Aerosol and Precipitation Chemistry at a Remote Himalayan Site in Nepal

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As a part of a year long aerosol measurement program in the Nepal Himalayas, a series of 12 h samples of aerosol and event-based samples of precipitation were collected in postmonsoon, 1996; premonsoon, 1997; and monsoon, 1997. Results show that diurnal variations in the regional valley wind system are responsible for variations in the major ion (Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, NO₃⁻, and SO₄²⁻) concentrations in the aerosol. On time scales greater than a day, changes in atmospheric circulation and associated changes in the precipitation regime have an important effect on aerosol ion concentrations.

Periods of high major ion concentration in the aerosol generally coincide with similar periods in precipitation chemistry, although a linear relationship between concentrations in these 2 media is not robust due to limited data. High scavenging ratio values are found for all species except SO₄²⁻. Nitrate, Cl⁻, and NH₄⁺ are enriched in the precipitation compared to the aerosol, implying the presence of gaseous acidic species (HNO₃ and HCl) and gaseous NH₃ in the air. Ammonium was also enriched with respect to SO₄²⁻ in aerosol during a dry episode in the monsoon season. This may represent relatively local sources of NH₃ (from neighboring villages) and was not scavenged due to the lack of precipitation.

Empirical orthogonal function (EOF) analysis clearly shows the presence of 2 dominant pollutant transport mechanisms for the premonsoon and monsoon seasons (i.e., valley wind system and monsoon circulation). Although physically different, these 2 transport mechanisms follow similar transport pathways and transport aerosol into the Himalayas from similar source regions. Further, EOF analysis suggests a southerly maritime signal in the aerosol during monsoon and a more distant westerly maritime signal during premonsoon. Our results support the potential for using glaciochemical records from the Himalayas to investigate variations in the strength of past monsoon circulation and westerly disturbances.

INTRODUCTION

Ice cores retrieved from Greenland and Antarctica contain atmospheric chemistry records ranging from seasons to hundreds of thousand of years, providing insight into climatic variations over these periods (De Angelis et al. 1987; Delmas and Legrand 1989; Jouzel et al. 1990; Mayewski et al. 1993, 1994, 1996). Tropical and sub-tropical glaciers do not contain records as far back in the past, however, they may provide information concerning past climatic changes in regions where such information is virtually nonexistent (e.g., Thompson et al. 1984; Lyons et al. 1991). The vast glaciated regions in the Himalayas contain valuable information on monsoon variations over the past several thousand years. Quantitative estimates of past atmospheric chemical composition based on glaciochemical data depend greatly on the knowledge of the relationship between the chemistry of the precipitation and that of the airmass within which it forms and deposition. These relationships are site specific, so an interpretation of glaciochemical data from the Himalayas requires knowledge of the relationship between aerosol and precipitation chemistry in the region.

Studies on the chemical composition of aerosol and precipitation in the Himalayas have been limited to date on both temporal and spatial scales. A short-term sampling program in the Nguzompa glacier basin near Mt. Everest showed low ion burdens in both aerosol and snow (Wake et al. 1994). A 2 week sampling project in Hidden Valley in the Himalayas of western Nepal showed that temporal variations in aerosol concentrations were related to the influx of air masses by monsoon circulation (Shrestha et al. 1997). Recently, a year-long sampling of atmospheric aerosol (with sampling intervals of 5 days) was conducted at a remote Himalayan site and a rural Middle-Mountain site in Nepal (Shrestha et al. 2000). This study showed...
marked seasonal variations in the aerosol concentrations due to changes in circulation and associated precipitation scavenging. As part of the same program, aerosol samples were collected over 6 and 12 h sample intervals at the Himalayan site during 3 different seasons: premonsoon, monsoon, and postmonsoon. Aerosol sampling was complemented by precipitation samples. This paper investigates the variations in aerosol concentrations during the intensive sampling programs and their connection with meteorological variables and transport mechanisms. A preliminary attempt is made to quantify the relationship between aerosol concentrations and concentrations in the precipitation.

EXPERIMENTAL

The Site

The sampling site was located near the remote village of Phortse in the Khumbu region of the Himalayas in Nepal (Figure 1). The sampling site stands at an elevation of 4100 m a.s.l. at 27°51' N latitude and 86°45' E longitude and is situated about 350 m above the village, close to where a northwest to southeast trending ridge merges with the mountain slope. The ridge continues down to the confluence of the Imja Khola and Dudh Kosi rivers, at an elevation of 3550 m a.s.l. A meteorological station was established 50 m below the aerosol sampling site, on the same ridge. Although the predominant wind direction over the valley is southwesterly, observations of the local wind reveal that wind near the sampling station blows predominantly from a south-south-east direction (across the ridge). Therefore the sampling site is well protected from sources of pollution in the village. The village of Phortse consists of about 60 permanent houses. There are small patches of farmland around the village, where potato and buckwheat are cultivated between April and September. There are also some forested areas dominated by juniper and different varieties of pine. A small airstrip at Syangboche is located at a distance of about a 4 h walk.

Figure 1. Location map of Phortse sampling station. The arrows show predominant daytime local wind directions. (Continued)
(5 km aerial distance) and a slightly larger airport, Lukla, is a 3 day walk from the Phortse village. The nearest road head, Jiri, is at a distance of a 7 day walk (ca. 70 km aerial distance).

**Aerosol Samples**

The sampling described in this paper was part of a year-long aerosol sampling program at Phortse. During 3 different periods in postmonsoon, premonsoon, and monsoon seasons, regular 5 day integrated sampling was replaced by intensive sampling programs during which samples were collected over time intervals of 6 to 12 h. These intensive sampling programs were conducted between September 24 to 29, 1996; March 11 to 29, 1997; and August 11 to 31, 1997, corresponding to postmonsoon, premonsoon, and monsoon periods. The first sampling period was relatively short due to a pump breakdown. Therefore only data for the premonsoon and monsoon samples are discussed in detail.

Aerosol samples were collected on 2 μm pore size, 90 mm diameter Zefluor Teflon filters (Gelman Sciences). The filters were placed facing downwards in a cylindrical polyethylene protective cover. The air was drawn by 24 high volume pumps, powered by a combination of photovoltaic cells and batteries. The volume of air sampled was measured by an inline flow meter. Corrections for ambient temperature and pressure allowed for conversion of the measured volumes to standard cubic meters (scm). For the mean flow rate of 0.40 scm h\(^{-1}\), the velocity at the face of the filter was sufficiently high so that the efficiency of collection for particles as small as 0.3 μm is >99% (Liu et al. 1984). The flow velocity at the opening of the protective cover was calculated to be 3 cm s\(^{-1}\), according to which the cutoff for large particles, as given by the sedimentation velocity of particles, is estimated at 8 μm (Barrie 1985; Davidson 1989; Warneck 1988).

Care was taken to minimize contamination both in the laboratory and in the field. The filter cartridges were loaded and packed in clean plastic bags in a class 100 clean lab at the University of New Hampshire. The 90 mm cartridges were packed in clean plastic bags and transported in air-tight containers. Earlier sampling in the Himalayas showed an abundance of NH\(_4\) in the aerosol, and it was thought that postsampling reaction with NH\(_3\) in the ambient air might have created a positive artifact for NH\(_4\)\(^+\) (Haagenson and Shapiro 1979; Hayes et al. 1980; Silvente and
To avoid contamination by ambient air as well as evaporation of sampled species during transport and storage, filters were removed from their holders and were individually placed in precleaned air-tight glass bottles immediately after sampling at Phortse. The filters were placed with the exposed side of the filters facing inside of the bottles. The glass bottles were then placed in air-tight dark containers. The filters were removed from the glass bottles just prior to chemical analysis. Loading and unloading of samples was carried out wearing a nonparticulating clean suit, hood, face mask, and plastic gloves. Blank filters were handled in the same manner as the samples. After sampling, filters were brought to Kathmandu, where they were stored for several days. The filters were then shipped to the Climate Change Research Center (CCRC) at the University of New Hampshire by air cargo for extraction of the filter and laboratory analysis.

The filters were analyzed for major water soluble ionic species (Na\(^+\), NH\(_4^+\), K\(^+\), Mg\(^{2+}\), Ca\(^{2+}\), Cl\(^-\), NO\(_3^-\), and SO\(_4^{2-}\)) at the CCRC laboratory. In order to analyze the major ion concentration, the sample and blank filters were wetted with 0.5 ml ultrapure methanol. The soluble components were then extracted with three 5 ml aliquots of deionized Milli-Q water. Major ion concentrations in the aqueous extracts were determined by ion chromatography using a Dionex model 4000 ion chromatograph. Cations were analyzed using a CS12 column, 22 mM MSA eluent, and CSRS suppresser, and anions were analyzed using an AS11 column, 6.6 mM NaOH eluent, and MMS suppresser. The sample loop was 250 \(\mu\)l, and the sample running time was approximately 9 min.

Ten field blanks and 5 lab blanks were collected. We define the detection limit for major inorganic ions as the standard deviation of all the blanks divided by the mean volume of all the samples (after Talbot et al. (1986)). The detection limits are presented in Table 1. Mean blank values were deducted from the sample values.

The mountainous terrain is characterized by distinct diurnal variations in the local wind pattern. Generally the wind is up-slope (valley wind) during the daytime and down-slope (mountain wind) during the nighttime (Nakajima 1976; Hindman 1995a, b). While this is valid for all seasons, the timing of the diurnal wind variation depends on the geometry of the valley and season. Initially, 3 samples were taken daily in the beginning of the postmonsoon sampling at 0800 to 1400, 1400 to 1800, and 1800 to 0800 h (local standard time). Major ion concentrations in the 2 daytime samples were similar for most species, except SO\(_4^{2-}\). The lack of significant and consistent differences between the 2 daytime samples combined with the study of local wind patterns indicates that the mountain wind dominates only after 1700 h and the daytime samples were affected primarily by valley wind. In the sampling programs thereafter, only 1 daytime (0800–1800 h) and 1 nighttime (1800–0800 h) sample was collected daily.

**Precipitation Samples**

Precipitation samples were collected in 500 and 1000 ml polypropylene jars with an orifice diameter of 150 mm (larger jars were used for collecting solid precipitation). The precleaned jars were packed and sealed in clean bags (Clean Room Products, New York). Prior to exposure, the jars, with caps on, were removed from plastic bags and mounted on a 1.5 m high stand. Next, the cap was removed from the jar and placed in the original plastic bag. Immediately after sample collection, the jar was sealed tightly by the cap to avoid dry deposition and was placed in air-tight dark containers. Storing in the container allowed solid precipitation to melt. Between 6 to 12 h after sampling, the precipitation samples were transferred to 30 ml polypropylene bottles. Depending on the amount of precipitation, 2–4 aliquots were prepared for each precipitation event. To avoid changes in concentrations due to bioconsumption, half of the aliquots were treated with ultrapure chloroform (1% of the aliquot volume; Galloway (1978)). The polypropylene bottles were then placed in dark air-tight containers. Samples were frozen soon after reaching Kathmandu and until they were dispatched to CCRC.

Precipitation samples were also analyzed at the CCRC laboratory using a Dionex ion chromatograph. Ammonium concentrations were determined as average values of aliquots treated with chloroform, while Cl\(^-\) values were determined from untreated samples.

### Table 1

Detection limits of aerosol and precipitation samples from Phortse

<table>
<thead>
<tr>
<th>Period</th>
<th>Na(^+)</th>
<th>NH(_4^+)</th>
<th>K(^+)</th>
<th>Mg(^{2+})</th>
<th>Ca(^{2+})</th>
<th>Cl(^-)</th>
<th>NO(_3^-)</th>
<th>SO(_4^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aerosol (neq cm(^{-1}))</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Sep. 1996</td>
<td>2.20</td>
<td>0.03</td>
<td>0.18</td>
<td>0.20</td>
<td>1.08</td>
<td>0.49</td>
<td>0.62</td>
<td>0.45</td>
</tr>
<tr>
<td>Mar. 1997</td>
<td>0.22</td>
<td>0.95</td>
<td>0.14</td>
<td>0.07</td>
<td>0.35</td>
<td>0.19</td>
<td>0.15</td>
<td>1.00</td>
</tr>
<tr>
<td>Aug. 1997</td>
<td>0.21</td>
<td>0.41</td>
<td>0.02</td>
<td>0.05</td>
<td>0.46</td>
<td>0.08</td>
<td>&lt;snzv</td>
<td>0.07</td>
</tr>
<tr>
<td><strong>Precipitation ((\mu)eq kg(^{-1}))</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sep. 1996</td>
<td>0.04</td>
<td>0.02</td>
<td>&lt;snzv</td>
<td>0.03</td>
<td>0.04</td>
<td>0.17</td>
<td>&lt;snzv</td>
<td>&lt;snzv</td>
</tr>
<tr>
<td>Mar. 1997</td>
<td>&lt;snzv</td>
<td>&lt;snzv</td>
<td>&lt;snzv</td>
<td>0.01</td>
<td>0.07</td>
<td>0.01</td>
<td>&lt;snzv</td>
<td>&lt;snzv</td>
</tr>
<tr>
<td>Aug. 1997</td>
<td>&lt;snzv</td>
<td>0.04</td>
<td>0.02</td>
<td>0.00</td>
<td>0.05</td>
<td>0.00</td>
<td>&lt;snzv</td>
<td>&lt;snzv</td>
</tr>
</tbody>
</table>

*snzv = specified nonzero value.*
samples. For other species, average values of all samples for the precipitation event were used. Standard deviations of multiple samples representing the same precipitation event were adequately low (<5% of the mean). The amount of precipitation was determined by the readings from a manual precipitation gauge. Detection limits, determined as described in Shrestha et al. (1997), are presented in Table 1. The first precipitationsample from the premonsoon sampling program is suspect because of unrealistically high (>200 times the average) concentrations for all species except NH$_4^+$ and NO$_3^-$ and were therefore not included in further analyses. The same procedure of sampling solid and liquid precipitation and missing initial small amounts of precipitation may have an impact on the data.

Meteorological Data
A meteorological station established and operated in conjunction with the aerosol sampling program included a thermohygrograph, an actinograph, an anemometer, a rain gauge, and an altimeter barometer. Melting was required to measure the amount of solid precipitation. General weather conditions at the site, such as cloud cover and movement, visibility, fog, mist, etc., were observed and noted twice daily at standard meteorological observation times for Nepal (0845 and 1745 h) during the sampling program. Synoptic weather maps prepared by the Department of Hydrology and Meteorology, Nepal, were acquired to obtain information on synoptic scale circulation during the sampling programs. Wind direction data was not obtained during the 1997 monsoon due to instrument malfunction. For that period, data from a permanent meteorological station at Dingboche (about 5 km northeast of Phortse) is used. The wind data from Dingboche was well correlated with wind data from Phortse during other sampling periods.

RESULTS AND DISCUSSION

Diurnal Variations in Aerosol Concentration
The nighttime samples generally show lower concentrations than daytime samples. We present events for dominant ionic species in aerosol (i.e., NH$_4^+$, NO$_3^-$, and SO$_4^{2-}$) when consecutive daytime and nighttime samples were taken (Figure 3). There are 19 (out of 28) such events with conspicuous differences in daytime and nighttime concentrations for all species. Among these, daytime samples show higher concentrations than nighttime for 12 events, while nighttime samples show higher concentrations for the remaining 7 events. In the premonsoon sampling program, only during the period between March 19/20 and 21/22 did nighttime samples for SO$_4^{2-}$ show considerably higher concentrations compared to daytime samples (Figure 3 left).

Apart from wind direction, precipitation plays an important role in variations in aerosol concentrations (Figures 2 and 4). Precipitation was generally nocturnal in Phortse (67% of the total precipitation events). Precipitation scavenging plays an important role in reducing aerosol concentration in the Himalayas (Shrestha et al. 1997, 2000), which could have resulted in the observed diurnal variations in aerosol concentration (Figure 3). However, there are several instances when nocturnal precipitation did not occur and nighttime concentrations are still reduced (e.g., March 15/16, 17/18, and 21/22). Besides precipitation, the diurnal variation in regional scale wind systems (Shrestha et al. 2000) could also affect the aerosol concentrations. Pollutants transported to the site by regional scale valley wind systems during the daytime are replaced by relatively cleaner air aloft by the mountain wind system in the nighttime. The northeasterly wind direction during the night on March 15 and 20 indicates the presence of mountain wind at the sampling site (Figure 4). The differences in daytime and nighttime samples, even when there was no precipitation event, suggests that the role of diurnal changes in the wind pattern is the dominant control on the diurnal fluctuation of aerosol concentrations. Coincidentally, after March 23 in the premonsoon samples, there was no precipitation and the mountain wind system also ceased (Figure 4).

In contrast, nighttime concentrations are substantially higher than daytime concentrations from August 21/22 to 23/24 and on August 27/28 for most species (Figure 3). Wind direction data from Dingboche shows the presence of mountain wind during this period (Figure 4). Mountain winds occur over a wide area in the Khumbu region (Hindman et al. 1996), and the observation of low level cloud movement at Phortse did show diurnal changes in the local winds. Occasionally during the early monsoon, the Phortse station experienced higher levels of pollution compared to a lower elevation station at Jiri. This was likely due to the intrusion of a polluted monsoon layer (Shrestha et al. 2000). Higher nighttime concentrations suggest that pollutants are brought to the sites during the night by the mountain wind flowing down the valley from northeast of the sampling site. The nocturnal mountain wind could readily transport air masses from the polluted layer to the Phortse site, causing nighttime rises in major ion concentrations during the periods when precipitation did not occur. An airborne measurement of aerosol species and meteorological parameters is planned in the near future in the Nepal Himalayas, which may provide valuable insight into the existence of a pollution layer overriding relatively clean air masses (Hindman).

Multiday Variations in Aerosol Concentration
Premonsoon concentrations of NH$_4^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, NO$_3^-$, and SO$_4^{2-}$ are 2 to 10 times greater than the monsoon concentrations (Figure 2) on average. The differences in aerosol concentrations between the 2 sampling periods (premonsoon and monsoon) are a part of greater seasonal variations. The discussion here focuses on concentration variations within each sampling season.

Concentration variations at multiday time scales (several samples) are characteristic of the premonsoon and monsoon concentration series (Figure 2). At these time scales (several days to a week), precipitation events were generally associated with
Figure 2. Time series of water soluble major ions in the aerosol (solid lines) and precipitation (stippled bars) measured at Phortse during premonsoon, 1997 (left), and monsoon, 1997 (right), seasons. Note the difference in vertical scales. Short breaks in aerosol data are due to a gap while changing filters. Longer data gaps are when samples are below detection, unless indicated as “md” (missing data). Data offscale is labeled in the plot.
Figure 3. Daytime and nighttime concentrations of major ionic species in aerosol samples collected at Phortse. Days without consecutive day and night samples are not presented in the figure. Daytime and nighttime precipitation events are indicated by “d” and “n” in (a) and (d), whereas “dn” indicates precipitation events covering both the daytime and the following night. Note the difference in vertical scales.
Figure 4. Meteorological data collected in Phortse during premonsoon, 1997 (left), and monsoon, 1997 (right). Here we use wind direction data from Dingboche for monsoon, 1997, as there is no wind direction data from Phortse for that period. Points in wind direction plots indicate hourly data, while a solid line is weighted mean with 5% smoothing factor.
decreases in aerosol concentrations. For example, during the premonsoon sampling program, concentrations of most ionic species decreased dramatically following precipitation events in March (i.e., March 13–14, 17/18, and 19/20) (Figure 4). However, the precipitation of March 23 was of low intensity and apparently did not significantly alter aerosol concentrations. In addition, the circulation pattern that is generally northwesterly in premonsoon (Figure 5a), and is relatively cleaner and does not support advective transport from the south, shifted to a southwesterly flow between March 20 and 25 (Figure 5b) (Mayewski et al. 1983). This shift in large-scale circulation is capable of incorporating more pollutants from distant southerly and southwesterly sources. After March 25, the 500 mb circulation reestablished the pattern similar to that at the beginning of the month (figure not shown).

The monsoon samples also display significant variations in major ion concentrations on time scales of a week. The monsoon samples can be divided into 2 parts, August 8–20 and August 20–28. The first period was characterized by low concentrations, close to or <1 neq cm⁻¹ for all species except Na⁺ and Cl⁻ (Figure 2 right). The sample of August 19/20 (night) shows a large increase in concentrations of all species except Cl⁻, although all ion concentrations remain significantly lower than those during the premonsoon period until the end of the sampling period, when they returned to the lower level characteristic of the first half of the monsoon sampling (August 8–20). The sequence of high and low concentrations of atmospheric aerosol on weekly time scales in the monsoon sampling period matches a similar sequence of variations in the amount of precipitation. Precipitation records for the monsoon sampling program show 2 distinct periods: a wet period between August 8 and 17 and a substantially drier period between August 18 and 27. The last days of the monsoon sampling program (August 28–30) shift back into a wet period. Analysis of synoptic weather maps shows that the monsoon trough shifted southward during that period (Figures 5c and d). This caused air masses reaching the site to change trajectories from southeasterly to easterly. The shift in air-mass trajectory elongated the travel distance from the Bay of Bengal such that the moisture got depleted in the earlier part of the path. It is suggested that the high aerosol concentrations were caused by incorporation of the pollutants into the relatively dry air masses in its path.

### Aerosol-Precipitation Relationship

Concentrations of chemical constituents in precipitation collected during the premonsoon and monsoon intensive sampling programs are shown in Figure 2. As with the aerosol samples, the concentrations of major ions in the precipitation were high during the premonsoon season as well as in the 2 isolated precipitation samples of August 21 and 21/22 and low in the first half of the monsoon sampling. In addition, the concentrations of water soluble species in the precipitation in the postmonsoon sampling were similar to those during the first half of the monsoon sampling (limited in time and samples). Figure 2 shows that periods with high aerosol concentrations generally correspond to similar periods in the precipitation concentration. As a preliminary step to quantify the relationship between concentrations in the precipitation and in the aerosol, scavenging ratios were calculated according to

\[
W = \frac{\rho_a C_s}{C_a},
\]

where \(C_s\) = concentrations in precipitation (ng g⁻¹); \(C_a\) = concentration of aerosol (ng m⁻³); and \(\rho_a\) = density of air (764 g m⁻³ after correcting for the standard temperature and pressure) (Davidson et al. 1993).

The mean scavenging ratios for most species were significantly higher than those found in Greenland (e.g., Davidson et al. 1993) or in the Swiss Alps (Baltensperger et al. 1993) (Table 2). The scavenging ratio for SO₄²⁻, although relatively low compared to scavenging ratios of other species, is comparable to values found in Greenland (350; Baltensperger et al. (1993)). The scavenging ratios are highly variable for all species. The variability may be attributed to differences in precipitation formation, gas and aerosol-phase atmospheric concentrations, and/or the extent of below cloud scavenging between individual events, as samples were collected during different weather conditions and seasons. Our data set does not allow assessment of the relative importance of the different processes controlling relationships between aerosol and precipitation composition. However, sample-to-sample variations in aerosol concentrations are not reflected in corresponding precipitation events. Although there is a high correlation between concentrations of most species in the aerosol and in the precipitation, this relationship is biased by a small number of samples with considerably higher concentrations than average concentrations in aerosol and in the precipitation (figure not shown). Table 3 shows that major ion concentrations for most species in aerosol covary with those in precipitation when concentrations are averaged over episodes of high and low concentrations and over the 2 sampling seasons (premonsoon and monsoon). While these results show that the concentration increase (decrease) in one medium is reflected by a similar increase (decrease) in the other, the magnitude of change is not consistent and the relationship is not linear. Since the relationship significantly improved by averaging over longer time periods, it is possible that the relationship will further improve and approach a linear relationship as more data are collected in the future. This would provide greater confidence when using glaciochemical data for interpreting atmospheric composition of the past as the glaciochemical data provides concentrations at seasonal or annual resolution.

The mean scavenging ratio of NO₃⁻ is relatively high. In the aerosol, NO₃⁻ concentrations were equivalent to only one third of the NH₄⁺ concentrations (Table 2), while in precipitation the NO₃⁻ concentrations were greater than NH₄⁺ (Figures 6a–b). The relative increase in NO₃⁻ concentrations was greater in the period of higher aerosol concentrations (e.g., during premonsoon). This suggests the presence of gaseous HNO₃ in the air.
Figure 5. Geopotential heights at 500 mb level. The dashed arrows indicate tentative isobaric trajectory of air masses arriving at the site.
Table 2
Scavenging ratios for water soluble major ions

<table>
<thead>
<tr>
<th>Period</th>
<th>Na⁺</th>
<th>NH₄⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>NO₃⁻</th>
<th>SO₄²⁻</th>
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</thead>
<tbody>
<tr>
<td>Mean</td>
<td>1393</td>
<td>1811</td>
<td>2436</td>
<td>2580</td>
<td>1805</td>
<td>2582</td>
<td>2502</td>
<td>487</td>
</tr>
<tr>
<td>S. Dev.</td>
<td>1593</td>
<td>2351</td>
<td>2092</td>
<td>2277</td>
<td>1873</td>
<td>2007</td>
<td>2007</td>
<td>326</td>
</tr>
</tbody>
</table>

(largely unsampled on our filters), especially when the air was more polluted. Relatively high scavenging ratios for NO₃⁻ could result from the scavenging of gas-phase HNO₃ by precipitation. Similarly, our results show enhancement of Cl⁻ with respect to Na⁺ in the precipitation. Chloride was in large deficit relative to Cl⁻ in aerosol, and there is no correlation between these species (Figure 6c). In contrast, Na⁺ and Cl⁻ were not only linearly related in the precipitation, but Cl⁻ was also enriched relative to Na⁺ (Figure 6d). The best fit line shows that Cl⁻:Na⁺ in precipitation was close to the mean sea-water ratio between Cl⁻ and Na⁺ (1.165; Drever (1988)). Such enrichment of Cl⁻ with respect to Na⁺ in the following precipitation could be due to 2 factors.

1) Presence and scavenging of gaseous HCl in air can cause enrichment of Cl⁻ in the precipitation. The Na⁺/Cl⁻ ratio in the precipitation will approach the average sea water ratio if both of these components originated as marine aerosol and underwent chemical fractionation by the reaction with, for example, H₂SO₄ as they traveled to the site. Evidence of fractionation of sea salt particles by H₂SO₄ was found in Hidden Valley, where similar enrichment of Cl⁻ in the precipitation was observed (Shrestha et al. 1997).

2) Air masses transported to the site by more vigorous circulation are likely to be less fractionated due to shorter travel time. Since air masses causing precipitation represent stronger circulation, enrichment of Cl⁻ in the precipitation could be because of the bias of sampling such air masses. When only the aerosol data during the precipitation events in Phortse were examined, the relationship between Cl⁻ and Na⁺ improved remarkably ($r = 0.83$) and the ratio between Cl⁻ and Na⁺ was 0.6. Although this ratio is only half of the mean sea-water ratio, it is significantly higher than when all aerosol data is considered. Further, when only aerosol data during monsoon precipitation events are considered, a similar ratio is obtained, while the correlation is significantly lower ($r = 0.63$).

It is common to observe enrichment of SO₄²⁻ relative to NH₄⁺ in precipitation due to SO₂ oxidation in clouds (e.g., Calvert et al. 1985). On the contrary, our samples display relative enrichment of NH₄⁺ in the precipitation with respect to SO₄²⁻ (Figures 6e and f and 7a and b (August 9–13)). The amount of NH₄⁺ is more than the sum of SO₄²⁻ and NO₃⁻ in the precipitation (Figure 7). Similar enrichment was also observed in Hidden Valley, although enrichment of NH₄⁺ occurred to a much higher extent (Shrestha et al. 1997). Poor scavenging of SO₂ could have been responsible for the relative enrichment of NH₄⁺. A low scavenging ratio of SO₂ compared to all other species in our samples supports this. However, different scavenging rates should not occur if SO₂ and NH₄ are internally mixed. Southerly air masses that bring in precipitation travel over populated areas, forests, and cultivated lands in the lower mountain and plains in Nepal before reaching the Phortse site. These air masses could accumulate additional gaseous NH₃ emitted from animal manure and fertilizers. As there are no industrial activities in this intermediate region (ca. 50 km from the site), additional sources of SO₂ are insignificant. Low SO₂ concentrations measured in rural and semiurban sites support the hypothesis that there are no

Table 3
Event-based geometric means of selected major ionic species in aerosol and precipitation

<table>
<thead>
<tr>
<th>Events</th>
<th>NH₄⁺</th>
<th>SO₄²⁻</th>
<th>Ca²⁺</th>
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</thead>
<tbody>
<tr>
<td>Aerosol Precipitation</td>
<td>Aerosol Precipitation</td>
<td>Aerosol Precipitation</td>
<td></td>
</tr>
<tr>
<td>Mar. 13–19</td>
<td>15.56 (4)</td>
<td>12.92 (5)</td>
<td>53.35 (3)</td>
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<tr>
<td>Mar. 19–23</td>
<td>58.05 (2)</td>
<td>21.10 (2)</td>
<td>152.79 (1)</td>
</tr>
<tr>
<td>Mar. 24–25</td>
<td>241.77 (1)</td>
<td>nd</td>
<td>33.93 (4)</td>
</tr>
<tr>
<td>Premonsoon average</td>
<td>38.68 (3)</td>
<td>15.21 (4)</td>
<td>73.74 (2)</td>
</tr>
<tr>
<td>Aug. 8–19</td>
<td>0.35 (8)</td>
<td>0.44 (8)</td>
<td>0.80 (8)</td>
</tr>
<tr>
<td>Aug. 20–28</td>
<td>7.18 (5)</td>
<td>20.66 (3)</td>
<td>3.40 (5)</td>
</tr>
<tr>
<td>Aug. 29</td>
<td>6.36 (6)</td>
<td>1.00 (6)</td>
<td>1.20 (7)</td>
</tr>
<tr>
<td>Monsoon average</td>
<td>1.72 (7)</td>
<td>0.61 (7)</td>
<td>1.41 (6)</td>
</tr>
</tbody>
</table>

Here, events are based on periods of distinct high and low aerosol concentrations. Values in parentheses indicate the rank of the mean concentration for this data set. There was no precipitation during the Mar. 24–25 event and this is indicated by “nd.” Ranks for precipitation concentrations were assumed to be the same as for aerosol for this event.
Figure 6. Relationships between water soluble major ions in aerosol (left) and precipitation (right). Concentrations in the aerosol are in neq cm⁻¹ and in the precipitation in μeq kg⁻¹. Solid lines represent common relationships between species, and dotted lines represent the best fit line.
Figure 7. NH$_4^+$/SO$_4^{2-}$ and NH$_4^+$/\((SO_4^{2-}+NO_3^-)\) ratios in the air and NH$_4^+$/SO$_4^{2-}$ ratios in the precipitation for the premonsoon sampling (a) and the monsoon sampling (b).
significant SO$_2$ (and thus SO$_2^{2-}$) sources in Nepal (e.g., Carmichael et al. 1995). While concentrations of all species were elevated in the period between August 20 and 28, this period is also characterized by enrichment of NH$_4^+$ with respect to SO$_2^{2-}$ in the aerosol (Figure 7b), supporting the presence of NH$_3$ in the ambient air.

**Interspecies Relationships, Sources, and Transport**

Multivariate analysis was performed on the aerosol data to investigate interspecies relations with respect to sources and transport mechanisms. We used multivariate empirical orthogonal function (EOF) analysis, rather than repeated simple linear regression or multiple linear regression, because of its ability to assess joint behavior of several species (variates). EOF decomposition provides objective representations of multivariate data by analyzing the covariance structure of its variates (Pixoto and Oort 1992; Mayewski et al. 1997; Meeker et al. 1997). This analysis was performed on the premonsoon samples and the monsoon samples. Aerosol concentrations below detection were represented by the detection limits.

The signs and magnitudes of variance explained by EOF1 shows that 6 of the major ions (excluding Na$^+$ and Cl$^-$) are strongly loaded in both premonsoon and monsoon samples (Table 4). The first EOF is interpreted to represent well-mixed air masses. High loading of 6 species indicates long travel distances from source regions (Heidam 1984; Mayewski et al. 1997; Meeker et al. 1997). Thermal advection (valley winds) represents the dominant transport mechanism during the premonsoon season, while monsoon air masses carry pollutants to the site during the monsoon season (Shrestha et al. 2000). While separate processes drive these 2 transport mechanisms, their transport pathways are similar in the sense that both flow from the south. This implies that the valley wind system, due to thermal advection, is relatively extensive, and the source regions are similar to those of large-scale monsoon circulation, hence it causes similar variations in aerosol concentrations.

Sodium and Cl$^-$ dominate the second EOF for both seasons, suggesting that sources/transport of Na$^+$ and Cl$^-$ are different from those of other species (Table 4). Premonsoon EOF1 explains 21% of variance in Na$^+$, while a majority of Na$^+$ variance is explained by EOF2 (55%). This implies that Na$^+$ has dual sources. The loading on EOF1 may support an association with a crustal source. The crustal source of Na$^+$ is insignificant during the monsoon season. High loading of Na$^+$ and Cl$^-$ on EOF2 for both seasons is a surprising result. Joint loading of these 2 species is indicative of marine aerosols. It is natural to expect some influence of marine aerosol in the monsoon season. Crustal sources of Na$^+$ and Cl$^-$ (evaporites) from arid regions of central Asia transported by the westerly circulation is precluded because of the lack of Ca$^{2+}$ and Mg$^{2+}$ loading in this EOF (Wake et al. 1994). The occasional precipitation during winter and premonsoon has its moisture source at the Mediterranean Sea (westerly disturbance; Mani 1981; Nayava, 1980). It is possible that the EOF2 during premonsoon is reflecting the distant maritime origin of moisture transported by a westerly flow. Although Mg$^{2+}$ is also a major component of sea salt, it is absent in the second EOF possibly because its crustal fraction is much larger than the sea salt fraction.

Unlike EOF1 and EOF2, EOF3 is different for the 2 seasons and shows mixed loading both in sign and magnitude (Table 4). The monsoon loading of NH$_4^+$ and K$^+$ may represent a biomass burning signal. The premonsoon is a season when biomass burning is common in the low-lands and hills of Nepal. Similar loading of Cl$^-$ could be because a fraction of NH$_4^+$ is associated with Cl$^-$. This can happen if NH$_4^+$ is in excess after completely neutralizing NO$_3^-$ and SO$_2^{2-}$ and there is gaseous HCl present in the ambient air (Harrison and Pio 1983).

**SUMMARY AND CONCLUSIONS**

Intensive aerosol sampling during postmonsoon, premonsoon, and monsoon seasons at Phortse in the Nepal Himalayas showed diurnal variations and variations at the time scale of several samples (i.e., a week) in the concentrations of water soluble inorganic chemical species. Generally, higher concentrations in the daytime and lower concentrations in the nighttime samples reflect the diurnal variation in the regional valley wind systems and also the influence of scavenging of particles by predominantly nighttime precipitation events. The influence of the former is dominant. Additionally, distinct variations in aerosol concentrations occurring at weekly time scales were related to precipitation events. This time-scale cleansing of atmospheric constituents by precipitation resulted in decreased concentrations. However, these precipitation events also coincided with considerable changes in circulation; changes in the source regions associated with the changes in the circulation may therefore also be affecting the aerosol concentrations.
Event-based precipitation sampling showed that precipitation chemistry in general mimics variability in aerosol chemistry. While the aerosol concentrations are not reflected in corresponding precipitation events on a sample-by-sample basis, the relationship between the ionic concentrations in the 2 media improves as the samples are averaged over several days to a season. This supports the potential for using glaciochemical time series from the Himalayas to infer the atmospheric composition of the past in that region. Scavenging ratios were found to be highly variable and the mean values were relatively high for most species, except \( \text{SO}_4^{2-} \). High scavenging ratios for \( \text{NO}_3^- \) suggest enrichment in precipitation due to the presence of gaseous \( \text{HNO}_3 \) in the air. Similarly, \( \text{Cl}^- \) is also enriched in precipitation compared to aerosol, and in precipitation it shows a close relationship with \( \text{Na}^+ \). This is attributed to the scavenging of HCl present in the ambient air, likely of the same source as \( \text{Na}^+ \) (i.e., sea salt particles, fractionated due to reaction with \( \text{H}_3\text{O}^+ \) in the air. Similarly, \( \text{Cl}^- \) is attributed to higher solubility of gaseous \( \text{NH}_3 \) in the air.

In addition, low fractionation of precipitating air masses due to vigorous circulation is also likely responsible for the apparent enhancement of \( \text{Cl}^- \) with respect to \( \text{Na}^+ \) in precipitation. Enrichment of \( \text{NH}_4^+ \) in the precipitation with respect to \( \text{SO}_4^{2-} \) is attributed to higher solubility of gaseous \( \text{NH}_3 \) compared to \( \text{SO}_4^{2-} \). Furthermore, similar enrichment in the aerosol during a dry episode in the monsoon sampling is attributed to the presence of \( \text{NH}_3 \) in the ambient air from areas in the neighborhood of the sampling site. The present data sets are too limited to suggest the observed relationships as conclusive. Continued observations of synchronous aerosol and precipitation chemistry in the future may substantiate such relationships, enabling us to better interpret the glaciochemical data from the Himalayas.

EOF analysis shows that there is a dominant transport mechanism controlling aerosol concentrations of all species except \( \text{Na}^+ \) and \( \text{Cl}^- \), both during premonsoon and monsoon seasons. While large-scale thermal winds and monsoon circulation are the predominant transport mechanism operating in the premonsoon and monsoon seasons, respectively, remarkable similarities between EOF1 for both seasons suggest that both transport mechanisms have similar pathways and incorporate pollutants from similar source regions. EOF2 during the monsoon represents marine contributions to the aerosol, transported by southeasterly monsoon circulation, while during premonsoon EOF2 likely depicts distant maritime sources transported by westerly disturbances. These results are promising concerning the use of glaciochemical data from the Himalayas to infer variations in continental contribution to the atmospheric composition of the regions and variation in relative strengths of monsoon and westerly circulation.

REFERENCES


