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Aerosol major ion record at Mount Washington

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[1] This study examined the seasonal cycles and regional-scale meteorological controls on the chemical properties of bulk aerosols collected from 1999 to 2004 at Mount Washington, the highest peak in the northeastern United States. The concentrations of NH_4^+ and SO_4^{2-} peaked during summer months. The pattern for aerosol NO_3^- was more complicated with relatively high median concentrations characterizing spring and summer months, but with major elevated events occurring during fall, winter, and spring. The seasonal relationship between NH_4^+ and SO_4^{2-} indicated that during warmer months a mixture of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 was present, while it was mainly the latter in winter. More acidity and higher concentrations of the major species were generally associated with winds from the southwest and west sectors. The highest (≥ 95 th percentile) concentrations of SO_4^{2-} and NH_4^+ were associated with air mass transport from major upwind source regions in the Midwest and along the eastern seaboard. The ionic composition and seasonal cycle observed at Mount Washington were similar to those measured at other northeastern sites, but the range and average concentrations were much lower. These differences were exaggerated during wintertime. Included in this paper are several Eulerian case studies of SO_2 conversion to SO_4^{2-} during transit from Whiteface Mountain, New York, to Mount Washington. The calculations suggest a gas-phase SO_2 oxidation rate of ~ 1 – 2% per hour and demonstrate the possibility of using these two sites to investigate the chemical evolution of air masses as they move from Midwestern source regions to northern New England.

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1. Introduction

[2] Atmospheric aerosols have been extensively measured because of their impact on human health, visibility, biogeochemical cycles, and climate. The aerosol record at Mount Washington, the highest peak (~ 1910 m) in the northeast, is unique because the majority of ground-based aerosol measurements have been conducted at lower elevations. Aerosols above the boundary layer can have a different composition than those within it because the air aloft may have a different air mass history, be isolated from surface pollution sources, and be subject to different rates

and mechanisms of chemical transformation [Tanner *et al.*, 1984]. The meteorology affecting aerosols at Mount Washington is also different from that influencing the more populated southern region of New Hampshire. This inland mountain site provides a unique perspective on large-scale aerosol transport to northern New England because it is free from local sea breeze influences, located further from major pollution source regions, and is situated above the boundary layer during most of the year.

[3] Fine aerosols over the eastern U.S. are dominated by substantial sulfate (SO_4^{2-}) [Malm *et al.*, 1994] and organic fractions [Quinn and Bates, 2003]. The transport of aerosol SO_4^{2-} to the northeast has been rigorously investigated and well established [Husain and Samson, 1979; Husain *et al.*, 1984; Poirot and Wishinski, 1986; Keeler and Pierson, 1994; Irons, 2004], and the SO_4^{2-} component comprises 50–60% of the total aerosol mass and reaches a maximum in summer months [Malm *et al.*, 2004]. Sulfate dominates the inorganic composition throughout the year, but the concentration of aerosol nitrate (NO_3^-) reaches a maximum in winter and early spring contributing 5–10% of the anion mass [Malm *et al.*, 1994; Malm *et al.*, 2004].

[4] Aerosol samples have been collected at the summit of Mount Washington consistently year round since 1999; thus this data set provides an opportunity to explore aerosol composition over a wide range of seasons, environmental

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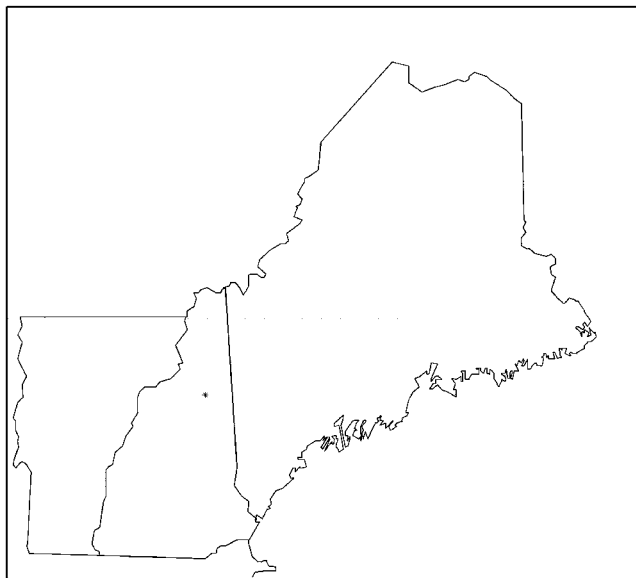


Figure 1. Location of Mount Washington.

conditions, and transport regimes. The aerosol data collected at Mount Washington has recently been used to explain several air pollution events in the region including those related to Asian dust [DeBell *et al.*, 2004b], Quebec forest fires [DeBell *et al.*, 2004a], and cold season ammonium nitrate episodes [Fischer and Talbot, 2005].

[5] The present paper is intended to provide a more comprehensive analysis of the summit aerosol record during all seasons in the context of similar measurements made by other groups in the northeast. The objectives of this study were to (1) identify the major ionic species in aerosols measured at this mountain site; (2) identify and explain the seasonal cycles of the major ionic species; (3) determine how aerosol composition varies with wind direction during each season; and (4) determine the air mass histories and source regions associated with the highest levels of the major ionic species in each season.

2. Methods

2.1. Mount Washington Sampling Site

[6] Mount Washington (44.27°N, 71.30°W) is located in the 3,035 km² White Mountain National Forest in northern New Hampshire (Figure 1). The tree line is approximately 600 m below the summit, with a surrounding rural landscape and nearby peaks reaching about 1500 m. Year-round bulk aerosol data have been collected at the summit of Mount Washington by the Atmospheric Investigation, Regional, Modeling, Analysis and Prediction (AIRMAP) program since December 1998. AIRMAP is a regional air quality and climate program based at the University of New Hampshire which operates an atmospheric observing network that includes Mount Washington as its highest-elevation site (www.airmap.unh.edu).

[7] Vehicles and an antique coal-fired locomotive are able to access the summit on most summer days; however, these combustion sources have a negligible influence on the local aerosol for the following reasons. With the exception of occasional service vehicles, cars are not allowed on the

summit cone where the aerosol measurements are conducted. Emissions from the antique coal-fired locomotive may interfere with aerosol measurements at points downwind (east of the summit), but they are not oxidized quickly enough to impact ionic aerosol measurements at Mount Washington. That is, if the plume from the locomotive reaches the summit, it usually occurs within tens of seconds after leaving the source. Furthermore, there is no indication from this analysis or visual inspection (color), that these emissions have affected our aerosol samples.

[8] The summit is home to the Mount Washington Observatory, which has been measuring temperature, dew point, visibility, sky cover, pressure, wind speed, and wind direction on the summit since 1932. The seasonal wind distribution for the years 1999 to 2004 at the summit of Mount Washington is given in Figure 2. The predominant wind directions during all seasons are westerly and northwesterly. During winter months the wind distribution favors northwesterly more than in other seasons. The average temperature on the summit is below 0°C from October to April, and the average annual temperature is -2.9°C [Grant *et al.*, 2005]. The maximum summer temperature recorded on the summit is 22°C and it has occurred twice, the first time in August 1975 and more recently in June 2003.

2.2. Sampling and Chemical Analysis

2.2.1. Mount Washington Sampling

[9] This study focuses on data collected by AIRMAP from January 1999 through October 2004. Twenty-four hour bulk aerosol filters were collected from ~1200–1200 UTC, with field blanks collected every seven days. Data were not collected from 09 February 2003 to 09 June 2003 due to a fire on the summit, which disrupted the electrical power supply.

[10] Aerosol samples are collected on 90-mm Teflon filters (Fluoropore, Millipore, Bedford, Massachusetts) using a custom manufactured sampling device. This device is mounted external to the meteorological observing tower facing into the prevailing westerly wind sector. Water-soluble aerosol ions are extracted and analyzed by ion chromatography at the University of New Hampshire using methods described recently by DeBell *et al.* [2004b]. Eight inorganic ions are quantified: Ca²⁺, Na⁺, Mg²⁺, K⁺, NH₄⁺, Cl⁻, NO₃⁻ and SO₄²⁻.

[11] Due to different air volumes for each sample, the detection limit concentration for each species was calculated separately for each sample as twice the standard deviation of the blanks associated with each sample divided by the air volume for that sample. This value was then adjusted to standard temperature and pressure, and converted to nmol m⁻³. The resulting average detection limits (in nmol m⁻³) for each species are: SO₄²⁻ (0.13), NH₄⁺ (0.21), NO₃⁻ (0.049), K⁺ (0.043), Mg²⁺ (0.049), Ca²⁺ (0.094), Na⁺ (0.37), and Cl⁻ (0.31).

[12] Sulfur dioxide was measured with a Thermo Environmental Instruments model 43C pulsed fluorescence detector modified following recommendations [Luke, 1997]. Briefly, ambient air entering the instrument was filtered using a 1-μm Fluoropore membrane and then dried using a Nafion drier with a zero air counterflow. The instrument was zeroed and calibrated every 12 hours using standards obtained from Scott-Marrin. As with all the

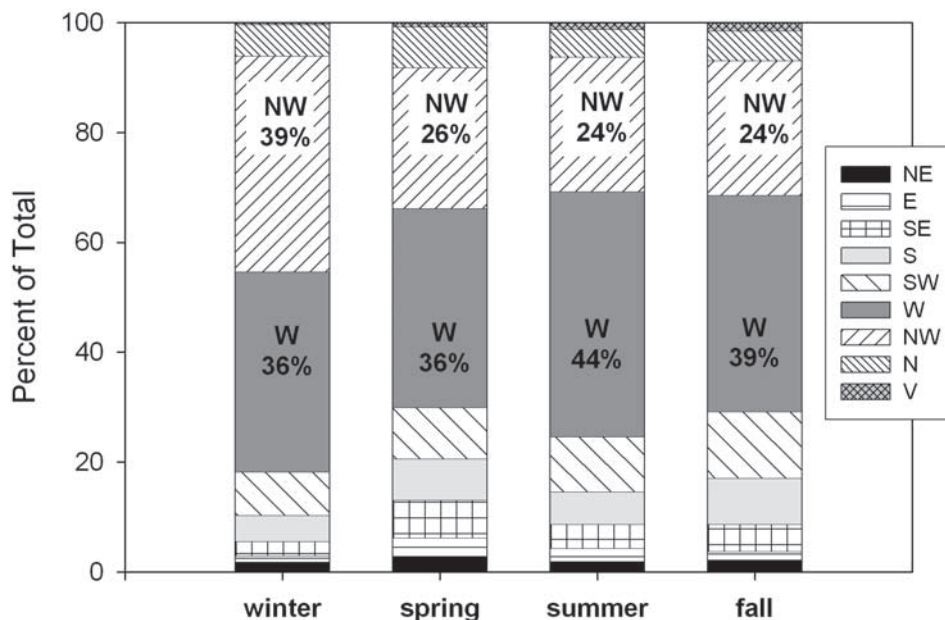


Figure 2. Hourly wind distribution at Mount Washington for the years 1999 through 2004 segregated by season. V indicates variable.

AIRMAP instrumentation, custom LabView software was used to automatically control these functions.

2.2.2. Whiteface Mountain Sampling

[13] Sulfur dioxide and aerosol SO_4^{2-} data was used from Whiteface Mountain, NY (44.4°N, 73.9°W, ~1500 m) to explore three summertime elevated SO_4^{2-} events at Mount Washington. At Whiteface Mountain aerosol SO_4^{2-} samples were collected daily using high-volume samplers on 20 cm x 25 cm Whatman 41 filters. The sampling system at Whiteface Mountain has been in continuous operation since June of 1978 [Husain and Dutkiewicz, 1990]. The suitability of the filter for aerosol SO_4^{2-} determination has been established [Canelli and Husain, 1982]. Daily filters were analyzed for SO_4^{2-} using ion chromatography [Husain et al., 1984]. Analytical performance was controlled by analyzing digestates of blank filters, standard SO_4^{2-} solution, samples spiked with known SO_4^{2-} , and quality control samples provided by a separate laboratory. Blank values were <0.01 mg SO_4^{2-} /liter, whereas recoveries for all quality control samples were 90–105%. At least 5% of the samples in each batch were analyzed in duplicate. Precision was within $\pm 5\%$ (rsd) and overall analytical uncertainty within $\pm 7\%$ for most samples. Sulfur dioxide was measured daily at Whiteface Mountain with a Thermo Environmental Instruments model 43C pulsed fluorescence detector.

2.3. Backward Trajectories and Associated Analysis

[14] 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. This EDAS archive grid covers the continental U.S., has a horizontal resolution

of about 80 km, and a vertical resolution of 22 pressure surfaces between 1000 and 50 hPa. The 80-km EDAS archive grid was only available through April 2004, thus starting in May 2004 trajectories were run using the EDAS 40-km archive grid which replaced the 80-km grid. This EDAS archive grid also covers the continental U.S., has a horizontal resolution of about 40 km, and a vertical resolution of 26 pressure surfaces between 1000 and 50 hPa.

[15] Backward trajectories were calculated from the summit of Mount Washington twice daily at 0000 and 1200 UTC (7 PM and 7AM Local Time (LT)) for the years 1999 through 2004. They were calculated in 1-hour time steps for 72 hours back in time. Because the EDAS grid defines the local terrain below the actual altitude of the summit of Mount Washington, all trajectories were initialized from 1,200 m above the model ground level.

[16] Linking trajectories to aerosol samples is inherently difficult because the samples were collected over a 24-hour period, and the trajectories represent the history of the air arriving at Mount Washington at a specific point during the sample collection interval. In this transport analysis, each aerosol sample was paired with three trajectories, one at the beginning, middle, and end of the sampling period. Aerosol sample trajectory sets were then sorted with respect to chemical species concentration.

2.4. Meteorological Data and Analysis

[17] The Mount Washington Observatory provided hourly averaged summit wind direction as one of the following directions: north (N), northeast (NE), east (E), southeast (SE), south (S), southwest (SW), west (W), and northwest (NW). Wind direction was paired with 24-hour aerosol samples using the following logic. If the wind was constantly out of a given direction for 18 of the 24 hours during

Table 1. Summary of the Ionic Species for Mount Washington for the Period Between 1 January 1999 and 3 October 2004^a

	Statistic	Summer N = 532	Fall N = 474	Winter N = 485	Spring N = 456
NH ₄ ⁺	5th %	0.68	0.31	-0.01	0.31
	25th %	6.6	3.4	0.8	3.6
	Median	18	10	2.7	9.2
	Mean	29	18	5.5	17
	s.d.	45	25	10	25
	75th %	35	23	6.0	21
SO ₄ ²⁻	5th %	0.32	0.15	0.01	0.17
	25th %	2.9	1.9	0.38	1.8
	Median	8.1	4.8	1.5	4.7
	Mean	18	11	2.9	9.2
	s.d.	34	17	4.3	13
	75th %	21	13	3.8	11
NO ₃ ⁻	5th %	0.01	-0.01	-0.04	0.01
	25th %	0.31	0.19	0.06	0.29
	Median	0.91	0.62	0.29	1.1
	Mean	2.2	2.7	1.4	3.5
	s.d.	3.1	6.0	5.1	7.6
	75th %	3.0	2.6	0.78	3.4
Cl ⁻	5th %	-0.28	-0.29	-0.31	-0.24
	25th %	-0.07	-0.07	-0.08	-0.06
	Median	-0.02	-0.02	-0.03	0.00
	Mean	0.07	0.05	0.10	0.13
	s.d.	0.31	0.31	0.65	0.37
	75th %	0.16	0.10	0.10	0.24
Na ⁺	5th %	-0.08	-0.09	-0.14	-0.07
	25th %	0.14	0.04	0.00	0.11
	Median	0.40	0.24	0.16	0.45
	Mean	0.62	0.53	0.47	0.88
	s.d.	0.85	1.0	1.0	1.4
	75th %	0.80	0.60	0.54	1.1
Ca ²⁺	5th %	-0.01	0.00	-0.02	0.00
	25th %	0.16	0.10	0.02	0.10
	Median	0.41	0.33	0.07	0.40
	Mean	0.96	0.87	0.22	0.95
	s.d.	1.7	1.9	0.52	1.5
	75th %	1.2	0.82	0.22	1.2
Mg ²⁺	5th %	0.00	0.00	-0.01	0.00
	25th %	0.04	0.03	0.00	0.04
	Median	0.14	0.09	0.03	0.14
	Mean	0.29	0.25	0.07	0.32
	s.d.	0.47	0.56	0.14	0.51
	75th %	0.37	0.24	0.09	0.40
K ⁺	5th %	0.02	0.00	-0.01	0.00
	25th %	0.15	0.05	0.02	0.06
	Median	0.34	0.16	0.05	0.17
	Mean	0.51	0.28	0.09	0.29
	s.d.	0.68	0.39	0.15	0.33
	75th %	0.65	0.37	0.12	0.39
	95th %	1.5	0.93	0.31	1.0

^aSamples with ions at concentrations below the detection limit were included in the statistics. Because of this, there is scatter around zero for the less prevalent ions, and negative numbers were calculated for the 5th percentile of some species. All values for ion concentrations are in nmol m⁻³.

the collection period (i.e., 75% of the sample time) the sample was paired with that direction. If the wind was not constant from one direction, but rather fluctuated between neighboring sectors 90% of the time, then the sample was

labeled as the sector between those two directions. For example, if the wind fluctuated between the W and NW over a 24-hour period, then the aerosol sample was classified as west-northwest (WNW).

3. Aerosol Composition and Seasonal Trends

3.1. Chemical Composition Summary

[18] In all seasons, the primary aerosol anion was SO₄²⁻, with NH₄⁺ as the principal cation. Nitrate was the second most abundant anion. With the exception of several large episodes during the cooler seasons [Fischer and Talbot, 2005], aerosol NO₃⁻ was present at concentrations nearly an order of magnitude less than aerosol NH₄⁺. Chloride, Na⁺, Ca²⁺, Mg²⁺ and K⁺ contributed less to the overall ionic composition, and they were often below the limit of detection. Chloride was only above its limit of detection in ~20% of the samples, while Na⁺ was above its limit of detection in ~60% of the samples. Calcium and Mg²⁺ were above their respective limits of detection in ~75% of the samples, while K⁺ was detectible ~80% of the time. These minor ions were below the limit of detection most frequently during wintertime.

[19] Table 1 presents a detailed statistical summary by season of all aerosol ionic species measured at Mount Washington. As explained in section 2.2, detection limits for each species varied from sample to sample. Samples with ion concentrations below the limit of detection were included in the statistical analysis. Therefore there was scatter around zero nmol m⁻³ for the less prevalent ions. The fluctuations around zero concentration were not important for SO₄²⁻, NO₃⁻, and NH₄⁺ except in winter. During the other seasons they were below the detection limit in ≤3% of the samples. Handling the statistics in this manner (i.e., using negative numbers) does affect the results for less prevalent species (i.e., makes them lower), but ignoring samples below the limit of detection creates artificially enhanced concentrations. For this reason the statistics in Table 1 have also been calculated using half the limit of detection values for ion concentrations below the limit of detection. The results calculated both ways are comparable except for the 5th percentile, and together they add robustness to our compositional summary.

[20] The aerosol ionic composition and seasonal cycle observed at Mount Washington was similar to that measured at other sites in the northeast [Malm et al., 1994; Malm et al., 2004; Schwab and Demerjian, 2004]. The data presented in Table 2 indicate that the major differences between aerosols measured at Mount Washington and at other sites were that the range and average concentrations were much lower at Mount Washington during all seasons [Malm et al., 1994; Jordan et al., 2000; Lefter and Talbot, 2001; Malm et al., 2004; L. D. Ziemba et al., Aerosol acidity in rural New England: Temporal trends and source region analysis, submitted to *Journal of Geophysical Research*, 2006; hereinafter referred to as Ziemba et al., submitted manuscript, 2006]. Annually SO₄²⁻, NO₃⁻, and NH₄⁺ concentrations at Mount Washington were a factor of 2 or 3 less than at monitoring sites in Maine, and at the nearby Great Gulf IMPROVE monitoring site. Concentrations were even lower compared to sites in New York. During summer months, average SO₄²⁻ concentrations at Mount Washington were

more than a factor of 2 less than concentrations measured at sites in southern New England and New York. Sulfate concentrations (mean = 2.9 nmol m⁻³) were an order of magnitude lower at Mount Washington compared to lower-elevation sites during winter months (Table 2).

[21] This large difference could be due to transport below the summit, low aerosol residence times on the summit or the fact that Mount Washington is located further from major pollution source regions to the west and southwest. Measurements in the continental atmosphere have indicated a gradual decrease in aerosol concentration with elevation within the boundary layer, with consistently lower concentrations in the free troposphere [Huebert, 1980; Gorzelska et al., 1994]. Mountain sites can experience lower particulate concentrations in comparison to low-elevation sites during winter because they are frequently above the mixed layer during these months [Dutkiewicz et al., 1987; Malm et al., 2002]. Mount Washington is only located well within the mixed layer on the warmest summer afternoons [Fischer et al., 2004; Grant et al., 2005], and winter on Mount Washington is characterized by high winds and precipitating conditions. A high frequency of freezing fog causes the summit to be covered in rime ice for a large portion of winter, which may reduce aerosol lifetimes on the summit. Wintertime rime ice samples collected during winters 2000–2001 and 2001–2002 indicate average SO₄²⁻ and NO₃⁻ mixing ratios of several thousand ppm [Ryerson et al., 2004]. Figure 3 provides an example of a regional aerosol NO₃⁻ event that occurred in early January 2002 that was not measured at Mount Washington likely due to the presence of heavy freezing fog. This type of occurrence likely accentuated the very low winter aerosol concentrations at this site.

3.2. Sulfate Seasonal Cycle

[22] Aerosol SO₄²⁻ exists primarily in the fine mode (<2.5 μm) in New England [Lefer and Talbot, 2001]. At Mount Washington over the period 1999–2004, the concentration of SO₄²⁻ peaked with a median of 8.1 nmol m⁻³ during the summer, dropped by 5-fold in winter to 1.5 nmol m⁻³, and was approximately equal in spring and fall at 4.7 nmol m⁻³ (Table 1). The highest monthly mean concentration generally occurred in August (23.2 nmol m⁻³) and the lowest in December (2.6 nmol m⁻³). The median concentrations of SO₄²⁻, NH₄⁺, and NO₃⁻ as a function of season and year are presented in Figure 4. The SO₄²⁻ seasonal cycle observed at Mount Washington agrees with other data for the eastern U.S. [Hidy, 1978; Malm et al., 2002], and measurements at both CASTNET [Baumgardner et al., 1999] and IMPROVE [Malm et al., 1994; Malm et al., 2004] monitoring sites in the northeast. The SO₄²⁻ seasonal cycle can be explained in general terms as a result of higher rates of summertime oxidation of SO₂ to SO₄²⁻ by photochemical intermediates such as the hydroxyl radical (OH) and aqueous-phase conversion by hydrogen peroxide (H₂O₂) and ozone (O₃) [Kunen et al., 1983; Botha et al., 1994; Baumgardner et al., 1999]. Trace element analyzed in conjunction with SO₄²⁻ data from Whiteface Mountain suggests that photochemical activity plays the dominant role in determining the SO₄²⁻ seasonal cycle in the northeast [Husain and Dutkiewicz, 1990].

[23] The 5-fold seasonal contrast between summer and winter at Mount Washington is more exaggerated than at other eastern U.S. sites. In addition to the harsh winter climate, a seasonal shift in prevailing winds from westerly to northwesterly during winter months (Figure 2) may also make a minor contribution to the SO₄²⁻ seasonal cycle at Mount Washington by transposing the upwind source region northward of major U.S. coal-fired steam generating plants. In previous work, the seasonal cycle of SO₄²⁻ at Underhill, VT was partially attributed to this regional shift in source region [Rahn and Lowenthal, 1985].

3.3. Ammonium Seasonal Cycle

[24] Ammonia emissions vary seasonally with a summer maximum [Gilliland et al., 2003] followed by spring, fall, and winter [Mathur and Dennis, 2003]. At Mount Washington NH₄⁺ concentrations track SO₄²⁻ concentrations in the summer and both NO₃⁻ and SO₄²⁻ concentrations during the cooler months. Similar to SO₄²⁻, the highest monthly mean NH₄⁺ concentration occurred in August (31.7 nmol m⁻³) and the lowest in December (4.7 nmol m⁻³) (Table 1). The seasonal cycle of NH₄⁺ is closely tied to SO₄²⁻ availability and seasonal patterns in NH₃ emissions at upwind locations. Overall, emissions of NH₃ in the U.S. are 75% smaller during colder seasons compared to summertime [Gilliland et al., 2003].

3.4. Nitrate Seasonal Cycle

[25] The median NO₃⁻ concentration was highest during spring, followed by summer. Aerosol NO₃⁻ can exist in both fine and coarse (≥2.5 μm) modes in sea salt and dust particles as described by Ziemba et al. (submitted manuscript, 2006). However, due to both the location and meteorology of the Mount Washington site, concentrations of both Ca²⁺ and Na⁺, indicators of soil dust and sea-salt aerosols respectively, were relatively low (Table 1), with the exception of Asian dust events in spring 2001 [DeBell et al., 2004b].

[26] Nitrate generally made a larger contribution to the total anion load during fall, winter, and spring compared to summer, when it contributed ≤10% of the anion load in ~40% of the samples (Figure 5). Figure 5 indicates that compared to summertime, there were more events in fall, winter and spring where NO₃⁻ contributed ≥50% of the anion load. Summer generally exhibited a higher median concentration, but large NO₃⁻ events occurred primarily in the colder seasons. High episodic concentrations of NO₃⁻ in winter and spring have been observed at AIRMAP [Fischer and Talbot, 2005] and Speciation Trends Network sites in the northeast [Chu, 2004]. These events correlate with anomalously warm wintertime temperatures in upwind regions. Similar to the other major ions, concentrations of NO₃⁻ were smaller at Mount Washington than at other northeastern monitoring sites (Table 2), especially in winter when average concentrations were nearly an order of magnitude lower at Mount Washington.

3.5. Relationships Between the Major Ionic Species and Particle Acidity

[27] A scatterplot of NH₄⁺ versus SO₄²⁻ by season (Figure 6) showed slopes ranging from 1.3 in summer to 2.3 in winter, indicating that during warmer months a

Table 2. Annual and Seasonal Means (nmol m^{-3}) for the Major Aerosol Ionic Species at Mount Washington and Other Monitoring Sites

Site	State	Year(s)	Annual Mean			Reference
			SO_4^{2-}	NO_3^-	NH_4^+	
Mount Washington	NH	99–04	11	2.5	18	This work
Mount Washington	NH	01	12	3.5	21	This work
Acadia	ME	01	20	5.2	45	Malm et al. [2004]
Acadia	ME	88–91	25	13	-	Malm et al. [1994]
Addison Pinnacle	NY	01	40	11	90	Malm et al. [2004]
Bridgeton	ME	01	23	5.0	51	Malm et al. [2004]
Cape Cod	MA	01	29	9.1	67	Malm et al. [2004]
Casco Bay	ME	01	26	7.4	58	Malm et al. [2004]
Connecticut Hill	NY	01	37	11	86	Malm et al. [2004]
Great Gulf	NH	01	21	3.5	46	Malm et al. [2004]
Lye Brook	VT	01	26	7.5	60	Malm et al. [2004]
Mohawk Mountain	CT	01	23	15	62	Malm et al. [2004]
Moosehorn	ME	01	19	4.4	43	Malm et al. [2004]
Old Town	ME	01	26	7.1	58	Malm et al. [2004]
Presque Isle	ME	01	18	4.5	41	Malm et al. [2004]
Proctor Maple	VT	01	22	9.1	54	Malm et al. [2004]
Quabin Reservoir	MA	01	28	10	67	Malm et al. [2004]
Whiteface Mountain	NY	86–89	24	3.7	39	Miller et al. [1993]
Winter Mean						
Mount Washington	NH	99–04	2.9	1.4	5.5	This work
Acadia	ME	88–91	27	6.5	-	Malm et al. [1994]
Ashland	ME	94	14	-	-	Baumgardner et al. [1999]
Howland	ME	94	15	-	-	Baumgardner et al. [1999]
Lye Brook	VT	94	21	-	-	Baumgardner et al. [1999]
New Castle	NH	96	-	18	41	Jordan et al. [2000]
New Castle	NH	97	-	15	50	Jordan et al. [2000]
Whiteface Mountain	NY	02	16	18	33	Schwab and Demerjian [2004]
Whiteface Mountain	NY	03	19	10	31	Schwab and Demerjian [2004]
Woodstock	NH	95	19	-	-	Baumgardner et al. [1999]
Spring Mean						
Mount Washington	NH	99–04	9.2	3.5	17	This work
Acadia	ME	88–91	34	4.9	-	Malm et al. [1994]
New Castle	NH	94	-	20	55	Jordan et al. [2000]
New Castle	NH	95	-	8	19	Jordan et al. [2000]
New Castle	NH	96	-	16	47	Jordan et al. [2000]
New Castle	NH	97	-	17	50	Jordan et al. [2000]
Whiteface Mountain	NY	02	23	4.8	36	Schwab and Demerjian [2004]
Summer Mean						
Mount Washington	NH	99–04	18	2.2	29	This work
Acadia	ME	88–91	23	6.5	-	Malm et al. [1994]
Ashland	ME	94	21	-	-	Baumgardner et al. [1999]
Ashland	ME	1995	17	-	-	Baumgardner et al. [1999]
Harvard Forest	MA	91–95	50	9.8	60	Lefer and Talbot [2001]
Howland	ME	94	29	-	-	Baumgardner et al. [1999]
Howland	ME	95	19	-	-	Baumgardner et al. [1999]
Lye Brook	VT	94	47	-	-	Baumgardner et al. [1999]
Lye Brook	VT	95	32	-	-	Baumgardner et al. [1999]
New Castle	NH	94	-	13	67	Jordan et al. [2000]
New Castle	NH	95	-	12	33	Jordan et al. [2000]
New Castle	NH	96	-	14	58	Jordan et al. [2000]
New Castle	NH	97	-	15	72	Jordan et al. [2000]
Whiteface Mountain	NY	01	42	1.6	44	Schwab and Demerjian [2004]
Whiteface Mountain	NY	02	28	3.2	44	Schwab and Demerjian [2004]
Woodstock	NH	95	23	-	-	Baumgardner et al. [1999]
Woodstock	NH	94	34	-	-	Baumgardner et al. [1999]
Fall Mean						
Mount Washington	NH	99–04	11	2.7	18	This work
Acadia	ME	88–91	27	8.2	-	Malm et al. [1994]
New Castle	NH	94	-	13	39	Jordan et al. [2000]
New Castle	NH	95	-	7.2	20	Jordan et al. [2000]
New Castle	NH	96	-	15	38	Jordan et al. [2000]
New Castle	NH	97	-	15	39	Jordan et al. [2000]
Whiteface Mountain	NY	01	22	6.5	28	Schwab and Demerjian [2004]
Whiteface Mountain	NY	02	23	8.1	39	Schwab and Demerjian [2004]
Woodstock	NH	94	17	-	-	Baumgardner et al. [1999]

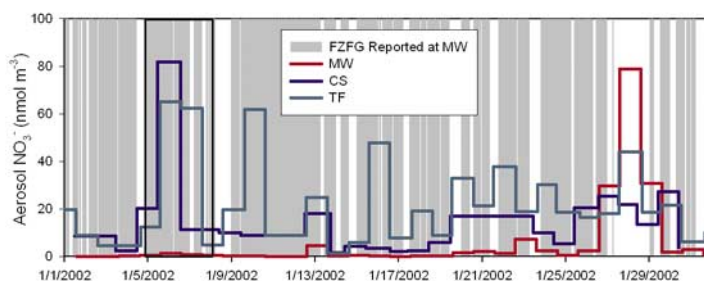


Figure 3. Aerosol NO_3^- at Mount Washington (MW) and two other Atmospheric Investigation, Regional, Modeling, Analysis and Prediction (Airmap) monitoring sites, Castle Springs (CS) and Thompson Farm (TF), for January 2002. The shading indicates periods where freezing fog (FZFG) was reported for Mount Washington. A regional NO_3^- event from 25 to 30 January is visible as a period with no fog on Mount Washington. The black box surrounds a regional NO_3^- event measured at the lower-elevation Airmap monitoring, but not at Mount Washington. During this period, freezing fog and blowing snow were reported at Mount Washington.

mixture of ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) and ammonium bisulfate (NH_4HSO_4) was likely present, but during winter $(\text{NH}_4)_2\text{SO}_4$ dominated. The slope of the summer data was 2.0 for the subset of data with SO_4^{2-} concentrations at or below 15 nmol m^{-3} , indicating that there was typically enough NH_3 encountered en route to Mount Washington to neutralize the H_2SO_4 completely at lower concentrations. The fraction of unneutralized 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 for summer. The slope was 1.3 for SO_4^{2-} concentrations above the 95th percentile and 2.6 for SO_4^{2-} concentrations below the 5th percentile.

[28] The aerosol hydrogen ion (H^+) concentration was roughly inferred using the following calculation: $[\text{H}^+] \sim 2 \times [\text{SO}_4^{2-}] + [\text{NO}_3^-] - [\text{NH}_4^+]$. As discussed by Ziemba et al. (submitted manuscript, 2006), we recognize that this type of calculation assumes that the only important cations at this site were H^+ and NH_4^+ and that there are more rigorous methods to determine aerosol acidity [Keene et al., 2004], but we lack the additional necessary measurements. A time series (Figure 7) for each sampling year indicates that the majority of aerosol samples were near neutral during the colder seasons. Events with elevated aerosol acidity occurred from spring through October, but the most acidic events during this period occurred during summer and early fall, specifically in August and September.

[29] Figure 8 is a scatterplot of $[\text{NH}_4^+]$ versus $(2[\text{SO}_4^{2-}] + [\text{NO}_3^-])$ measured at Mount Washington. The reduced major axis regression slopes are given by season, and they indicate the approximate degree of aerosol neutralization. Aerosol acidity is highest in summer and lowest in winter, which agrees with a similar analysis for the 2001 CASTNET data [Park et al., 2004]. The notable difference between the data for Mount Washington and the aggregated CASTNET data, was that there was a lower degree of acid neutralization at Mount Washington over the period 1999 to 2004. Previous studies have suggested that rural sites can have more acidic aerosol compositions than urban sites [Schwab and Demerjian, 2004]. Note that a slope of 2.0 indicates neutrality in Figure 6 while a slope of 1.0 indicates neutrality in

Figure 8. Comparing slopes between these two plots for all seasons indicates that aerosol NO_3^- made a negligible contribution to the estimated acidity during summer but contributed $\sim 30\%$ of the estimated acidity during winter and spring.

4. Seasonal Source Region Impacts

4.1. Summer

[30] In summer (Table 3), 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 flows. The highest median concentrations of NH_4^+ and SO_4^{2-} were found during periods with winds from the southwest (180° to 245°). The relationship between these ions for summer (Figure 9 and Table 4) indicates that aerosols from the south to southwesterly wind sectors were the least neutralized and that a mixture of H_2SO_4 and NH_4HSO_4 may have been present under these conditions. Aerosol NH_4^+ concentrations under southwesterly and southerly events rarely exceeded 65 nmol m^{-3} , which may indicate the limited amount of NH_x ($\text{NH}_3 + \text{NH}_4^+$) that is typically encountered en route to Mount Washington. The slope increased from the southwest to the northwest wind sector, as shown by the colored regression lines in Figure 9a. Although transport from this direction was not as common as transport from the predominant west and northwesterly sectors, pollution transported from the southwest contributed aerosol acidity in excess of $100 \text{ nmol H}^+ \text{ m}^{-3}$.

[31] During summer months, samples associated with winds from the northwest sector had the highest median concentration of aerosol NO_3^- . We speculate that this summer peak in aerosol NO_3^- concentrations in the northwesterly sector reflected both distant forest fires in the region and the lack of SO_4^{2-} (SO_2) in that sector, which allowed excess NH_3 to react with HNO_3 after the H_2SO_4 has been fully neutralized. For example, forest fire emissions were transported from Quebec to New England in early July 2002 [DeBell et al., 2004a], and explain the high NO_3^- concentration for that summer (Figure 4). Aerosol NO_3^- remained below 10 nmol m^{-3} during summertime

periods of elevated SO_4^{2-} and NH_4^+ with the exception of the period influence by these fires.

[32] Periods of summertime elevated ($\geq 75\%$) SO_4^{2-} and NH_4^+ at Mount Washington lasted from 1 to 6 days, and

occurred throughout the summer season. Over our six year study period, the maximum summertime SO_4^{2-} and NH_4^+ concentrations occurred during 12 August to 19 August 2002 where they reached 432 and 566 nmol m^{-3} respectively. A major air pollution event during this time was characterized by very elevated O_3 levels (i.e. >100 ppbv) both regionally and at the summit [Angevine et al., 2004; Fischer et al., 2004].

[33] The duration and frequency of summer SO_4^{2-} events was consistent with measurements at other sites in the northeast [Hidy, 1978; Rahn and Lowenthal, 1985; Keeler and Pierson, 1994]. Rahn and Lowenthal [1985] explained pollution aerosol in the northeast as the synergy of northeastern foreground pollution with midwestern components that appear as superimposed pulses with durations of 1 to 4 days. In addition to having higher median concentrations during summer months, westerly and southwesterly transport were also associated with the extremely elevated SO_4^{2-} and NH_4^+ events. The 95th percentile concentrations of SO_4^{2-} and NH_4^+ occurred simultaneously $>80\%$ of the time. The trajectories associated with samples exceeding the 95th percentile concentrations for these ions are shown in Figures 10a and 10c. Although the majority of the trajectories 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. There were also trajectories that traversed southern Ontario. Smelting in Sudbury, Ontario, and other Canadian SO_2 sources may explain the relatively few cases where trajectories traversed north of the Great Lakes, winds were from the northwest, and summertime SO_4^{2-} concentrations were greater than the 95th percentile. While mainly associated with trajectories traversing northwestern source regions (Figures 10b and 10d), the lowest concentrations of SO_4^{2-} and NH_4^+ were also associated with air masses from the east. It is possible to have low SO_4^{2-} with fast moving trajectories that pass through large SO_2 source regions, during periods with low SO_2 to SO_4^{2-} conversion rates [Pierson et al., 1989]. Our analysis of the transport associated with samples with SO_4^{2-} less than the 5th percentile also indicates that this is reflected in the aerosol record at Mount Washington.

[34] Examination of the trajectories associated with the 95th percentile concentrations showed that they traveled at a slightly higher altitude than those associated with the 5th percentile of SO_4^{2-} along the entire length of the trajectories. However, the difference may not be significant because it was never more than 300 m and reached this maximum difference at the furthest point from Mount Washington. Trajectories associated with the 95th and 5th percentile of summer aerosol NO_3^- concentrations did not show predominant source regions as clearly as those for SO_4^{2-} and NH_4^+ (not shown).

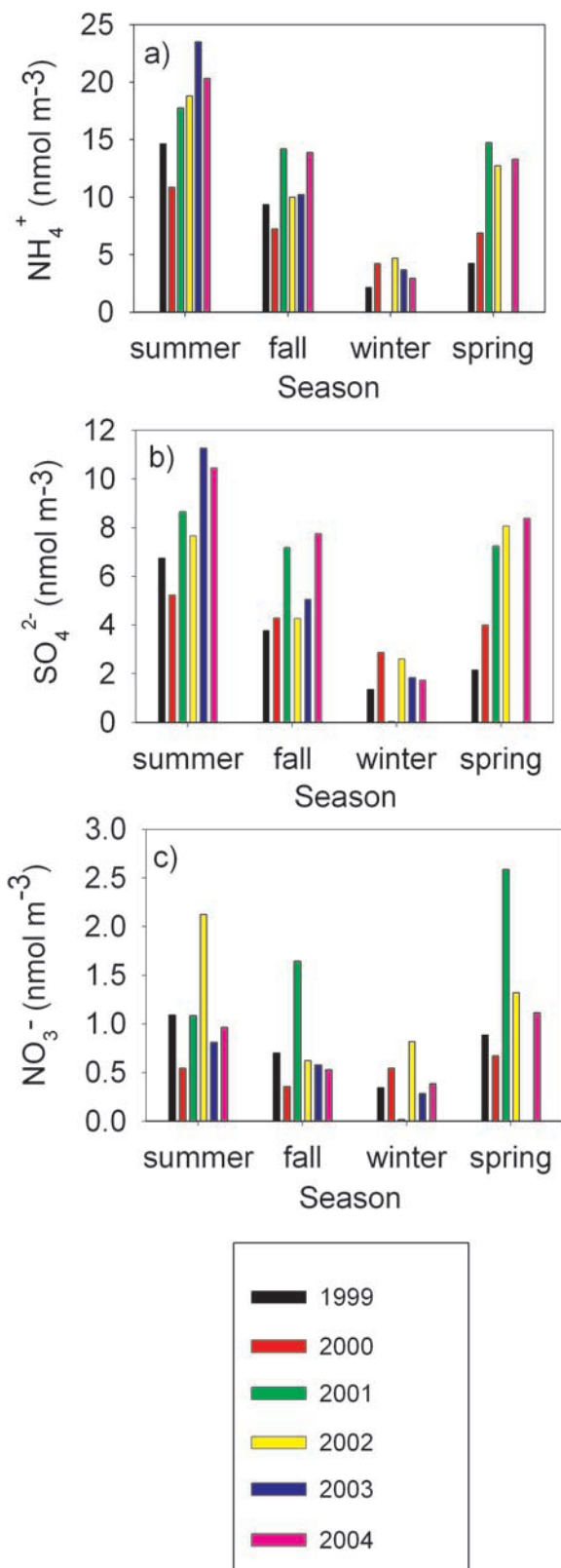


Figure 4. Median (a) NH_4^+ , (b) SO_4^{2-} , and (c) NO_3^- as a function of year and season. Note that the scale is different for each plot. The four seasons are on the x axis, and the different colors indicate different years. The winter seasons are labeled by the January year. For example, winter 2000 includes December 1999, January 2000, and February 2000.

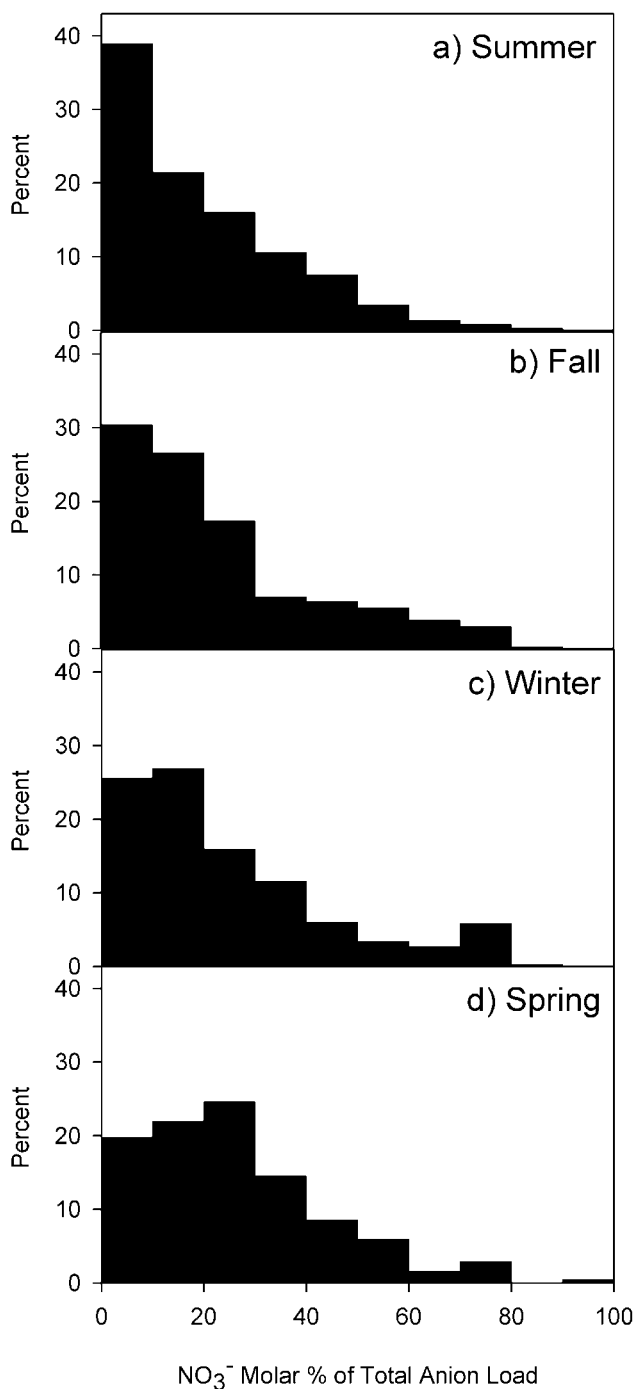


Figure 5. Histogram of the molar percent contribution of NO_3^- to the total anion load for (a) summer, (b) fall, (c) winter, and (d) spring. The y axis represents the percent of total samples collected during each season over the period January 1999 to October 2004.

[35] Our results confirm previous observations that the concentration of summertime SO_4^{2-} generally reflects the dominant SO_2 source regions especially during the summer months [Parekh and Husain, 1982; Poirot and Wishinski, 1986; Lefer *et al.*, 1999; Slater and Dibb, 2004]. Also consistent with our analysis, summertime wind segregated measurements of NH_3 and aerosol NH_4^+ at Harvard Forest

for the period 1991 to 1995 indicated high mean NH_3 concentrations from the northwest, but higher total NH_x concentrations from the southwest indicating larger total NH_3 emissions from the southwest sector with a large fraction of NH_3 converted to NH_4^+ [Lefer *et al.*, 1999]. Similar summertime source regions have been noted for O_3 and other anthropogenic gas-phase pollutants at Harvard Forest [Munger *et al.*, 1996] and Mount Washington [Fischer *et al.*, 2004].

4.2. Eulerian Case Studies of SO_2 Conversion to SO_4^{2-}

[36] As evident from Table 2, average summertime SO_4^{2-} concentrations at Mount Washington were slightly lower than recent results from Whiteface Mountain [Schwab and Demerjian, 2004]. They are also much lower than concentrations measured at Whiteface Mountain during other previous measurement intensives [Kelly *et al.*, 1984; Miller *et al.*, 1993]. The present day lower concentrations of SO_4^{2-} compared to these older data may be partially explained by historic changes in SO_2 emissions [Husain *et al.*, 1998; Husain *et al.*, 2004].

[37] Three events with elevated SO_4^{2-} at Mount Washington and westerly transport, occurring from 21–22 June 2002, 13–15 July 2002, and 20–22 August 2003, were

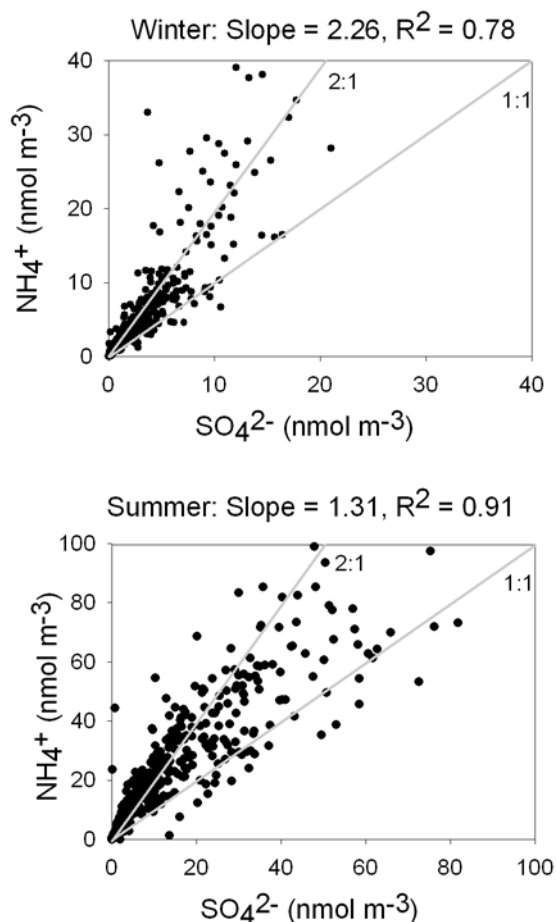


Figure 6. Scatterplots of NH_4^+ versus SO_4^{2-} for winter and summer. For fall, slope = 1.51 and $R^2 = 0.85$. For spring, slope = 1.91 and $R^2 = 0.83$.

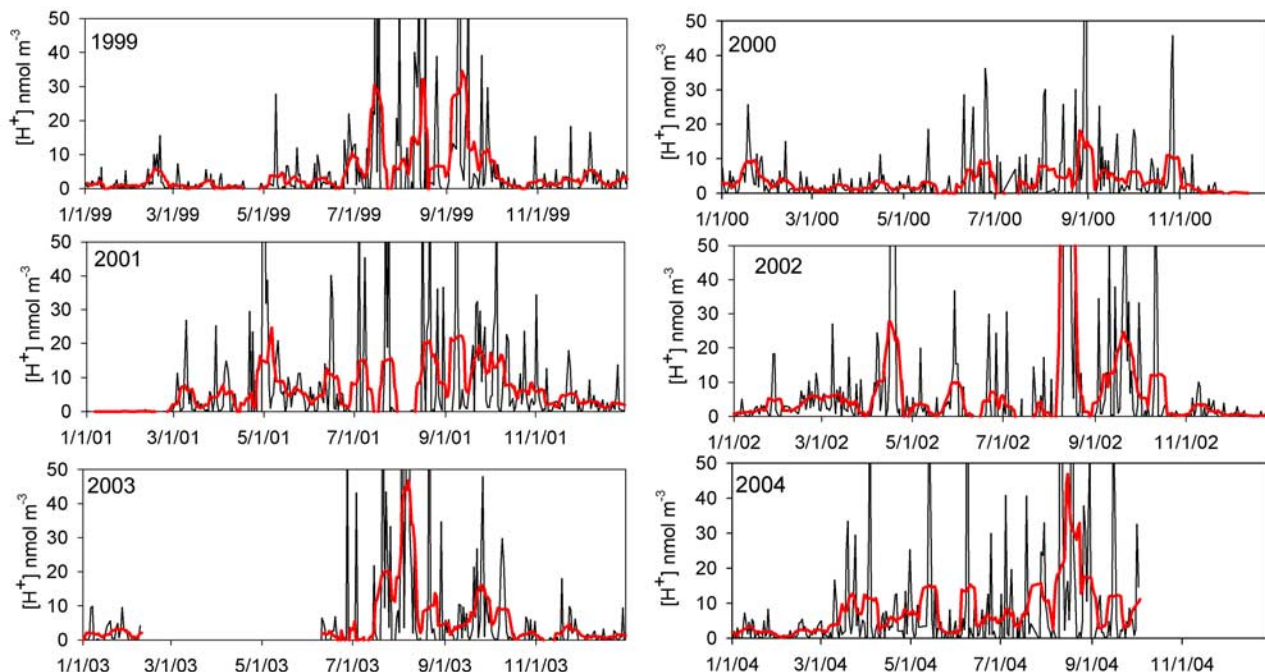


Figure 7. Yearly time series of $[H^+]$ in nmol m^{-3} estimated from $[H^+] = 2 \times [SO_4^{2-}] + [NO_3^-] - [NH_4^+]$. The red line presents a 10-day running mean.

used in conjunction with data from Whiteface Mountain to explore potential dilution and SO_4^{2-} formation from SO_2 oxidation between the sites (Figure 11). Whiteface Mountain lies ~ 210 km to the west of Mount Washington, and thus provides an opportunity to explore the evolution of these air masses as they traveled from high SO_2 emission regions (e.g. the Ohio Valley) to Mount Washington. As air masses travel from Whiteface Mountain to Mount Washington they pass over northern Vermont where the SO_2 emission density per county ranges from 0.54–2.7 tons per square mile. In contrast, the emissions in western New York are ~ 20 tons SO_2 per square mile (www.epa.gov/oar/data/geosel.html).

[38] The amount of dilution and oxidation that occurs between Whiteface and Mount Washington can be estimated using simultaneous aerosol SO_4^{2-} and SO_2 measurements at both sites. We can define two useful unknowns: (1) C, the fraction of SO_2 measured at Whiteface that is oxidized to SO_4^{2-} between Whiteface and Mount Washington and (2) D, the dilution factor, accounting for fractional loss of total sulfur between the two sites.

[39] In defining and using these two unknowns, some assumptions are necessary: (1) air mass transport between the sites occurred near or at the top of the boundary layer, so that dry deposition was a minor loss process compared to dilution, (2) the same dilution factor can be applied to both SO_2 and SO_4^{2-} , (3) SO_2 sources between Whiteface and Mount Washington are significantly less than those upwind of Whiteface Mountain, (4) the only loss processes for SO_2 are due to dilution and oxidation, so that one mole of aerosol SO_4^{2-} at Mount Washington

represents the loss of 1 mole of SO_2 , and (5) the transport pathway was cloud free so that the principal oxidation mechanism was

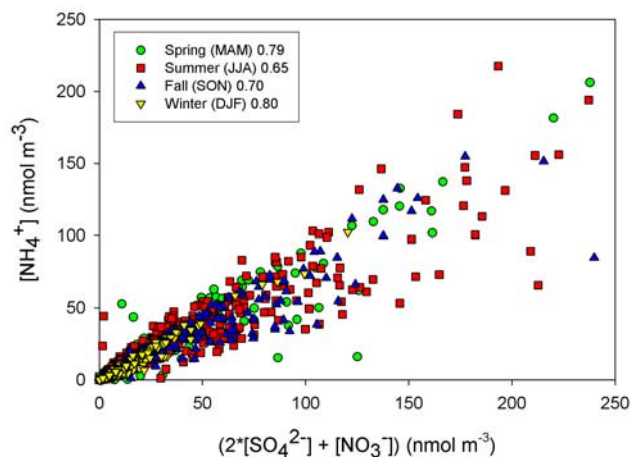


Figure 8. Scatterplot of $[NH_4^+]$ versus $(2 \times [SO_4^{2-}] + [NO_3^-])$ at Mount Washington segregated by season. The reduced major axis regression slopes are given by season. They indicate the degree of acid neutralization at the site.

Table 3. Median Concentration (nmol m^{-3}) of the Major Ionic Species for Each Major Wind Sector for Summer (1999–2004), Fall (1999 to 4 October 2004), Winter (Jan 1999 to 2003), and Spring (1999 to 2004, Missing 2003)

	W	WNW	NW	WSW → S
Summer	N = 143	N = 87	N = 40	N = 56
NH_4^+	23	12	13	30
SO_4^{2-}	13	5.1	4.2	22
NO_3^-	1.0	0.56	1.8	0.63
Fall	N = 101	N = 66	N = 48	N = 65
NH_4^+	13	7.4	4.5	22
SO_4^{2-}	6.1	4.1	2.2	16
NO_3^-	0.92	0.42	0.64	0.61
Winter	N = 96	N = 69	N = 110	N = 25
NH_4^+	3.7	1.8	2.1	5.3
SO_4^{2-}	2.1	1.1	1.5	4.6
NO_3^-	0.53	0.23	0.22	0.39
Spring	N = 88	N = 66	N = 42	N = 29
NH_4^+	10	7.2	7.1	15
SO_4^{2-}	4.8	4.5	3.1	12
NO_3^-	1.0	0.58	0.87	2.5

[40] Using these assumptions, we can mathematically express the relationship between concentrations at each site as,

$$\text{ST}_{\text{mw}} = \text{ST}_{\text{wf}}(1 - D) \quad (2)$$

where ST_{wf} is the total sulfur (nmol m^{-3}) measured at Whiteface Mountain ($\text{SO}_{2\text{wf}} + \text{SO}_{4\text{wf}}^{2-}$), and likewise at Mount Washington $\text{ST}_{\text{mw}} = (\text{SO}_{2\text{mw}} + \text{SO}_{4\text{mw}}^{2-})$. Then at Mount Washington,

$$\text{SO}_{4\text{mw}}^{2-} = \text{SO}_{4\text{wf}}^{2-} - D(\text{SO}_{4\text{wf}}^{2-}) + C(\text{SO}_{2\text{wf}}). \quad (3)$$

The mean concentrations of the measured sulfur species and the calculated variables for the three events are given in Table 5. We recognize that this method is a first-order approximation and represents total SO_4^{2-} production between the sites. It is possible to estimate the required OH concentration using C and by calculating the effective second-order rate constant for reaction (1). The results of these estimations are also given in Table 5. This simple model suggests a gas-phase oxidation rate of $\sim 1\text{--}2\%$ per hour based on an approximate 10 hour travel time. The

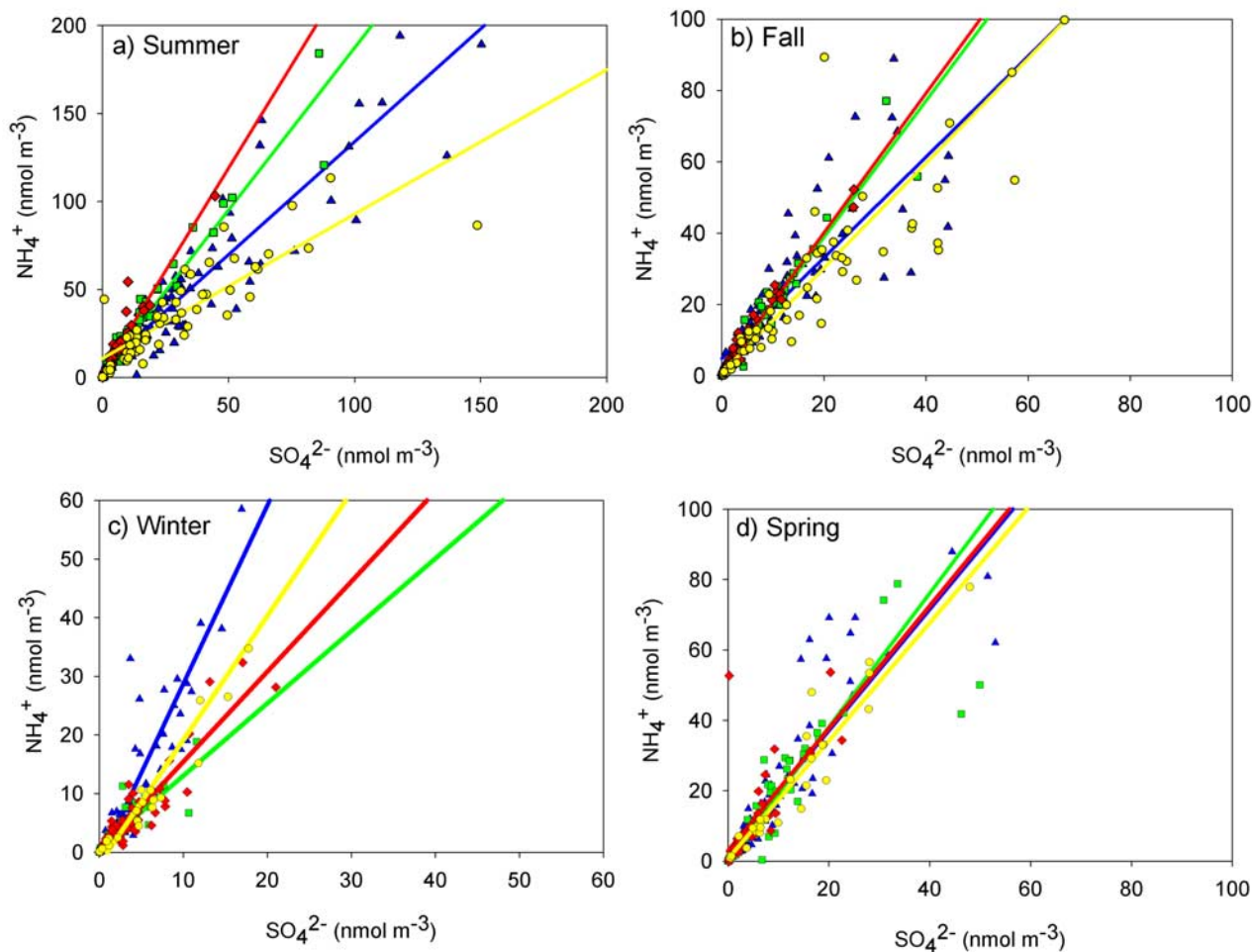


Figure 9. Relationship between NH_4^+ and SO_4^{2-} as a function of wind sector and season. The colors indicate the prominent wind directions: W (blue), WNW (green), NW (red), and WSW to S (yellow). The slope, R^2 values, and number of points in each category are given in Table 4.

Table 4. Slope, Number of Points, and R^2 Values Corresponding to Figure 9 for Each Major Wind Sector^a

	WSW → S (180°–245°)			W			WNW			NW		
	Slope	<i>n</i>	R^2	Slope	<i>n</i>	R^2	Slope	<i>n</i>	R^2	Slope	<i>n</i>	R^2
Summer	0.96	56	0.73	1.3	143	0.96	1.9	87	0.95	2.5	40	0.91
Fall	1.6	60	0.82	1.5	101	0.88	1.9	66	0.98	2.0	48	0.98
Winter	2.2	25	0.95	3.3	96	0.84	1.4	69	0.76	1.6	110	0.87
Spring	1.7	29	0.94	1.8	88	0.87	2.0	66	0.91	2.4	42	0.51

^aThe slopes are reported in molar ratios.

results discussed here are in agreement with those of *Husain and Dutkiewicz* [1992] although a different estimation technique was used [*Husain and Dutkiewicz*, 1992].

[41] Haze was reported at Mount Washington during all three events and maximum afternoon temperatures reached $\sim 17^\circ\text{C}$. Other meteorological conditions recorded

at Mount Washington during each of the events support and explain the relative changes in the calculated values of *D* and *C*. There were clouds reported above Mount Washington during all three events; however, the August 2003 event stood out with more clouds and reported fog. The increased oxidation rate in this event cannot be explained solely by the higher average temperature, so the high humidity and low clouds may explain the higher SO_2 conversion rates and indicate that cloud processing played a significant role during this event. There were also different average wind speeds measured at the summit of Mount Washington during each event, which indicates that the transport time also varied by event. The lowest average wind speeds were measured during the June 2002 event. The distance between the two sites divided by the average wind speed indicates that there was likely a longer travel time for this event of ~ 15 hours, which may explain the larger value of *D* for this event. When a longer transport time was used for

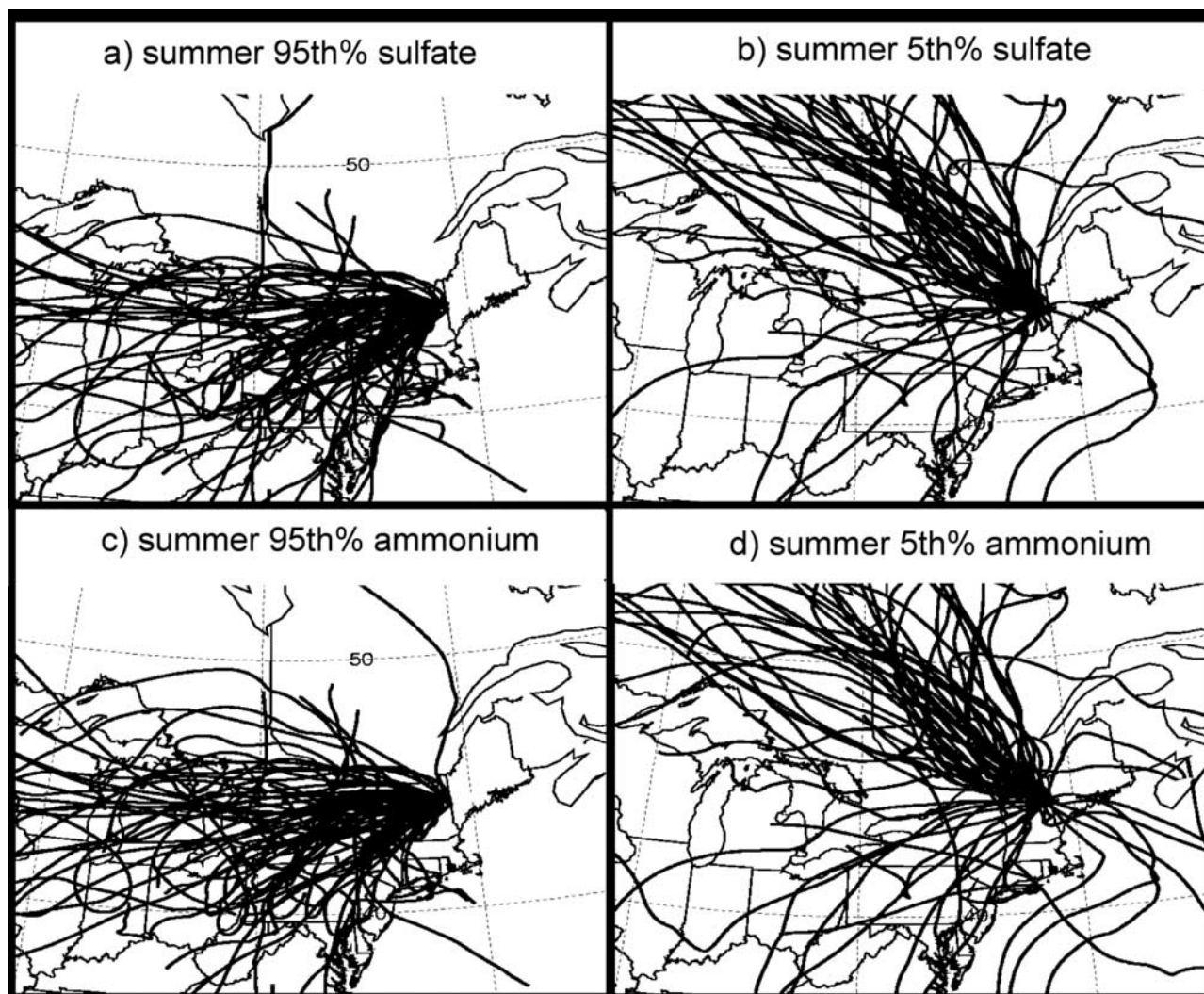


Figure 10. Trajectories associated with the beginning, middle, and end of samples with summertime (a) sulfate above the 95th percentile, (b) sulfate below the 5th percentile, (c) ammonium above the 95th percentile, and (d) ammonium below the 5th percentile.

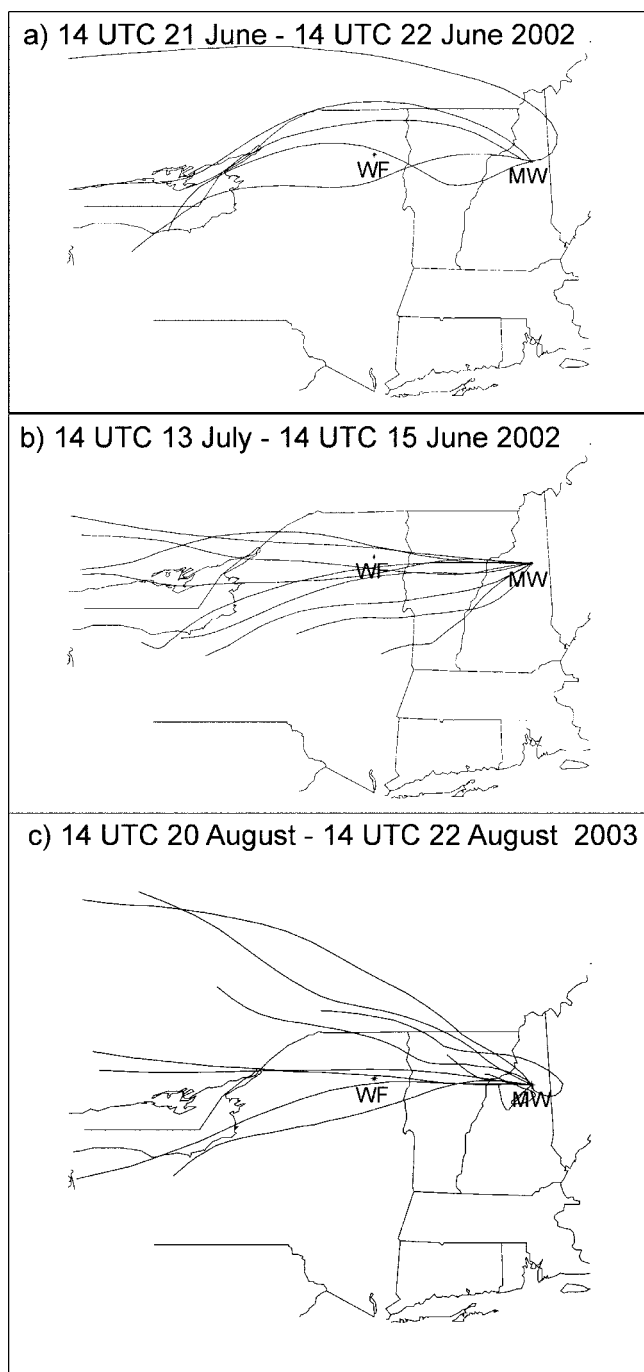


Figure 11. Twenty-four hour backward trajectories from Mount Washington during each of the three chosen high- SO_4^{2-} events. Trajectories were run every 6 hours from the start to the end of the Mount Washington sampling periods that were included in the calculations presented in Table 5. The dots indicate the location of Mount Washington and Whiteface Mountain.

this calculation (~ 15 hours), the oxidation rate per hour was reduced to 1.4%. The event during August 2003 had the highest average wind speed of the three events, which yielded a travel time of ~ 10 hours, and is likely reflected in the lowest value of D for these three events.

4.3. Fall, Winter, and Spring

[42] Periods of SO_4^{2-} and NH_4^+ $>$ 95th percentile during the cooler seasons showed similar transport as summer episodes. During fall, winter, and spring the major ionic composition varied with wind direction similar to summer, with the exception of aerosol NO_3^- . Unlike summer, during fall samples collected under winds from the west and southwest sectors had the highest mean and median concentrations of aerosol NO_3^- . The $\text{H}_2\text{SO}_4\text{-HNO}_3\text{-NH}_3$ thermodynamic framework implies that NH_4NO_3 aerosols form when excess NH_3 is available beyond that required for the neutralization of H_2SO_4 [Seinfeld and Pandis, 1998]. Particulate NH_4NO_3 formation is more favorable and stable during cooler months and the SO_2 to SO_4^{2-} conversion rate is reduced. Data from Mount Washington imply that the reduction in SO_4^{2-} during winter months exceeded the reduction in NH_3 due to temperature. A similar trend was discerned for Thompson Farm, an AIRMAP monitoring site in southern New Hampshire (Ziemba et al., submitted manuscript, 2006).

[43] During fall, samples collected under winds from west-northwesterly and northwesterly sectors were completely neutralized (similar slopes ~ 2), and samples collected under winds from westerly and southwesterly sectors contained a mixture of NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$ (similar slopes ~ 1.6). During winter months the pattern was reversed, and samples collected under winds from westerly and southwesterly sectors had larger slopes than samples collected under winds with a northwesterly component. The slope reversal in winter appears to be caused by the increased contribution from NO_3^- to the anion load during winter.

[44] In contrast to summer, spikes in aerosol NH_4^+ and SO_4^{2-} during the cooler months were accompanied by levels of aerosol $\text{NO}_3^- > \sim 10 \text{ nmol m}^{-3}$. Several of the notably high years in Figure 4 can be attributed to these types of events. In a few extreme cases, the aerosol composition shifted from a SO_4^{2-} to a NO_3^- dominated regime [Fischer and Talbot, 2005]. Closer examination of trajectories associated with elevated NO_3^- events during fall winter and spring (not shown) indicated that they were generally associated with winds from westerly and southwesterly sectors; however, events with west-northwesterly winds were also identified. It was rare to have $\text{NO}_3^- >$ 95th percentile associated with synoptic-scale transport from the eastern seaboard.

5. Conclusions

[45] This study confirmed that SO_4^{2-} , NO_3^- , 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 the seasonal wind shift and was likely the result of seasonal oxidation rates of SO_2 . Aerosol NO_3^- displayed a different cycle with more prominent peaks during the cooler seasons. Aerosol composition also varied with wind direction. More acidity and higher concentrations of the major species were generally associated with wind from southwest and west sectors. The highest concentrations of SO_4^{2-} and NH_4^+ were associated with transport traversing pollution source regions

Table 5. Measured Average Concentration of Aerosol SO_4^{2-} and SO_2 at Whiteface and Mount Washington During Three Summertime Events^a

	21–22 June 2002		13–15 July 2002		20–22 August 2003	
	WF	MW	WF	MW	WF	MW
Mean SO_4^{2-} (nmol m^{-3})	109	87	33	42	57	69
Mean SO_2 (nmol m^{-3})	96	38	78	44	89	47
Fraction of Total Sulfur Lost (D)		0.39		0.22		0.20
% SO_2 Oxidized per hour		2.1		2.2		2.7
Average Temperature at MW ($^{\circ}\text{C}$)		12		10		13
Rate constant ($\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$)		9.4×10^{-13}		9.5×10^{-13}		9.4×10^{-13}
OH (molecule cm^{-3})		6.2×10^6		6.5×10^6		8.0×10^6

^aAlso included are the calculated dilution factors and the percent of SO_2 measured at Whiteface that was oxidized per hour en route to Mount Washington. The percent oxidized assumes a 10 hour travel time between the sites. An air density of 2.6×10^{19} was used to calculate the OH concentration.

in the Midwest and along the eastern seaboard. The dominant anion during summer events was almost exclusively SO_4^{2-} . As SO_4^{2-} concentrations decreased during the cooler seasons, particulate NO_3^- made a larger contribution to elevated events at this site.

[46] Future research should continue to compare aerosol and gas precursor measurements at Mount Washington with those collected closer to upwind source regions, such as Whiteface Mountain, to investigate the chemical evolution of air masses as they move from Midwestern source regions, through upstate New York, and to northern New England. We have demonstrated the potential for such comparisons; however, shorter sampling intervals at both sites are necessary to improve future calculations. Aerosol composition and the seasonal cycles of the major ions have been established for Mount Washington. Future research should be directed toward understanding the interannual variability by exploring the link between regional climate and the aerosol burden at this site.

[47] **Acknowledgments.** We would like to thank AIRMAP team members together with the observers and interns at the summit of Mount Washington for operation of the AIRMAP monitoring sites. Financial support for our work was provided through the Office of Oceanic and Atmospheric Research of the National Oceanic and Atmospheric Administration under grants [#]NA17RP2632 and [#]NA03OAR4600122.

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