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Title: A 16-year comparison of fine particle and aerosol strong acidity at the interface zone (1,540 m) and within (452 m) the planetary boundary layer of the Great Gulf and Presidential-Dry River Class I Wildernesses on the Presidential Range, New Hampshire USA

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Abstract: Mount Washington, NH in the White Mountain National Forest, is flanked to the north-northeast and south by two Class I Wilderness areas, the Great Gulf and Presidential Range-Dry River Wildernesses, respectively. The Clean Air Act protects Class I area natural resource values from air pollution. Aerosol sulfate, a fine particulate component that is often transported long distances, is a known contributor to visibility degradation and acidic deposition. We examined summertime fine particulate aerosol mass and sulfate, strong acidity and ammonium concentrations from 1988 to 2004 on Mount Washington at two elevations, 452 and 1,540 meters (msl). The former site is within, and the latter at the interface of, the planetary boundary layer. Comparisons of sampling interval durations (10 and 24 hours), site vs. site, and different sampling methods are made. We also examine the extent to which aerosol sulfate is neutralized. Ten hour (daytime) compared to 24 hour samples have higher mass and aerosol sulfate concentrations, however paired samples are well correlated. Fine mass concentrations compared between the 452 m and 1,540 m sites (standard temperature and pressure corrected) show a weak positive linear relationship with the later being approximately 34% lower. We attribute the lack of a strong correlation to the facts that the

1,540 m site is commonly at the interface of and even above the regional planetary boundary layer in summer and that it can intercept different air masses relative to the 452 m site. Sulfate is ~19% lower at the higher elevation site, but comprises a greater percentage of total fine mass; 42% compared to 35% for the high and low elevation site, respectively. Aerosol strong acidity was found to increase with increasing sulfate concentrations at both sites. At the high elevation site, elevated mass and sulfate concentrations are associated with westerly and southwesterly regional flows.



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Dr. Singh,

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Please accept the manuscript entitled: *A 16-year comparison of fine particle and aerosol strong acidity at the interface zone (1,540 m) and within (452 m) the planetary boundary layer of the Great Gulf and Presidential-Dry River Class I Wildernesses on the Presidential Range, New Hampshire USA* submitted on line for consideration to be published in the journal Atmospheric Environment. I will be the corresponding author and have obtained agreement from all co-authors to submit this manuscript on their behalf. Please contact me with any questions.

Sincerely,

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1 1. INTRODUCTION

2 In the 1977 amendments to the Clean Air Act (CAA), the US Congress designated existing
3 National Parks greater than 6,000 acres and federal Wilderness and wildlife refuge lands greater
4 than 5,000 acres as "Class I areas" (Section 162 (a)) and provided protections against
5 degradation of air quality under the prevention of significant deterioration (PSD) provisions.

6 The PSD program has a permit process for major new and modified emission sources to
7 determine if they will cause an "adverse impact" on the air quality related values (AQRV) of
8 Class I areas. Those values are established by the federal land manager and can include scenic,
9 cultural, biological, and recreational resources. Visibility, an AQRV, was also singled out by
10 Congress not only to prevent future degradation through the PSD program but to improve
11 conditions back to natural conditions.

12
13 The Great Gulf (2,247 ha) and Presidential Range-Dry River (8,094 ha¹) Wildernesses (Figure 1) on the
14 Presidential Range, NH in the White Mountain National Forest (WMNF) are such designated Class I
15 areas. The AQRV's for these areas include visibility, vegetation health, and water and soil chemistry as
16 it relates to watershed health. The WMNF is one of the most visited of federal lands in the US, seeing
17 more than 6 million visitors annually. The Great Gulf and Presidential Range - Dry River Wildernesses
18 also comprise part of the largest alpine ecosystem in the eastern US (Kimball and Weihrauch, 2000).

19 [FIGURE 1 ABOUT HERE]

20
21 Suspended fine particulates, ≤ 2.5 micrometers in size ($PM_{2.5}$), cause visibility degradation by absorbing
22 and scattering light (Malm et al., 2004). Additionally, they are a regulated air pollutant under the
23 National Ambient Air Quality Standards (NAAQS) provisions of the CAA (Section 109) for human
24 health and welfare protections. Adverse human health effects of $PM_{2.5}$ include difficulty breathing,

1 decreased lung function, aggravated asthma and even premature death in people with heart or lung
2 disease (EPA, 2005). Ozone, PM_{2.5} and strong aerosol acidity exposure were associated with declines in
3 lung function in vigorously exercising hikers in a study on the Presidential Range (Korrick et al., 1999).
4 Korrick et al. (1999) found that the effects of PM_{2.5} and strong aerosol acidity persisted after adjustment
5 for ozone and were of the same magnitude as the ozone related impacts. PM_{2.5}, when deposited on
6 vegetation and other surfaces, contributes to acid loading of ecosystems, resulting in loss of important
7 nutrients and mobilization of toxins such as aluminum (Driscoll et al, 2001).

8

9 Interagency Monitoring of Protected Visual Environments (IMPROVE) compliance monitoring for
10 visibility protections in Class I areas in the northeast occurs at lower elevations well within the planetary
11 boundary layer (BL), due to sampling and electrical power infrastructure needs. Unlike the four other
12 designated Class I areas in the northeastern US, the Great Gulf and Presidential Range-Dry River
13 Wilderness areas occupy much higher topography, from 268 to 1,770 m, putting them within and above
14 the regional BL. Summer mixed-layer height of the atmosphere in the northeast typically ranges from
15 1,100 to 1,500 m (Freedman et al. 2001). Our monitoring program for PM_{2.5} using the MST Area
16 sampler² (herein referred to as the “Harvard Impactor”) at two elevations, which bracket the elevational
17 range of the Great Gulf and Presidential Range-Dry River Wilderness areas respectively, was initiated in
18 1988. In 1995 IMPROVE installed a sampler at our low elevation sampling site, considering it a
19 representative proxy of conditions in the two Wilderness areas.

20

21 It has been well established that air pollutant concentrations can differ with altitude, using airborne
22 observations, and that above versus within the BL air masses can have different origins, composition and
23 chemistry (Tanner et al., 1984, Taubman et al., 2004a, Peltier et al., 2007). However, little long-term

¹ Presidential Range - Dry River Wilderness area was expanded in 1984 to 11,080 ha but the new additional area is designated Class II.

1 work has been done at mountainous land-based locations that are at the interface of the BL and
2 influenced by the lower free troposphere (FT). Previous work has shown that ozone concentrations at
3 land sites on the Presidential Range, NH exhibit considerably different trends at the base and summit of
4 the mountain, with strong diurnal changes at the former and weak diurnal changes and higher nighttime
5 concentrations at the latter (Hill and Allen, 1994, Fischer et al., 2004). These differences in diurnal
6 ozone patterns are influenced by long-range transport, anabatic processes, the strength of nocturnal
7 temperature inversions in the region, and the consequent mixing downward of air masses aloft as such
8 inversions breakup during the daytime. Here, we examine how fine particulate aerosol mass and
9 chemistry, at land-based sample sites on complex terrain, vary with elevation and compare these results
10 with data obtained from altitudinal transects from aircraft.

11

12 The objectives of this study are (1) to compare summertime total PM_{2.5} mass and aerosol chemistry in
13 samples from within the BL and at the BL/FT interface of the BL on the Presidential Range over a 16
14 year period; (2) to compare co-located Harvard Impactor and IMPROVE results; (3) to understand how
15 much of the aerosol acidic SO₄⁻² is neutralized (by surface level sources of ambient ammonia) in these
16 Wilderness airsheds; and (4) to test how measured hydrogen ion associated with aerosols compares to
17 the inferred hydrogen ion calculations used in other studies (Malm et al., 1994, Ziemba et al. 2007). Our
18 study also benefits from and builds on the extensive meteorological measurements from the Mount
19 Washington Observatory and the recent analysis of how seasonal cycles and regional-scale meteorology
20 influence bulk aerosol chemistry on the summit of Mount Washington (Fischer et al. 2007).

21

22

²Specification by manufacturer: http://www.airdiagnostics.com/indoor_samp equip.html

1 **2. METHODS**

2 **2.1 Site Location**

3 The high elevation monitoring site is located 377 m below and approximately 1.7 km SW of the summit
4 cone of Mount Washington, NH (44° 16'N, 71° 18'W, 1,914 m ASL) and ~ 100 m E of the Appalachian
5 Mountain Club's Lakes of the Clouds (LOC) Hut at an elevation of 1,540 m (Figure 1). This remote site
6 does not have electrical grid service, which limits the scope of the monitoring to instruments operated by
7 batteries with solar panels. It is, however, more distant from tourist amenity pollutant sources on the
8 summit of Mount Washington. The lower elevation site (Camp Dodge) is at the base of Mount
9 Washington and 9.8 km northeast of the LOC site at 452 m elevation³. Mount Washington is ~250 km
10 north-northeast of the metropolitan Boston area and about 125-175 km northeast of the New Hampshire
11 cities of Nashua, Manchester and Concord.

12
13 The regional, summertime BL typically is 1,100 – 1,500 m above msl (Freedman et al., 2001) and on
14 Mount Washington it exhibits diurnal and vertical migration that is influenced by daily solar heating,
15 changing weather fronts, and the complex terrain of the surrounding mountain region. Above this
16 mixing-layer is the “free troposphere” where the approaching winds to the Presidential Range are more
17 geostrophic. The LOC sample site at 1,540 m is located in the alpine zone on the mountain, more
18 isolated from potential local pollution sources, and at the regional BL/FT interface. The Camp Dodge
19 site is located in a northern hardwood ecosystem and is more representative of atmospheric and pollutant
20 conditions within the BL.

³ This site was temporarily located ~0.5 km from Camp Dodge in 1990 and 1991 at the Base of the Mount Washington Auto Road.

1 **2.2 Sampling Regime**

2 Fine particulate mass and acid aerosol sampling began at Camp Dodge (452 m), in 1988 with day-time
3 10-hour (7am-5pm, EST) sampling intervals to relate PM_{2.5} concentrations with visibility conditions. A
4 midnight to midnight (EST) sampling interval was established for a small number of samples in 1995
5 and 1997, and then for all samples beginning in 1998, to be consistent with the Federal Reference
6 Method (FRM) and IMPROVE methodologies. The total number of days sampled at Camp Dodge
7 varied by year and ranged from 15 to 93 days. IMPROVE monitoring began in 1995 at Camp Dodge
8 with sampling every Wednesday and Saturday until late August 2000, when sampling switched to an
9 every third day schedule.

10

11 The LOC site (1,540 m) day-time 10-hour sampling began in 1990 and continued through 2003. In 1998
12 24-hour samples were also collected at LOC but due to electric power limitations 10-hour and 24-hour
13 samples were collected on alternate days with no overlap. Total number of samples collected at LOC
14 varied by year and ranged from 14 to 59 days. In 2002 and 2003 sampling was biased towards hazy days
15 to capture and document the acidity level of haze events that the IMPROVE method might miss due to
16 the every third day schedule. The number of high and low PM_{2.5} samples (above and below 10 PM_{2.5} μg
17 m⁻³) are well distributed in these years compared to others; therefore while this bias must be recognized
18 when interpreting the data it may not dramatically skew the dataset. In 2004 both sites switched to
19 sampling 24-hour intervals every third day to match sample schedule with the IMPROVE network.

20

21 **2.3 Harvard Impactor (HI) PM_{2.5} Method**

22 The Harvard Impactor (HI) monitoring system (Koutrakis et al., 1988; Marple et al., 1988; Turner et al.,
23 2000) is an inertial impactor based device operated in combination with a 10 liter per minute (lpm)
24 pump and used to sample aerosol particles ≤2.5 μm in diameter. The HI sampler, as used for acidic

1 sampling, consists of three parts: an aluminum honeycomb denuder inlet, a 2.5 μm diameter cut
2 impactor stage with an oiled porous stainless steel plate, and a base which holds a 37 mm diameter
3 Teflon filter. Particles $\leq 2.5 \mu\text{m}$ in diameter pass down into the base where they are collected on the
4 Teflon filter. The honeycomb denuder is coated with citric acid, which removes $\sim 93\%$ of ambient
5 ammonia gas that might neutralize the acid aerosol on the sample filter (Koutrakis et al., 1988). Due to
6 this efficiency and other small negative artifacts, all particle strong acidity measurements should be
7 considered minimum estimates. Pump flows were checked and adjusted daily using rotameters
8 calibrated for each of the two elevations. Field blanks were set out throughout the season and treated the
9 same as a sample but without drawing flow through the impactor unit. Filters were handled exclusively
10 within a glove box containing citric acid-coated cellulose paper to remove any ammonia and were
11 shipped to the Harvard School of Public Health laboratory enclosed in sealed plastic bags with fresh
12 citric acid-coated paper.

13
14 The mass of each filter was measured before and after sampling on an electronic microbalance in an
15 ammonium-free environment and a temperature and relative humidity-controlled laboratory set at
16 $40\% \pm 5\%$ RH. Uncertainties in RH measurements reported with each set of data were estimated to be
17 $\pm 3\%$ for the equilibration of the filters prior to mass measurement. Following gravimetric analysis,
18 select filters were subjected to an aqueous extraction. Hydrogen ion (H^+), sulfate ion (SO_4^{2-}), and
19 ammonium ion (NH_4^+) were analyzed using a pH meter for H^+ and ion chromatography for SO_4^{2-} and
20 NH_4^+ (Koutrakis et al., 1988). Filters were wetted with a small amount of ethanol, then extracted in
21 water with 10^{-4}N perchloric acid. The acid was added to dissolve the water soluble particle species.
22 This extract was tested for pH, with the addition of KCl that increases the ionic strength to stabilize the
23 pH electrode. The pH of the perchloric acid extraction solution is determined after the pH of each
24 sample extract is measured. The net amount of hydrogen ion is calculated using the log relation between

1 pH and concentration, based on a standard curve determined by adding known amounts of sulfuric acid
2 to the extraction solution. This method limits the measurements to strong acidity, i.e. weak organic
3 acids are not measured with this approach. The remaining extract was analyzed by ion chromatography
4 for SO_4^{2-} and NH_4^+ ions. Lab blanks were subtracted from the reported values.

5
6 All data were corrected to standard temperature and pressure, to adjust for differences due to elevation,
7 and reported in micrograms per meter cubed ($\mu\text{g m}^{-3}$). Average field blanks, when collected, were
8 subtracted from values. Finally, results were reviewed using quality assurance criteria to validate data
9 relative to sample run time and flow consistency. Voided samples were removed from the data set using
10 the following criteria: 1) on or off flows were $> \pm 8\%$ of 10 lpm, 2) run time for either 10 or 24-hours $>$
11 ± 2 hrs, or if 3) there was apparent filter contamination or the filter was processed incorrectly.

12
13 Other published studies on Mount Washington are compared with our results; methods are summarized
14 in Table 1. The IMPROVE methodology is described further in Malm et al., 2004 and the Atmospheric
15 Investigation, Regional Modeling, Analysis and Prediction (AIRMAP) method is described in Fischer et
16 al., 2007. All IMPROVE data is reported at local temperature and pressure, therefore it was corrected to
17 STP by multiplying the flow rate using a constant pressure correction for the site, based on elevation,
18 and daily ambient average temperature values provided by IMPROVE staff. For example fine mass
19 $\text{PM}_{2.5}$ STP corrected = $\text{PM}_{2.5} \times (\text{Flow Rate} / (\text{Flow Rate} \times 1/1.052 \times 293/273 + T_{\text{average ambient in Celsius}}))$.
20 IMPROVE data that had flow rates $>$ than $\pm 8\%$ of the target of 22.8 L/min were excluded. [TABLE 1
21 ABOUT HERE]

22 **2.4 Meteorology Measurements**

23 Wind speed and direction on Mount Washington were measured using several instruments and recording
24 devices by trained observers. All instruments are mounted atop the Mount Washington Observatory's

1 tower (approximately 20 m above local topography) on the northwest section of the summit of Mount
2 Washington (Grant et al., 2005). The majority of wind speed measurements were made using a custom
3 built pitot static anemometer mounted on a vane connected to a differential pressure measuring device
4 (Thoren, 2001). When the station experienced above freezing temperatures and light winds (<32 km
5 hr⁻¹) a standard NWS F420C 3-cup anemometer was used in conjunction with a 4305-C strip chart.
6 Hourly average wind speed was determined by manual interpretation of the paper trace. Wind direction
7 was measured using a custom built all-weather wind vane. Prevailing wind direction for each hour was
8 determined by manual inspection of wind direction displays and recorders and recorded at the end of
9 each hour.

10

11 Twenty-four hour and 10-hour resultant wind direction was calculated using vector averaging where
12 mean wind direction was weighted by wind speed. These data were paired with concurrent LOC samples
13 only to represent regional air flows at the high elevation site.

14 **2.5 Statistics**

15 Statistical calculations were done with either SYSTAT 11.0 or MS Excel. The variables are log
16 normally distributed and therefore were log transformed before standard t-tests were run. Regression
17 analyses were done and resultant linear equations reported for general discussion and comparison with
18 other work. Outliers were removed before statistical analysis was conducted but are noted in scatter plot
19 captions.

20

21 **3. RESULTS AND DISCUSSION**

22

1 **3.1 Within and at the interface zone of the planetary boundary layer comparisons**

2

3 **3.1.1 Summary statistics**

4 Summary statistics (Tables 2 and 3) for all years of monitoring are presented by length of sampling
5 interval (10 and 24-hours) and by site (Camp Dodge and Lakes of the Clouds). Total PM_{2.5} mass and
6 aerosol SO₄⁻² mass values are reported in μg m⁻³ and chemical concentrations for aerosol SO₄⁻², NH₄⁺
7 and H⁺ ions are in nmol m⁻³ (nmol m⁻³ = μg m⁻³ /10.4). Data are corrected to STP. All parameters are
8 log normally distributed and median values are reported, however, mean and standard deviation values
9 are provided and discussed in comparison with other published work. Direct comparisons of statistics to
10 others work should be done with the recognition that the number of samples varied year-to-year and
11 there was a slight bias towards our sampling more polluted days in 2002 and 2003 as described in
12 Section 2.2. [TABLE 2 AND 3 ABOUT HERE]

13

14 For all samples, median summertime PM_{2.5} and SO₄⁻² mass ranged from 4.8 to 12.6 μg m⁻³ and 1.6 to 2.3
15 μg m⁻³, respectively. Median PM_{2.5} was greatest at the low elevation site and 10-hour intervals were
16 greater than 24-hour samples at both sites. Statistical comparisons of the 2 intervals are discussed in
17 section 3.1.2 for overlapping sample years. Mean PM_{2.5} mass concentrations reported in this study are
18 similar, but slightly lower than, mean summertime values from a 2001-2002 study at two rural New
19 York (NY) mid-elevation sites, Whiteface Mountain lodge (600 m) and Pinnacles State Park (515 m)
20 that ranged from 10-18 μg m⁻³ (Schwab et al, 2004). New York is closer to a large eastern US source
21 region of sulfur dioxide emissions, the main precursor to aerosol SO₄⁻². Tanner et al. (2005) at a rural
22 southern Appalachian mountain site, Look Rock Great Smoky National Park, TN, (810 m) report PM_{2.5}
23 and SO₄⁻² mass mean summertime values ranging from 16-21 μg m⁻³ and 7.6-9.5 μg m⁻³, respectively,

1 both of which are higher than observed in our study. This is expected as the TN site is closer to a
2 number of large sulfur dioxide emitting sources, such as coal-burning power plants.
3

4 The range of mean values for aerosol SO_4^{-2} and NH_4^+ concentrations at both locations of this study, 31-
5 41 and 43-64 nmol m^{-3} respectively, are within the range of means for other northeastern US studies
6 summarized in Fischer et al., 2007 (between 17-50 and 29-72 nmol m^{-3} for aerosol SO_4^{-2} and NH_4^+ ,
7 respectively). That study, conducted as part of AIRMAP using methods reported in Table 1, monitored
8 aerosol chemistry on the summit of Mount Washington (1,917 m) during a 6 year period from
9 1999-2004 (Fischer et al., 2007). Median SO_4^{-2} and NH_4^+ concentrations in 24-hour samples reported
10 from the LOC site (1,540 m), 16.7 and 59.4 nmol m^{-3} respectively, were higher than values reported in
11 the AIRMAP study, 8.1 and 18 nmol m^{-3} respectively (Fischer et al., 2007). While this study and that of
12 Fischer et al. (2007) include similar temporal spans and are located on the same mountain approximately
13 370 m elevation difference, our study had a much lower sample size for 24-hour samples, especially for
14 aerosol NH_4^+ . AIRMAP 24-hour samples were collected from approximately 7 AM to 7AM EST so
15 direct paired sample analysis was not done.
16

17 Fischer et al. (2007) states that the summit of Mount Washington is thought to be only in the BL on the
18 hottest of summer days. Taubman et al. (2004a) discuss a daytime partitioning between the BL and the
19 Lower Free Troposphere (LFT) where the former often has more particles (smaller in size) while the
20 latter has fewer particles but that they are well aged, larger, and scatter and absorb light more efficiently.
21 If chemistry at LOC is more often influenced by the BL than the summit during summer, then its aerosol
22 concentrations at LOC would be expected to be higher on average. Large altitudinal differences in
23 aerosols were also observed during an aircraft flight near our mountain site (see Figure 2, methods
24 described in Taubman et al., 2004a and Taubman et. al., 2004b). During this “instantaneous” altitudinal

1 profile by aircraft, between 9 and 10 AM on August 13th, 2002, the summit of Mount Washington was
2 actually within the BL. The data do not reflect the dynamic diurnal patterns but do show an example of
3 lower light scattering (Mm^{-1} at 550 nm wavelength) and particle counts at higher elevations (Figure 2).
4 This vertical pattern is due to dilution by the LFT airmass aloft with increasing levels at lower altitudes
5 where downward mixing of overnight transport shows a mid-elevation peak of different air pollution
6 parameters. This profile was taken during a regional pollution event (Taubman et al., 2004a). [FIGURE
7 2 ABOUT HERE]

8
9 Camp Dodge 24-hour SO_4^{-2} and NH_4^+ median concentrations of 24.0 and 45.8 $nmol\ m^{-3}$, respectively,
10 agree well with a study by Ziemba et al. (2007) who reported summertime median values of 23.7 and
11 41.3 $nmol\ m^{-3}$ respectively, at a coastal NH rural low elevation site in Durham, NH (24 m ASL) over a
12 similar time frame. Ziemba et al. (2007) also calculated inferred acidity and found a summertime
13 median value of 6.6 $nmol\ m^{-3}$. Sulfate aerosol associated strong acidity was measured in this study, as
14 aqueous hydrogen ion concentrations, ranging from 8.9-13.0 $nmol\ m^{-3}$ with higher median values at the
15 low elevation site, Camp Dodge (452 m).

16 **3.1.2 Ten hour versus 24-hour sampling intervals**

17 A comparison of the full dataset (all years) shows significant differences between 10 and 24-hour $PM_{2.5}$
18 mass samples ($p < 0.001$) at both sites, with the 10-hour samples having a higher median value (Tables 2
19 and 3). This could be in part due to the disparity in the years sampled rather than solely due to
20 differences in sample intervals. National and regional concentrations of direct and precursor emissions
21 of $PM_{2.5}$ have decreased since 1990 (EPA, 2008; EPA, 2007). Because of this temporal trend,
22 comparisons between 10-hour and 24-hour datasets at the same location were made by examining only a
23 subset of data with overlapping years. Samples are not paired however (with the exception of a set from

1 Camp Dodge in 1997), therefore this comparison is not direct but does reduce the influence of the
2 general trend in decreasing pollution from 1990 to 2004.

3
4 The median PM_{2.5} mass concentration in 10-hour samples at Camp Dodge was 11.9 µg m⁻³ (n=124) and
5 was found to be significantly greater than the median concentration for 24-hour samples, 10.1 µg m⁻³
6 (n=32), for the overlapping years dataset, p=0.04 (includes data from 1995 and 1997 only). Comparison
7 of the chemical parameters, SO₄⁻², NH₄⁺, and H⁺, resulted in no significant differences at Camp Dodge
8 (although there is some suggestion for H⁺ being greater in 24-hour samples, p=0.08). In contrast to this
9 are the results from the paired measurements in 1997 which include n=17 for PM and n=12 for
10 chemistry. Ten-hour values were well correlated with 24-hour values of PM_{2.5} mass and chemistry with
11 regression slopes near 1 (with the exception of H⁺ which had a slope of 0.93) but with positive y-
12 intercepts. This suggests that 10-hour samples were generally higher in mass concentration, and SO₄⁻²
13 and NH₄⁺ concentrations. In both of the t-test and regression comparisons, n was small for 24-hour
14 samples and this could be contributing to the conflicting results.

15
16 LOC overlapping years datasets (2000-2003) showed 10-hour median values to be significantly greater
17 than 24-hour samples for PM_{2.5} mass (10-hour: 5.3 µg m⁻³ with n=115; 24-hour: 1.3 µg m⁻³ with n=103),
18 SO₄⁻² (10-hour: 35.4 nmol m⁻³ with n=29; 24-hour: 13.0 nmol m⁻³ with n=70) and H⁺ ion (10-hour: 23
19 nmol m⁻³ with n=29; 24-hour: 7.0 nmol m⁻³ with n=64). There was insufficient NH₄⁺ data from this
20 location to make a comparison. Sulfate aerosols have been shown to have a weak diurnal pattern, with
21 mid-day peaks, on the summit of Mount Washington (G. Allen, unpublished data) and at a rural mid
22 elevation site in the Great Smoky Mountain National Park Look Rock, TN (Tanner et al., 2005). Greater
23 daytime concentrations of aerosol SO₄⁻² and strong acidity have been observed at a semi-rural site in
24 Pennsylvania that is near significant SO₂ emission sources (Liu et al., 1996). Daytime SO₄⁻² maxima

1 could be caused by conversion of sulfur dioxide and water to sulfuric acid in condensed phases or from
2 photochemical transformation involving gas phase oxidation by the hydroxyl radical. Furthermore, fresh
3 aerosol sulfate formation is likely to be more acidic, due to limited time for neutralization by ammonia at
4 these locations. This is supported by the greater concentrations of H^+ in 10-hour compared to 24-hour
5 samples. Meteorological conditions could arise, with rapid transport from emission source areas, that
6 bring fresh SO_2 to higher elevations at night that are transformed during the photochemically active
7 daytime. The August 13th 2002 altitude profile (Figure 2) shows an example of mid-elevation pollution
8 (ozone and SO_2) maxima at about 1,000 m between 9:00 and 10:00 EST. It is likely that this pollution
9 was transported to this rural location aloft overnight, due to a nocturnal temperature inversion, and then
10 mixed downward due to the break-up of the inversion with daytime heating. Further evidence of
11 downward mixing was the 10:00 EST ozone concentration peak at Camp Dodge, whereas typical diurnal
12 peaks are between 12:00 and 13:00 EST (data not shown).

13

14 Local SO_2 sources are expected to be limited at this rural location. However possible influences on LOC
15 include the diesel-powered electricity generators at the summit of Mount Washington and the soft-coal
16 burning cog railway locomotives which emits mostly large particulates that fall out of the atmosphere
17 quickly. More extensive concurrent measurements at high and low elevations are necessary to determine
18 if the differences observed between daytime and 24-hour samples are characteristic and what
19 meteorological conditions enhance these differences.

20

21 **3.1.3 Lakes of the Clouds vs. Camp Dodge**

22 Comparisons of paired samples showed that LOC and Camp Dodge have statistically different $PM_{2.5}$
23 mass concentrations (STP corrected) with the latter being greater. This is also reflected in the regression
24 results for $PM_{2.5}$ mass at the high and low elevation sites shown in scatter plots, Figure 3a, (24-hour and

1 10-hour samples are combined in the regression analysis because there is little difference if split). The
2 weak r^2 and scatter plots suggest that the two sites are positively correlated they can have unlinked $PM_{2.5}$
3 mass concentrations. Relatively lower $PM_{2.5}$ mass levels at higher elevations have been seen in the
4 southern Appalachians in the cooler months relative to low elevation urban areas. The mountains there
5 are often above the mixing layer and stay cleaner from lack of source pollution while urban areas have
6 local emissions, largely organic aerosols that contribute to higher $PM_{2.5}$ mass levels. Organic aerosols
7 comprise a significant portion of the fine mass at this rural northeastern location (IMPROVE database)
8 with likely sources including a mix of anthropogenic and local biogenic emission sources (terpenes,
9 natural and anthropogenic wood smoke, etc.). Local biogenic emissions would be more represented
10 within the BL while above this layer more regional sources, including from downwind urban areas,
11 would contribute. The Camp Dodge site in this study is usually within the mixing layer in the summer
12 while the higher elevation site is in and out of the mixing layer. Therefore there are likely differences in
13 meteorology and air mass history between the two sites. As noted earlier, this divergence has been
14 observed for ozone concentrations, where the Mount Washington summit (1,917 m) and base have
15 different background concentrations, diurnal patterns, and peak concentrations during pollution events
16 (Fischer et al., 2004). [FIGURE 3 ABOUT HERE]

17
18 High and low elevation SO_4^{-2} mass concentrations ($\mu g\ m^{-3}$), STP corrected, show a slightly tighter
19 regression than $PM_{2.5}$, that includes both 24-hour and 10-hour samples. The $r^2=0.70$ and slope =0.81
20 (See Figure 3b) suggests 20% less SO_4^{-2} mass concentration at the high elevation site. This indicates
21 that, while SO_4^{-2} does explain some of the variation in total $PM_{2.5}$ mass, another component, e.g. local
22 emissions of organics or crustal materials, is contributing to the elevation differences. This also
23 indicates that while the higher elevation site has lower total $PM_{2.5}$ mass it has proportionally more SO_4^{-2}
24 than the lower elevation site. [TABLE 4 ABOUT HERE]

1 **3.2 Comparison of Harvard Impactor and IMPROVE samplers**

2 The 24-hour summary statistics from this study's HI impactor and the co-located IMPROVE sampler at
3 Camp Dodge (452 m) are shown in Table 4. A regression between co-located PM_{2.5} mass methods show
4 that the IMPROVE sampler method results in approximately 34% lower PM_{2.5} mass concentration
5 (Teflon filter from Module A, see Table 1) compared to the HI levels (Figure 4a). Yet, a comparison of
6 the SO₄⁻² mass concentrations from the IMPROVE sampler (Nylon filter from Module B and analyzed
7 by Ion Chromatography) and HI show a 1:1 agreement, slope =1.01 (Figure 4b). [FIGURE 4 ABOUT
8 HERE]

9
10 The cause of disagreement between co-located IMPROVE and Harvard Impactor total PM_{2.5} mass
11 concentrations at Camp Dodge is difficult to pinpoint and likely multifaceted. There are differences in
12 sample processing that may contribute minimally to water associated mass differences. IMPROVE
13 weighs filters within a range of approximately 30 to 40% relative humidity, with approximately 10
14 minutes equilibration time. The HI method calls for a 48 hour equilibration at a higher RH of 40%±5%.
15 If IMPROVE samples are often weighed at 35% after a short equilibration, while HI is weighed at 40%
16 after a longer equilibration, then there may be more water associated with the particulates from the latter
17 method especially if there is significant amounts of acidic SO₄⁻² present, which is considerably more
18 hygroscopic than neutralized SO₄⁻² (Koutrakis et al., 1989). However, the IMPROVE program is not
19 designed to quantify acidity and takes no precautions to protect samples against neutralization from
20 ammonia (such as shipping with citric acid paper). Therefore samples that may have been acidic in the
21 ambient atmosphere may not be as acidic when they reach the laboratory. Overall it is expected that
22 difference due to sample processing would be minimal and not be of the magnitude of the disparity
23 observed. The IMPROVE program has had good general agreement of comparisons of PM_{2.5} mass with

1 EPA methods in audits conducted by the EPA National Air and Radiation Environmental Laboratory (C.
2 McDade, pers. communications).
3
4 Teflon filters have been found to lose NH_4NO_3 through its conversion to ammonia and nitric acids with
5 changes in temperature and RH contributing to this process (Yu et al., 2006). The two methods both use
6 Teflon filters for mass measurements, however, differ in that the IMPROVE filters are not stabilized for
7 up to a week, from fluctuating temperature and RH conditions, while HI filters are consistently collected
8 and stabilized by the next morning (Table 1). This may result in the IMPROVE Teflon Channel A
9 samples experiencing more loss of nitrate aerosol than the HI setup. However, differences in nitrate
10 aerosol loss may only be a small contributor to the total mass disagreement. It has been estimated that in
11 summertime aerosol nitrate loss is on average 2% of the total fine mass at the Great Gulf Camp Dodge
12 site using the IMPROVE method (Ashbaugh and Eldred, 2004). Further, rural inland northeastern sites
13 have been shown to have little aerosol NO_3^- and nitric acid present even on the most polluted days (Lefer
14 and Talbot, 2001; Hill and Allen, unpublished data). On the summit of Mount Washington the
15 summertime 95th percentile aerosol nitrate concentration was found to be 8.2 nmol m^{-3} from 1999-2004
16 (Fischer et al., 2007). Further examination is required to verify the differences in methodologies and to
17 assess the ramifications toward reconstruction of mass and the visibility metric.

18

19 **3.3 Percent of SO_4^{2-} in total fine particulates and its acidity**

20 **3.3.1 Sulfate vs. $\text{PM}_{2.5}$**

21 Sulfate plotted against fine mass ($\mu\text{g m}^{-3}$) showed positive significant regressions at both sites and both
22 sample intervals (Figure 5 a and b). As discussed earlier, sulfate at LOC constitutes a greater percentage
23 of $\text{PM}_{2.5}$. This is supported when the slopes of the regressions for LOC and Camp Dodge were

1 compared and found to be significantly different for the 24-hour dataset (0.42 and 0.35 respectively).
2 Comparison of the slopes for the 10-hour dataset showed no significant difference between sites. There
3 does appear to be a subset of data, especially prominent in the 10-hour data sets, where SO_4^{-2} remains
4 low ($<5 \mu\text{g m}^{-3}$) and $\text{PM}_{2.5}$ increases to moderate levels ($20 \mu\text{g m}^{-3}$ or greater). This subset pulls the
5 slope of the regressions downward and is contributing to the lower r^2 values for 10-hour dataset
6 regressions and likely the lack of a difference between sites. Local sources of organic or crustal aerosols
7 could result in elevated $\text{PM}_{2.5}$ levels with relatively less SO_4^{-2} . Organic aerosols and/or local source dust
8 and soot could contribute more to daytime total $\text{PM}_{2.5}$, especially at lower elevations, but this study lacks
9 the measurements to verify this hypothesis. [FIGURE 5 ABOUT HERE]

10 3.3.2 Sulfate acidity

11 All strong acid aerosol particles are SO_4^{-2} , therefore the stoichiometric ratio of the NH_4^+ and SO_4^{-2}
12 species would be 2:1 for fully neutralized sulfate ($(\text{NH}_4)_2\text{SO}_4$) and 1:1 for acidic ammonium bisulfate
13 (NH_4HSO_4). Figures 6 a and b show scatter plots of Camp Dodge NH_4^+ vs. SO_4^{-2} and H^+ vs. SO_4^{-2} for
14 24-hour and 10-hour samples. Figures 7 a, b are similar graphs for the LOC site. Both sites show that
15 the SO_4^{-2} aerosol is more acidic than neutralized, i.e. the slopes are closer to 1:1 ratio for $\text{NH}_4^+:\text{SO}_4^{-2}$
16 (Figures 5a and 6a). LOC aerosol is statistically more acidic than that measured at Camp Dodge based
17 on 24-hour sampling periods when the slopes were compared (0.97 and 1.3 respectively, $p<0.01$).
18 [FIGURE 6 ABOUT HERE] The slopes for H^+ vs. SO_4^{-2} for LOC and Camp Dodge were significantly
19 different in the 24-hour dataset (0.89 and 0.71 respectively, $p<0.01$) again providing evidence that LOC
20 aerosol is more acidic in 24-hour samples. There was no difference detected between the slopes in the
21 10-hour data at a p-value of 0.01 or less (Figures 6-7). Regressions of NH_4^+ vs. SO_4^{-2} have positive y-
22 intercepts due to low SO_4^{-2} values ($<50 \text{ nmol m}^{-3}$) having higher associated NH_4^+ concentrations, i.e.
23 more neutralized, while higher SO_4^{-2} values are more acidic. Fischer et al. (2007) found this to be true
24 for the Mount Washington summit and suggest that in summertime there is enough ammonia to

1 neutralize up to 15 nmol m^{-3} of SO_4^{-2} in air masses reaching that high elevation location. That study
2 reported the slopes of NH_4^+ vs. SO_4^{-2} regressions to be 1.3 and 2.6 when data were parsed into the 95th
3 and 5th percentile SO_4^{-2} concentrations respectively. The present study shows a much higher
4 neutralization point of approximately 35 nmol m^{-3} of SO_4^{-2} based on inspection of the NH_4^+ to SO_4^{-2}
5 scatter plot. Measured H^+ concentrations plotted against SO_4^{-2} also reflected this phenomenon, where
6 the y-intercept is negative as low SO_4^{-2} concentrations have less associated hydrogen and higher SO_4^{-2}
7 concentrations have more. Ziemba et al. (2007) found a NH_4^+ to SO_4^{-2} ratio at Durham, NH, about 15
8 km from the Atlantic Ocean, to be 1.6 but this included year round data. As stated previously this
9 study's low elevation site and that of Ziemba et al. (2007) had similar summertime NH_4^+ concentrations.

10 [FIGURE 7 ABOUT HERE]

11

12 **3.4 Hydrogen ion; measured vs. inferred**

13 Few studies measure hydrogen ion associated with aerosols in rural settings (Keeler et al., 1991, Lui et
14 al., 1996). Hydrogen ion is often calculated, or “inferred” from other parameters. This study has a
15 significant amount of hydrogen ion data, therefore we tested the rudimentary method used to calculate
16 inferred hydrogen ion (Ziemba et al., 2007) for the Camp Dodge site. The equation to calculate inferred
17 hydrogen concentration is: $[\text{H}^+] = 2[\text{SO}_4^{-2}] + [\text{NO}_3^-] - [\text{NH}_4^+]$. Nitrate values were obtained from the
18 co-located IMPROVE dataset as we did not measure it in our study. All other parameters were from the
19 Harvard Impactor dataset. A linear regression showed a 1:1 relationship with an r^2 of 0.95 ($r^2 = 0.88$ with
20 one influential outlier removed, data not shown) indicating that the crude method of inferring hydrogen
21 ion is appropriate at this rural northeast site.

22

23 It should be noted that the IMPROVE program does not measure sample acidity but does measure total
24 elemental hydrogen which includes hydrogen associated with largely aerosol sulfur and organic matter.

1 While estimates of aerosol acidity have been made using the IMPROVE dataset (Malm, et al., 1994)
2 IMPROVE samples are not protected from ammonia during collection and transport, and likely do
3 experience aerosol neutralization. For the purposed of the Regional Haze requirements IMPROVE
4 program assumes that all aerosol sulfate is neutralized. This effectively lead to total SO_4^{-2} associated
5 mass being overestimated while the associated visibility degradation would be underestimated as acidic
6 SO_4^{-2} is more hygroscopic than neutralized SO_4^{-2} . The hygroscopic growth curves are similar for
7 ammonium sulfate and ammonium bisulfate up to an RH of about 70%. Above this RH the curves
8 diverge such that a bisulfate aerosol is approximately 1.2 times greater than a neutralized sulfate aerosol
9 of the same dry size. The aerodynamic diameters of sulfuric acid droplets are consistently greater than
10 the diameters of ammonium bisulfate and ammonium sulfate aerosols at all RH values (Koutrakis et al.,
11 1989, Hand and Malm, 2006). While this is offset somewhat by the mass scattering efficiencies of the
12 various sulfate compounds the differences could be significant under certain conditions.

13 **3.5 Wind direction and associated mass and acidity**

14 Lakes of the Clouds 10 and 24-hour $\text{PM}_{2.5}$, SO_4^{-2} , H^+ , and NH_4^+ concentrations, from 1990-2004, were
15 grouped into 7 vector averaged wind directions (N-ESE, S-SE, SW-SSW, WSW, W, WNW, and NW).
16 Results showed that median values of all parameters were greatest from regional westerly and
17 southwesterly flows as compared to other wind directions. Maximum median values were $13.8 \mu\text{g m}^{-3}$
18 for $\text{PM}_{2.5}$, 41.3 nmol m^{-3} SO_4^{-2} , 17.4 nmol m^{-3} H^+ , and 59.4 nmol m^{-3} NH_4^+ (n varied for each vector
19 group). Wind speed and direction data from the summit of Mount Washington were used as data from
20 the LOC site are strongly influenced by the local topography. This study's results agree with the more
21 in-depth back trajectory analysis on bulk aerosol chemistry from the summit of Mount Washington from
22 1999 to 2004 by Fischer et al. (2007) that showed relatively higher SO_4^{-2} concentrations coming from
23 the southwesterly quarter in the summertime. Another study by Slater et al. (2002), conducted at a

1 nearby mid-elevation site on Cranmore Mountain (508 m), found higher aerosol SO_4^{-2} concentrations
2 from the W/SW flows as compared to winds from the N/NE.

3

4 **4.0 CONCLUSIONS**

5 Results from this long-term record of summertime $\text{PM}_{2.5}$ mass and aerosol chemistry at two rural
6 northeast sites, adjacent to two Class I Wilderness areas, demonstrates that haze-causing pollution
7 aerosol can vary dramatically with elevation. The higher elevation site often experiences lower $\text{PM}_{2.5}$
8 mass concentrations but it is comprised of relatively more SO_4^{-2} aerosol that can be more acidic (24-hour
9 samples). Results highlight the need for altitudinal evaluations of aerosol pollution distributions in
10 mountainous areas but do show that, while land-based sites are influenced by the complex terrain and
11 anabatic flows etc., the general patterns are consistent with the limited information available on vertical
12 profiles of aerosols concentrations and associated parameters.

13

14 Comparison of the Harvard Impactor method with a co-located IMPROVE sampler at the low elevation
15 site revealed a disparity in $\text{PM}_{2.5}$ mass, especially for the higher values, yet results show a 1:1
16 relationship for aerosol SO_4^{-2} measurements. This divergence may not drastically impact the IMPROVE
17 visibility metric calculations necessary for establishing baseline and reasonable progress trajectories as
18 part of the EPA Regional Haze requirements, as that method calculates reconstructed ambient light
19 extinction based on the speciated values of aerosol SO_4^{-2} and other individual ions. However, if the total
20 mass is underestimated then other speciated chemistry measure with the Module A filter, elements and
21 hydrogen, may also be underestimated. Furthermore, IMPROVE reconstruction of fine mass assumes all
22 aerosol SO_4^{-2} is neutralized as ammonium sulfate; while this study shows that much of the SO_4^{-2}
23 reaching this location is acidic. Acidic aerosol SO_4^{-2} absorbs more water and hence has a higher light
24 scattering efficiency relative to neutralized aerosol SO_4^{-2} .

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We confirm that estimating aerosol strong acidity (as hydrogen ion) using a rudimentary mass balance equation is a sufficient method for this rural location by comparing it with actual measured acidity. Further we demonstrate that the highest aerosol mass and acidic SO_4^{-2} concentrations are from flows from the south and west-southwest where the largest source regions exist. This work is one of the longest records of strong aerosol acidity at a rural mountain location and it contributes significant information on summertime air pollution conditions at two highly visited Northeast Class I areas, valued for their scenic views and unique alpine ecosystems. Finally, our work underscores the need for continued state and federal efforts to reduce interstate transport of sulfur and nitrogen emissions that affect the higher elevations of the region.

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1 TABLE CAPTIONS

2 Table 1. Method of aerosol PM_{2.5} and chemistry measurements near 2 Class I areas, Mount Washington,
3 NH

4
5 Table 2. Camp Dodge (452 m) 10-hour and 24-hour summertime statistics. All corrected to STP

6
7 Table 3. Lakes of the Clouds (1,540 m) 10-hour and 24-hour summertime statistics. All corrected to
8 STP

9
10 Table 4. Summary statistics for co-located HI and IMPROVE methods at Camp Dodge between
11 1995-2004, June, July, August data only. Percent SO₄⁻² of total mass statistics are also shown. All
12 corrected to STP.

13

1 **FIGURE CAPTIONS**

2

3 Figure 1. Location of the aerosol PM_{2.5} and chemistry sample sites and two NH Class I areas.

4

5 Figure 2. Airborne observations of total particle counts (cm³/100), Bscat 550 nm (Mm⁻¹ *10⁵), RH (%),
6 ozone (ppbv), SO₂ (ppbv*10) and temperature (*C) during a altitude transect near Mount Washington,
7 NH on August 13th, 2002 from 09:19-09:43 EST. Methods are described in Taubman et al., 2004a and
8 Taubman, et. al., 2004b.

9

10 Figure 3. Scatter plots of (a) PM_{2.5} mass, n=302 and (b) SO₄⁻² mass, n=206 for Lakes of the Clouds
11 (1,540 m) vs. Camp Dodge (452 m). Includes data from summertime 1990-2004. Regressions (solid
12 line) include 24-hour and 10-hour samples. All data are corrected to STP.

13

14 Figure 4 Comparison of IMPROVE vs. Harvard Impactor methods for (a) PM_{2.5} mass, n=130 (b) and
15 SO₄⁻² mass, n=98 at Camp Dodge (452 m). IMPROVE PM_{2.5} are from Module A and SO₄⁻² data are
16 from Module B, see Table 1 for more details. Data include summertime 1995 through 2004. All data are
17 corrected to STP.

18

19 Figure 5. Scatter plot of (a) Sulfate vs. PM_{2.5} (μg m⁻³) for Camp Dodge 10 and 24-hour datasets (4
20 outliers removed) and (b) Sulfate vs. PM_{2.5} (μg m⁻³) for LOC 10 and 24-hour datasets (2 outliers
21 removed). Regression equations are shown for 10, 24 and 10+24-hour datasets but a regression line is
22 shown only for the latter. Data include summertime 1990 through 2004. All data are corrected to STP.

23

24 Figure 6 a and b. Scatter plot of NH₄⁺ vs. SO₄⁻² (nmol m⁻³) for (a) Camp Dodge and (b) LOC for 10 and
25 24-hour samples. Regression equations are shown for 10, 24 and 10+24-hour datasets but a regression
26 line is shown only for the latter. Data include summertime 1991 through 2004. All data are corrected to
27 STP.

28

29 Figure 7 a and b. Scatter plot of H⁺ vs. SO₄⁻² (nmol m⁻³) for (a) Camp Dodge and (b) LOC for 10 and
30 24-hour samples. Regression equations are shown for 10, 24 and 10+24-hour datasets but a regression
31 line is shown only for the latter. Data include summertime 1991 through 2004. All data are corrected to
32 STP.

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Table 1
[Click here to download Table: Table1.doc](#)

Method parameter	AMC Harvard Impactor	IMPROVE Module A	IMPROVE Module B	UNH AIRMAP
Site Location (elevation ASL)	Camp Dodge (452 m) and LOC (1,540 m)	Camp Dodge (452 m)	Camp Dodge (452 m)	Summit of Mount Washington (1,917 m)
Sample History	1988-2007	1995-present	1995-present	2001-present
Sampler Type	Impactor 2.5 cut with citric acid denuder	Cyclone 2.5 cut	Cyclone 2.5 cut with carbonate denuder	Bulk Aerosol
Filter Type	37-mm Teflon	25-mm Teflon	25-mm Nylon before 5/24/00, 37-mm Nylon beginning 5/24/00	90-mm Teflon
Duration & time of day sampled	10-hour: 7am-5pm EST 24-hour: 12am – 12am EST	24-hour: 12am – 12am EST	24-hour: 12am – 12am EST	24-hour: 7am – 7am EST
Post sampling time filter was collected & stabilized	6-8 hrs	1-6 days	1-6 days	2-5 hrs
Target flow rate (valid flows are target \pm 8%)	10 L/min	22.8 L/min	22.8 L/min	undefined
Measurements	PM _{2.5} , SO ₄ ⁻² , NH ₄ ⁺ , H ⁺	PM _{2.5} , S and other elements	SO ₄ ⁻² , NO ₃ ⁻ and other ions (no NH ₄ ⁺ or H ⁺)	SO ₄ ⁻² , NH ₄ ⁺ plus other major cations and anions (no H)
Mass methods	48 hour equilibration period in RH and temperature controlled environment. RH 40% \pm 5%	~10 minute equilibration period in RH and temperature controlled environment. RH within a range of 30 to 40%	~10 minute equilibration period in RH and temperature controlled environment. RH within a range of 30 to 40%	None
Citations	This study	Malm et al, 2004 & Charles McDade (pers. Comm.)	Malm et al, 2004 & Charles McDade (pers. Comm.)	Fischer et al., 2007

Table 2

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	10-hour ($\mu\text{g m}^{-3}$)		10-hour (nmol m^{-3})			24-hour ($\mu\text{g m}^{-3}$)		24-hour (nmol m^{-3})		
	PM _{2.5} 1988-1997	SO ₄ ⁻² 1991-1997	SO ₄ ⁻² 1991-1997	NH ₄ ⁺ 1991-1997	H ⁺ 1991-1997	PM _{2.5} 1995, 1997-2004	SO ₄ ⁻² 1995, 1997-2004	SO ₄ ⁻² 1995, 1997-2004	NH ₄ ⁺ 1995, 1997-2004	H ⁺ 1995, 1997-2004
5 th %	4.2	0.3	3.6	4.2	0.0	2.2	0.4	4.2	9.4	3.0
25 th %	8.1	1.0	10.3	12.4	4.3	4.6	1.1	11.4	28.3	7.0
Median	12.6	2.3	23.5	30.8	12.0	8.2	2.3	24.0	45.8	13.0
75 th %	19.0	4.8	49.8	69.6	24.8	13.9	5.1	53.6	80.0	31.4
95 th %	38.9	13.4	140.1	160.7	98.6	32.1	10.8	112.5	143.3	87.0
Mean	15.4	3.9	40.7	48.6	24.9	11.0	3.7	38.1	59.0	24.4
StdDev.	11.5	4.7	49.3	48.9	43.4	9.4	3.7	38.7	46.2	29.6
N	424	316	316	289	316	470	325	325	170	320

Table 3
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	10-hour ($\mu\text{g m}^{-3}$)		10-hour (nmol m^{-3})			24-hour ($\mu\text{g m}^{-3}$)		24-hour (nmol m^{-3})		
	PM _{2.5} 1990-2003	SO ₄ ⁻² 1991-2003	SO ₄ ⁻² 1991-2003	NH ₄ ⁺ 1991-2003	H ⁺ 1991-2003	PM _{2.5} 1998-2004	SO ₄ ⁻² 2000-2004	SO ₄ ⁻² 2000-2004	NH ₄ ⁺ 2000-2004	H ⁺ 2000-2004
5 th %	1.3	0.2	2.4	3.3	0.0	1.1	0.2	2.1	13.6	1.0
25 th %	4.0	0.9	9.2	11.1	2.0	2.5	0.6	6.3	31.9	4.0
Median	8.5	2.1	21.7	30.3	8.9	4.8	1.6	16.7	59.4	9.0
75 th %	14.1	4.5	46.9	58.9	23.1	10.1	4.0	41.4	77.8	32.8
95 th %	27.5	14.6	152.5	125.0	91.8	21.2	9.7	101.0	149.8	95.1
Mean	10.5	3.6	37.4	42.9	21.2	7.4	2.9	30.6	63.5	23.8
StdDev.	8.9	4.0	42.2	44.4	34.3	7.3	3.4	35.2	42.0	33.3
N	352	206	206	174	212	160	105	105	31	99

Table 4

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	24-hour ($\mu\text{g m}^{-3}$) Camp Dodge 1995-2004			24-hour ($\mu\text{g m}^{-3}$) IMPROVE 1995-2004		
	PM _{2.5}	SO ₄ ⁻²	% SO ₄ ⁻²	PM _{2.5}	SO ₄ ⁻²	% SO ₄ ⁻²
5 th %	2.2	0.4	7.3	2.3	0.3	7.8
25 th %	4.7	1.1	16.2	3.9	0.6	16.2
Median	8.2	2.3	23.5	6.9	1.3	25.2
75 th %	14.2	5.1	30.7	12.2	3.8	37.7
95 th %	32.4	10.8	39.6	26.0	10.8	49.3
Mean	11.2	3.6	23.4	9.3	3.0	26.6
Std. Dev.	9.7	3.7	9.4	7.5	3.7	13.4
N	473	328	322	225	219	188

Figure 1
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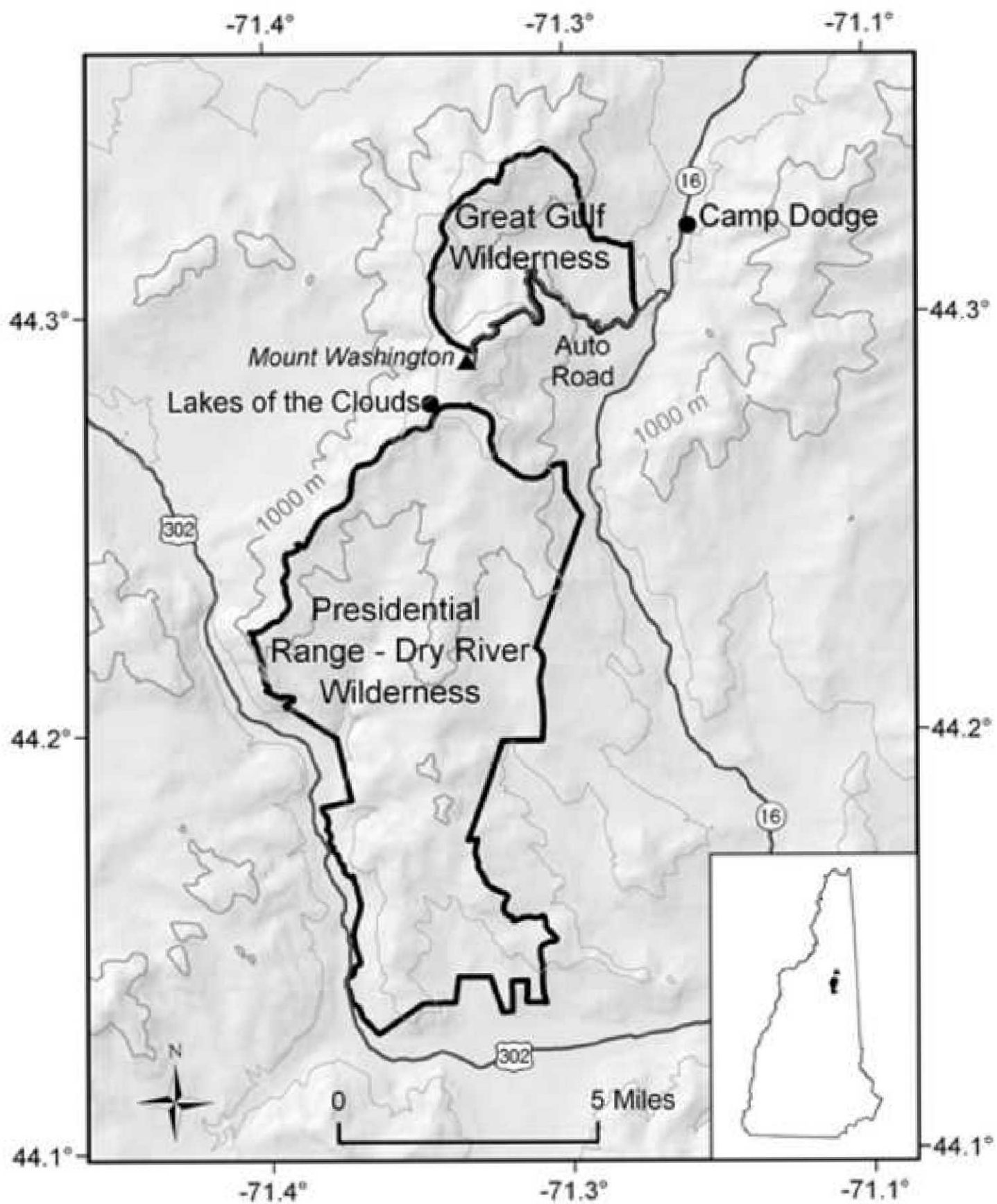


Figure 2
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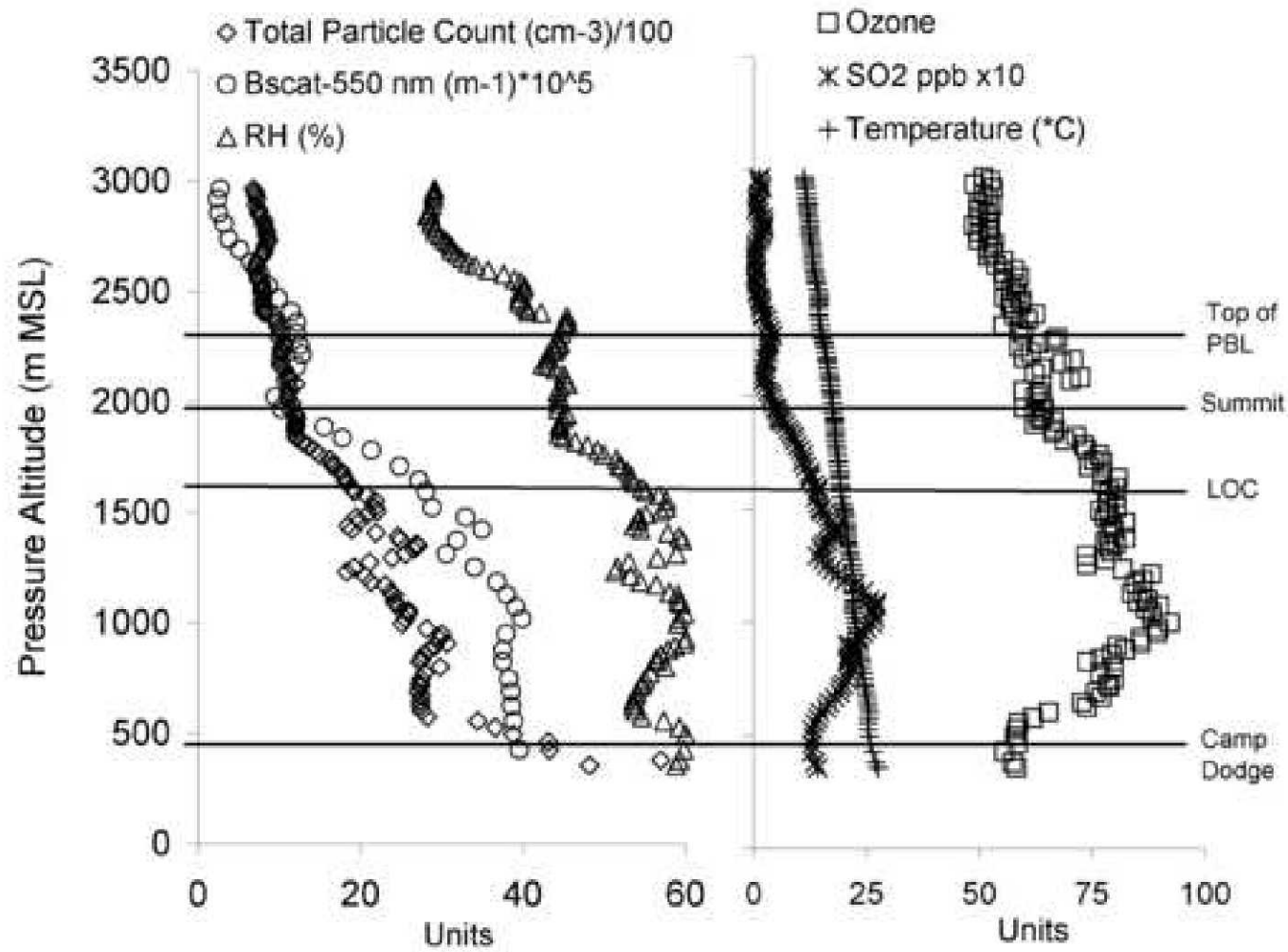


Figure 3
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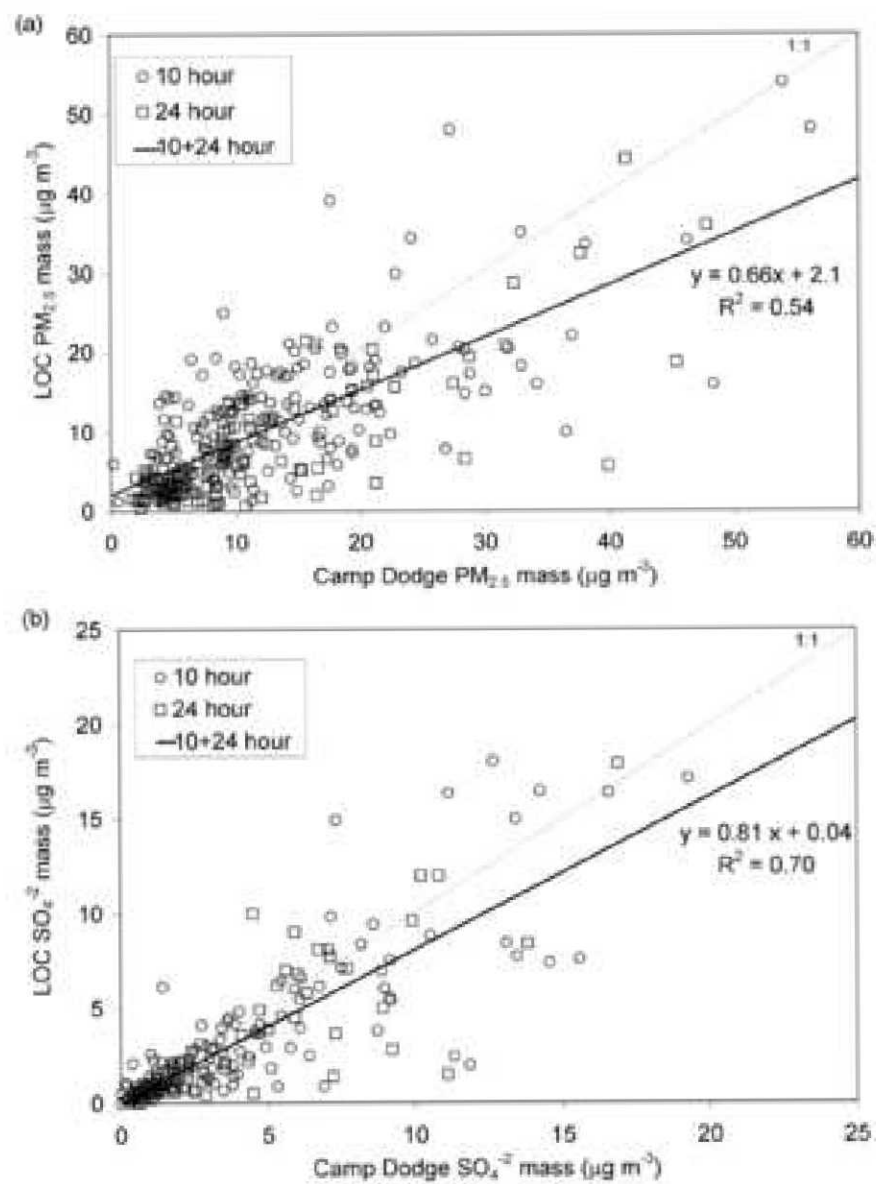


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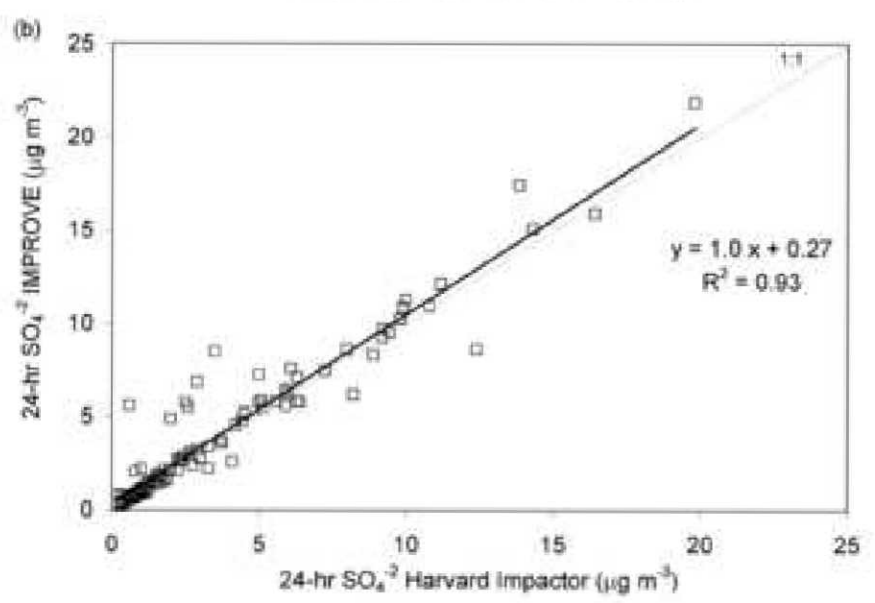
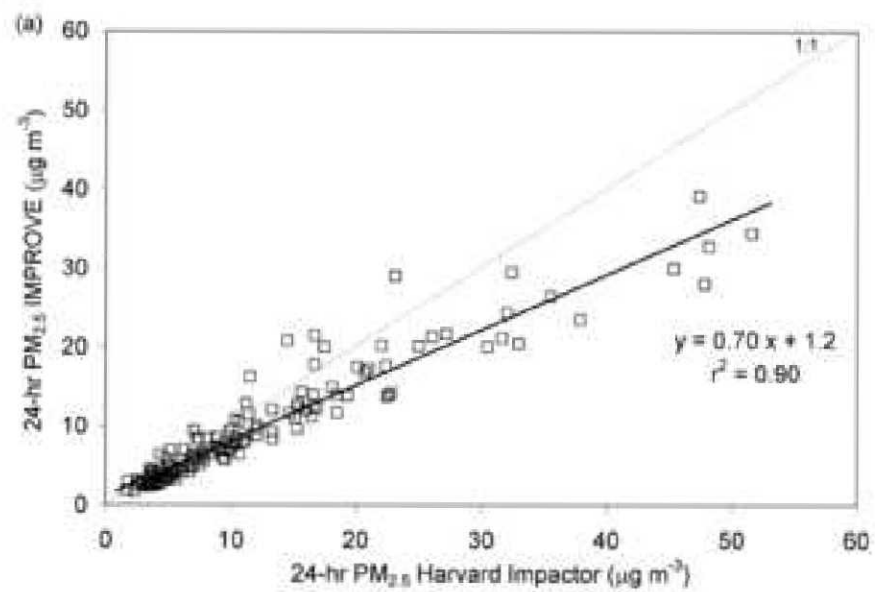


Figure 5
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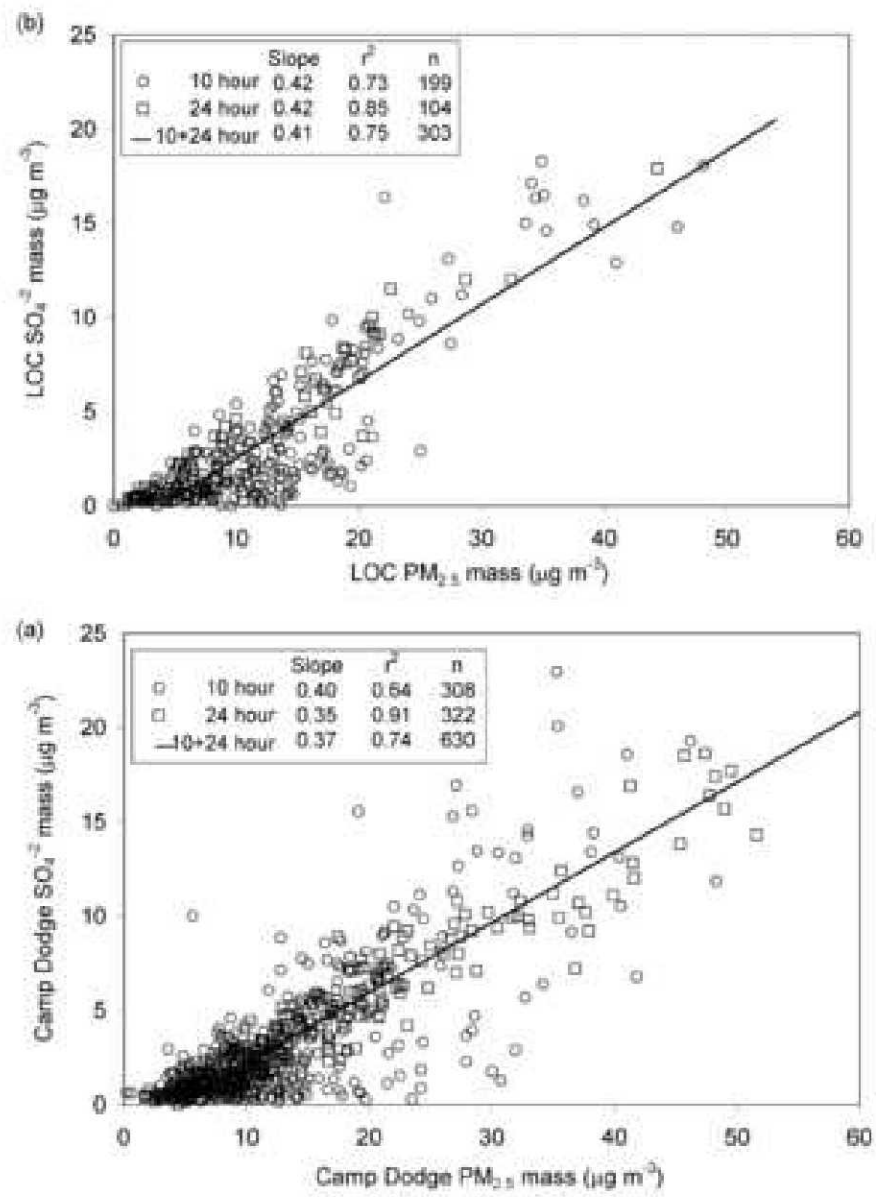


Figure 6

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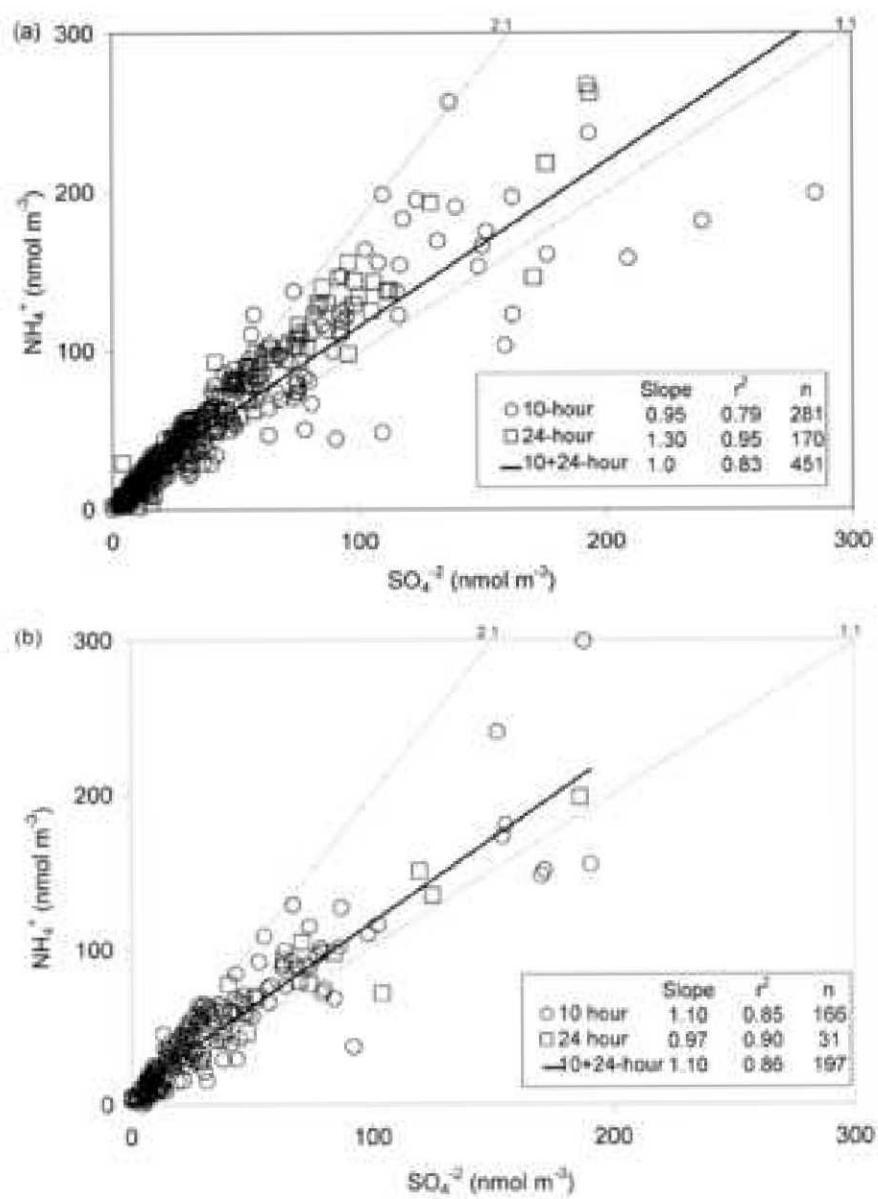


Figure 7

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