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Loss of fine particle ammonium from denuded nylon filters

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Abstract

Ammonium is an important constituent of fine particulate mass in the atmosphere, but can be difficult to quantify due to possible sampling artifacts. Losses of semivolatile species such as NH_4NO_3 can be particularly problematic. In order to evaluate ammonium losses from aerosol particles collected on filters, a series of field experiments was conducted using denuded nylon and Teflon filters at Bondville, IL (February 2003), San Gorgonio, CA (April 2003 and July 2004), Grand Canyon NP, AZ (May, 2003), Brigantine, NJ (November 2003), and Great Smoky Mountains National Park (NP), TN (July–August 2004). Samples were collected over 24 h periods. Losses from denuded nylon filters ranged from 10% (monthly average) in Bondville, IL to 28% in San Gorgonio, CA in summer. Losses on individual sample days ranged from 1% to 65%. Losses tended to increase with increasing diurnal temperature and relative humidity changes and with the fraction of ambient total $N(-III)$ (particulate NH_4^+ + gaseous NH_3) present as gaseous NH_3. The amount of ammonium lost at most sites could be explained by the amount of NH_4NO_3 present in the sampled aerosol. Ammonium losses at Great Smoky Mountains NP, however, significantly exceeded the amount of NH_4NO_3 collected. Ammoniated organic salts are suggested as additional important contributors to observed ammonium loss at this location.
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1. Introduction

Atmospheric fine particles are significant contributors to air pollution in many environments. Measuring the concentrations and composition of atmospheric aerosols is key to understanding their sources and effects, including impacts on human health, visibility, pollutant deposition, and climate forcing (Watson and Chow, 2001). Results of long-term monitoring of particle composition by various programs reveal that particle composition varies from one location to another and on various time scales (Malm et al., 1994).

One common approach to characterizing particle composition is collection of aerosol particles on filters followed by extraction and chemical analysis. Filter-based measurement approaches can be problematic in accurate determination of semivolatile aerosol components, including ammonium nitrate (Appel, 1993; Appel and Tokiwa, 1981; Appel et al., 1984), due to the occurrence of both positive and negative sampling artifacts. Positive artifacts

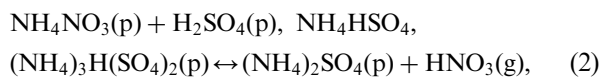*Corresponding author. Tel.: +1 970 491 8697;
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resulting from uptake of relevant gases by collected particles or by the filter medium itself can be reduced by the use of upstream denuders (e.g., to remove gaseous ammonia and nitric acid) (Ali et al., 1989; Allegrini and Desantis, 1989; Allegrini et al., 1994; Baltensperger, 1997; Forrest et al., 1980; Quinn and Bates, 1989).

Negative artifacts, resulting from volatilization of collected particles, can be accounted for by monitoring the volatilized component. In the case of NH_4NO_3, a negative bias can result from volatilization of nitric acid and ammonia via equilibrium 1 (Appel, 1993; Appel et al., 1981, 1980; Richardson and Hightower, 1987; Spicer, 1977; Spicer and Schumacher, 1977):

$$NH_4NO_3(p) \leftrightarrow NH_3(g) + HNO_3(g). \qquad (1)$$
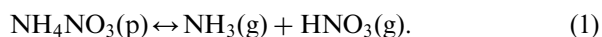
Another source of particulate nitrate loss from filters is via collected ammonium nitrate particles reacting with strong acids releasing HNO_3 (g) following equilibria 2 and 3 (Appel and Tokiwa, 1981; Appel et al., 1981, 1980; Cheng and Tsai, 1997; Harker et al., 1977; Koutrakis et al., 1992; Lawson, 1988; Stelson and Seinfeld, 1982b; Zhang and McMurry, 1987, 1992):

$$NH_4NO_3(p) + H_2SO_4(p), \ NH_4HSO_4,$$
$$(NH_4)_3H(SO_4)_2(p) \leftrightarrow (NH_4)_2SO_4(p) + HNO_3(g), \qquad (2)$$

$$NH_4NO_3(p) + HCl(g) \leftrightarrow NH_4Cl(p) + HNO_3(g). \qquad (3)$$

Thus, accurate determination of NH_4NO_3 is a challenging task.

In the case of ammonium nitrate, volatilized ammonia and nitric acid can be measured using downstream denuders or filters designed to collect these gases. Nylon membrane filters are composed of thin layers of porous nylon (Lee and Ramamurthi, 1993). They have often been utilized for $HNO_3(g)$ collection due to their strong affinity for this species (Babich et al., 2000). In some large networks, such as the Interagency Monitoring of PROtected Visual Environments (IMPROVE) network and the EPA aerosol speciation trends network (Malm et al., 1994; USEPA, 2003), particles are collected directly on nylon filters because of the nylon filter's affinity for nitric acid. In principle, a single nylon filter can be used to collect fine particles and retain any nitric acid that volatilizes from those particles. We recently reviewed the performance of a denuded nylon filter sampling system (Yu et al., 2005b) and found

essentially no nitrate loss from the nylon filter under a wide variety of conditions.

While the nylon filter is efficient at retaining volatilized nitric acid, there is no good reason to expect the nylon filter to retain volatilized ammonia. Little work has been done previously, however, to determine the extent of the negative bias in fine particle ammonium measurement using nylon filters (Solomon et al., 2000). Most previous research on NH_4NO_3 loss focused on Teflon filters (Anlauf et al., 1985; Appel et al., 1981, 1984, 1980; Babich et al., 2000; Fitz and Motallebi, 2000; Quinn and Bates, 1989; Sickles, 1999; Sickles et al., 1990; Tsai et al., 2000; Van Loy et al., 2000) and significant losses of both nitrate and ammonium have been observed. Solomon et al. (2000) examined $PM_{2.5}$ ammonium, sulfate, and nitrate determination for a Federal Reference Method (FRM) low volume air sampler using quartz-fiber filters (Rupprechet and Patashnick Co. Inc.), a Reference Ambient Air Sampler (RAAS) using Teflon filters (Andersen Instruments Incorporated), a Spiral Ambient Speciation Sampler (SASS) using Teflon filters (Met One Instruments), a Mass Aerosol Speciation Sampler (MASS) using quartz-fiber filters (URG Corporation), a Versatile Air Pollution Sampler (VAPS) using quartz-fiber filters (URG Corporation), and an IMPROVE sampler using nylon filters in four different urban locations. Although percentage losses for each species were not explicitly reported, IMPROVE nylon filters had lower ammonium concentrations than the others, suggesting that the basic nature of nylon filters may enhance ammonium volatilization (Solomon et al., 2000).

The extent of ammonium loss can be influenced by several factors that affect equilibrium gas–particle partitioning in the atmosphere. For example, the magnitude of diurnal variations in temperature and relative humidity can strongly influence the position of the equilibrium associated with reaction (1). Changes in air mass composition during the course of sample collection can also influence the magnitude of resulting sampling artifacts. Further, the likelihood of ammonia loss from sampling media also depends on the composition of collected aerosol particles. While ammonium nitrate particles can readily volatilize under changing environmental conditions, for example, loss of ammonia from acidic ammonium bisulfate particles is very unlikely (Bassett and Seinfeld, 1983).

Here we report on the magnitude of ammonia volatilization from daily denuded nylon and Teflon

filter samples collected at several rural locations in the IMPROVE network. Included in the study is a diverse assortment of environments ranging from those where ammonium nitrate is a dominant component of fine particle composition to those where acidic sulfate particles comprise much of the inorganic aerosol mass. Findings of this effort represent an important contribution to understanding potential sampling biases of particulate ammonium, a key component in atmospheric aerosols.

2. Experimental section

A series of field experiments was conducted at several IMPROVE monitoring locations in order to determine potential sampling biases associated with various aerosol sampling configurations. Here we report on the aspects of those field campaigns most directly related to improving understanding of ammonium loss from both Teflon and nylon filter sampling media.

2.1. Field sites

Field campaigns, each approximately 1 month in duration, were carried out at Bondville, IL (February 2003), San Gorgonio Wilderness Area, CA (April 2003 and July 2004), Grand Canyon National Park, Arizona (May, 2003), Brigantine National Seashore, NJ (November 2003) and Great Smoky Mountains National Park (NP), TN (July/August 2004). Bondville was chosen because of its historically high winter nitrate concentrations. The San Gorgonio site, located in the San Bernardino National Forest east of Los Angeles historically has the highest NH_4NO_3 concentrations among all IMPROVE sites (Malm et al., 1994). Grand Canyon was selected to represent sites in the Southwestern US and a spring measurement period was selected as a period when fine particle nitrate concentrations are typically higher in the IMPROVE data record. The Brigantine site was selected to represent a rural location on the Atlantic seaboard, where nitrate is historically high in autumn and where sea salt may be an important aerosol constituent. The final study at Great Smoky Mountains NP was designed to evaluate ammonium loss under polluted summertime conditions when the local aerosol is usually strongly acidic. The selected study sites are mapped in Fig. 1.

2.2. Denuder/filter pack sampling trains

Samples were collected continuously 24 h from 8:00 to 8:00 a.m. local standard time. Annular denuder/filter pack systems (URG-3000C) were manufactured by University Research Glassware, Incorporated. A schematic diagram of the denuder/filter pack sampling train configurations is shown in Fig. 2. Two sampling configurations were utilized, as described below, in the experiments reported here.

The first sampling configuration consisted of a $PM_{2.5}$ cyclone, a carbonate-coated annular denuder to remove gaseous HNO_3, a phosphorous acid-coated annular denuder to remove gaseous NH_3, a filter pack containing two nylon (Nylasorb, pore size 1.0 μm, 37 mm, Pall Corporation) filters in series, and another phosphorous acid-coated annular denuder to capture any ammonia volatilized from collected particles (Rosenberg et al., 1988). The first nylon filter is designed to collect fine particles (those passing through the cyclone), while the second is included to determine whether volatilized nitric acid is lost from the particle collection filter (Yu et al., 2005b). The second sampling configuration is similar to the first except that a Teflon (Teflo, pore size 2.0 um, 37 mm, Pall Corporation)–nylon (T–N) filter pair was used to evaluate potential differences in ammonia and nitric acid loss from Teflon vs. nylon filters. Denuders used in both configurations were 242 mm long (URG-2000-30 × 242-3CSS). The first sampling train was operated daily. The second configuration was operated every 3–4 days. Replicate sampling trains identical to module 1 were also operated periodically to determine measurement precision. Blanks were regularly collected from all filter and denuder types to determine minimum detection limits (MLD) for particle and gas phase species of interest.

2.3. Denuder and filter pack handling

Denuders were cleaned and coated daily. The coating solution to collect nitric acid and other acidic gases contains 10 g Na_2CO_3, 10 g glycerol, 500 ml deionized water, and 500 ml methanol. To remove $NH_3(g)$, the coating solution is made of 10 g phosphorous acid, 100 ml deionized water, and 900 ml methanol. The denuders were dried following coating using a zero air system (Yu et al., 2005b). All filters were handled in an ammonia free

Fig. 1. Locations of study field campaigns.

glove box, an enclosed Plexiglas box with ammonia scrubber (Perma Pure Inc.). Denuders were extracted using 10 ml deionized water immediately in the field and the aliquots were refrigerated before ion chromatography (IC) analysis. Filters were stored in clean sample tubes in a freezer inside clean Ziploc bags with ammonia removing towels (1% phosphorous acid) until extraction. The front nylon filter was extracted using 5 ml deionized water for 30–45 min in an ultrasonic bath. The back-up nylon filter was extracted ultrasonically using 5 mL 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ solution (anion IC eluent) to recover collected nitric acid volatilized from the first filter. We have shown elsewhere (Yu et al., 2005b) that particle nitrate collected on nylon filters in this campaign was removed as efficiently with water extraction (using sonication) as with the alkaline anion IC eluent. Teflon filters were extracted using deionized water and sonication. Then 50 μl ethanol was added to wet the hydro-

phobic Teflon filter surface before extraction (Wolfson, 1980).

2.4. Sample analysis

The aliquots from filter and denuder extraction were analyzed using two Dionex cation and anion IC systems. The cation IC included an IP 20 isocratic pump, CD 20 conductivity detector, CG12A guard column, CS12A separation column and a CSRS-ULTRAI suppressor. The anion IC consisted of a GP 40 gradient pump, CD 20 conductivity detector, AG4A-SC guard column, AS4A-SC separation column, and an ASRS-ULTRA suppressor. The cation eluent was 20 mM methanesulfonic acid at a flow rate of $1.0\,ml\,min^{-1}$; the anion eluent was 1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$ at a flow rate of $2.0\,ml\,min^{-1}$. An autosampler was used for sample injection. The ion chromatographs were calibrated daily by injection of aqueous
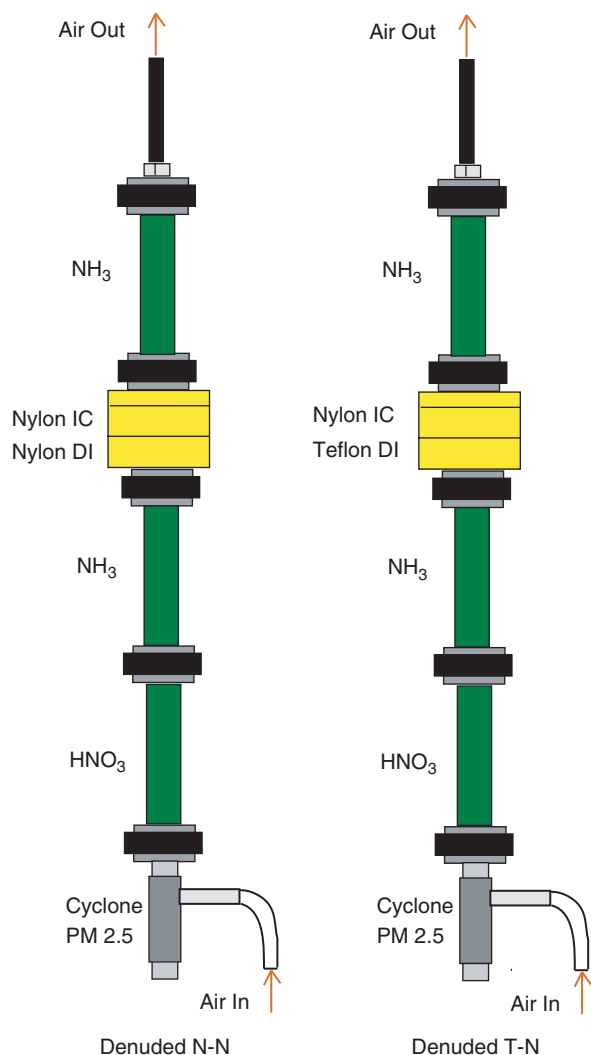
Fig. 2. A schematic diagram of the URG denuder/filter pack configurations.

Table 1
Minimum detection limits (MDL) and pooled relative standard deviations (RSD) of major aerosol species determined from denuded N–N filter packs and denuders

Species	MDL ($\mu g/m^3$)	RSD (%)
Cl^-	0.018	14.4
NO_3^-	0.068	6.74
SO_4^{2-}	0.046	5.19
Na^+	0.008	11.6
NH_4^+	0.030	4.53
K^+	0.015	23.6
Mg^{2+}	0.022	13.9
Ca^{2+}	0.039	12.0
$HNO_3(g)$	0.058	6.06
$SO_2(g)$	0.037	3.24
$NH_3(g)$	0.083	11.9

deviation, RSD) of measured species based on nylon filter blanks and denuded N–N filter pack replicates are listed in Table 1. The MDL of SO_4^{2-}, NO_3^-, and NH_4^+ are 0.05, 0.07, and 0.03 $\mu g\,m^{-3}$. The precisions (RSD) for measuring these species are 5.2%, 6.7%, and 4.5%, respectively. These values are similar to results obtained in a previous study using a similar experimental setup (Lee et al., 2004). Error bars shown in subsequent figures represent $\pm$ one standard deviation.

3. Results and discussion

3.1. Ammonium nitrate loss on denuded nylon filters

Particulate ammonium nitrate collected on a nylon filter is prone to phase transformation following equilibrium 1 with changing environmental conditions, including operation of upstream denuder for ammonia and nitric acid collection. We define the ammonium loss percentage ($BNH_4^+\%$) as the ratio of ammonium captured by the denuder downstream of the filter pack (BNH_4^+) to total NH_4^+, defined as the sum of the ammonium concentration obtained from the first filter (either Teflon or nylon, $NH_4^+{}_{filter}$) and the ammonium concentration obtained from the backup ammonia denuder (BNH_4^+):

$$BNH_4^+\% = \frac{BNH_4^+}{NH_4^+(filter) + BNH_4^+} \times 100\%. \qquad (4)$$

Nitrate loss from denuded nylon filters was negligible in our experiments. In contrast, ammonium loss was observed in all experiments. The degree of ammonium loss varies from site to site as
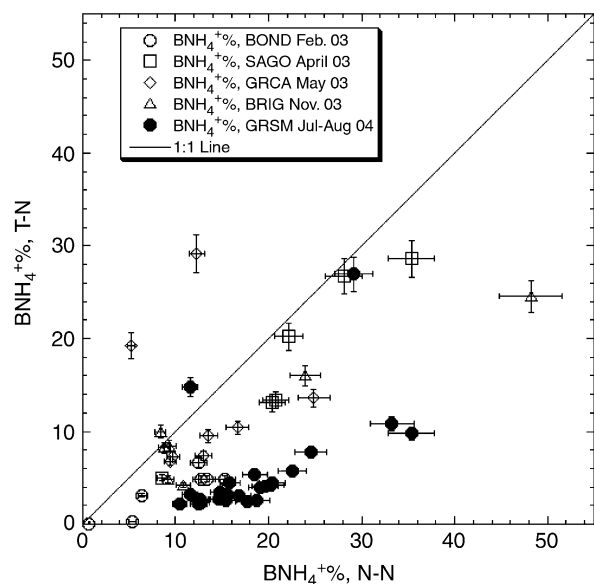
standards prepared in our laboratory from analytical-grade salts. A standard solution was analyzed after every ten samples to monitor any shifts in instrument calibration response. Independent NIST-traceable anion and cation standards (Dionex Corporation) were injected at least daily to verify calibration accuracy.

2.5. Data analysis

MDL for each species were determined from sample blanks. Similar values were obtained for nylon and Teflon filters. Measurement precision was evaluated based on replicate measurements. The MDL and precision (expressed as relative standard

Fig. 3. Ammonium loss comparison between denuded T–N and N–N filter packs. Errors are propagated representing ±one standard deviation.

Table 2
Ammonium nitrate loss from the denuded N–N filter pack in six field experiments

Site	BNH_4^+ %			
	Max	Min	Avg	Std
Bondville, February 03	18	0.7	9.7	5
San Gorgonio, April 03	45	8.6	24	9
Grand Canyon NP, May 03	65	5.2	18	14
Brigantine, November 03	52	5.8	24	14
San Gorgonio, July 04	48	16	28	9
Great Smoky Mountains NP, July–August 04	35	10	18	6

shown in Fig. 3. The maximum, minimum, and average ammonium losses from denuded nylon front filters are summarized in Table 2. Average ammonium losses in the field campaigns range from as low as 10% in Bondville in winter to as high as 28% at San Gorgonio in summer. Intermediate average losses were observed at San Gorgonio in April (24%), Grand Canyon (18%), Great Smoky Mountains (18%), and Brigantine (24%). Daily ammonium losses vary from 1% to 65%.

3.2. Ammonium loss from denuded Teflon vs. nylon filters

A comparison of ammonium loss differences between denuded T–N and N–N filter packs operated simultaneously is summarized in Fig. 3. Average ammonium loss amounts in the paired comparisons are similar for Teflon and nylon filters at Grand Canyon (12.9% and 13.1%), but losses from nylon filters are generally higher at Bondville (9.5% (N–N) and 3.5% (T–N)), San Gorgonio (22.6% (N–N) and 17.8% (T–N), only April data available for this comparison), Brigantine (16.9% (N–N) and 10.9% (T–N)), and Great Smoky Mountains (18.3% (N–N) and 5.5% (T–N)).

A higher pressure drop across the filter may promote dissociation of collected semivolatile particles (Peters et al., 2000). The measured pressure drop

across the nylon–nylon filter pairs is typically 10 in of Hg, whereas the pressure drop across the Teflon–nylon filter pairs is typically 5 in of Hg, suggesting most of the pressure drop results from the nylon filter(s). Differences between the initial and final pressure filter pack drops are typically less than 0.1 in of Hg. The higher pressure drop across the nylon filters probably enhances ammonium loss. Previous theoretical work concluded that evaporation loss of particles from filter samplers depends primarily on pressure drop across the filter and the vapor-to-particle mass distribution of volatile species (Zhang and McMurry, 1991). This idea was later reinforced by Cheng and Tsai (1997). The effect of gas–particle partitioning is discussed in more detail below. It is also possible that the high affinity of the nylon filter medium for nitric acid enhances the loss of ammonium from ammonium nitrate by quickly and tightly binding any nitric acid that dissociates, perhaps promoting further dissociation. If one is measuring only particulate nitrate, our studies indicate this is not problematic (Yu et al., 2005b). Measurement of ammonium, however, clearly can be.

3.3. Temperature, RH, and gas-to-particle partition

The temperature and RH of the sampling environment affect NH_4NO_3-phase transformation (Appel, 1993; Stelson and Seinfeld, 1982a). We examined effects of changing temperature and RH on ammonium loss from the denuded nylon filters. Fig. 4 compares ammonium loss vs. the change in temperature during the 24 h sampling period ($\Delta T = T_{max} - T_{min}$), where T_{max} and T_{min} are maximum and minimum hourly temperatures. Although there is a lot of scatter in the data, there does appear to be a tendency at several sites for ammonium loss to increase as the diurnal temperature swing
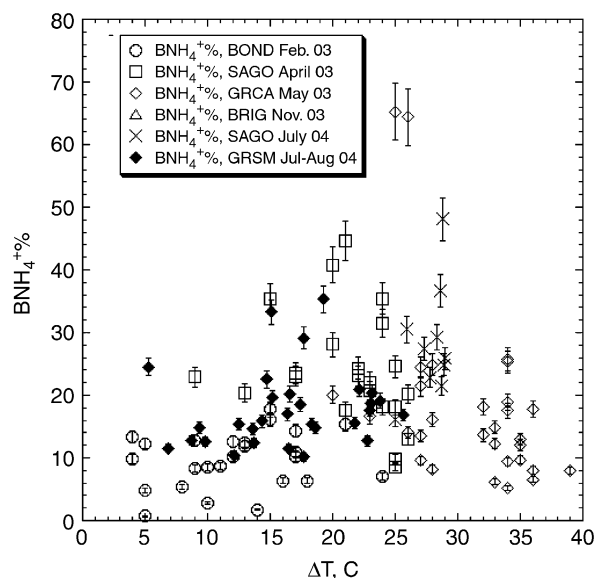
Fig. 4. Scatter plot of ammonium loss from denuded N–N filter packs vs. daily temperature difference. Errors are propagated representing ±one standard deviation.
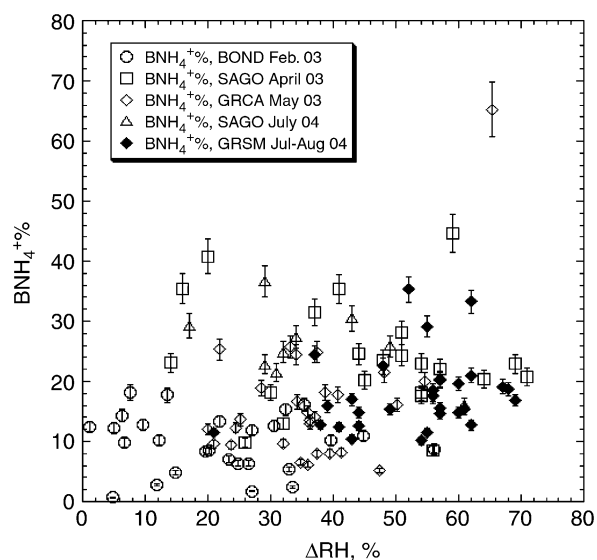

Fig. 5. Scatter plot of ammonium loss from denuded N–N filter packs vs. daily RH difference. Errors are propagated representing ±one standard deviation.

of ΔRH and ΔT on ammonium loss. The global fit for 118 data points is $BNH_4^+\% = (7.85 \pm 2.93) + (0.17 \pm 0.06) \cdot \Delta RH + (0.16 \pm 0.10) \cdot \Delta T$. The resulting, low correlation coefficient ($R^2 = 0.11$) indicates that this simple, linear model does not explain very much of the observed variance in the data. The same 2-parameter model was also tested on individual campaign data sets, yielding similar results.

Undoubtedly temperature and RH have an impact on NH_4NO_3 dissociation (Appel, 1993; Stelson and Seinfeld, 1982b). However, their combined effects are probably not well captured in a simple linear regression analysis, as observed above. This is partly due to the fact that the dependence of the equilibrium constant for gas–particle partitioning of ammonium nitrate does not exhibit a simple linear dependence on T and RH. In addition, by removing nitric acid and ammonia from the gas stream in the two upstream denuders, we are perturbing the gas–particle partitioning state that existed in the ambient air and promoting dissociation of ammonium nitrate.

Assuming the ambient air parcel sampled was at gas–particle partitioning equilibrium, the departure from that equilibrium caused by the sampling system denuders will increase as the fraction of total ammonia (N(−III) = particulate NH_4^+ + gaseous NH_3) present as gaseous ammonia increases. Fig. 6 compares ammonium loss from the denuded
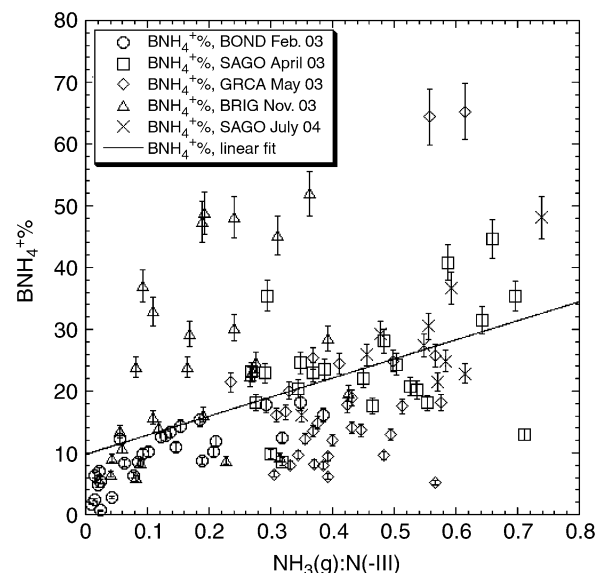

Fig. 6. Scatter plot of ammonium loss from denuded N–N filter packs vs. $NH_3(g):N(-III)$. Errors are propagated representing ±one standard deviation. The solid line is a linear least squares regression fit to all data points.

increases. Fig. 5 depicts a similar comparison of ammonium loss vs ΔRH ($\Delta RH = RH_{max} - RH_{min}$). Brigantine results are not included due to a lack of local RH data. A positive correlation between ammonium loss and change in RH is apparent for individual sites once again. We used multiple linear regression analysis to examine the combined effects

Table 3
Linear least squares regression analyses of $BNH_4^+\%$ vs. $NH_3(g)$: $N(-III)$

Field location	Intercept	Slope	R^2
Bondville, February 03	5.05 ± 0.87	35.97 ± 5.19	0.66
San Gorgonio, April 03	12.56 ± 6.17	25.00 ± 12.95	0.16
Grand Canyon, May 03	-12.16 ± 10.62	25.00 ± 12.95	0.16
Brigantine, November 03	14.25 ± 5.16	52.85 ± 23.56	0.17
San Gorgonio, July 04	-6.08 ± 11.44	62.71 ± 20.52	0.54
Great Smoky Mountains, July–August 04	8.11 ± 1.68	87.69 ± 13.64	0.60
Global regression analysis	11.66 ± 1.54	27.47 ± 4.62	0.20

nylon filter to the ratio $NH_3(g):N(-III)$ in the ambient air. We do see that ammonium loss ($BNH_4^+\%$) increases as the ratio of $NH_3(g):N(-III)$ increases overall and within each campaign. Linear least squares regression ($BNH_4^+\% =$ intercept + slope∗[$NH_3(g):N(-III)$]) was used to fit all campaign data sets. Intercept, slope and correlation coefficient (R^2) are summarized in Table 3. Our observations of ammonium loss from denuded nylon filters are generally consistent with Zhang and McMurry's (1992) theoretical prediction that losses on denuded Teflon filters become significant when the ratio $NH_3(g):N(-III)$ exceeds a value in the range of 0.05–0.5. Of course, in the real world, there are many additional factors that complicate this relationship. Above, we talked about the importance of diurnal changes in T and RH. Below, we address issues related to aerosol composition.

3.4. Aerosol chemical composition and acidity

Ammonium nitrate is generally considered the major species responsible for ammonium loss from filter media due to its semivolatile nature. Ammoniated forms of sulfate, which dominate inorganic aerosol composition in many regions of the country, have much lower vapor pressures suggesting that ammonium loss from particles of this type (e.g., ammonium sulfate, ammonium bisulfate, or others) should be negligible (Bassett and Seinfeld, 1983).

We compared the amount of ammonium lost for each filter sample to the amount of particulate nitrate measured in the same sample, in order to determine whether volatilization of ammonium nitrate could fully explain the observed ammonium loss. Results are summarized in Table 4. In most of the field campaigns sufficient fine particle nitrate was present to explain observed ammonium loss. This was not the case at Great Smoky Mountains,

Table 4
Comparison of measured NH_4^+ loss with measured NO_3^-

Site	NH_4^+ loss/NO_3^-	
	Mean	Std Dev
Bondville, February 03	0.05	0.04
San Gorgonio, April 03	0.12	0.07
Grand Canyon, May 03	0.24	0.14
Brigantine, November 03	0.28	0.18
San Gorgonio, July 04	0.45	0.19
Great Smoky Mountains, July–August 04	1.98	0.76

where more ammonium was lost than could be explained by measured nitrate concentrations.

If insufficient nitrate is available to account for ammonium loss and volatilization of ammoniated sulfate particles is unimportant (Bassett and Seinfeld, 1983), we need to consider other possible contributors to the observed ammonium loss at Great Smoky Mountains NP. One possibility is decomposition of other ammonium salts contained in collected particles, such as ammonium salts of semivolatile organic acids (Ferek et al., 1983; Grosjean et al., 1978; Kawamura et al., 1996; Limbeck and Puxbaum, 1999). Grosjean et al. (1978) identified six dicarboxylic acids: glutaric, adipic, malonic, succinic, methyl adipic, and azelaic from 24-h filter samples collected in Riverside, CA using GC–MS. High concentrations of weak acids including succinic, glutaric, and adipic acids were identified in filter samples collected over the Northeastern United States (Ferek et al., 1983). Succinic or oxalic acid was found to be the dominant diacid species in Antarctic aerosols, followed by azeleic, adipic, or malonic acid (Kawamura et al., 1996). Oxalic, malonic, and succinic acid were the dominant compounds in continental background aero-

sols, followed by lower amounts of glutaric, adipic, and phthalic acid (Limbeck and Puxbaum, 1999). In order to investigate this possibility, we selected a group of nylon filter extracts and their corresponding acidic gaseous denuder aliquots collected in Great Smoky Mountains NP to analyze their organic acid composition. Selected samples were chosen based on large observed ammonium losses. The nylon filter aliquots analyzed were stored remainders of extracts originally analyzed for inorganic ions. No precautions were taken at the time of extraction to preserve these solutions for later organic acid analysis, although the extracts were refrigerated during storage. Consequently, some loss of organic acids may have occurred due to microbial activity during approximately 5 months storage between extraction and analysis. Results presented, therefore, should be considered conservative estimates of initial organic acid concentrations. In contrast, portions of the denuder aliquots from the carbonate denuder designed to collect gaseous acidic species were preserved for possible later organic acid anion analysis by adding a small amount of chloroform immediately after on-site extraction (Morales et al., 1994). The denuder samples can help us get an idea of the prevalence of low molecular weight carboxylic (e.g., formic and acetic) and dicarboxylic (e.g., oxalic) acids in the local atmosphere during the campaign as many of these species are volatile enough to exist partly or mostly in the gas phase (Khwaja, 1995; Limbeck et al., 2001; Souza et al., 1999). Mono and dicarboxylic acids have also been identified as major organic aerosol constituents (Limbeck and Puxbaum, 1999; Malm et al., 2005). The nylon filter and carbonate denuder extracts were analyzed using gradient NaOH elution IC to quantify a suite of organic acid anions (Dionex, 1997, 1998, Revision 04).

Significant amounts of formate and oxalate were found in the Great Smoky Mountains preserved denuder aliquots in addition to lower concentrations of glutarate, succinate, maleate, butyrate, and pinate. Although the nylon filter aliquots were not preserved, we still found significant amounts of residual oxalate and lactate. Lower concentrations of organic acids tentatively identified are malonate, valerate, and butyrate. These findings, while not conclusive, suggest that ammoniated organic salts, such as ammonium oxalate, ammonium lactate, or others may have been present in sampled particles. During the Southeastern Aerosol and Visibility

Study (SEAVS) in Great Smoky Mountains NP in 1995, investigators also found important contributions to submicron organic aerosol from polar organic compounds (Blando et al., 1998; Yu et al., 2005a). In the current study, the ratio of residual oxalate to nitrate on the front nylon filter ranged from 0.2 to 120; 75% of the samples had ratios higher than 1, suggesting that ammonium loss from organic ammonium salts could make a contribution to ammonium loss at least comparable to that from ammonium nitrate volatilization. Certainly this is an issue worth carefully examining in future studies.

4. Conclusions

Ammonium loss from denuded nylon and Teflon filter media was examined in five rural field studies. The degree of ammonium loss from denuded nylon filters varied between campaigns, ranging from an average of 10% in Bondville, IL in February to 28% in San Gorgonio, CA in July. Ammonium losses from denuded Teflon filters were generally somewhat lower than observed for nylon filters, possibly reflecting higher pressure drops across nylon filters. Losses of ammonium tended to increase with increasing diurnal temperature and relative humidity swings, although these relationships were often weak. Ammonium loss also increased with the degree of gas–particle equilibrium perturbation caused by upstream removal of gaseous ammonia, as predicted by previous investigators. For sampling approaches where ammonia is not denuded upstream, losses are probably lower than observed here although positive artifacts resulting from ammonia collection by acidic particles can be problematic in this approach.

Although NH_4NO_3 volatilization is typically considered the major source of ammonium loss, observations in Great Smoky Mountains NP indicate that more ammonium is lost than can be explained by this mechanism. It is hypothesized that organic ammonium salts, such as ammonium oxalate, may also contribute to observed losses of ammonium from filter media. Relatively large amounts of oxalate and succinate were observed in Great Smoky Mountains NP particle extracts where ammonium losses exceeded aerosol nitrate concentrations.

While loss of nitrate has been demonstrated to be negligible from denuded nylon filters, loss of ammonium cannot be ignored and should be considered in future sampling system design. One

possible remedy is to capture volatilized ammonia with a backup acid-coated filter or denuder, an approach often used in intensive research air sampling efforts. The costs of implementing such a solution for existing large monitoring networks, however, could be substantial.

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