Loss of PM$_{2.5}$ Nitrate from Filter Samples in Central California

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ABSTRACT
Evaporative loss of particulate matter (with aerodynamic diameter <2.5 μm, [PM$_{2.5}$]) ammonium nitrate from quartz-fiber filters during aerosol sampling was evaluated from December 3, 1999, through February 3, 2001, at two urban (Fresno and Bakersfield) and three nonurban (Bethel Island, Sierra Nevada Foothills, and Angiola) sites in central California. Compared with total particulate nitrate, evaporative nitrate losses ranged from <10% during cold months to >80% during warm months. In agreement with theory, evaporative loss from quartz-fiber filters in nitric acid denuded samplers is controlled by the ambient nitric acid-to-particulate nitrate ratio, which is determined mainly by ambient temperature. Accurate estimation of nitrate volatilization requires a detailed thermodynamic model and comprehensive chemical measurements. For the 14-month average of PM$_{2.5}$ acquired on Teflon-membrane filters, measured PM$_{2.5}$ mass was 8–16% lower than actual PM$_{2.5}$ mass owing to nitrate volatilization. For 24-hr samples, measured PM$_{2.5}$ was as much as 32–44% lower than actual PM$_{2.5}$ at three California Central Valley locations.

INTRODUCTION
The U.S. Environmental Protection Agency (EPA) has established National Ambient Air Quality Standards for PM$_{2.5}$ (particles with aerodynamic diameter <2.5 μm) and has published a Federal Reference Method (FRM) for measuring it that entails collecting PM$_{2.5}$ on a Teflon-membrane filter and determining its mass gravimetrically. Some PM$_{2.5}$ components, such as ammonium nitrate (NH$_4$NO$_3$), are volatile and can leave the filter before gravimetric analysis. NH$_4$NO$_3$ is a major component of PM$_{2.5}$ and PM$_{10}$ (particles with aerodynamic diameters <10 μm) in California's Central Valley.

Ambient particulate NH$_4$NO$_3$ is formed by a reversible reaction between gaseous ammonia (NH$_3$) and nitric acid (HNO$_3$). At equilibrium:

\[ \text{NH}_4\text{NO}_3(s) \rightleftharpoons \text{NH}_3(g) + \text{HNO}_3(g) \]  

Stelson and Seinfeld described the dependence of this equilibrium on temperature and relative humidity (RH). Dissociation of NH$_4$NO$_3$ increases with increasing temperature and remains constant for a given temperature below the deliquescence RH, which is 62% at 25 °C. Above the deliquescence RH, dissociation decreases rapidly with increasing RH.

It has long been recognized that NH$_4$NO$_3$ is lost through evaporation from filters during sampling. This has important implications for accurate assessment of PM$_{2.5}$ under federal and state regulations. During the California Regional PM$_{10}$/PM$_{2.5}$ Air Quality Study (CRPAQS) and Fresno Supersite operations from December 1999 through January 2001, nitrate (NO$_3^-$) concentrations ranged from 0 to 60 μg/m$^3$, constituting as much as 54% of PM$_{2.5}$ mass. The highest NO$_3^-$ concentration was found in winter. Chow et al. reported elevated wintertime PM$_{2.5}$ and PM$_{10}$ NO$_3^-$ concentrations in the San Joaquin Valley (SVJ) during the Valley Air Quality Study in 1988–1989. NO$_3^-$ episodes were regional, with corresponding peak concentrations at urban and nonurban sites. NH$_3$NO$_3$ was also a major component of PM$_{2.5}$ during the 1995 Integrated Monitoring Study at two urban (Fresno and Bakersfield) and two nonurban (Chowchilla and Kern Wildlife Refuge) sites in the SVJ.

Zhang and McMurry presented theoretical relationships describing evaporative loss of volatile compounds such as NH$_4$NO$_3$ from filter-substrate and impactor.
The degree of volatilization depended mainly on the relative abundances of ambient gaseous HNO₃ and particulate NO₃⁻, the amount of gas denuded during sampling, and on the pressure drop through the sampler. Cheng and Tsai conducted laboratory experiments with monodisperse NH₄NO₃ particles and found that evaporative losses decreased as the thickness of the particle “cake” on the filter increased. Losses were higher at low particle concentrations. Chang et al. tested a particle preconcentrator for use in cascade impactor and filter samplers. Reducing the gas-to-particle ratio by preconcentrating the particles reduced NH₄NO₃ evaporation in both types of samplers.

Hering and Cass assessed the impact of NO₃⁻ volatilization on PM₂.₅ mass acquired from Teflon-membrane filters during the 1986 Caltech study and the 1987 Southern California Air Quality Study in the South Coast Air Basin. They found that NO₃⁻ volatilization was greatest during the warm months and during the warmest periods of the day. Volatilized NH₄NO₃ was up to 60% of measured PM₂.₅ mass. Volatilization was driven by depletion of the gas phase (i.e., denuding of NH₃ or HNO₃ before the particle filter) and by an increase in the temperature of the filter substrate relative to the ambient temperature. John et al. demonstrated that anodized aluminum inlets on dichotomous samplers effectively remove gaseous HNO₃.

Ashbaugh and Eldred examined data from the California Acid Deposition Monitoring Program (CADMP) from 1988 to 1994. The CADMP sampler collects total particulate NO₃⁻ on a nylon-membrane filter preceded by a HNO₃ denuder and collects particulate NO₃⁻ on a parallel Teflon-membrane filter in an undenuded channel. They conducted an experiment during winter 1997 in Bakersfield, CA, using an Interagency Monitoring of Protected Visual Environments (IMPROVE) sampler with a configuration similar to the CADMP sampler. The face velocities of the CADMP and IMPROVE samplers were 23.8 and 100 cm/sec, respectively. In general, both samplers lost similar amounts of NO₃⁻. Although the CADMP and IMPROVE samplers were not collocated, Ashbaugh and Eldred concluded that differences in face velocity did not affect NH₄NO₃ volatilization.

In this article, the spatial and temporal variations of PM₂.₅ NH₄NO₃ volatilization in the SJV during CRPAQS are examined. The factors responsible for this sampling artifact are evaluated and reconciled with theory. Additional measurements at the Fresno Supersite during and after the CRPAQS are used to facilitate this analysis.

**EXPERIMENTAL WORK**

Aerosol sampling was conducted at two urban (Fresno and Bakersfield) and three nonurban (Bethel Island, Sierra Nevada Foothills, and Angiola) anchor sites (Figure 1). DRI (Reno, NV) sequential filter samplers (SFS) were operated at all five sites. An Andersen Instruments (Smyrna, GA) multiple channel reference ambient air sampler (RAAS, a speciation sampler) and two Andersen Instruments single-channel FRM samplers, equipped with Teflon-membrane (Pall Sciences, R2PJ047, Ann Arbor, MI) and quartz-fiber (Pall Sciences, QAT2500-VP, Ann Arbor, MI) filters, were operated at the Fresno Supersite. All of the samplers were preceded by PM₂.₅ size-selective inlets: Sensidyne Bendix 240 cyclone for the SFS; AIHL cyclone for the RAAS; and EPA WINS impactor for the FRM. The SFS and RAAS samplers were preceded by aluminum oxide tubular and sodium carbonate-coated glass annular denuders, respectively, to remove gaseous HNO₃. Experiments with the CADMP sampler, which is similar to the SFS sampler, showed that the efficiency of the aluminum oxide denuder exceeded 90% for HNO₃. Similar efficiencies were reported for a sodium carbonate honeycomb denuder with respect to HNO₃ and HONO. The RAAS sampler also contained an undenuded channel in which NO₃⁻ was collected on a quartz-fiber filter.

Sampler configurations are shown in Figure 2. Non-volatilized NO₃⁻ was collected on 47-mm front quartz-fiber filters in the SFS, RAAS, and FRM samplers. Volatilized NO₃⁻ was collected in HNO₃-denuded channels on back-up sodium chloride impregnated cellulose-fiber filters (31ET, Whatman, Hillsboro, OR) and back-up nylon-membrane (Nylasorb, Pall Sciences, Ann Arbor, MI) in the SFS and RAAS samplers, respectively. NO₃⁻ was analyzed on distilled-deionized water extractions of the filters by ion chromatography. A citric acid impregnated cellulose-fiber filter following the Teflon-membrane filter in the SFS

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**Figure 1.** Locations of CRPAQS anchor sites.
captured ambient NH₃ and particulate ammonium (NH₄⁺) volatilized to NH₃ from the Teflon-membrane filter. The sum of the SFS quartz-fiber filter NH₄⁺ (adjusted to equivalent NH₃) and citric acid impregnated filter NH₃ provides the “total equivalent NH₃” (particle plus gas).

Twenty-four-hour samples were collected on the EPA every-sixth-day schedule starting on December 2, 1999, at the Fresno, Angiola, and Bakersfield sites and on December 2, 2000, at the Bethel Island and Sierra Nevada Foot-hills sites, and ending on February 3, 2001. Daily SFS samples were collected at Fresno and Angiola during a 2000 fall intensive study on the following dates: October 14, October 16–20, October 22–24, and November 2–9. A winter intensive study was conducted at all five anchor sites from December 15 to 18 and December 26 to 28, 2000, and from January 4 to 7 and January 31 to February 3, 2001, when SFS samples were collected from 12:00 a.m. to 5:00 a.m., 5:00 a.m. to 10:00 a.m., 10:00 a.m. to 1:00 p.m., and 1:00 p.m. to 5:00 p.m. HNO₃ and NH₃ were also determined on the same schedule using DRI sequential gas samplers. Total NO₃⁻ (TNO₃⁻ = gaseous HNO₃ [as equivalent NO₃⁻] plus nonvolatilized and volatilized NO₃⁻) in the sequential gas samplers was collected on sodium chloride impregnated cellulose-fiber filters in an undenuded sampling stream. Particulate NO₃⁻ was collected on the same filters in a parallel HNO₃-denuded channel, and HNO₃ was determined by the difference between the undenuded and denuded NO₃⁻ concentrations (i.e., by denuder difference). NH₃ was also determined by denuder difference using citric acid impregnated cellulose-fiber filters and citric acid coated denuder. Hourly HNO₃ was measured continuously at the Fresno Supersite using a TEI-42C chemiluminescence analyzer (Thermal Electron Corp., Franklin, MA) with undenuded and HNO₃-denuded channels. Meteorological measurements of temperature and RH were available for the Fresno and Bakersfield sites.

**RESULTS AND DISCUSSION**

Figure 3 shows a linear, inverse relationship between 24-hr average temperature and RH at the Fresno and Bakersfield sites. Trends were similar at both sites. Given the dependence of the NH₄NO₃ equilibrium on temperature and RH, this variation should control the distribution of gaseous and particulate NO₃⁻ and influence NH₄NO₃ sampling artifacts in the SJV.
Seasonal averages of nonvolatilized and volatilized NO$_3^-$ from 24-hr average SFS samples at the Fresno, Angiola, and Bakersfield sites are shown in Figure 4. The highest and lowest total particulate NO$_3^-$ (PNO$_3^-$, the sum of nonvolatilized and volatilized NO$_3^-$) occurred during winter and summer, respectively, at the Bakersfield and Angiola sites. The lowest concentrations were similar during spring and summer at Fresno. Seasonal average volatilized NO$_3^-$ in PNO$_3^-$ ranged from 3.5% at Angiola during winter to 84% at Fresno during summer. These results are consistent with those observed by Shaw et al., Her and Cass, and Ashbaugh and Eldred. Monthly average ratios of volatilized NO$_3^-$ : PNO$_3^-$ at the Fresno, Angiola, and Bakersfield sites, along with average temperature at Fresno and Bakersfield, are plotted in Figure 5. Monthly volatilized NO$_3^-$ is low during winter and reached 60–80% in summer. As shown in Table 1, monthly average volatilized NO$_3^-$ as a percentage of PNO$_3^-$ was highly correlated among sites and also with Fresno monthly average temperature. Monthly average temperature at Fresno and Bakersfield was also highly correlated.

Figure 6 examines daily average fraction of volatilized NO$_3^-$ at the Fresno and Angiola sites along with daily average temperature at Fresno during the 2000 fall intensive period. The fraction of volatilized NO$_3^-$ decreased substantially at both sites, whereas temperature at Fresno decreased by ~10 °C over the intensive period. Figure 7 shows period-average temperature at Fresno and Bakersfield and the fraction of volatilized NO$_3^-$ at those sites during the 2000–2001 winter intensive period. Again, the fraction of volatilized NO$_3^-$ at the Fresno and Bakersfield sites was correlated with temperature and the fraction peaked during the afternoon sampling period (1:00 p.m. to 4:00 p.m. PST). This corresponded to an increase in temperature of 5–6 °C from the previous period at both sites.

Figure 8 compares daily nonvolatilized NO$_3^-$ from the front quartz-fiber filters in the denuded and unde-nuded channels of the RAAS sampler (Figure 2) in Fresno during winter and summer, respectively, at the Bakersfield and Angiola sites. The lowest concentrations were similar during spring and summer at Fresno. Seasonal average volatilized NO$_3^-$ in PNO$_3^-$ ranged from 3.5% at Angiola during winter to 84% at Fresno during summer. These results are consistent with those observed by Shaw et al., Her and Cass, and Ashbaugh and Eldred. Monthly average ratios of volatilized NO$_3^-$ : PNO$_3^-$ at the Fresno, Angiola, and Bakersfield sites, along with average temperature at Fresno and Bakersfield, are plotted in Figure 5. Monthly volatilized NO$_3^-$ is low during winter and reached 60–80% in summer. As shown in Table 1, monthly average volatilized NO$_3^-$ as a percentage of PNO$_3^-$ was highly correlated among sites and also with Fresno monthly average temperature. Monthly average temperature at Fresno and Bakersfield was also highly correlated.
for warm (May–September) and cold (November–March) months over several years. The largest difference is seen during the warmer months when the average ratio of denuded-to-undenuded NO$_3^-$ to H$_2$SO$_4$ was 0.41/0.21. These ratios were much higher (1.08/0.34) during the colder months.

**Consistency with Theory**

According to Zhang and McMurry,$^{11}$ the sampling efficiency ($\eta_e$) for particulate NH$_4$NO$_3$ at equilibrium with gaseous NH$_3$ and HNO$_3$ at the sampler inlet (saturation ratio [SR] = 1) is:

$$\eta_e = \exp\left( \frac{P_o - \Delta P}{T P_o} \right) \frac{P_o}{C_m}$$

(2)

where $P_o$ and $\Delta P$ are the ambient atmospheric pressure and pressure drop across the filter, respectively; $\rho_e$ is the ambient HNO$_3$ concentration over the sampling period; and $C_m$ is the particulate NO$_3^-$ concentration measured on an unreactive filter. The SR is the actual partial pressure of the gas above the filter divided by its partial pressure at equilibrium.

When both NH$_3$ and HNO$_3$ have been removed (e.g., by denuders) at the sampler inlet (SR = 0), the $\eta_e$ is:

$$\eta_e = \left( 1 + \frac{P_o - \Delta P}{2P_o} \right) \frac{\rho_e}{C_m}$$

(3)

Corresponding RAAS filter samples (every-sixth-day schedule) and continuous HNO$_3$ concentrations in Fresno are available from December 2000 through April 2002. Figure 9 compares daily and monthly average NO$_3^-$ evaporative losses with those expected from theory. Because NH$_3$ was not removed in the RAAS NO$_3^-$ sampling channel, the effective SR should lie between 0 and 1. A laboratory experiment showed that the pressure drop across a quartz-fiber filter at the flow rate of 20 L/min was 2.7%. Theoretical sampling efficiencies for SR = 0 and SR = 1, calculated according to eq 3 and eq 2, respectively, and assuming a pressure drop of 2.7%, are plotted in Figure 9. As shown in Figure 6 of Zhang and McMurry,$^{11}$ the experimental results for Fresno are bracketed by the theoretical curves for SR = 0 and SR = 1.

The effect of the ambient gas-to-particle distribution on NO$_3^-$ volatilization is illustrated by Figure 10, which is based on monthly average RAAS filter and continuous HNO$_3$ measurements in Fresno. Figure 10a shows that the highest HNO$_3$ concentrations occurred during the warmest (and driest) months, when PNO$_3^-$ concentrations were lowest. This follows from the dependence of the gas-particle equilibrium for NH$_4$NO$_3$ (eq 1) on temperature and RH. Figure 10b shows a strong correlation ($r = 0.93$) between the fraction of particulate NO$_3^-$ volatilized during sampling and the ratio of ambient HNO$_3$-to-total NO$_3^-$. The relationship is nearly 1:1, in which:

**Table 1.** Intersite correlations between monthly average ratios of volatilized NO$_3^-$ to total PNO$_3^-$ (which is the sum of nonvolatilized and volatilized NO$_3^-$ in HNO$_3$-denuded channel) at the Fresno, Angiola, and Bakersfield sites and monthly average temperature (T in °C) at Fresno.

<table>
<thead>
<tr>
<th>Fresno Ratio</th>
<th>Angiola Ratio</th>
<th>Bakersfield Ratio</th>
<th>Fresno T</th>
</tr>
</thead>
<tbody>
<tr>
<td>—</td>
<td>1</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Angiola ratio</td>
<td>0.88</td>
<td>1</td>
<td>Fresno —</td>
</tr>
<tr>
<td>Bakersfield ratio</td>
<td>0.91</td>
<td>0.92</td>
<td>0.95</td>
</tr>
<tr>
<td>Fresno T</td>
<td>0.91</td>
<td>0.92</td>
<td>0.95</td>
</tr>
</tbody>
</table>

**Figure 6.** Daily ratio (%) of volatilized NO$_3^-$ to total PNO$_3^-$ at the Fresno (solid circle) and Angiola (solid bar) sites, along with temperature (°C; triangle) at Fresno during the 2000 fall intensive study.

**Figure 7.** Average diurnal variation of the ratio (%) of volatilized NO$_3^-$ to total PNO$_3^-$ (which is the sum of nonvolatilized and volatilized NO$_3^-$), along with temperature (°C) at Fresno and Bakersfield during the 2000–2001 winter intensive study.
Volatilized NO$_3^-$ from the RAAS in Fresno, CA, for: (a) warm months (May to September 2000–2001); and (b) cold months (November to March 1999–2002).

Volutilized NO$_3^-$ /PNO$_3$ = 1.13 (HNO$_3$/ [HNO$_3$ + PNO$_3$]) - 0.05

For HNO$_3$-denuded RAAS filter samples, volatilization of NH$_4$NO$_3$ from the front quartz-fiber filter represents the re-establishment of the NH$_3$–HNO$_3$ equilibrium that existed in the ambient atmosphere. Equilibrium is not attained when all of the PNO$_3$ evaporates.

Hering and Cass$^{14}$ estimated volatilized NO$_3^-$ for samples collected in Los Angeles using thermodynamic equilibrium constants ($K$) derived by Mozurkewich$^{22}$ as a function of temperature ($T$), where:

$$\ln K = 118.87 - \frac{24084}{T} - 6.025 \ln T \quad (5)$$

Mozurkewich$^{22}$ also specified additional terms to eq 5 that account for the effects of RH on $K$, but these were not applied by Hering and Cass.$^{14}$ $K$ defines the maximum (saturation) concentrations of NH$_3$ and HNO$_3$ in equilibrium with solid- or aqueous-phase NH$_4$NO$_3$ in a system that contains only these species. Hering and Cass$^{14}$ presented the following equation to convert $K$ in units of squared nano-bars (nb$^2$) to volatilized NO$_3^-$ ($\Delta$NO$_3^-$) concentrations ($\mu$g/m$^3$):

$$\Delta$NO$_3^-$ = $\frac{745.7}{T} \sum_{i=1}^{24} \frac{1}{\sqrt{K_{amb,i}}} \quad (6)$$

where $K_{amb,i}$ is the equilibrium constant for the $i$th hour. Eq 6 assumes complete removal of NH$_3$ and HNO$_3$ before the filter and that volatilized NO$_3^-$ approaches equilibrium with particulate NH$_4$NO$_3$ remaining on the filter. Hering and Cass$^{14}$ noted that $K^{1/2}$ approximately doubles with a 5 °C increase in temperature. To account for an increase in the sample filter temperature with respect to ambient temperature, they defined $\kappa$ as:

$$\kappa = \frac{K_{filter}}{\sqrt{K_{amb}}} \quad (7)$$

where $K_{filter}$ and $K_{amb}$ are the NH$_4$NO$_3$ dissociation constants at the filter and ambient temperatures, respectively. To account for partial depletion of NH$_3$ and HNO$_3$ at equal molar concentrations before the filter, Hering and...
Cass\textsuperscript{14} defined $\gamma$ as the fraction of vapor penetrating through the inlet to the filter. To account for the effects of temperature increase and removal of vapor before the filter, Hering and Cass\textsuperscript{14} expanded eq 6 as follows:

$$\Delta NO_3^- = \left[ \frac{745.7}{T} \right] (\kappa - \gamma) \frac{1}{24} \sum_{i=1}^{24} K_{amb,i} \tag{8}$$

They applied eq 8 to data from Los Angeles and Upland, CA, with $\kappa - \gamma = 1$ and found good agreement between estimated and measured volatilized $NO_3^-$ under the constraint that the estimated value could not exceed $PNO_3^-$. This constraint is necessary because eq 6 or eq 8 overestimate volatilized $NO_3^-$ when the gas phase is completely denuded under conditions where the ambient gas concentrations are much higher than particulate $NH_4NO_3$ concentrations. This is illustrated in Figure 10a at the Fresno Supersite for the month of September. In this case, if all of the ambient $HNO_3$ was denuded and all of the particulate $NH_4NO_3$ on the filter evaporated, the resulting $HNO_3$ concentration behind the filter would be much lower than its initial ambient concentration. Whereas the assumption that $\kappa - \gamma = 1$ can represent a range of cases of increased filter temperature and fractional penetration of $NH_3$ and $HNO_3$ gases to the filter, it reduces eq 8 to eq 6 in practice.

Because all of the $HNO_3$ and possibly none of the $NH_3$ was removed by the $HNO_3$ denuder in the SFS, neither eq 6 nor eq 8 strictly represents $NO_3^-$ volatilization at the Fresno Supersite. To illustrate this, eq 6 was applied to warm (May–September) and cold (November–March) months for daily Fresno and Bakersfield SFS samples taken from December 2, 1999, through February 3, 2001. $NH_4NO_3$ thermodynamic equilibrium constants ($K$) as a function of temperature only and both temperature and RH were calculated according to eq 5 of Mozurkewich.\textsuperscript{22} As in Hering and Cass,\textsuperscript{14} daily average $K$ were obtained from hourly average $K$. As expected, volatilized $NO_3^-$ was overestimated during the warm months in every sample by an average factor of 11. Values estimated from equilibrium constants based on temperature and on temperature and RH are compared with measurements for the cold months, as shown in Figure 11, which demonstrates that volatilized $NO_3^-$ based on $K$ was overestimated in most cases. This is probably because of the presence of $NH_3$ in the sampling stream, which suppresses volatilization of $NH_4NO_3$ even when all of the $HNO_3$ has been denuded and/or to the presence of nonvolatilized $NO_3^-$ associated with sea salt or mineral aerosols.

To account for the complete removal of $HNO_3$ but not of $NH_3$ and for the effects of heating in the sampler, the Simulating Composition of Atmospheric Particles at Equilibrium (SCAPE) thermodynamic equilibrium model of Kim et al.\textsuperscript{23} was applied. This model describes the

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**Figure 10.** (a) Monthly ratio of RAAS total $PNO_3^-$ and $HNO_3$ at the Fresno Supersite from December 2000 through April 2002; and (b) monthly ratio of $HNO_3$ to total $NO_3^-$ ($TNO_3^-$, which is $HNO_3$ as equivalent $NO_3^-$ + $PNO_3^-$) and monthly ratio of volatilized $NO_3^-$ to $PNO_3^-$ in Fresno from December 2000 through April 2002.

**Figure 11.** Comparison of volatilized $NO_3^-$ estimated from $K$ with volatilized $NO_3^-$ measured with SFS at the Fresno and Bakersfield sites during the cold months (November to March). $K$ is a function of temperature in the closed circles; $K$ is a function of temperature and RH in the open circles.
gas-particle equilibrium for complex gas and particle mixtures. The model input requires water-soluble cations and anions, such as sodium (Na\(^+\)), calcium (Ca\(^{2+}\)), magnesium (Mg\(^{2+}\)), sulfate (SO\(_4^{2-}\)), carbonate (CO\(_3^{2-}\)), total equivalent NH\(_3\) (gaseous NH\(_3\) plus particulate NH\(_4^+\)), total equivalent HNO\(_4\) (gaseous HNO\(_3\) plus particulate NO\(_3^-\)), and chloride (Cl\(^-\)) as hydrochloric acid (HCl). Total NH\(_3\) was measured on SFS samples. Because HNO\(_3\) was denuded, PNO\(_3^-\) is used as model input, and the model estimates the retained and volatilized NO\(_3^-\). Ca\(^{2+}\), Mg\(^{2+}\), and CO\(_3^{2-}\) were not measured, and zero concentrations are assumed. Twenty-four-hour average chemical concentrations at the Fresno and Bakersfield sites were applied with corresponding hourly average temperature and RH, and the estimated equilibrium concentrations were used to calculate 24-hr averages.

Estimated and measured volatilized NO\(_3^-\) are plotted in Figure 12 for warm and cold months. The results are summarized in Table 2. During the warm months, when NO\(_3^-\) volatility is high, the agreement is good, with an average absolute difference (AAD) of 24% and a correlation (r) of 0.95. During the cold months, however, volatilized NO\(_3^-\) was underestimated. Underestimation of volatilized NO\(_3^-\) was also seen for the 15-day winter-intensive periods. Because the winter-intensive samples captured the diurnal variation of gas and particle concentrations, underestimation of volatilized NO\(_3^-\) in the 24-hr average RAAS samples during cold months cannot be explained by such variation. Hering and Cass\(^{14}\) demonstrated that filter temperatures that are higher than ambient temperatures can increase NO\(_3^-\) volatilization in undenuded and denuded samples. Underestimation of NO\(_3^-\) during cold months may be related to heating of the sampler plenum during daylight hours. To test this, the model was rerun with hourly temperatures increased by 5 °C between the hours of 10:00 a.m. and 6:00 p.m. PST. The corresponding reduction in RH was estimated using the relationships between temperature and RH presented in Figure 3. As shown in Table 2, this increased the average estimated cold months volatilized NO\(_3^-\) from 0.41 to 1.21 μg/m\(^3\) and increased the correlation between estimated and measured volatilized NO\(_3^-\) from 0.75 to 0.91.

These results suggest that the utility of thermodynamic models for estimating volatilized NO\(_3^-\) depends on the available measurements and sampling strategy. Knowledge of the ambient gas concentrations is required for eq 2 and eq 3. The use of simple thermodynamic constants is precluded unless both NH\(_3\) and HNO\(_3\) have been denuded from the sample air, and reactions of these gases with other species have been accounted for.\(^{24}\) This was not the case in Fresno, where NH\(_3\) concentrations exceeded those of total NO\(_3^-\). NH\(_3\) concentrations can be estimated for SFS samples as the difference between the back-up citric acid-impregnated filter NH\(_3\) and the NH\(_3\) equivalent of volatilized NO\(_3^-\). Average warm- and cold-month NH\(_3\) concentrations in Fresno were 9.3 ± 3.2 and 10.5 ± 4.6 μg/m\(^3\), respectively. The corresponding average HNO\(_3\) concentrations based on continuous measurements were 3.6 ± 1.7 and 2.1 ± 1.6 μg/m\(^3\), respectively.

Table 2. Estimation of volatilized NO\(_3^-\) in SFS samples from Fresno and Bakersfield during the CRPAQS using the SCAPE thermodynamic equilibrium model.

<table>
<thead>
<tr>
<th>Season</th>
<th>Avg. Measured Volatilized NO(_3^-) (μg/m(^3))</th>
<th>Avg. Estimated Volatilized NO(_3^-) (μg/m(^3))</th>
<th>Avg. Measured % Volatilization(^a)</th>
<th>Avg. Estimated % Volatilization(^a)</th>
<th>r(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>May-Sep.</td>
<td>2.4</td>
<td>2.5</td>
<td>77</td>
<td>84</td>
<td>0.95</td>
</tr>
<tr>
<td>Nov.-Mar.</td>
<td>1.51</td>
<td>0.41</td>
<td>22</td>
<td>8.3</td>
<td>0.75</td>
</tr>
<tr>
<td>Nov.-Mar.  (^c)</td>
<td>1.51</td>
<td>1.21</td>
<td>22</td>
<td>22</td>
<td>0.91</td>
</tr>
</tbody>
</table>

\(^a\)Volatilized NO\(_3^-\)/total particulate NO\(_3^-\) [PNO\(_3^-\)], which is the sum of nonvolatilized and volatilized NO\(_3^-\) in a HNO\(_3\)-denuded channel] × 100; \(^b\)Correlation between estimated and measured volatilized NO\(_3^-\); \(^c\)Assume 5 °C heating in the sampler.
For comparison, daily average NH$_3$ and HNO$_3$ measured by denuder difference during the winter-intensive study were 9.3 ± 2.3 and 2.1 ± 1.6 μg/m$^3$, respectively. Detailed thermodynamic equilibrium models, such as SCAPE require total equivalent NH$_3$ and HNO$_3$ as model input, which include the retained and volatilized particulate and gas concentrations, if the gases have not been denuded. Such models also assume that the particle chemistry is internally mixed. Thus, NO$_3^-$ volatilization may not be accurately simulated in the presence of externally mixed sodium nitrate (NaNO$_3$), for example. Whereas measurement of NH$_3$ and HNO$_3$ is useful in understanding the relationships between gaseous precursors and particles in the atmosphere, it is more cost-effective to measure volatilized NO$_3^-$ directly.

**Implications for PM$_{2.5}$ Standards**

The state of California has drafted a proposal for a 24-hr average PM$_{2.5}$ standard of 25 μg/m$^3$. Hering and Cass$^{14}$ and Ashbaugh and Eldred$^{8}$ demonstrated that NO$_3^-$ volatilization causes a negative bias for PM$_{2.5}$ mass by filter measurements. This is also the case in California’s Central Valley. Figure 13 presents the daily average ratio of volatilized NH$_4$NO$_3$ to actual PM$_{2.5}$ mass concentration (sum of measured PM$_{2.5}$ mass and volatilized NH$_4$NO$_3$) on SFS Teflon-membrane filters and measured PM$_{2.5}$ mass concentrations (vertical bars) at the Fresno, Angiola, and Bakersfield sites from December 2, 1999, to February 3, 2001.

**Figure 13.** Daily SFS volatilized ammonium nitrate (NH$_4$NO$_3$ is 1.29 × NO$_3^-$) as a percentage of actual PM$_{2.5}$ mass (sum of measured PM$_{2.5}$ mass and volatilized NH$_4$NO$_3$) on SFS Teflon-membrane filters and measured PM$_{2.5}$ mass concentrations (vertical bars) at the Fresno, Angiola, and Bakersfield sites from December 2, 1999, to February 3, 2001.

Nitrate volatilization from Teflon-membrane filters in FRM samplers is related to the ratio of ambient HNO$_3$ to sampled NO$_3^-$ concentration, deposition of HNO$_3$ in the sampler inlet, the pressure drop across the filter, and potential heating in the sampler.$^{11,14}$ If it is true that the inlet of the FRM sampler acts as an efficient denuder for HNO$_3$, as suggested by Hering and Cass,$^{14}$ losses in the FRM because of evaporation of NH$_4$NO$_3$ could be similar to those found in other HNO$_3$-denuded filter-based samplers. A comparison between the SFS and FRM samplers in Fresno suggests that this is indeed the case. Figure 14a shows that the SFS (denuded) nonvolatilized front quartz-fiber filter NO$_3^-$ concentrations (0.52 ± 0.26 μg/m$^3$) were similar to the (undenuded) FRM quartz-fiber filter NO$_3^-$ concentrations (0.81 ± 0.33 μg/m$^3$) during the warm months at Fresno. Figure 14b shows that the SFS PNO$_3$ concentrations, which averaged 3 ± 1.9 μg/m$^3$, were much higher than the corresponding FRM NO$_3^-$ concentrations during the warm months at Fresno. These results suggest that the FRM sampler effectively removes gaseous HNO$_3$ from the sampling stream and that volatilization of particulate NO$_3^-$ from the front quartz-fiber filter and, by implication, the FRM Teflon-membrane filter, should be similar to that observed in the SFS.

**CONCLUSIONS**

Volatilization of NH$_4$NO$_3$ during aerosol sample collection in SJV was evaluated using measurements from CRPAQS and the Fresno Supersite. Particulate NO$_3^-$ distributions were spatially and temporally consistent in the SJV. On a seasonal basis, the amount of particulate NO$_3^-$ lost to evaporation during sampling at the Angiola, Fresno, and Bakersfield sites ranged from 3.5 to 6.5%
daily losses with respect to actual PM$_{2.5}$ mass occurred during spring and summer and reached 44% in Fresno. If, as these results suggest, the FRM sampler inlet efficiently removes HNO$_3$ during sampling, then NO$_3^-$ volatilization must be considered when using such measurements to evaluate compliance with emerging PM$_{2.5}$ air quality standards. Such losses cannot be accurately estimated from NH$_4$NO$_3$ equilibrium constants alone. Detailed thermodynamic models, such as SCAPE, require comprehensive gas and particle measurements. The most straightforward means of correcting FRM PM$_{2.5}$ mass for NO$_3^-$ volatilization is to measure it directly.

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