauty,

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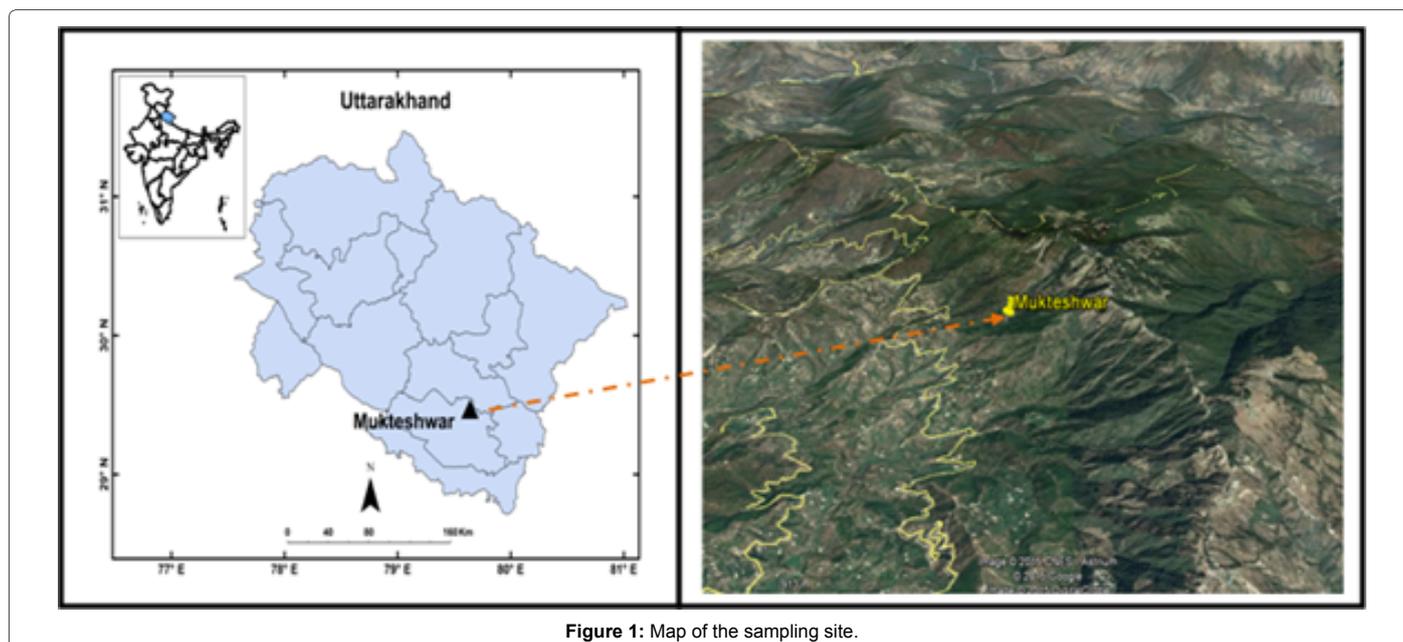


Figure 1: Map of the sampling site.

with magnificent views of the central Himalayas. It is one of the most famous tourist spots in north India which receive domestic as well as foreign tourists every year. The mean minimum temperature in this village ranges from -5°C to 0°C during January whereas the mean maximum temperature ranges from 25°C to 30°C during the month of June. There are no any major industrial units around this site. Most of the people use biomass as a source of energy for domestic heating and cooking purposes. The major sources of air pollution at this site include vehicular pollution used for tourist activities and emissions from agricultural activities.

Collection of snowfall samples

Fresh snowfall samples were collected with the help of plastic trays (30 cm diameter) on event basis during winter season of 2012-2013. Generally, winter season spreads between November and February but the site receives maximum snowfall during December and January. The tray was washed properly with high quality deionized water and dried before collection of snowfall. Sampler was placed at ~ 2 m height above the ground level. The collector tray was kept outside just before the start of snowfall and was removed immediately after snowfall to avoid contamination. In order to cover entire Mukteshwar area, the collection was done at five points at same time on the day of snowfall event. These points are located at around 100 m distance between each point. Fresh snowfall samples deposited on tray were transferred into pre-cleaned polypropylene bottles using polyethylene gloves. These samples were stored in the refrigerator at the site which was later transferred to the laboratory within 15 days from the collection period. Samples were later processed for analysis of pH, Electrical Conductivity (EC) and major ions.

Analysis of samples

The collected samples were brought to the laboratory and analysed for major anions, cations, EC and pH. Determination of major cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) and major anions (F^- , Cl^- , NO_3^- and SO_4^{2-}) were performed by using ion chromatography (Metrohm 883 Basic IC Plus). Metrosep A SUPP 4, 250/4.0 column and an eluent of 1.8 mmol/L Na_2CO_3 and 1.7 mmol/L NaHCO_3 at a flow rate of 1.0 with Metrohm suppressor technique were used for determination

of anions. While Metrosep C4-100/4.0 column and an eluent of 1.7 mmol/L Nitric acid and 0.7 mmol/L Dipicolinic acid at a flow rate of 0.9 without suppressor was used for determination of cations. HCO_3^- was determined by using 0.0025 N H_2SO_4 [33].

Quality analysis

Quality control and Quality Assurance (QA/QC) of chemical analysis was performed by checking ion balance and conductivity balance [24,34,35]. A significant correlation ($R^2 = 0.81$) was found between sum of anions (F^- , Cl^- , NO_3^- , SO_4^{2-} and HCO_3^-) and sum of cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} and Mg^{2+}) which indicated good ion balance for samples. A very good correlation between measured Electrical Conductivity (EC) and calculated conductivity ($R^2 = 0.87$) further confirmed good quality of dataset.

Results and Discussion

pH variation in snowmelt samples

The pH of the snowmelt samples ranged from 5.47 to 7.95 with an average of 6.37. Approximately, 95% samples had pH more than 5.6. The pH of precipitation in a clean atmosphere is generally 5.6 due to its equilibration with atmospheric CO_2 [36]. The snowmelt samples with pH more than 5.6 indicating inputs of alkaline components at this sampling site, which has been discussed in subsequent sections. Alkaline precipitation is a typical feature of Indian region due to suspended atmospheric dusts rich in calcium carbonate [2]. Similar range of pH distribution has been reported by many workers in global precipitation (Table 1). At this site, only 5% acidic precipitation has been observed. Results of this site were compared with other sites in Indian region. Satyanarayana et al. [30] have reported 11% acidic precipitation at Hudegade in ecologically sensitive region of Western Ghats, India. The frequency distribution of pH of snow samples showed that approx. 17% samples were acidic at Kothi in north western Himalayan region of India [16]. Very high frequency of acid rain occurrence has been reported over Indian Ocean during INDOEX due to high concentration of non-sea salt sulphate [37].

Ionic composition of snowmelt samples

Table 2 gives statistical parameters of major ions of snowfall. The ion concentration followed the following sequence- $\text{Ca}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NH}_4^+ > \text{NO}_3^- > \text{Mg}^{2+} > \text{K}^+ > \text{F}^-$ (Figure 2). Among cations, the percent concentration followed the sequence - $\text{Ca}^{2+} > \text{Na}^+ > \text{NH}_4^+ > \text{Mg}^{2+} > \text{K}^+$ while anions followed the sequence- $\text{Cl}^- > \text{SO}_4^{2-} > \text{HCO}_3^- > \text{NO}_3^- > \text{F}^-$.

The most abundant ion was Ca^{2+} , with concentrations ranging from 43 to 111 $\mu\text{eq/L}$. The average concentration of Ca^{2+} was 87 $\mu\text{eq/L}$ accounts for approximately 24% of all ions and 44% among all cations. We compared snowfall concentration of Ca^{2+} at this site with global reports. It was observed that the average concentration of Ca^{2+} at Mukteshwar was higher than Khumbu-Himal [9]. The highest concentration of Ca^{2+} indicating the dominance of crustal and marine sources which has been discussed in source contribution section. High levels of Ca^{2+} due to local as well as transported dust have been reported in precipitation [30,38]. The suspended soil dust might be significant local source for Ca^{2+} since the soil in this region are loosely bound in the earth crust. Since, the site is very fascinating place for tourists attracting its scenic beauty. The ongoing construction activities

especially building resorts to accommodate the maximum number of tourists. Besides this, road dust also contributes Ca^{2+} in precipitation. These activities are considered as significant sources of Ca^{2+} [16,20]. Very high concentration of Ca^{2+} due to suspended dust has been reported in Indian precipitation [24].

After Ca^{2+} and Na^+ , NH_4^+ ion has been most abundant. NH_4^+ concentrations ranged from 4 to 52 $\mu\text{eq/L}$. The average concentration of NH_4^+ was recorded as 24 $\mu\text{eq/L}$ which accounted for approximately 7% of all ions and 12% among all cations. Very high concentration of NH_4^+ among all cations indicated a significant influence of anthropogenic sources at Mukteshwar. The most important sources of NH_4^+ are agriculture activities, livestock, excreta of human and animal etc. [19,39]. Local people in this region are dependent upon mainly agriculture activities for their livelihood. Due to this region, agriculture activities and livestock might be a significant source of NH_4^+ at this site. Apart from these sources, local people as well as tourists reaching here also might be significant source for NH_4^+ in this region. Singh and co-workers [39] reported that humans are also a significant source of NH_3 . Since many local people are forced to go in the open field for excretion since they don't have proper toilet facility. Open excreta of human and animal also might be a good source of NH_4^+ at Mukteshwar. Apart from above mentioned sources, some contribution of long range transport can't be ruled out at this site which has not been discussed in this paper.

SO_4^{2-} also had relatively higher concentrations ranging from 2.11 to 99.95 $\mu\text{eq/L}$. The average concentration was observed to be 34.74 $\mu\text{eq/L}$ which accounted for approximately 9% of all ions and 21% among all anions. A comparison with other global data, we found that average concentration of SO_4^{2-} at this site was lower than Yulong snow [40] but higher than Mt. Everest [11] and Mt. Logan Massif [41]. Since,

Sampling site	Country	pH	Reference
Mukteshwar, Uttarakhand	India	6.37	Present study
Gulmarg, Jammu & Kashmir	India	6.70	[31]
Kothi, Himachal Pradesh	India	5.69	[16]
Central and Southern Californis	USA	5.20	[59]
Scottish Catchment	Europe	4.20	[60]
Larsemann Hills	Antarctica	5.71	[58]

Table 1: Geographical comparison of pH of snowmelt samples.

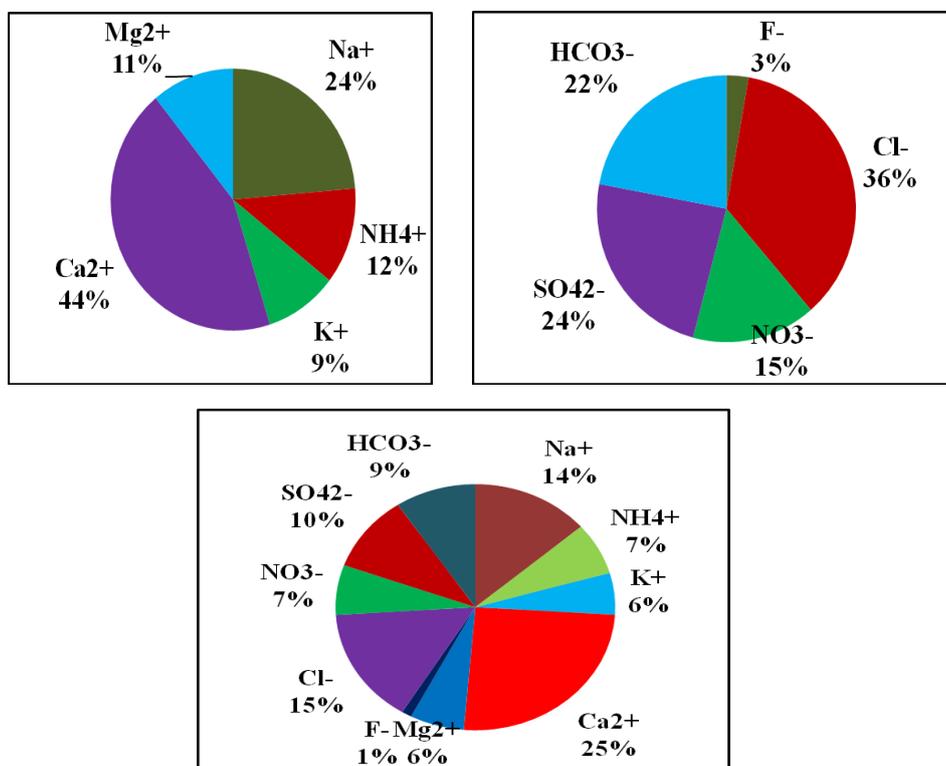


Figure 2: Percent contribution of ions (a) Cations (b) Anions (c) Total ions.

there is no any industrial activities at this site. Due to this reason, the maximum contribution of SO_4^{2-} might be due to transported SO_4^{2-} from other site in India or transboundary and long range transport SO_4^{2-} . Very similar range of SO_4^{2-} concentration has been reported worldwide [2,26,30,38,42,43]. High concentration of SO_4^{2-} indicated a significant influence of anthropogenic sources emitting SO_2 . Among local sources, diesel driven vehicular traffic might be the possible source of SO_4^{2-} . Vehicular flow due to increased tourist activities during winter season might be considered as a good source of SO_2 at Mukteshwar.

NO_3^- was found to have concentrations ranging from 2.8 to 48.8 $\mu\text{eq/L}$. The average concentration was observed to be 22.6 $\mu\text{eq/L}$ accounts approximately 6% of total ions and 14% of total anions. NO_3^- in snowfall samples might be due to emission of NO_x mainly from vehicular sources which is transformed into the atmosphere which give rise to NO_3^- in precipitation samples [44,45]. Another local source might be biomass burning during winter season to produce heat by local people cannot be ruled out [46]. Apart from local emissions, very high concentration of NO_3^- might be due to long range transport of $\text{NO}_x / \text{NO}_3^-$ from various air masses approaching at Mukteshwar.

Figure 3 compares NO_3^- in precipitation samples of Mukteshwar (snowmelt) with urban site, Delhi (rain water) [47]. On an average, it is very clear from the Figure that urban sites had 3 times high NO_3^- in precipitation. As compared to the size of town and local activities NO_3^- values in snowmelt at Mukteshwar are significantly high when we compare the size and the amount of local activities of Delhi city. This indicates that even though Mukteshwar is a remote hilly site, it is significantly affected by long range transport of pollution while most of NO_3^- in the precipitation of Delhi can be considered as local vehicular contributions. The varying composition of precipitation samples at different sites might be due to differences in local emission, meteorological conditions, methods of sampling, regional and global scale transport of pollutants in relation to air masses, type of sampling site, elevation from sea level etc. [9,24]. In order to understand the possible reason behind the variation of NO_3^- concentration in precipitation samples, we are comparing our study site i.e. Mukteshwar (rural characteristics) with Delhi city (urban characteristics). Mukteshwar is a small village with no major vehicular pollution except those by tourist activities. Apart from local vehicular emission, significant contribution of NO_3^- in precipitation at Mukteshwar might be due to transported $\text{NO}_x / \text{NO}_3^-$ from other places within India as well as long range transport of pollutants. Raatikainen and co-workers also observed the transport of pollution from Indo-Gangetic plain to Mukteshwar in Himalayan region of India. Delhi had very high NO_3^- in precipitation which might be due to a vast increase in vehicular population. In 1994, Delhi had 24,32,295 mobile vehicles which reached to 69,32,706 in 2010 [48]. This has increased the consumption of petrol by 44.7%. In addition, NO_3^- might also be contributed by increased number of industrial units. According to Delhi statistics, the number of industries is increased by 39.54% in Delhi region from 1994-2010 [48].

Source contribution

In order to find out the contribution of various sources categories, marine and non-marine fractions have been calculated. Further non-marine fraction has been calculated as crustal associated and anthropogenic fractions following the approach as reported by Kulshrestha et al. [49].

Marine contribution: The maximum fraction of sea salt is composed of Na^+ , Cl^- and Mg^{2+} with some fraction of Ca^{2+} , SO_4^{2-} and K^+ . In order to estimate the marine contribution in snowmelt samples, sea salt ratios were calculated by assuming Na^+ as a sea salt tracer

with marine origin only [50]. The sea salt ratios deviated considerably for all components from standard sea salt ratios (Table 3) indicating significant influence of non-marine contribution. The results showed that Cl^-/Na^+ ratio is very close to sea water ratios indicating its major contribution from marine sources (Table 3). $\text{Mg}^{2+}/\text{Na}^+$ ratios are slightly higher than the standard sea water ratio reflecting contribution of marine sources with some contribution from non-marine sources. Sodium ratios of SO_4^{2-} , K^+ and Ca^{2+} are higher than standard sea water ratios indicating their likely contribution from soil or anthropogenic sources. Elevated ratios of $\text{SO}_4^{2-}/\text{Na}^+$, K^+/Na^+ and $\text{Ca}^{2+}/\text{Na}^+$ have been reported at various other sites in Indian region [2,26,29].

In order to estimate sea salt fraction (ssf) and non-sea salt fraction (nssf) the following formula were used:

$$\%ssf = \frac{100}{EF_{sea\ water}} \quad (1)$$

$$\text{Here } EF_{sea\ water} = \frac{\left[\frac{X}{Na^+} \right]_{snowfall}}{\left[\frac{X}{Na^+} \right]_{sea\ water}} \quad (2)$$

Where, [X] is the concentration of desired ionic species in $\mu\text{eq/L}$.

$$\%nssf = 100 - \%ssf$$

The percent contribution of sea salt fraction and non-sea salt fraction of Cl^- , SO_4^{2-} , K^+ , Ca^{2+} and Mg^{2+} in snowfall samples has been given in Table 3. It is very clear from the table that the maximum fraction of SO_4^{2-} , K^+ and Ca^{2+} originated from non-marine sources. Similar to our results, large fraction of nssSO_4^{2-} and nssCa^{2+} have been

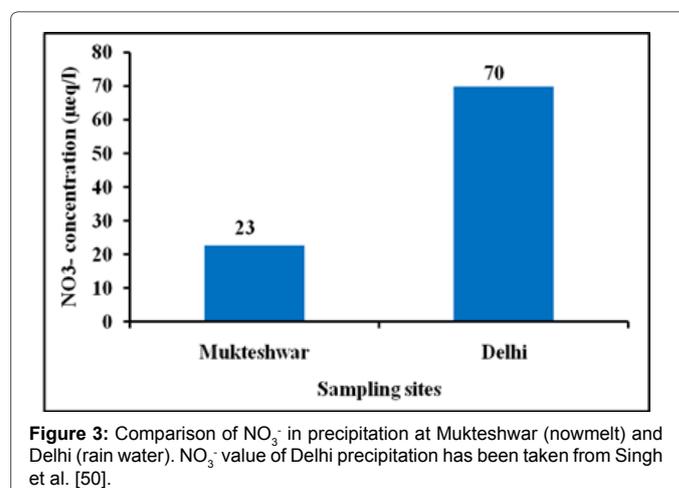


Figure 3: Comparison of NO_3^- in precipitation at Mukteshwar (nowmelt) and Delhi (rain water). NO_3^- value of Delhi precipitation has been taken from Singh et al. [50].

	Average	Min	Max
pH	5.47	7.95	6.37
EC	27.6	20.9	42.5
Na^+	47	22	82
NH_4^+	24	4	52
K^+	19	5	42
Ca^{2+}	87	43	111
Mg^{2+}	22	6	56
F^-	4	1	9
Cl^-	52	26	85
NO_3^-	23	10	38
SO_4^{2-}	35	13	49
HCO_3^-	32	5	78

Table 2: pH, EC and ionic composition ($\mu\text{eq/L}$).

	Cl ⁻	SO ₄ ²⁻	K ⁺	Ca ²⁺	Mg ²⁺
Sea water ratios (Keene et al. 1986)	1.16	0.125	0.022	0.044	0.227
Snowmelt ratios	1.12	0.74	0.40	1.86	0.46
EF (sea water)	0.97	5.93	18.36	42.30	2.03
%ssf	100	17	5	2	49
%nssf	0	83	95	98	51

Table 3: Sodium ratios of snowmelt and percent sea salt fraction and non sea salt fraction of major ions at Mukteshwar

Ions	Marine	CF	Anthropo
Cl ⁻	100	0	0
NO ₃ ⁻	0	12.3	87.7
SO ₄ ²⁻	16.7	22.4	60.9
K ⁺	5.4	94.6	0
Ca ²⁺	2.3	97.7	0
Mg ²⁺	48.9	51.1	0
Na ⁺	100	0.0	0
NH ₄ ⁺	0	4.2	95.8
F ⁻	0	1.0	99.0

Table 4: Percent contribution of marine, crustal (CF) and anthropogenic fraction (Anthropo) of all ions.

reported at various sites in snow samples [12,31,40,51].

Non-marine contribution: Further, non-marine fraction was differentiated into two categories- i) crustal associated and ii) anthropogenic sources. It is well known that anthropogenic sources are mainly responsible for lowering the pH of precipitation i.e. enhancing acidity while crustal sources i.e. alkaline species increases the pH and decrease the acidity of precipitation [3,52,53]. The contribution of crustal associated fraction (CF) and anthropogenic fraction (Anthro) of ionic species was calculated by the same approach as it was used by Kulshrestha et al. [49] which is an appropriate approach to explain pH value in Indian precipitation.

The nss Ca²⁺ was considered as reference element in snowfall samples in order to determine the crustal associated fraction (CF) of major ions [2]. The percent contribution of CF was calculated by the following formula:

$$\%CF_x = \frac{100}{EF_{soil}}$$

$$\text{Where, } EF_{soil} = \frac{\left[\frac{y}{nss Ca^{2+}} \right]_{snowfall}}{\left[\frac{y}{nss Ca^{2+}} \right]_{soil}} \quad (3)$$

y= (nss SO₄²⁻, nss Ca²⁺, nss K⁺, nss Mg²⁺, NO₃⁻, NH₄⁺ and F⁻) in µeq/L.

The percent contribution of Anthro fractions of each ion was calculated by the following formula-

$$\%Anthro_x = \%nss_x - \%CF_x \quad (4)$$

Using the above mentioned formula, the source characterization for different ions of snowfall has been calculated as given in Table 4. It is very clear from the table that the maximum contribution of Ca²⁺ is associated with crustal fraction. The percent contribution of SO₄²⁻, NH₄⁺ and NO₃⁻ was the highest in Anthro in comparison to CF. The highest contribution of crustal Ca²⁺ might be due to contribution from local sources such as local soil, construction activities, road dust etc. as well as long range transport of fine dusts. The significant contribution of long range transport has been reported in snow samples globally

[7,54]. Very high percent contribution of Anthro SO₄²⁻ at this site might be due to transported SO₂/SO₄²⁻ mainly since there is no any significant source of SO₂ nearby the sampling site. The crustal SO₄²⁻ at this site might be due to reaction of SO₂ with CaCO₃ rich dust particles forming calcium sulphate [2,3] which is very common in Indian region. The highest contribution of NH₄⁺ by anthropogenic sources might be due to significant contribution from local sources like agricultural activities, animal and human excreta, biomass burning, biogenic sources etc. with some contribution due to transported NH₄⁺ carried out by various air masses at this site.

Very high fraction of Anthro NO₃⁻ might be due to the emissions of NO_x from fossil fuel combustion and biomass burning. Among local sources, vehicles used by tourist might be the major source of NO_x. The significant contribution of NO₃⁻ has been reported in air masses due to long range transport of NO_x/NO₃⁻ in precipitation samples [16,30].

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

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

Here $\sum X_{ssf}$ = Sum of concentration of all ssf values in each air mass cluster in µeq/L.

$\sum X_{Total}$ = Sum of concentration of all components in each air mass cluster in µeq/L

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

Here $\sum X_{CF}$ = Sum of concentration of all CF values in each air mass cluster in µeq/L.

$$\text{Average Anthro}\% = 100 - \text{Average marine}\% - \text{Average crustal}\%$$

Using the above approach, the average percent contribution of marine, crustal and anthropogenic sources was calculated and given in Figure 4. The order of dominance followed the sequence- Crustal (40%) > Marine (38%) > Anthropogenic (22%). The significant contribution of crustal fraction has been observed in snow samples which might be due to local contribution with long range transport [15,16]. After crustal contribution, it was observed that the marine contribution dominated over anthropogenic sources. A very similar kind of observation has been reported in precipitation samples in Indian region [38]. The pH of snowmelt samples at this site suggesting significant dominance of alkaline species (crustal components) over acidic species (anthropogenic components) since sea salt don't play any important role in deciding pH of precipitation samples.

Neutralization factor

It is well known that NO₃⁻ and SO₄²⁻ are the major acidic species while nss Ca²⁺, nss Mg²⁺ and NH₄⁺ are the major alkaline species in precipitation samples. Due to this fact, nss Ca²⁺, nss Mg²⁺ and NH₄⁺ are mainly considered for calculation of neutralization factor.

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

$$NF_{xi} = \frac{[X_i]}{[NO_3^- + nssSO_4^{2-}]}$$

Where [X_i] = The concentration of desired ionic species i.e. nss Ca²⁺, nss Mg²⁺ and NH₄⁺ in µeq/L.

Using the above mentioned formula, the neutralization factor of nss Ca²⁺, nss Mg²⁺ and NH₄⁺ was calculated and are given in Figure 5.

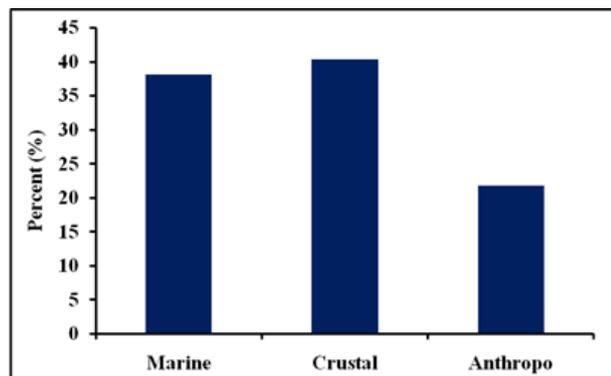


Figure 4: Average contribution of marine, crustal and anthropogenic sources.

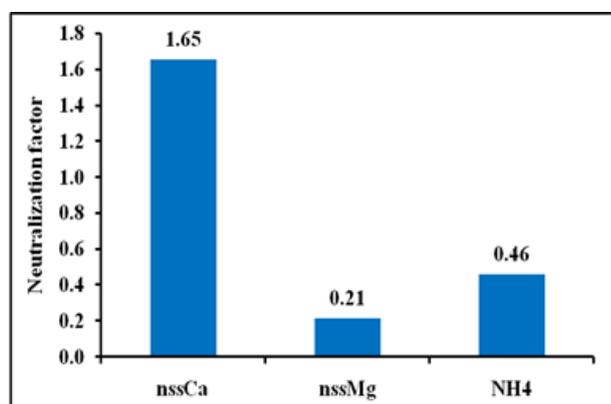


Figure 5: Neutralization factor of nss Ca²⁺, nss Mg²⁺, NH₄⁺.

The neutralization factor for these species followed the order- nss Ca²⁺ > NH₄⁺ > nss Mg²⁺.

The maximum neutralization of snowfall acidity occurs by nssCa²⁺ which might be due to suspended soil dust rich in CaCO₃ in Indian atmosphere [29]. These soil dusts might be contributed significantly by long range transport. The importance of transported dust in the neutralization of acidic components in precipitation samples has been observed globally [30,38]. Very high value of neutralization factor for nssCa²⁺ and NH₄⁺ has been reported in precipitation samples globally [2,30,53,55-60].

Conclusion

The pH of fresh snowfall collected at Mukteshwar was noticed in the range of 5.47-7.95 with an average of 6.37 which is similar to the pH of precipitation reported in other studies in this region. This is mainly due to the interferences of crustal sources. Among all ionic species, Ca²⁺ dominated. CaCO₃ rich aerosols are contributed by the suspension of soil, road dusts and construction activities. Scavenging of such aerosols gives rise to high pH of precipitation due to buffering action. Even at high SO₄²⁻ levels, the pH is relatively higher as the acidity created by sulphuric acid is buffered by the presence of Ca²⁺. Relative source contribution to the snowmelt was calculated as crustal 40%, marine 38% and anthropogenic 22% at the site. Comparison of NO₃⁻ values revealed that precipitation at Delhi is highly influenced by vehicular sources showing very high NO₃⁻ as compared to Mukteshwar. Interestingly, in spite of small town having lesser vehicular activities, precipitation at Mukteshwar has relatively high NO₃⁻ values which

might be due to long range transport of NO_x/NO₃⁻.

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