2.6 BULK AEROSOL SO_4^{2-} AND NH_4^+: RELATIONSHIP TO AIR MASS TRANSPORT AT MOUNT WASHINGTON

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1.0 INTRODUCTION

Aerosols transported in the free troposphere can have a different composition than those transported in the boundary layer. Air transported in the free troposphere may have a different history, be isolated from surface sources, and be subjected to different rates and mechanisms of chemical transformation (Tanner et al., 1984). The aerosol record at Mount Washington (44.27°N, 71.30°W, ~1910 m), the highest peak in the northeastern United States, is unique because the majority of previous aerosol measurements have been made at lower altitudes. This study examined the seasonal cycles and regional scale meteorological controls on the chemical properties of bulk aerosols at the summit of Mount Washington. The site is operated by AIRMAP, a UNH air quality and climate program, and is part of an atmospheric observing network located in New Hampshire, USA.

2.0 METHODS

This study focused on data collected by AIRMAP from January 1999 through October 2004. During this period 24-hour bulk aerosol filters were collected from ~1200 – 1200 UTC, with field blanks collected every seven days. Data was not collected from 09 February 2003 to 09 June 2003 due to a fire on the summit, which disrupted the electrical power supply. Aerosol samples were collected on 90 mm Fluropore Teflon filters using a custom manufactured sampling device that was mounted external to the meteorological observing tower facing into the prevailing westerly wind sector. Water-soluble aerosol ions were extracted and analyzed by ion chromatography at the University of New Hampshire using methods recently described by DeBell et al. (2004b).

Backward trajectories were calculated with the Hybrid Single Particle Lagrangian Integrated Trajectories (HY-SPLIT) model (Draxler, 1999; Draxler and Rolph, 2003). Meteorological data from the Eta Data Assimilation System (EDAS) archive was used to calculate trajectories from January 1999 through April 2004. Starting in May 2004, trajectories were run using the EDAS 40-km archive grid. Seventy-two hour backward trajectories were calculated from the summit of Mount Washington twice daily at 0000 and 1200 UTC for the years 1999 through 2004. Aerosol-trajectory pairs were then sorted with respect to the concentration of aerosol chemical constituents. NOAA daily weather maps (NOAA, 1999-2004) were used to examine the meteorological features associated with several events, and samples collected during periods with winds from a consistent source sector were also examined.

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3.0 AEROSOL COMPOSITION AND TRENDS

The primary aerosol anion was sulfate (SO_4^{2-}), with ammonium (NH_4^+) as the principal cation. The concentrations of NH_4^+ and SO_4^{2-} peaked during the summer months, and the lowest concentrations occurred during the winter months (Figure 1). Sulfur dioxide oxidation rates are typically an order of magnitude lower in winter than in summer, consistent with our observed seasonal trend in aerosol SO_4^{2-}. In addition, a larger component of the wind distribution at this site is northwesterly during winter as compared to summer when it is westerly. The median aerosol nitrate (NO_3^-) concentration was highest in spring, followed by summer. The dominant anion during summer periods with elevated aerosol concentrations was SO_4^{2-}, but as SO_4^{2-} concentrations decreased during the cooler seasons, particulate NO_3^- made a larger contribution to the anion aerosol composition.

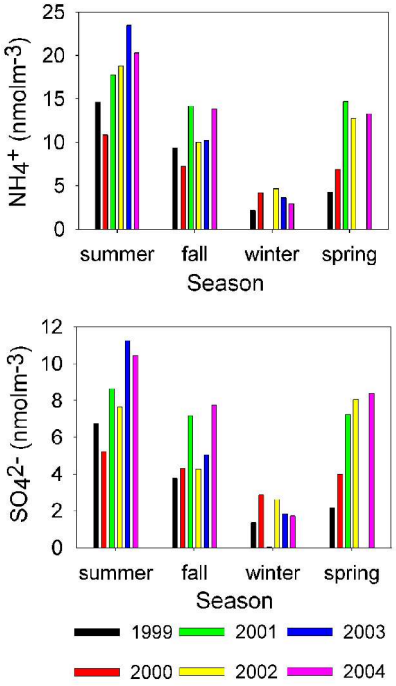

Figure 1: Median a) NH_4^+ and b) SO_4^{2-} as a function of year and season. Note that the scale is different for each plot. The four seasons are on the x-axis and the different colors indicate different years. The winter seasons are labeled by the January year. For example, winter 1999 includes January and February 1999, and Winter 2000 includes December 1999, January 2000 and February 2000.

This seasonality in aerosol ion concentrations may also reflect that Mount Washington is in the continental boundary layer during summer, but above the mixed layer and under the influence of the free troposphere during winter. In wintertime this may decouple the site from the surface, preventing direct reception of surface pollution. The summit is also covered in rime ice for a large portion of winter, and the low residence time of aerosols under icing conditions could depress winter concentrations and enhance observed seasonal differences.

The seasonal relationship between NH_4^+ and SO_4^{2-} showed slopes ranging from 1.3 in summer to 2.3 in winter (Figure 2). This indicates that during warmer months a mixture of $(NH_4)_2SO_4$ and NH_4HSO_4 was present, while it was mainly the latter in winter. Adding NO_3^- to the regression indicated that this ion made a notable contribution during winter and spring. The slope of the summer data in Figure 2 was 2 for the subset of data with SO_4^{2-} concentrations at or below 15 $nmolm^{-3}$, which indicates that there was typically enough NH_3 encountered en route to Mount Washington to neutralize the H_2SO_4 completely to $(NH_4)_2SO_4$ at these low concentrations. The fraction of un-neutralized or partially neutralized H_2SO_4 increased with summer SO_4^{2-} concentrations, and was reflected in the different slopes between samples with SO_4^{2-} concentrations above and below the 95th percentile in summer. The slope was 1.26 for SO_4^{2-} concentrations above the 95th percentile and 2.56 for SO_4^{2-} concentrations below the 5th percentile.

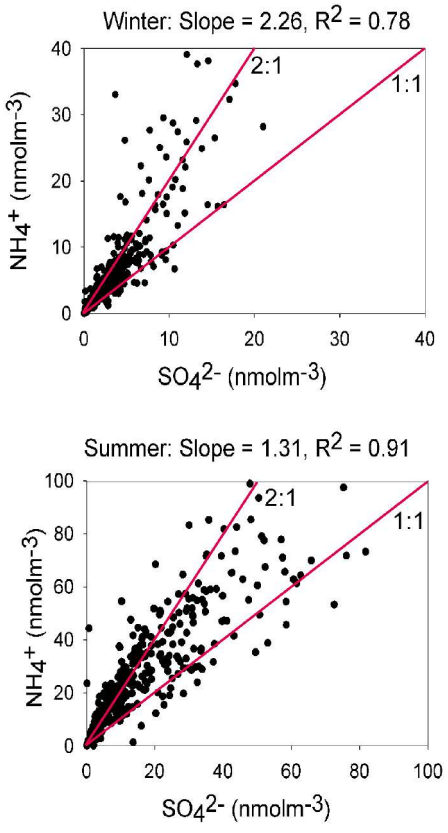

Figure 2: Scatter plots of 24-hour NH_4^+ versus SO_4^{2-} for winter and summer.

4.0 INTER-ANNUAL VARIABILITY

As indicated in Figure 1, the highest summer median concentration of aerosol NH_4^+ and SO_4^{2-} occurred during 2003. It should be noted that the highest summer mean concentration of these species and aerosol NO_3^- occurred during summer 2002. The high mean can be attributed to a major regional air pollution event that occurred in the second half of August (Angevine et al., 2004; Fischer et al., 2004), and to forest fire smoke transported from Quebec to New England in early July (Debell et al., 2004a). The lowest summertime median concentrations of all three ions were measured during summer 2000. The highest median fall concentrations of aerosol NH_4^+, SO_4^{2-}, and NO_3^- were measured in 2001. Higher than normal acidity was simultaneously measured during fall 2001 at rural monitoring sites in New York (Schwab and Demerjian, 2004).

5.0 REGIONAL TRANSPORT

In summer, samples associated with winds from the northwest sector and rural Canadian source regions typically contained a factor of 2 lower concentrations of NH_4^+ and SO_4^{2-} compared to samples collected under southwesterly and westerly winds. The highest median concentrations of NH_4^+ and SO_4^{2-} were found during periods with winds from the southwest (180° to 245°). Trajectory analysis (Figure 3) showed that high ($\geq$ 95th percentile) SO_4^{2-} and NH_4^+ ion concentrations were generally associated with westerly and southwesterly transport, and low ($\leq$ 5th percentile) SO_4^{2-} and NH_4^+ ion concentrations were generally associated with northwesterly transport. Periods of elevated SO_4^{2-} and NH_4^+ during the cooler seasons showed transport scenarios similar to those observed during summer episodes. Although the majority of the trajectories associated with elevated levels of these ions traversed the Midwestern source region south of the Great Lakes, there were a small number of trajectories which traversed the Atlantic seaboard. The 95th percentile concentrations of SO_4^{2-} and NH_4^+ occurred simultaneously more than 80 percent of the time.

6.0 CONCLUSIONS

This study confirmed that SO_4^{2-} and NH_4^+ were the dominant aerosol ionic species measured at Mount Washington. The seasonal cycles of these species, indicated a summer maximum and winter minimum for SO_4^{2-} and NH_4^+. This seasonality could not be explained by either the seasonal wind shift or changing SO_2 emissions, and was likely the result of seasonal oxidation rates of SO_2. The highest concentrations of SO_4^{2-} and NH_4^+ were associated with transport traversing pollution source regions in the Midwest and along the eastern seaboard. At Mount Washington, there was a notable difference between summer elevated aerosol events and those occurring during the cooler seasons. Sulfate was the dominant anion during summer; however, in cooler months NO_3^- was also present and contributed up to 98 % of the anion load.

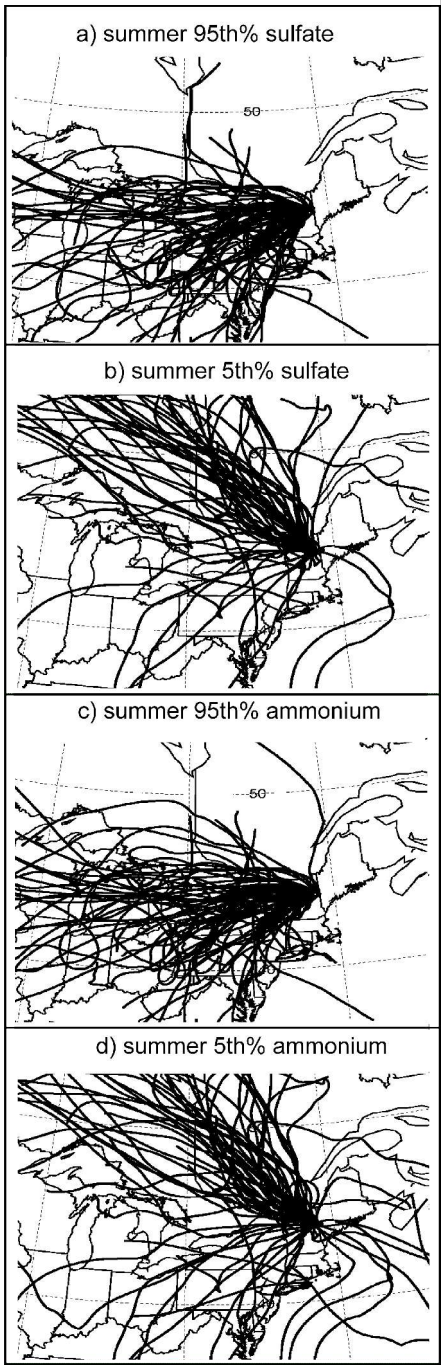

Figure 3: Backward trajectories associated with the beginning, middle, and end of summertime samples with: a) SO_4^{2-} above the 95th percentile, b) SO_4^{2-} below the 5th percentile, c) NH_4^+ above the 95th percentile, and d) NH_4^+ below the 5th percentile.

7.0 REFERENCES

Angevine, W. M., C. J. Senff, et al. (2004). Coastal boundary layer influence on pollutant transport in New England, *J. of App. Met.*, 43, doi:10.1175/JAM2148.1.

DeBell, L. J., R. W. Talbot, et al. (2004a). A major regional air pollution event in the northeastern United States caused by extensive forest fires in Quebec, Canada, *J. of Geophys. Res.*, 109, doi:10.1029/2004JD004840.

DeBell, L. J., M. Vozzella, et al. (2004b). Asian dust storm events of spring 2001 and associated pollutants observed in New England by the Atmospheric Investigation, Regional, Modeling, Analysis and Prediction (AIRMAP) monitoring network, *J. of Geophys. Res.*, 109, doi:10.1029/2003JD003733.

Draxler, R. R. (1999). Hybrid single-particle Lagrangian integrated trajectories (HYSPLIT): Verson 4.0 -- User's Guide and model description., *NOAA Technical Memorandum ERL ARL-230*, Air Resources Laboratory, 45 pp.

Draxler, R. R. and G. D. Rolph (2003). HYSPLIT (Hybrid Single-Partilce Lagrangian Integrated Trajectory) model access vial NOAA ARL READY Website (http://www.arl.noaa.gov/ready/hysplit4.html). Silver Springs, MD, NOAA Air Resources Lab.

Fischer, E. V., R. W. Talbot, et al. (2004). Summertime ozone at Mount Washington: Meteorological controls at the highest peak in the northeast, *J. of Geophys. Res.*, 109, doi:10.1029/2004JD004841.

National Oceanic and Atmospheric Administration (NOAA), 1999-2004: Daily Weather Maps, Weekly Series 1999-2004, Washington, D.C.

Schwab, J. J. and K. L. Demerjian (2004). Aerosol chemical composition in New York state from integrated filter samples: Urban/rural and seasonal contrasts, *J. of Geophys. Res.*, 109, doi:10.1029/2003JD004078.

Tanner, R. L., R. Kumar, et al. (1984). Vertical distribution of aerosol strong acid and sulfate in the atmosphere, *J. of Geophys. Res.*, 89, 7149-7158.

8.0 ACKNOWLEDGEMENTS

Funding for this work was provided through the Office of Oceanic and Atmospheric Research at the National Oceanic and Atmospheric Administration under grants NA03OAR4600122 and NA04OAR4600154. We would also like to thank AIRMAP team members Kevan Carpenter, Pieter Beckman, Sallie Whitlow, Karen Garrison, Don Troop, and Sean Wadsworth, together with the observers and interns at the summit of Mount Washington for their help in generating the data used in this work.