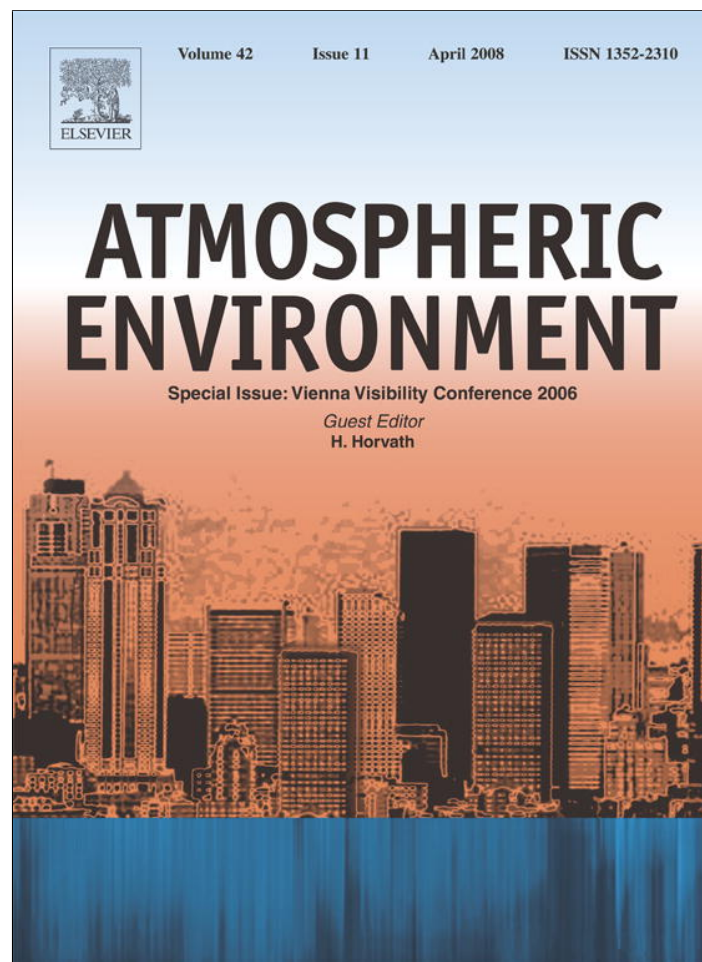


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# Observations of fine and coarse particle nitrate at several rural locations in the United States

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## Abstract

Nitrate comprises an important part of aerosol mass at many non-urban locations during some times of the year. Little is known, however, about the chemical form and size distribution of particulate nitrate in these environments. While submicron ammonium nitrate is often assumed to be the dominant species, this assumption is rarely tested. Properties of aerosol nitrate were characterized at several IMPROVE monitoring sites during a series of field studies. Study sites included Bondville, Illinois (February 2003), San Geronio Wilderness Area, California (April and July 2003), Grand Canyon National Park, Arizona (May 2003), Brigantine National Wildlife Refuge, New Jersey (November 2003), and Great Smoky Mountains National Park, Tennessee (July/August 2004). Nitrate was found predominantly in submicron ammonium nitrate particles during the Bondville and San Geronio (April) campaigns. Coarse mode nitrate particles, resulting from reactions of nitric acid or its precursors with sea salt or soil dust, were more important at Grand Canyon and Great Smoky Mountains. Both fine and coarse mode nitrate were important during the studies at Brigantine and San Geronio (July). These results, which complement earlier findings about the importance of coarse particle nitrate at Yosemite and Big Bend National Parks, suggest a need to more closely examine common assumptions regarding the importance of ammonium nitrate at non-urban sites, to include pathways for coarse mode nitrate formation in regional models, and to consider impacts of coarse particle nitrate on visibility. Because coarse particle nitrate modes often extend well below 2.5  $\mu\text{m}$  aerodynamic diameter, measurements of  $\text{PM}_{2.5}$  nitrate in these environments should not automatically be assumed to contain only ammonium nitrate.

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**Keywords:**  $\text{PM}_{2.5}$ ; Nitrate; Coarse particle; Acidity; Visibility; IMPROVE

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## 1. Introduction

Particulate nitrate comprises a significant fraction of airborne particulate matter at many locations. Measurement of nitrate ion in aerosol samples, unfortunately, provides no information about the form of nitrate. In many cases, it is assumed that the nitrate is present in the form of submicron

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ammonium nitrate, a semi-volatile compound reversibly formed from gas phase nitric acid and ammonia. Several investigators, however, have observed formation of coarse particle nitrate resulting from reaction of nitric acid, or its precursors, with sea salt or soil dust, both in laboratory and field environments (e.g., Abbatt and Waschewsky, 1998; De Haan and Finlayson-Pitts, 1997; Gard et al., 1998; Goodman et al., 2000; Grassian, 2002; Hanisch and Crowley, 2001; Jordan et al., 2003; Laskin et al., 2002, 2005; Ooki and Uematsu, 2005; Pakkanen et al., 1996; Sullivan et al., 2006; ten Brink, 1998; Umann et al., 2005; Underwood et al., 2001; Zhuang et al., 1999).

In aerosol monitoring networks where composition measurements focus on  $PM_{2.5}$  samples, interpretation of measured nitrate can be complex. The  $PM_{2.5}$  size fraction can contain submicron ammonium nitrate and/or the lower tail of a coarse mode of nitrate present with reacted sea salt or soil dust. In the United States, the Interagency Monitoring of PROtected Visual Environments (IMPROVE) program historically has measured  $PM_{2.5}$  nitrate and assumed this represented ammonium nitrate. A similar assumption is often made in other monitoring networks. More detailed investigations of aerosol composition at two IMPROVE measurement locations, Big Bend National Park, Texas and Yosemite National Park, California, however, revealed that much of the nitrate measured in summertime aerosol was actually reacted sea salt with periodic contributions from reacted soil dust. In Big Bend (Lee et al., 2004), the fine particle aerosol fraction was dominated by acidic sulfate particles and summertime temperatures were hot, both factors that limit formation of ammonium nitrate. Nitric acid in the gas phase, however, was available to react with sea salt transported to the site from the Gulf of Mexico and with dust aerosol. During summer measurements at Yosemite (Malm et al., 2005), there was sufficient ammonia to neutralize aerosol sulfate, but warm dry conditions prevented significant formation of ammonium nitrate during most of the 2 months measurement period. Particulate nitrate concentrations were found to correlate strongly with  $Na^+$  concentrations, both temporally and as a function of particle size, and significant loss of chloride was observed in the aerosol, all evidence of nitric acid reaction with sea salt at this location.

The results at Big Bend and Yosemite National Parks suggested a need to further explore the

dominant forms of nitrate at a variety of rural monitoring locations. Here, we describe results from an investigation of the forms of particulate nitrate present at several IMPROVE monitoring sites. The findings represent new insight into characteristics of particle nitrate at several rural measurement locations in different parts of the United States. Understanding the form of nitrate present in the aerosol is important for understanding mechanisms controlling particle nitrate formation, the atmospheric lifetime of the nitrate, and its hygroscopic and optical properties.

## 2. Methods

A series of intensive field experiments was designed and conducted to investigate aerosol particle characteristics at five IMPROVE monitoring sites in the United States in 2003 and 2004. Measurements were made at Bondville, Illinois (February 2003), Brigantine National Wildlife Refuge, New Jersey (November 2003), San Geronio Wilderness Area, California (April and July 2003), Grand Canyon National Park, Arizona (May 2003), and Great Smoky Mountains National Park, Tennessee (July/August 2004). Each field campaign lasted approximately 1 month. Most of the campaigns were scheduled to examine locations where historical IMPROVE observations suggested important  $PM_{2.5}$  contributions from nitrate and time periods when nitrate concentrations were near their annual historic peak at each study location. Two campaigns were scheduled for the nitrate-rich San Geronio, CA site to investigate changes in particle composition and gas-particle partitioning moving from spring to summer. Table 1 summarizes location information and measurement periods for each field campaign.

Measurements were made at Bondville in order to examine wintertime, Midwest US aerosol properties. This region experiences high nitrate concentrations during the cooler months of the year. The San Geronio site was included because of heavy impacts from the Los Angeles air basin located to the west, which result in the highest nitrate concentrations of any IMPROVE site. Grand Canyon was included in the study to investigate aerosol nitrate properties at a site located on the Colorado Plateau. This region is of interest in part because it is home to the so-called *Golden Circle* of National Parks prized for their scenic vistas, making good visual air quality a high

Table 1  
Study site information

Location	State	Longitude	Latitude	Elevation (m)	Study period
Bondville	IL	−88.3719	40.0514	211	2/01/03–2/27/03
San Geronio Wilderness Area	CA	−116.9013	34.1924	1705	4/04/03–4/26/03 7/01/03–7/30/03
Grand Canyon National Park	AZ	−111.9841	35.9731	2267	5/01/03–5/30/03
Brigantine National Wildlife Refuge	NJ	−74.4492	39.465	5	11/4/03–11/30/03
Great Smoky Mountains National Park	TN	−83.9416	35.6334	810	7/26/04–8/18/04

priority. The Brigantine site was included in the study to represent an eastern US coastal location, where mixing of polluted continental and marine air masses might produce interesting aerosol chemistry situations. The final campaign was conducted at Great Smoky Mountains National Park in summertime, to characterize aerosol nitrate and potential, associated sampling artifacts, in a highly polluted, acidic, sulfate-dominated environment.

PM<sub>2.5</sub> inorganic ion species (Cl<sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, NO<sub>3</sub><sup>−</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) and gas phase concentrations of HNO<sub>3</sub>, NH<sub>3</sub>, and SO<sub>2</sub> were measured using an URG annular denuder/filter-pack system. Several sampling configurations were operated in parallel, as described in detail elsewhere (Yu et al., 2005, 2006), to address a variety of broader study objectives. Briefly, measurements presented here were obtained using a configuration featuring a PM<sub>2.5</sub> cyclone, two annular denuders for collection of acidic (sodium carbonate coating) and basic (phosphorous acid coating) trace gases, a nylon filter (Gelman Nylasorb, 1.0 μm pore size), and a backup phosphorous acid-coated denuder (to collect any ammonia volatilized from particles collected on the nylon filter). The nylon filter was demonstrated to efficiently retain any nitric acid volatilized from collected nitrate particles (Yu et al., 2005).

In order to observe temporal changes in aerosol characteristics, a Particle Into Liquid Sampler (PILS) coupled to two ion chromatographs (IC) was used to measure PM<sub>2.5</sub> concentrations of Cl<sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, NO<sub>3</sub><sup>−</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup> at 15-min time resolution. The overall approach of PILS/IC is to collect aerosol particles into a small continuous flow of water for on-line ion analysis. This is accomplished by generating supersaturated water vapor and mixing it with a denuded sample air stream. Particles ( $D_p > 50$  nm) nucleate and grow to several μm in a growth chamber and are inertially collected in a liquid stream (Orsini et al., 2003; Sorooshian et al., 2006; Weber et al., 2001, 2003).

The liquid stream was injected into two ICs every 15 min for measurement of aerosol anions and cations. A LiBr internal standard was used to account for dilution of the liquid carrier stream resulting from water vapor condensation on collected particles. System denuders were changed approximately every 5–6 days, at which time a system blank was determined and IC calibration verified.

Aerosol particle ion (Cl<sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, NO<sub>3</sub><sup>−</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) size distributions were determined using a Micro-Orifice Uniform Deposit Impactor (MOUDI) operated at 30 L min<sup>−1</sup>. Samples were typically collected over 48 h periods to ensure adequate mass collection at these rural sites. To reduce particle bounce, silicone spray-coated aluminum foil was used as the impaction substrates with a 37 mm Teflon after-filter following the last impaction stage. The MOUDI was operated with eight stages with aerodynamic diameter size ranges:  $D_p > 18$  μm, 18–10 μm, 10–5.6 μm, 5.6–3.2 μm, 3.2–1.8 μm, 1.8–1.0 μm, 1.0–0.56 μm, 0.32–0.18 μm and after-filter ( $D_p < 0.18$  μm).

Replicate denuder/filter-pack samples were collected periodically during the field experiments for determination of measurement precision (5–9% RSD for major aerosol ion species SO<sub>4</sub><sup>2−</sup>, NO<sub>3</sub><sup>−</sup>, and NH<sub>4</sub><sup>+</sup> and trace gases HNO<sub>3</sub>, SO<sub>2</sub>, and NH<sub>3</sub>; 8–22% RSD for lower concentration species). URG and MOUDI sampler blanks were also collected periodically to determine method detection limits. Samples collected by the URG and MOUDI samplers were analyzed in our laboratory at Colorado State University using two Dionex DX-500 automated ICs employing standard techniques of IC (see Yu et al., 2005).

### 3. Results and discussion

Measurements at each of the five study sites were examined in order to investigate the main form(s) of

aerosol nitrate at each location and to compare with previous findings at Big Bend and Yosemite National Parks. Principal pieces of information used in this approach include analysis of general aerosol characteristics (e.g., is  $\text{NH}_4^+$  present at levels greater than needed to neutralize observed  $\text{SO}_4^{2-}$  concentrations? Is there evidence of chloride loss from sea salt?), comparison of individual species' size distributions (e.g., is  $\text{NO}_3^-$  found in coarse particles, fine particles, or both?), and analysis of temporal covariance in species concentrations (e.g., do nitrate concentrations co-vary at high time resolution with  $\text{NH}_4^+$  concentrations? with  $\text{Na}^+$  concentrations?). Because space limitations preclude showing all study data in this manuscript, we will highlight selected pieces of information from each site that provide the best insight into the forms of nitrate present in the aerosol. Drawing on the full suite of study observations, we then draw some conclusions about the relative contribution of various forms of nitrate to aerosol measured at each location.

### 3.1. San Geronio Wilderness Area

Concentrations of  $\text{PM}_{2.5}$  nitrate, sulfate, and ammonium measured at San Geronio in April and July are compared in Fig. 1. It is apparent for both periods that the  $\text{NH}_4^+$  concentration significantly exceeds the amount needed to neutralize measured sulfate. During April, one sees that  $\text{NH}_4^+$  closely balances with the sum of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$ , suggesting the  $\text{PM}_{2.5}$  aerosol fraction contains a mix of ammonium sulfate and ammonium nitrate. A similar picture is seen on many days in July; however, for some days there is insufficient  $\text{NH}_4^+$  to neutralize both sulfate and nitrate, suggesting another cation species may be important in the  $\text{PM}_{2.5}$ .

Fig. 2 shows  $\text{PM}_{2.5}$   $\text{Cl}^-$  concentrations  $[\text{Cl}^-]$  plotted against  $\text{PM}_{2.5}$   $[\text{Na}^+]$  for April and July. The observed  $[\text{Cl}^-]/[\text{Na}^+]$  equivalent ratio in April is close to the ratio of  $[\text{Cl}^-]$  to  $[\text{Na}^+]$  in seawater (1.164), suggesting some sea salt is reaching the site. This picture changes significantly in July, however, when the  $[\text{Cl}^-]/[\text{Na}^+]$  ratio falls far below the seawater ratio, indicating significant loss of chloride from sea salt aerosol transported to San Geronio. Ratios of the sum of  $\text{PM}_{2.5}$   $[\text{Cl}^-]$  and  $[\text{NO}_3^-]$  to  $[\text{Na}^+]$  in July, by contrast, fall at or above the seawater ratio of  $[\text{Cl}^-]/[\text{Na}^+]$ . This pattern indicates likely replacement of sea salt aerosol chloride by

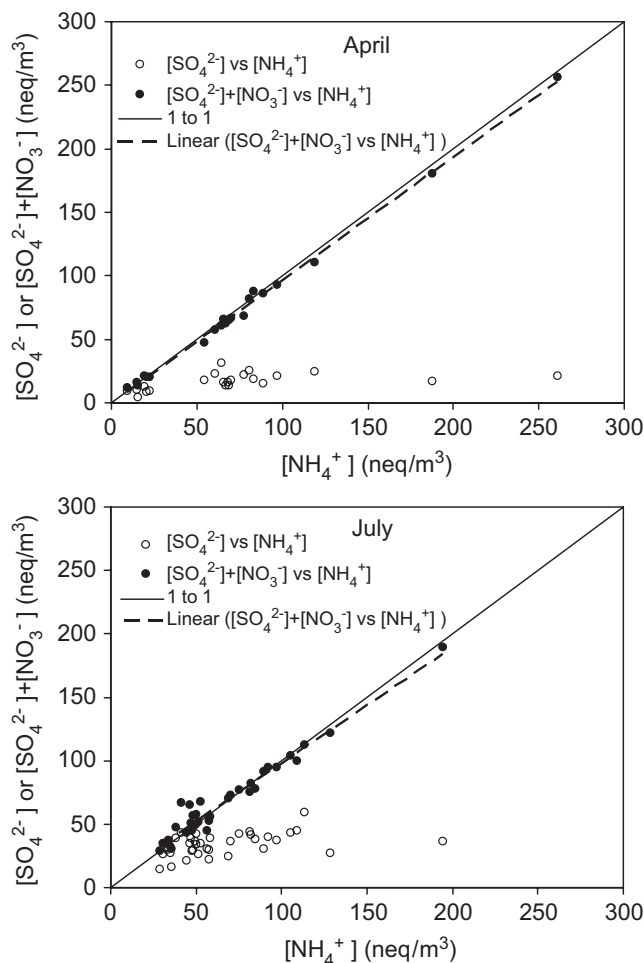


Fig. 1. Relationship of URG  $\text{PM}_{2.5}$  concentrations of sulfate, nitrate, and ammonium at San Geronio in April and July. Concentrations are expressed in nanoequivalents  $\text{m}^{-3}$ .

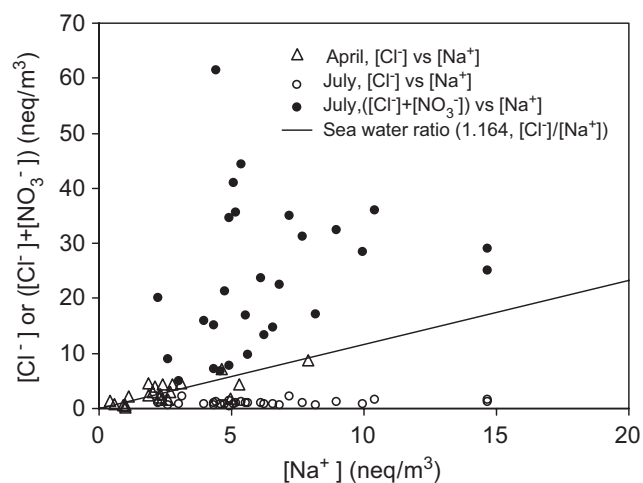


Fig. 2. Comparison of URG  $\text{PM}_{2.5}$   $\text{Cl}^-$  or  $\text{NO}_3^- + \text{Cl}^-$  concentrations and URG  $\text{PM}_{2.5}$   $\text{Na}^+$  concentrations at San Geronio in April and July.



nitrate, reflecting reaction of sea salt with nitric acid or its precursors. Formation of  $\text{NaNO}_3$  is also consistent with the observation that insufficient ammonium was present to balance the sum of nitrate and sulfate on some days in July (Fig. 1). Ratios of  $[\text{Cl}^-] + [\text{NO}_3^-]$  to  $[\text{Na}^+]$  greater than the seawater  $[\text{Cl}^-]/[\text{Na}^+]$  ratio reflect the presence of  $\text{PM}_{2.5} \text{NH}_4\text{NO}_3$ .

Further insight into the properties of San Gorgonio particulate  $\text{NO}_3^-$  is possible through examination of the MOUDI and PILS observations. Fig. 3 depicts the campaign-averaged measured size distributions for  $\text{SO}_4^{2-}$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{Na}^+$ . The MOUDI  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  size distributions are very similar to the shape of the ammonium size distribution in April, with a submicron mode peaked at 0.4–0.5  $\mu\text{m}$  aerodynamic diameter. Some nitrate is seen in supermicron particles. On the other hand,  $\text{NO}_3^-$  and  $\text{Na}^+$  size distributions mainly cover the coarse mode in July, with an aerodynamic mode diameter of  $\sim 4 \mu\text{m}$ . The similarity of the size

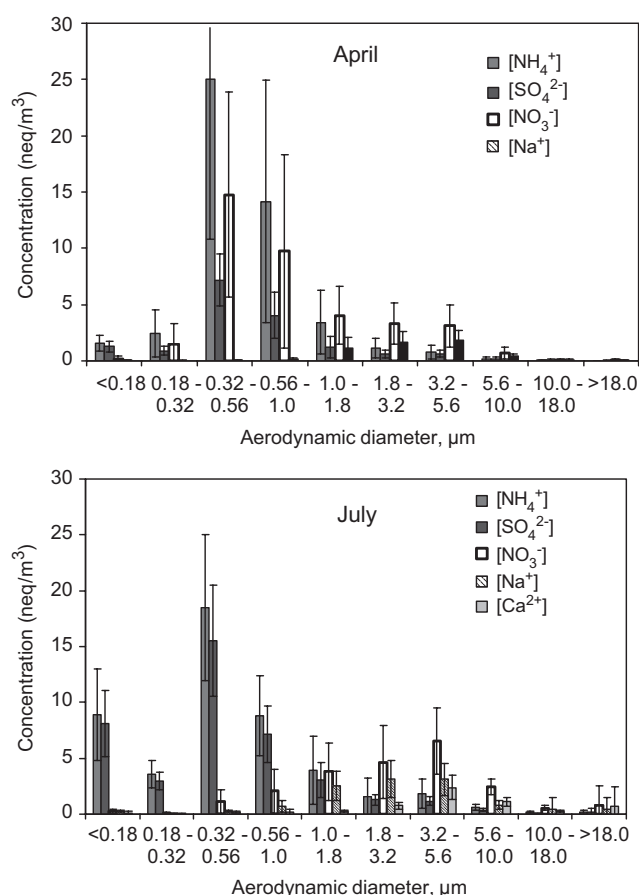


Fig. 3. Study average size distributions of key inorganic ion species measured in aerosol at San Gorgonio in April (top panel) and July (bottom panel). The error bars shown indicate the standard deviation of observed concentration ranges.

distributions for these two species further supports the interpretation above that significant particle  $\text{NO}_3^-$  in July was formed by sea salt particle reaction with gaseous nitric acid. Note that the coarse modes of  $\text{NO}_3^-$  and  $\text{Na}^+$  extend below 2.5  $\mu\text{m}$ , meaning they will be partially included in  $\text{PM}_{2.5}$  observations. The excess of  $\text{NO}_3^-$  over  $\text{Na}^+$  in some particle size bins and the coexistence of  $\text{Ca}^{2+}$  in these particle sizes suggest that some formation of  $\text{Ca}(\text{NO}_3)_2$  from nitric acid reaction with soil dust might also be important. Higher temperatures and lower humidities in summer are less favorable to ammonium nitrate formation, leaving more nitric acid available to react with sea salt or soil dust. Measurements of gas-particle partitioning for nitric acid/nitrate indeed reveal a much larger fraction in the gas phase in July than in April. Loss of semi-volatile ammonium nitrate from submicron aerosol collected by the MOUDI during the summer period, however, exaggerates the relative importance of coarse vs. fine mode nitrate during this season. The loss is apparent by comparison with the URG  $\text{PM}_{2.5}$  measurements, which are designed to retain volatilized nitric acid. Although coarse particle nitrate formation occurs in the atmosphere, fine particle ammonium nitrate remains an important contributor to summertime nitrate concentrations at this location.

Temporal variability in concentrations of  $\text{PM}_{2.5} \text{NO}_3^-$  and  $\text{Na}^+$  is evident in PILS observations from the site (Fig. 4). The diurnal variability evident in the plotted data is driven largely by mountain-valley wind patterns. During daytime upslope flow typically brings increased pollution levels to the site; these decrease again in the evening with the onset of downslope flow. Concentrations of  $\text{Na}^+$  in the measured  $\text{PM}_{2.5}$  far exceed  $\text{PM}_{2.5} \text{Cl}^-$  concentrations much of the time, indicating a loss of  $\text{Cl}^-$  from the precursor sea salt aerosol. This is consistent with other evidence, presented above, suggesting chloride loss due to nitric acid reaction with sea salt particles. Further examination of the PILS timelines, however, reveals that far more nitrate is present in the peak maximum than can be balanced by  $\text{Na}^+$ . A spike in  $\text{Ca}^{2+}$  concentrations (not shown) often accompanies the afternoon nitrate spike, but is also far too small to balance the observed levels of nitrate. PILS measurements of  $\text{NH}_4^+$  (not shown) suggest that a significant fraction of the observed afternoon nitrate peaks is comprised  $\text{NH}_4\text{NO}_3$ , even during the warm conditions experienced in July.

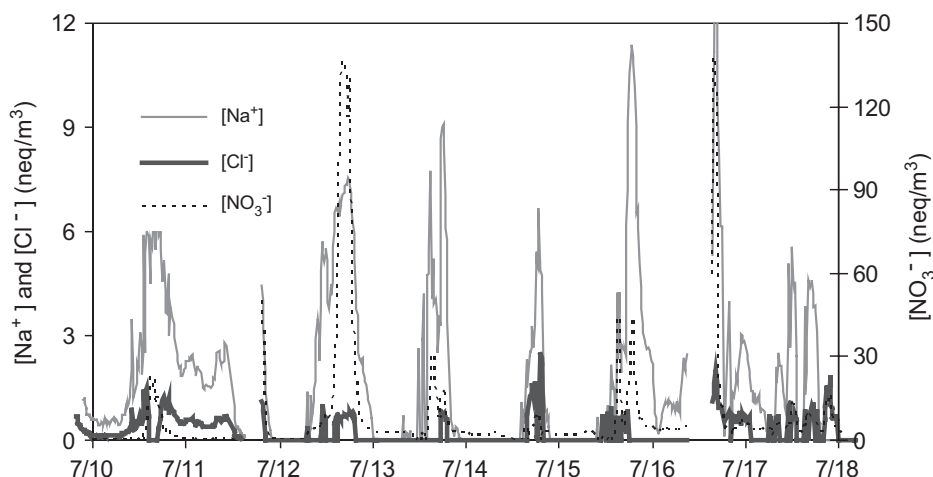


Fig. 4. Timelines of PM<sub>2.5</sub> Na<sup>+</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup> measured using the PILS at San Gorgonio in July. Note the difference in scales used for displaying NO<sub>3</sub><sup>-</sup> (right axis) vs. Na<sup>+</sup> and Cl<sup>-</sup> (left axis) concentrations.

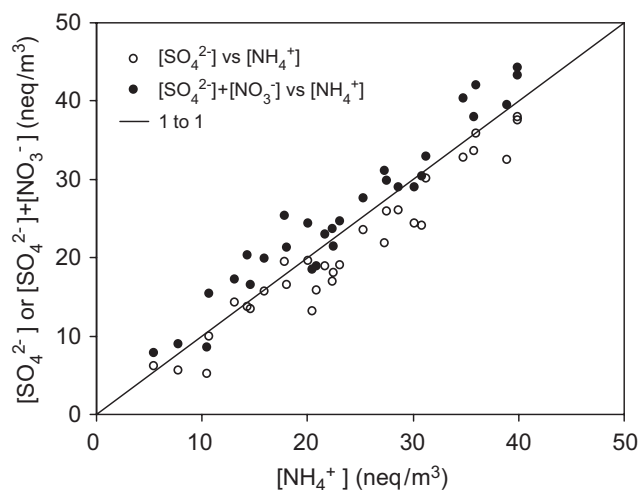


Fig. 5. Relationship of URG PM<sub>2.5</sub> concentrations of sulfate, nitrate, and ammonium at Grand Canyon National Park.

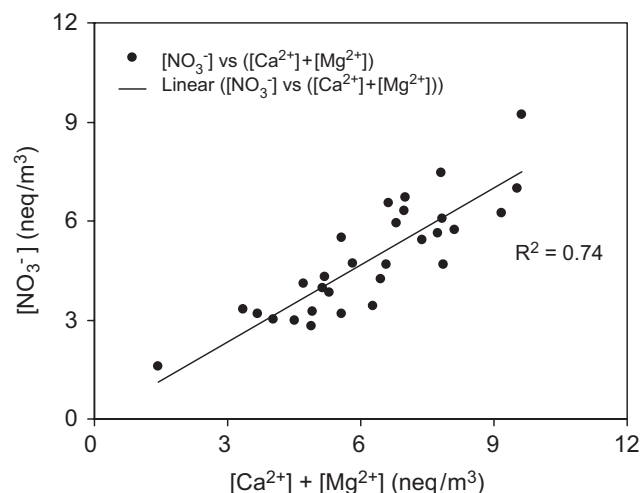


Fig. 6. Relationship of [NO<sub>3</sub><sup>-</sup>] and the sum of [Ca<sup>2+</sup>] and [Mg<sup>2+</sup>] from Grand Canyon URG PM<sub>2.5</sub> measurements.

### 3.2. Grand Canyon National Park

Grand Canyon PM<sub>2.5</sub> ammonium concentrations are compared with PM<sub>2.5</sub> sulfate concentrations and with sums of PM<sub>2.5</sub> sulfate and nitrate concentrations in Fig. 5. The observations indicate that sufficient ammonium is typically present to fully neutralize sulfate but not to balance the sum of sulfate and nitrate, suggesting that other forms of nitrate may be important in this environment. Fig. 6 shows a strong correlation of PM<sub>2.5</sub> nitrate with the sum of PM<sub>2.5</sub> Ca<sup>2+</sup> and Mg<sup>2+</sup>, presumably derived at this location mainly from soil dust. The strength of this correlation suggests that regional soil particles may act as important sinks for gas phase nitric acid. The PILS observations of PM<sub>2.5</sub>

composition (not shown) provide further support for this idea, with nitrate concentrations often tracking changes in Ca<sup>2+</sup> and Mg<sup>2+</sup> and some apparent tracking between Na<sup>+</sup> and nitrate as well. The ratio of Cl<sup>-</sup> to Na<sup>+</sup> in PM<sub>2.5</sub> was observed to consistently fall well below the sea water ratio, indicating possible chloride loss from sea salt transported to this inland site; more than enough nitrate was present to balance the chloride loss, consistent with the apparent importance of mineral forms of nitrate as well.

A strong correlation between particulate nitrate and Na<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> was also observed as a function of particle size in the MOUDI measurements (Fig. 7). While impactor measurements indicated the presence of a largely submicron,

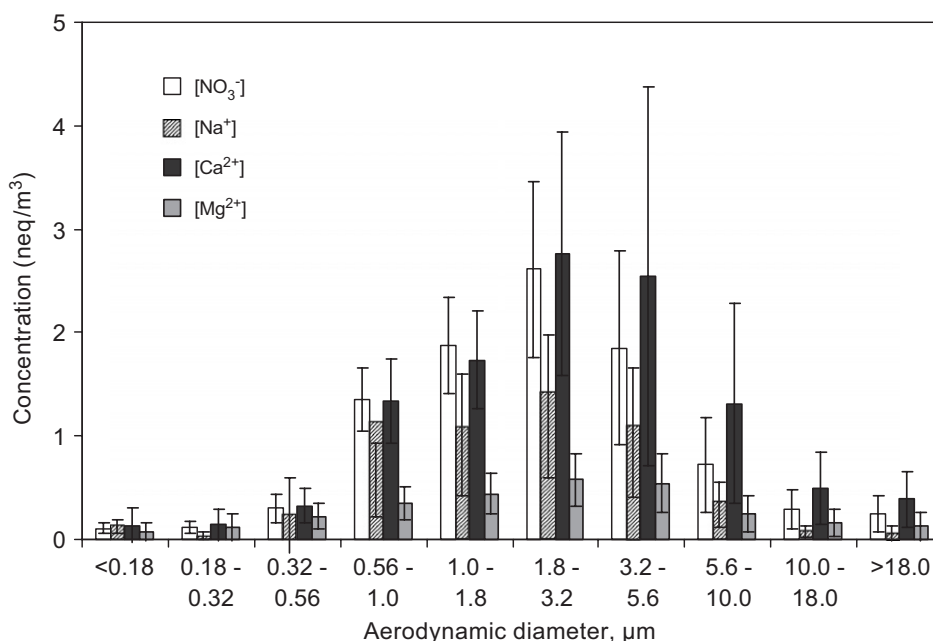


Fig. 7. The study average size distributions of key aerosol ion species at Grand Canyon National Park. Error bars represent the observed standard deviation among individual 48 h measurements.

neutral ammonium sulfate aerosol (not shown), nitrate,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Na}^+$  size distributions peak in the coarse mode with a mode diameter in the 1.8–3.2  $\mu\text{m}$  size bin. Interestingly, there was also some sulfate in coarse particles at this site (in excess of coarse mode ammonium), suggesting either naturally occurring mineral sulfate was present or some sulfate was incorporated into soil dust and/or sea salt particles transported to the site.

### 3.3. Bondville, Illinois

Sulfate, nitrate, and ammonium were the dominant ionic species in daily  $\text{PM}_{2.5}$  at Bondville. Modest correlations between ammonium and sulfate were observed in the daily  $\text{PM}_{2.5}$  URG ( $r^2 = 0.40$ ) and 15 min  $\text{PM}_{2.5}$  PILS ( $r^2 = 0.43$ ) observations. The URG observations are shown in Fig. 8. When nitrate concentrations are added to sulfate concentrations, the correlation with ammonium concentrations improves substantially ( $r^2 = 0.90$  for URG and 0.94 for PILS). The slopes of these latter correlations are also close to one much of the time, indicating sufficient ammonia was usually present to neutralize the aerosol nitrate and sulfate although an acidic sulfate plume sometimes intercepted the site. Average nitrate, sulfate, and ammonium particle size distributions observed using the MOUDI are shown in Fig. 9. The nitrate distribution, like those for ammonium and sulfate,

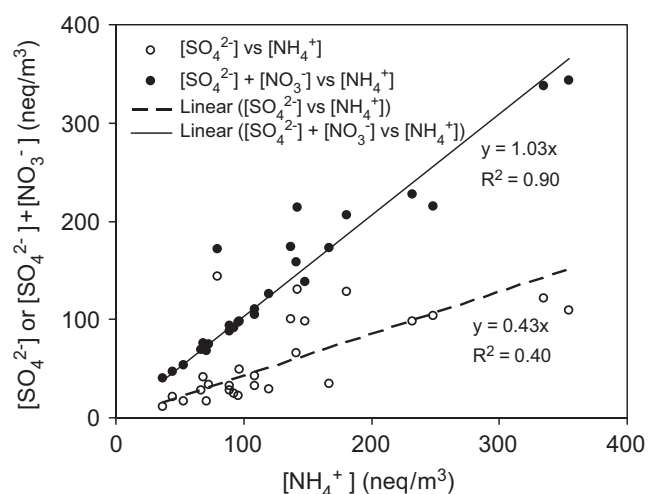


Fig. 8. Relationship of URG  $\text{PM}_{2.5}$  concentrations of sulfate, nitrate, and ammonium at Bondville.

exhibits a clear peak in the 0.32–0.56  $\mu\text{m}$  size bin. A small nitrate coarse mode is also apparent.

All of the measurements made at Bondville are consistent in indicating that ammonium nitrate is the dominant contributor to wintertime particulate nitrate at this location, except during occasional periods when the aerosol is strongly acidic. The prevalence of ammonium nitrate in this environment is consistent with expectations, given the relatively large sources of ammonia in regions often upwind of central Illinois and the low-temperatures characteristic of this region in winter.



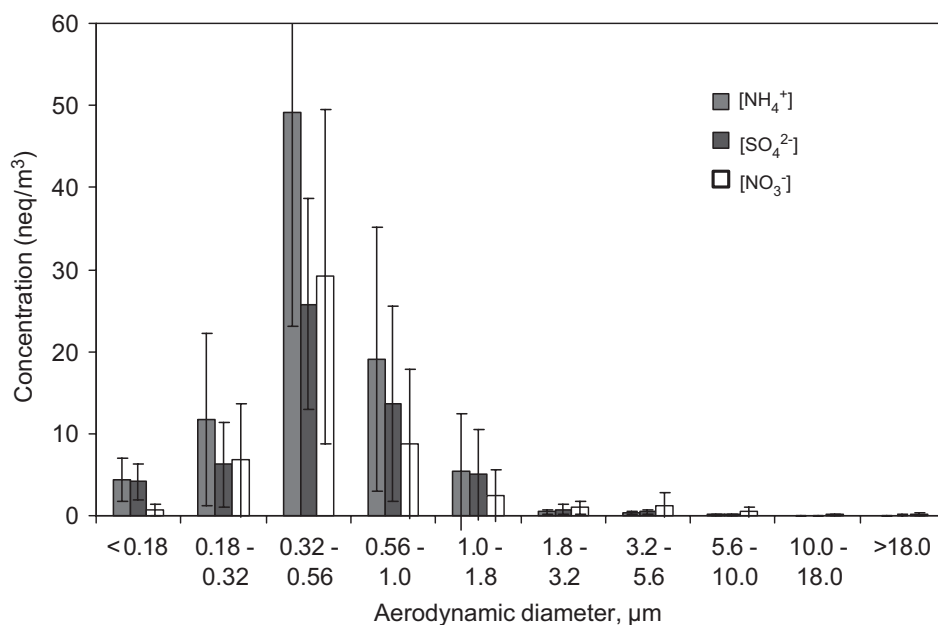


Fig. 9. The study average size distributions of key aerosol ion species at Bondville. Error bars represent the observed standard deviation among individual 48 h measurements.

### 3.4. Brigantine National Wildlife Refuge

Observations at Brigantine National Wildlife Refuge, located along the Atlantic Coast in New Jersey, reveal a mix of influences from coarse and fine particle nitrate. URG  $\text{PM}_{2.5}$  measurements indicate that enough  $\text{NH}_4^+$  is often present to balance the sum of nitrate and sulfate (see Fig. 10), although there are, as at Bondville, a few days where this is not the case. In contrast to Bondville, however, the study average MOUDI observations reveal a bimodal nature to the nitrate particle size distribution (see Fig. 11). Sulfate and ammonium exhibit very similar size distributions, peaking in the 0.32–0.56  $\mu\text{m}$  size bin, with a slight excess of ammonium appearing to balance nitrate concentrations in submicron particles. In supermicron particles, we see a second mode of nitrate that peaks in the 3.2–5.6  $\mu\text{m}$  size bin.  $\text{Na}^+$  and  $\text{Cl}^-$  have similar size distributions in the coarse mode, with the relatively large particle sizes reflecting the proximity of this measurement site to the ocean. A deficit of  $\text{Cl}^-$  relative to  $\text{Na}^+$  is an indicator of sea salt aging through reaction with nitric acid. Looking at individual MOUDI samples for this location (not shown), one can see that a coarse particle nitrate mode is sometimes dominant while in other periods the nitrate is primarily found in submicron particles. Even at

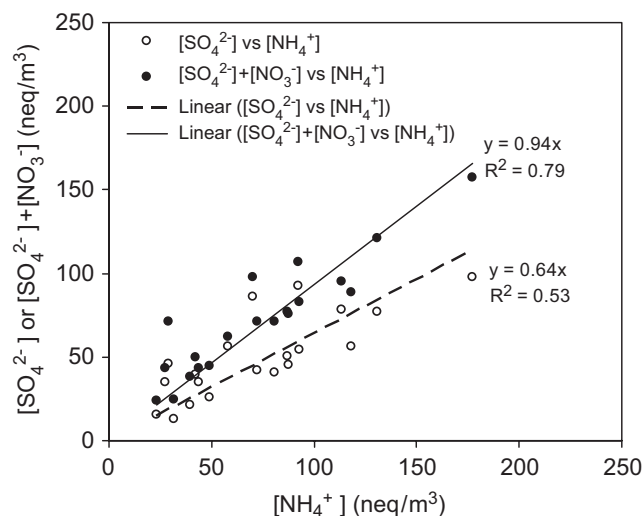


Fig. 10. Relationship of URG  $\text{PM}_{2.5}$  concentrations of sulfate, nitrate, and ammonium at Brigantine.

the 48 h timescale of these measurements, however, we often observed a mix of fine and coarse mode nitrate.

### 3.5. Great Smoky Mountains National Park

Sulfate and ammonium were the dominant ionic species in daily  $\text{PM}_{2.5}$  at Great Smoky Mountains (GRSM), with smaller contributions

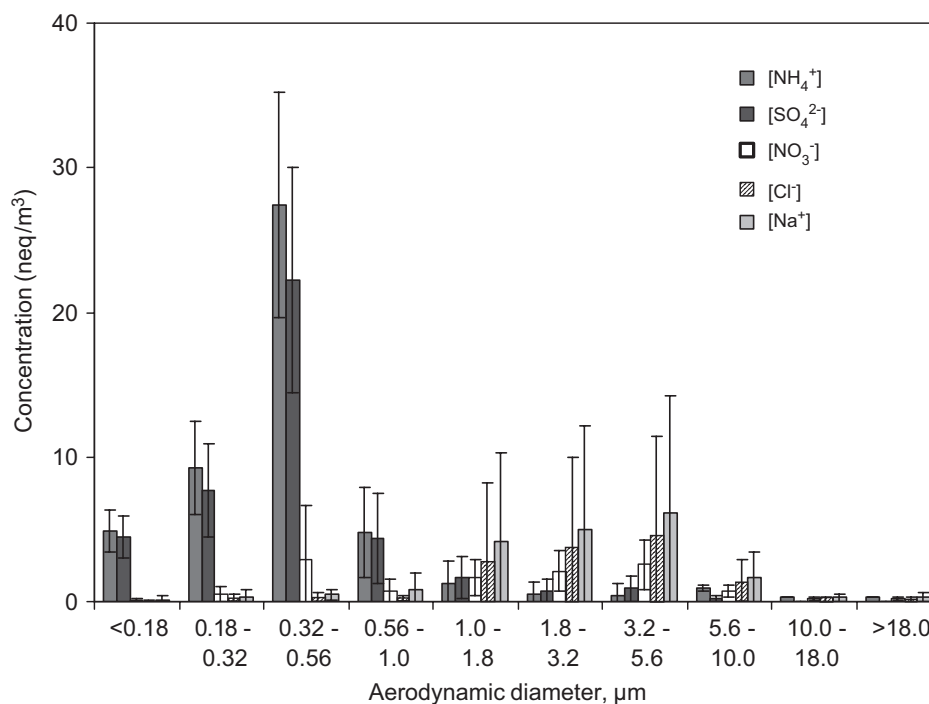


Fig. 11. The study average size distributions of key aerosol ion species at Brigantine. Error bars represent the observed standard deviation among individual 48 h measurements.

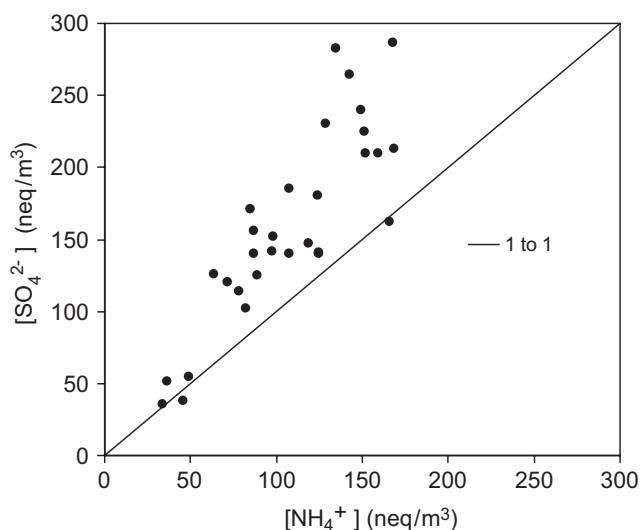


Fig. 12. Relationship of URG  $PM_{2.5}$  concentrations of sulfate and ammonium at Great Smoky Mountains National Park.

from  $NO_3^-$  and  $Na^+$ . Fig. 12 shows  $PM_{2.5}$  sulfate concentrations plotted against ammonium concentrations. Consistent with past observations in this region, there clearly is insufficient ammonium present to neutralize the sulfate acidity in summertime aerosol. The average aerosol acidity in the study was determined to be  $63.3 \text{ nmol m}^{-3}$  of  $H^+$  with a range of  $12.8\text{--}129.8 \text{ nmol m}^{-3}$ . These values are relatively high compared to average urban and

non-urban aerosol acidities measured in several other studies, including locations like Chicago, St. Louis, Boston and Big Bend National Park (Brauer et al., 1991; Koutrakis et al., 1988; Lee et al., 1993, 2004; Spengler et al., 1989). Because the aerosol is so acidic, formation of particulate ammonium nitrate is not favored thermodynamically (Seinfeld and Pandis, 1998). Observed gas/particle phase distributions at GRSM are consistent with the observed aerosol acidity. While on average only 11% of the total N(-III) (gaseous  $NH_3$  plus particulate  $NH_4^+$ ) was observed in the gas phase, 83% of the total N(V) (gaseous  $HNO_3$  plus particulate  $NO_3^-$ ) was in the gas phase.

Acidic sulfate aerosol was observed in fine aerosol particles, with a peak in the  $0.32\text{--}0.56 \mu\text{m}$  size bin. Fig. 13 depicts the study average particle size distributions at GRSM for  $Ca^{2+}$ ,  $Na^+$ , and  $NO_3^-$ . All three species are contained primarily in a coarse particle mode, although the  $Na^+$  distribution peaks one bin smaller in size ( $1.8\text{--}3.2 \mu\text{m}$ ) than the  $NO_3^-$  and  $Ca^{2+}$  modes ( $3.2\text{--}5.6 \mu\text{m}$ ). The amount of nitrate measured in each of the coarse particle size bins is approximately balanced (on a charge equivalent basis) by the amounts of  $Na^+$  and  $Ca^{2+}$ , suggesting a mix of reacted soil dust and reacted sea salt are important for particulate nitrate formation at this location.

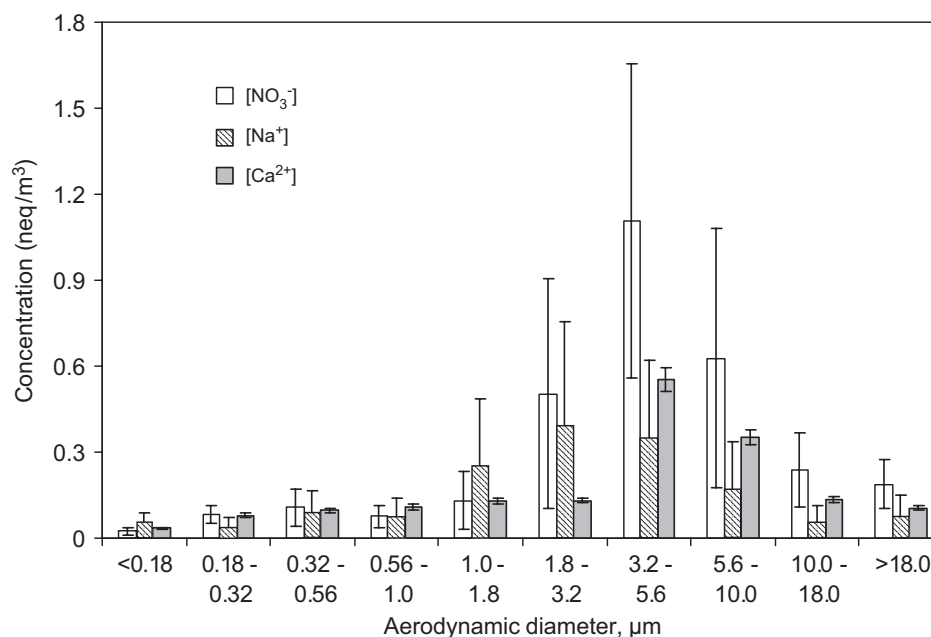


Fig. 13. Study average size distributions of key aerosol ion species at Great Smoky Mountains National Park. Error bars represent the observed standard deviation among individual 48 h measurements.

#### 4. Summary and conclusions

Observations of particulate nitrate at five rural locations in the United States reveal a composition dominated by submicron ammonium nitrate at some locations and times (Bondville, Illinois in winter, San Geronio Wilderness Area, California in spring and summer) while observations at other locations and times (Brigantine, New Jersey in fall, Great Smoky Mountains in summer, Grand Canyon in spring) revealed the presence of significant coarse particle nitrate which appeared to have formed as a result of reactions of nitric acid or its precursors with sea salt and/or soil dust. Observations of important contributions by coarse particle nitrate at these locations are consistent with earlier observations at Big Bend National Park, Texas and Yosemite National Park, California, where high temperatures and/or the acidic nature of fine particles limited ammonium nitrate formation.

To provide a more quantitative overview of the forms of nitrate present at different times and locations, observations of aerosol composition from each field campaign were analyzed to summarize the fraction of fine and coarse particle nitrate present in the form of ammonium nitrate or in other forms. This was done by examining ion concentrations for different particle size ranges measured with the URG or MOUDI sampler. The amount of ammonium nitrate was estimated by first pairing ammo-

Table 2

Summary of the fraction of mineral nitrate in each field campaign

Site	URG PM <sub>2.5</sub> (%)	MOUDI coarse ( $D_p > 1.8 \mu\text{m}$ ) (%)
San Geronio (April)	3	92
San Geronio (July)	6	91
Grand Canyon National Park (May)	50	99
Bondville (February)	15	99
Great Smoky Mountains National Park (July and August)	93	98
Brigantine (November)	15	81

nium with sulfate (as  $(\text{NH}_4)_2\text{SO}_4$ ) and pairing any additional ammonium with nitrate. Remaining nitrate was then assumed to be present as the result of reaction with sea salt or soil dust. This fraction is termed here as “mineral nitrate.” The fraction of nitrate in this “mineral” form is listed by field campaign in Table 2 for PM<sub>2.5</sub> (URG samples) and coarse particles (MOUDI,  $D_p > 1.8 \mu\text{m}$ ). Between 81% and 99% of the coarse particle nitrate appears to be in mineral form in the various studies. Not surprisingly, more variability is seen in PM<sub>2.5</sub> nitrate composition. At San Geronio, Bondville, and Brigantine, two-thirds or more of PM<sub>2.5</sub> nitrate is present as ammonium nitrate. At the other extreme, 93% of PM<sub>2.5</sub> nitrate at GRSM appears to be

present in mineral form, consistent with the acidic fine particles at this location.

Using additional ion measurements (URG PM<sub>2.5</sub> and MOUDI stages with  $D_p > 1.8 \mu\text{m}$ ) we estimated the fraction of total particle nitrate at each study location in the form of ammonium nitrate, reacted sea salt nitrate, and reacted soil dust nitrate. This was done by first pairing nitrate with excess ammonium (beyond that needed to neutralize sulfate, as above), then pairing nitrate with chloride deficient  $\text{Na}^+$  (total  $\text{Na}^+$  minus  $\text{Cl}^-$  multiplied by the sea water ratio of  $\text{Na}^+/\text{Cl}^-$ ), then assuming remaining nitrate is present as calcium nitrate. Although it has been suggested that nitric acid reacts more quickly with soil dust than with sea salt (Evans, 2003; Evans et al., 2004), we made the assignment of  $\text{NaNO}_3$  first in this analysis because additional information about the extent of sea salt reaction was available from measured chloride deficiencies. Results of these calculations are shown in Fig. 14 for the six studies presented here and for

our earlier measurements at Big Bend and Yosemite National Parks. Ammonium nitrate appears to comprise half or more of total particle nitrate at Bondville in winter, at San Gorgonio in spring, at Brigantine in fall, and at Yosemite in summer. (Note: Because  $\text{NH}_4\text{NO}_3$  concentrations occasionally rise to very high levels at some locations, the apparent importance of fine vs. coarse mode nitrate is weighted somewhat toward fine particle nitrate when considering average nitrate concentrations. Looking at the number of days where coarse nitrate is a large contributor to total particulate nitrate provides a somewhat different perspective.) The smallest contributions of ammonium nitrate are at two sites with strongly acidic aerosol: GRSM (2% study average) and Big Bend (1%).

By our estimates, sea salt nitrate is generally a larger contributor to total particle nitrate than nitrate associated with reacted soil dust.  $\text{NaNO}_3$  is estimated to comprise 39% or more of total particle nitrate at Yosemite (summer, 59%), Grand Canyon

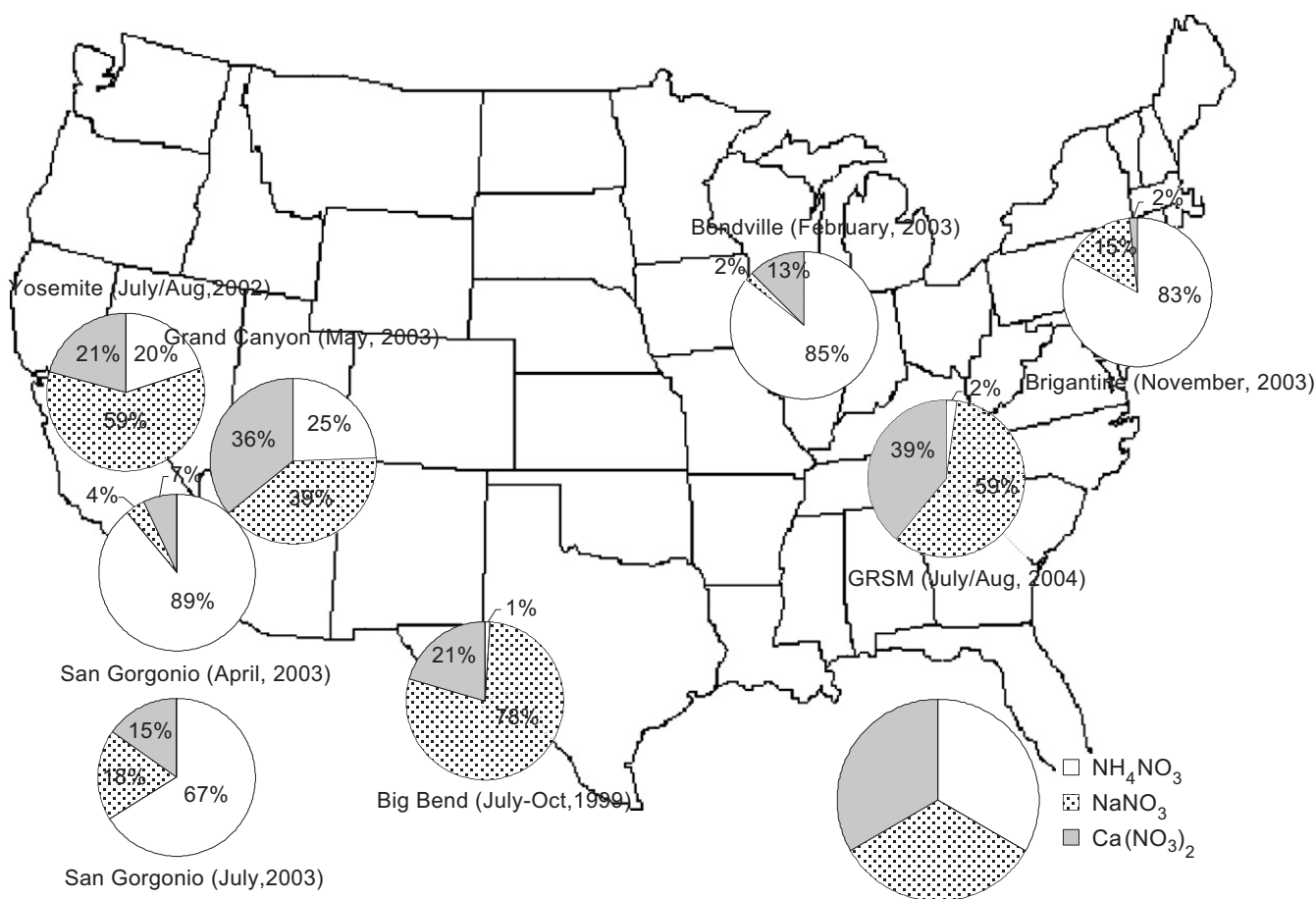


Fig. 14. Estimated fractions of total particulate nitrate during each field campaign comprised ammonium nitrate, reacted sea salt nitrate (shown as  $\text{NaNO}_3$ ), and reacted soil dust nitrate (shown as  $\text{Ca}(\text{NO}_3)_2$ ). The method for estimating the fractional contribution from each nitrate form is described in the text.

(spring, 39% (if we neglect the possible presence of sodium sulfate)), Big Bend (summer and fall, 78%), and GRSM (summer, 59%). Important contributions of reacted sea salt to total particle nitrate are also apparent at San Gorgonio (summer, 18%) and Brigantine (fall, 15%). Significant inputs to total particle by nitrate associated with reacted soil dust are estimated at several locations as well, with values of 15% or more at Yosemite (summer), Grand Canyon (spring), San Gorgonio (summer), Big Bend (summer/fall), and GRSM (summer). The importance of soil dust nitrate at Grand Canyon and Big Bend, in particular, is not surprising, given the arid regions that reside upwind of these parks. In looking at all these patterns, it is important to keep in mind the relative importance of nitrate to total aerosol at these sites. On a mass fraction basis, nitrate contributed nearly 60% on average to  $PM_{2.5}$  measured ions at San Gorgonio in April and approximately 30% in July, approximately 45% in Bondville in February, a little over 20% at Brigantine in November, approximately 15% at Grand Canyon in May and <5% at GRSM in July/August.

Overall, the findings reported here indicate that it is not uncommon at rural locations US for a significant fraction of particulate nitrate to be present in forms other than ammonium nitrate. This situation, as one would expect, is more likely in environments where the aerosol is acidic and/or temperatures are high. The presence of a coarse particle sink for nitric acid is also, of course, an important ingredient for coarse particle nitrate formation. These results suggest a need to more closely examine common assumptions regarding the importance of ammonium nitrate at rural locations, to include pathways for coarse mode nitrate formation in regional models, and to consider impacts of coarse particle nitrate on visibility, nitrogen deposition, and other issues. Further, since coarse particle nitrate modes often extend well below  $2.5\ \mu\text{m}$  aerodynamic diameter, measurements of  $PM_{2.5}$  nitrate in these environments should not automatically be assumed to contain only ammonium nitrate.

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### References

- Abbatt, J.P.D., Waschewsky, G.C.G., 1998. Heterogeneous interactions of HOBr,  $\text{HNO}_3$ ,  $\text{O}_3$ , and  $\text{NO}_2$  with deliquescent NaCl aerosols at room temperature. *Journal of Physical Chemistry A* 102 (21), 3719–3725.
- Brauer, M., Koutrakis, P., Keeler, G.J., Spengler, J.D., 1991. Indoor and outdoor concentration of inorganic acidic aerosols and gases. *Journal of Air & Waste Management Association* 41 (2), 171–181.
- De Haan, D.O., Finlayson-Pitts, B.J., 1997. Knudsen cell studies of the reaction of gaseous nitric acid with synthetic sea salt at 298 K. *Journal of Physical Chemistry A* 101 (51), 9993–9999.
- Evans, M.C.F., 2003. Characterization and formation of particulate nitrate in a coastal area. Ph. D. Thesis, University of South Florida.
- Evans, M.C., Campbell, S.W., Bhethanabotla, V., Poor, N.D., 2004. Effect of sea salt and calcium carbonate interactions with nitric acid on the direct dry deposition of nitrogen to Tampa Bay, Florida. *Atmospheric Environment* 38 (29), 4847–4858.
- Gard, E.E., Kleeman, M.J., Gross, D.S., Hughes, L.S., Allen, J.O., Morrical, B.D., Fergenson, D.P., Dienes, T., Galli, M.E., Johnson, R.J., Cass, G.R., Prather, K.A., 1998. Direct observation of heterogeneous chemistry in the atmosphere. *Science* 279 (5354), 1184–1187.
- Goodman, A.L., Underwood, G.M., Grassian, V.H., 2000. A laboratory study of the heterogeneous reaction of nitric acid on calcium carbonate particles. *Journal of Geophysical Research* 105 (D23), 29053–29064.
- Grassian, V.H., 2002. Chemical reactions of nitrogen oxides on the surface of oxide, carbonate, soot, and mineral dust particles: implications for the chemical balance of the troposphere. *Journal of Physical Chemistry A* 106 (6), 860–877.
- Hanisch, F., Crowley, J.N., 2001. Heterogeneous reactivity of gaseous nitric acid on  $\text{Al}_2\text{O}_3$ ,  $\text{CaCO}_3$ , and atmospheric dust samples: a Knudsen cell study. *Journal of Physical Chemistry A* 105 (13), 3096–3106.
- Jordan, C.E., Dibb, J.E., Anderson, B.E., Fuelberg, H.E., 2003. Uptake of nitrate and sulfate on dust aerosols during TRACE-P. *Journal of Geophysical Research-Atmospheres* 108 (D21), 1–10.
- Koutrakis, P., Wolfson, J.M., Spengler, J.D., 1988. An improved method for measuring aerosol strong acidity—results from a 9-month study in St-Louis, Missouri and Kingston, Tennessee. *Atmospheric Environment* 22 (1), 157–162.
- Laskin, A., Iedema, M.J., Cowin, J.P., 2002. Quantitative time-resolved monitoring of nitrate formation in sea salt particles



- using a CCSEM/EDX single particle analysis. *Environmental Science & Technology* 36 (23), 4948–4955.
- Laskin, A., Wietsma, T.W., Krueger, B.J., Grassian, V.H., 2005. Heterogeneous chemistry of individual mineral dust particles with nitric acid: A combined CCSEM/EDX, ESEM, and ICP-MS study. *Journal of Geophysical Research-Atmospheres* 110 (D10), D10208.
- Lee, H.S., Wadden, R.A., Scheff, P.A., 1993. Measurement and evaluation of acid air pollutants in Chicago using an annular denuder system. *Atmospheric Environment* 27A, 543–553.
- Lee, T., Kreidenweis, S.M., Collett Jr., J.L., 2004. Aerosol ion characteristics during the Big Bend regional aerosol and visibility observational study. *Journal of Air & Waste Management Association* 54, 585–592.
- Malm, W.C., Day, D.E., Carrico, C., Kreidenweis, S.M., Collett Jr., J.L., McMeeking, G., Lee, T., Carrillo, J., Schichtel, B., 2005. Intercomparison and closure calculations using measurements of aerosol species and optical properties during the Yosemite aerosol characterization study. *Journal of Geophysical Research-Atmospheres* 110 (D14), D14302.
- Ooki, A., Uematsu, M., 2005. Chemical interactions between mineral dust particles and acid gases during Asian dust events. *Journal of Geophysical Research-Atmospheres* 110 (D3), D03201.
- Orsini, D.A., Ma, Y.L., Sullivan, A., Sierau, B., Baumann, K., Weber, R.J., 2003. Refinements to the particle-into-liquid sampler (PILS) for ground and airborne measurements of water soluble aerosol composition. *Atmospheric Environment* 37 (9–10), 1243–1259.
- Pakkanen, T.A., Kerminen, V.-M., Hillamo, R.E., Mäkinen, M., Mäkelä, T., Virkkula, A., 1996. Distribution of nitrate over sea-salt and soil derived particles—Implications from a field study. *Journal of Atmospheric Chemistry* 24, 189–205.
- Seinfeld, J.H., Pandis, S.N., 1998. *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*. Wiley, New York.
- Sorooshian, A., Brechtel, F.J., Ma, Y.L., Weber, R.J., Corless, A., Flagan, R.C., Seinfeld, J.H., 2006. Modeling and characterization of a particle-into-liquid sampler (PILS). *Aerosol Science and Technology* 40 (6), 396–409.
- Spengler, J.D., Keeler, G.J., Koutrakis, P., Ryan, P.B., Raizenne, M., Franklin, C.A., 1989. Exposures to acidic aerosols. *Environmental Health Perspectives* 79, 43–51.
- Sullivan, R.C., Guazzotti, S.A., Sodeman, D.A., Prather, K.A., 2006. Direct observations of the atmospheric processing of Asian mineral dust. *Atmospheric Chemistry and Physics Discussions* 6, 4109–4170.
- ten Brink, H.M., 1998. Reactive uptake of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> in sea-salt (NaCl) particles. *Journal of Aerosol Science* 29 (1–2), 57–64.
- Umann, B., Arnold, F., Schaal, C., Hanke, M., Uecker, J., Aufmhoff, H., Balkanski, Y., Van Dingenen, R., 2005. Interaction of mineral dust with gas phase nitric acid and sulfur dioxide during the MINATROC II field campaign: first estimate of the uptake coefficient  $\gamma(\text{HNO}_3)$  from atmospheric data. *Journal of Geophysical Research—Atmospheres* 110 (D22), D22306.
- Underwood, G.M., Song, C.H., Phadnis, M., Carmichael, G.R., Grassian, V.H., 2001. Heterogeneous reactions of NO<sub>2</sub> and HNO<sub>3</sub> on oxides and mineral dust: a combined laboratory and modeling study. *Journal of Geophysical Research—Atmospheres* 106 (D16), 18055–18066.
- Weber, R.J., Orsini, D., Daun, Y., Lee, Y.N., Klotz, P.J., Brechtel, F., 2001. A particle-into-liquid collector for rapid measurement of aerosol bulk chemical composition. *Aerosol Science and Technology* 35 (3), 718–727.
- Weber, R., Orsini, D., Duan, Y., Baumann, K., Kiang, C.S., Chameides, W., Lee, Y.N., Brechtel, F., Klotz, P., Jongejan, P., ten Brink, H., Slanina, J., Boring, C.B., Genfa, Z., Dasgupta, P., Hering, S., Stolzenburg, M., Dutcher, D.D., Edgerton, E., Hartsell, B., Solomon, P., Tanner, R., 2003. Intercomparison of near real time monitors of PM<sub>2.5</sub> nitrate and sulfate at the US Environmental Protection Agency Atlanta Supersite. *Journal of Geophysical Research—Atmospheres* 108 (D7), 8421.
- Yu, X.-Y., Lee, T., Ayres, B., Kreidenweis, S.M., Collett Jr., J.L., 2005. Particulate nitrate measurement using nylon filters. *Journal of the Air & Waste Management Association* 55, 1100–1110.
- Yu, X.-Y., Lee, T., Ayres, B.R., Kreidenweis, S.M., Collett Jr., J.L., 2006. Loss of fine particle ammonium from denuded nylon filters. *Atmospheric Environment* 40, 4797–4807.
- Zhuang, H., Chan, C.K., Fang, M., Wexler, A.S., 1999. Formation of nitrate and non-sea-salt sulfate on coarse particles. *Atmospheric Environment* 33 (26), 4223–4233.