

# Depositional characteristics of $\text{NH}_4^+$ on Ürümqi glacier No. 1, eastern Tien Shan, China

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**ABSTRACT.** Investigation into the depositional and post-depositional processes of atmospheric  $\text{NH}_4^+$  on Ürümqi glacier No. 1 (UG1), China, was implemented within the Program for Glacier Processes Investigation (PGPI) campaign. Aerosol and surface snow samples were collected concurrently on a weekly basis from March 2004 to March 2005 in the UG1 accumulation zone at the headwaters of the Ürümqi river, eastern Tien Shan. All samples were analyzed for  $\text{NH}_4^+$  and other chemical species. This paper investigates the seasonal variations of  $\text{NH}_4^+$ . A significant linear relationship ( $R^2 = 0.70$ ,  $N = 21$ ,  $P < 0.01$ ) between  $\text{NH}_4^+$  concentrations in surface snow and aerosol was found during spring and summer, indicating that the warm–wet condition facilitates the air–snow exchange of  $\text{NH}_4^+$ . Humidity was found to be a significant meteorological factor influencing  $\text{NH}_4^+$  in deposition in autumn and winter. The  $\text{NH}_4^+$  concentration in aerosol clearly shows a trend similar to that in surface snow, suggesting that the variation of atmospheric  $\text{NH}_4^+$  might have been preserved in the surface snow. The possible source of  $\text{NH}_4^+$  is discussed in this paper.

## INTRODUCTION

As an atmospheric species, gaseous ammonia ( $\text{NH}_3$ ; most of which is the result of human activities) plays an important role in atmospheric chemistry (Fuhrer and others, 1996). The short turnover time of atmospheric ammonia species makes its variability in a location's precipitation an indicator of changes in the regional source, sink strengths and transportation or any combination of these changes (Hou and others, 2003). Ammonium ( $\text{NH}_4^+$ ), the ionic form of ammonia that forms when the latter is absorbed by water or reacts with acidic species in the atmosphere, presents relatively steady seasonality in snow and ice cores (Sigg and others, 1994). In recent years, increasing interest has been generated by the  $\text{NH}_4^+$  record preserved in glaciers, because of its advantage for ice-core dating and potential for evaluating anthropogenic influence (Sigg and others, 1994; Fuhrer and others, 1996).  $\text{NH}_4^+$  passes through two steps from the atmosphere to the ice-core record: (1) transfer from the atmosphere to snow; and (2) post-depositional processes in the snow after deposition. As a reversibly deposited species in the snow, the depositional processes of  $\text{NH}_4^+$  involve complex exchange between atmosphere and snow.

To further investigate the depositional processes of  $\text{NH}_4^+$  in alpine glaciers, this study – as a part of the Program for Glacier Processes Investigation (PGPI; Li and others, 2006; Wang and others, 2006; Zhao and others, 2006) – examines the characteristics and variations of  $\text{NH}_4^+$  in aerosol and surface snow on Ürümqi glacier No. 1 (UG1) at the headwaters of the Ürümqi river in eastern Tien Shan, northwestern China, during the period March 2004 to March 2005.

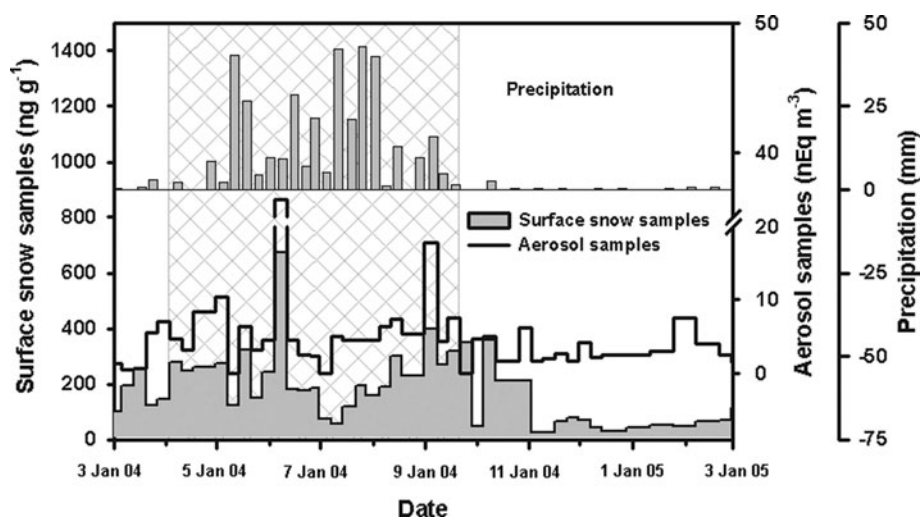
## SAMPLING SITE

UG1 (43°06' N, 86°49' E) is located in the eastern Tien Shan, central Asia, at the headwaters of the Ürümqi river. The eastern Tien Shan are surrounded by vast desert areas: the Taklimakan Desert to the south, the Gurbantungut Desert in

Junggar basin to the north and the Gobi Desert to the east. With a typical continental climate, the westerly jet stream prevails high above the mountains. The glacier is a north-west-facing valley glacier composed of east and west branches covering 1.677 km<sup>2</sup>. From 1959 to 2003, the annual equilibrium-line altitude has averaged approximately 4055 m a.s.l., where mean annual precipitation is about 645.8 mm a<sup>-1</sup> on the east branch (Wang and Zhang, 1985; Yang and others, 1988, 1992). The PGPI aerosol and snow-sampling site is located at 4130 m a.s.l., with no direct exposure to sunshine in winter due to the overshadowing of mountain ridges. The mean annual air temperature and precipitation at the site was –9.1°C and 700 mm w.e. between 1985 and 2003. The maximum precipitation occurred during June–September every year at the same time as the snowmelt. Spring, summer, autumn and winter were defined as April–May, June–September, October–November and December–March, respectively, in terms of the climate regime in the study area. There is only one large city and a few towns with industrial facilities in the area surrounding UG1. Ürümqi, the provincial capital of Xinjiang Uygur Autonomous Region, China, with more than two million inhabitants, is 105 km northeast of the PGPI site. Houxia, a small town in which two power plants, a cement plant and various other factories have been built since 1958, lies 50 km northeast, in the Ürümqi valley.

## METHODS

A total of 47 aerosol samples was retrieved from March 2004 to March 2005 on a weekly basis during dry clear weather. Samples were collected using 47 mm diameter Zefluor<sup>TM</sup> (2 mm pore size) Teflon filters (Gelman Sciences). Filtered air volumes were measured by an in-line flowmeter and converted into standard cubic meters (m<sup>3</sup>) using ambient temperature and pressure data. The particle collection efficiency (for particles as small as 0.035 µm) was estimated



**Fig. 1.**  $\text{NH}_4^+$  concentrations in aerosol and surface snow samples collected on UG1. The precipitation is included to categorize the dry and wet seasons (shaded portion).

to be >97%, based on the mean flow rate of  $1.27 \text{ m}^3 \text{ h}^{-1}$  over the filter (Liu and others, 1983). Strict trace-chemistry procedures were followed during sampling and transportation to prevent contamination, both in the field and the laboratory; this included the use of disposable polyethylene gloves, oronasal masks and pre-cleaned polyethylene sample containers (Zhao and others, 2006).

A total of 47 surface snow samples (usually 1–5 cm of uppermost snow) were collected at the PGPI site at 7 day intervals from March 2004 to March 2005. The surface snow consisted mainly of fresh snow during spring and summer (wet season) and of relatively old snow during autumn and winter because of sporadic precipitation (dry season). Every effort was made to collect fresh, well-preserved surface snow (i.e. snow not affected by post-depositional processes such as sublimation or melting). During the winter season, when there was insufficient snowfall the top 3 cm were sampled. However, if an accumulation event occurred prior to the scheduled sampling, the top 1 cm of fresh snow was collected. During the summer, sufficient fresh snow was usually available, and samples no more than 2 days old were collected from the top 3–5 cm. Details of the collecting procedure are reported by Li and others (2006).

Samples were kept frozen in the field, during transportation and in the laboratory until analysis. Analysis of duplicate samples, as well as of field and laboratory blanks, indicates that sample contamination during sample collection, transport and subsequent analytical procedures is negligible. Both aerosol and snow samples were analyzed in the Tien Shan Glaciological Station laboratory using a Dionex Ion Chromatograph model DX-320. Detailed methods are described by Buck and others (1992), Wake and others (1992) and Zhao and Li (2004).

## RESULT AND DISCUSSION

### Variations in aerosol and surface snow

The concentrations of  $\text{NH}_4^+$  in aerosol samples and surface snow samples, as well as of precipitation, are presented in Figure 1. In aerosol,  $\text{NH}_4^+$  concentrations averaged  $5.1 \text{ nEq m}^{-3}$ , fluctuating from values below the detection limit to a maximum of  $36.4 \text{ nEq m}^{-3}$  and showing an apparent

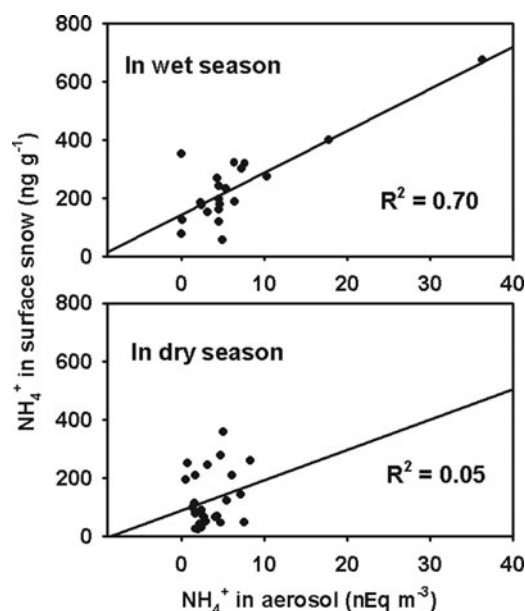
seasonal difference. The mean values of spring, summer, autumn and winter are  $5.4$ ,  $6.8$ ,  $5.9$  and  $2.9 \text{ nEq m}^{-3}$ , respectively. Thus, higher concentrations are found in summer. However, the mean concentration for this season is somewhat biased by the highest concentration (11 June 2004), which is believed to result from extreme pollution or transportation events. Atmospheric pollutants from Ürümqi are carried to the glacier by the low-level regional atmospheric circulations. Cloud from the factories in Houxia drifts in the river valley and can readily reach UG1 in the valley wind (Lee and others, 2003).

Surface snow  $\text{NH}_4^+$  concentrations (Fig. 1) were high from March to the end of June 2004. The highest peak in surface snow occurred on 11 June 2004, after which the concentration is characterized as less fluctuating and decreasing to a low level by the beginning of July 2004. From March to October 2004, despite an extremely low concentration on 5 October 2004, the concentration was characterized by high levels with a gradual change in the baseline.

Throughout the research period, the surface snow  $\text{NH}_4^+$  level demonstrated an explicit seasonality. The average concentrations in spring and summer were very similar, at  $214.0 \text{ ng g}^{-1}$  and  $210.4 \text{ ng g}^{-1}$ , respectively. Unlike in the aerosol, the surface snow  $\text{NH}_4^+$  concentration in autumn (an average of  $262.8 \text{ ng g}^{-1}$ ) was much higher than in the other seasons. During the winter,  $\text{NH}_4^+$  appeared to be relatively stable, the lowest average value being  $89.3 \text{ ng g}^{-1}$ . The mean concentration for all samples is  $173.4 \text{ ng g}^{-1}$  ( $9.6 \text{ nEq m}^{-3}$ ).

Several studies have reported aerosol data of  $\text{NH}_4^+$  on glaciers. In comparison with the results obtained from UG1, lower atmospheric  $\text{NH}_4^+$  concentrations, averaging  $0.6$ – $1.2 \text{ nEq m}^{-3}$  and  $2.33 \text{ nEq m}^{-3}$ , were found in the Summit region of central Greenland in 1990 (Silvente and Legrand, 1993) and, in Hidden Valley, Nepal Himalaya in 1994 (Shrestha and others, 1997). Similar summer maxima were found at coastal Antarctic sites, ranging from  $0.7$  to  $7.8$ – $14.4 \text{ nEq m}^{-3}$  (1991–94; Legrand and others, 1998). The concentration in Nunavut, Canada, which averaged  $5.0$ – $6.9 \text{ nEq m}^{-3}$  (Ianniello and others, 2002) is also comparable with those in UG1.

Comparison of  $\text{NH}_4^+$  concentrations in fresh snow samples from UG1 and other areas in the world demonstrates



**Fig. 2.** Linear correlation between aerosol and surface snow  $\text{NH}_4^+$  in both wet and dry seasons.

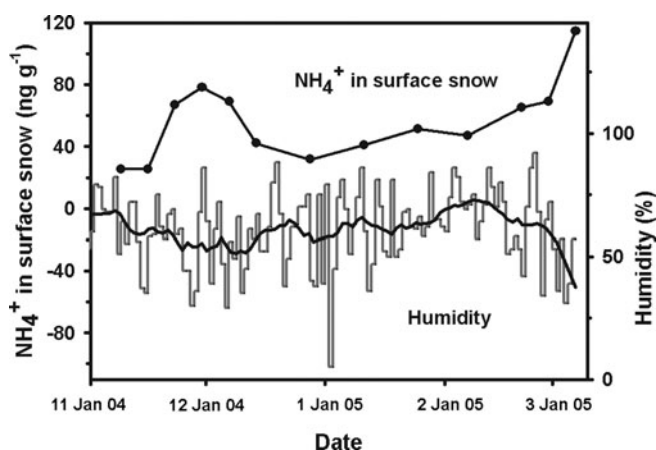
that UG1 has the highest mean value: about 26 times higher than the mean concentration found in the Summit region of central Greenland ( $6.3 \text{ ng g}^{-1}$ ; Silvente and Legrand, 1993). The concentrations at the South Pole are also much lower than those in UG1, with a mean concentration of  $18 \text{ ng g}^{-1}$  (Delmas and others, 1982). Snow collected from the Himalaya (Tibetan Plateau) shows relatively higher mean  $\text{NH}_4^+$  concentrations than other regions, except for UG1, ranging from values below detection to  $174.6 \text{ ng g}^{-1}$  (Mayewski and others, 1983; Shrestha and others, 1997).

The precipitation data shown in Figure 1 were obtained from the Daxigou Meteorological Station (3539 m a.s.l.), located 3 km from UG1. Most precipitation – over 80% of the annual value – occurred during June–August 2004. By contrast, precipitation seldom occurred during the periods March 2004 and October 2004–February 2005. According to the annual distribution of precipitation, the study period was divided into wet season (April–September 2004) and dry season (the other months).

### Relationship between surface snow and aerosol

The atmospheric flux of  $\text{NH}_4^+$  to the Earth's surface occurs by both dry and wet deposition processes. Both types of deposition depend strongly on meteorological parameters (e.g. precipitation, wind). Surface snow samples collected in summer (wet season) consisted mainly of fresh snow, whereas winter (dry season) surface snow samples were relatively old because of sporadic precipitation. The impact of dry deposition and post-depositional processes, such as wind erosion, sublimation and condensation, should be greater for the winter surface snow than for the summer, due to the low precipitation rate.

A significant linear relationship ( $R^2 = 0.70$ ,  $N = 21$ ,  $P < 0.01$ ) between  $\text{NH}_4^+$  concentrations in the surface snow and aerosol was found in the wet season (April–September 2004; Fig. 2). Poor correlation between aerosol and surface snow  $\text{NH}_4^+$  was found during the dry season (October–March;  $R^2 = 0.05$ ,  $N = 23$ ,  $P < 0.01$ ). Opposite relationships between aerosol and surface snow  $\text{NO}_3^-$  have



**Fig. 3.** Comparison between surface snow  $\text{NH}_4^+$  in dry season and humidity. The smoothed curve is generated from negative exponential smoother with sampling proportion 0.1 and polynomial degree 1.

been observed at the PGPI site (Zhao and others, 2006). In spring and summer, the  $\text{NH}_4^+$  concentration in the fresh surface snow is determined by two sources:  $\text{NH}_4^+$  within precipitation and  $\text{NH}_4^+$  scavenged from air by precipitation. The good correlation between aerosol and surface snow  $\text{NH}_4^+$  suggests a relatively stronger exchange of  $\text{NH}_4^+$  between atmosphere and snow surface than a scavenging effect. Spring and summer on UG1 are characterized by abundant precipitation, high humidity, high atmospheric temperature and intensive melting of the upper snowpack. Under certain meteorological conditions, deposited species with high vitality (like  $\text{NH}_4^+$ ) will quickly reach equilibrium with air (Andersen and others, 1999; Lee and others, 2003), leading to significant correlation between  $\text{NH}_4^+$  concentrations in aerosol and surface snow samples.

The relationship between  $\text{NH}_4^+$  in the aerosol and snow during the dry season is very complex and may be non-linear as a result of a disequilibrium between the air or snow and vertical  $\text{NH}_4^+$  gradients in the air above the area. To explore the cause of the poor correlation, data from the Daxigou Meteorological Station were compared with  $\text{NH}_4^+$  concentrations in surface snow. The results show that the temperature and local valley wind strength were not significantly related to the deposition of  $\text{NH}_4^+$ . The relationship can be seen in Figure 3, in which the  $\text{NH}_4^+$  is inversely associated with humidity (the data segment from 11 November 2004 to 7 March 2005 was selected because of the total absence of precipitation in this period). Further study is needed to probe the reasons for the relationship. In this case, the dry-deposited  $\text{NH}_4^+$  in snow did not reflect its level in the atmosphere as well as in months with high precipitation, probably because of perturbation resulting from humidity.

The  $\text{NH}_4^+$  concentration in the aerosol shows a trend similar to that in surface snow (Fig. 1), suggesting that the variation in atmospheric  $\text{NH}_4^+$  might have been preserved in the surface snow.

Investigation of the source of  $\text{NH}_4^+$  was made via its aerosol and surface snow values. In previous studies,  $\text{NH}_4^+$  has been reported to be a regionally and locally originated species due to the short turnover time of  $\text{NH}_3$  in the atmosphere (Hou and others, 2003). It arises primarily from the biological emissions of plants, soils and animals, and from the burning of biological material (forest and grass fires;

Adams and others, 1999). Anthropogenic emissions of ammonia arise mainly from the application of chemical fertilizer, bacterial decomposition of livestock wastes and energy consumption (Davidson and others, 1986; Buijsman and others, 1987; Bouwman and others, 1997). With the exception of energy consumption, all of the anthropogenic sources have explicit seasonality, with strengthened emissions in warm seasons, i.e. spring and summer. In a recent study of UG1 (Li and others, 2006),  $\text{NH}_4^+$  was categorized as an anthropogenic pollutant from the city of Ürümqi, and the town of Houxia; it was carried by the valley wind. In the course of our inspection, we found that de-pasturing of livestock is in progress from early spring (April–May) and again in the early autumn (around September). During both periods, thousands of sheep, cattle and horses migrate through the vicinity of UG1. These timings are concurrent with the two elevated periods in atmospheric  $\text{NH}_4^+$  variation. Hence, a hypothesis, which needs future study for confirmation, is that shepherding activities could be associated with the increased emission of  $\text{NH}_4^+$  in the study area.

## CONCLUSION

Year-round  $\text{NH}_4^+$  concentrations from aerosol and surface snow samples were examined to determine the seasonal variations and depositional behaviour of  $\text{NH}_4^+$  on UG1. The results show that the concentrations of  $\text{NH}_4^+$  in surface snow samples and aerosol varied in a similar way, having high mean values in spring, summer and autumn and low mean values in winter. Correlation analysis of  $\text{NH}_4^+$  in surface snow and aerosol was implemented. A significant linear relationship was detected during the wet season (spring and summer;  $R^2 = 0.70$ ,  $N = 21$ ,  $P < 0.01$ ), suggesting that high temperature and humidity facilitate the air–snow exchange of  $\text{NH}_4^+$ . A poor relationship was found during the dry season (autumn and winter;  $R^2 = 0.05$ ,  $N = 23$ ,  $P < 0.01$ ), which might be a result of perturbation as a result of humidity. Compared with other regions, the  $\text{NH}_4^+$  concentrations on UG1 are relatively high.

The potential sources of  $\text{NH}_4^+$  have been discussed in this study. The periods of high accumulation are thought to be associated with shepherding activities in the study area.

## ACKNOWLEDGEMENTS

This research was supported by the Knowledge Innovation Project of the Chinese Academy of Sciences (grant KZCX2-YW-127), the China National '973' Project (grant 2007CB411501), the National Natural Science Foundation of China (grants 40631001, 40571033, 40701034, 40701035 and J0630966), and the Fok Ying Tong Education Foundation (grants 101019). Support for this research was provided under the Program for Glacier Processes Investigation (PGPI), conducted by the Tien Shan Glaciological Station, Chinese Academy of Sciences.

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