

Particle Nitrate Sampling Artifacts in California's San Joaquin Valley

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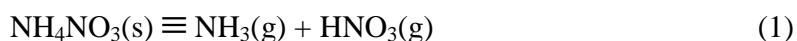
ABSTRACT

Evaporative loss of ammonium nitrate during aerosol sampling was evaluated during the California Regional Particulate Air Quality Study (CRPAQS). PM_{2.5} sampling was conducted using Desert Research Institute (DRI) sequential filter samplers (SFS) from December 1999 through February 2001 at three urban (Bethel Island, Fresno, Bakersfield) and two rural (Sierra Nevada Foothills, Angiola) sites in the San Joaquin Valley (SJV). Additional filter-based and continuous sampling was done in Fresno as part of the U.S. Environmental Protection Agency (EPA) Supersites program. Nitrate losses ranged from less than 10% to more than 80% in winter and summer, respectively. Evaporative loss in nitric acid-denuded samplers is controlled by the ratio of ambient nitric acid to particle nitrate, which is determined mainly by ambient temperature. Nitrate volatilization was estimated with a detailed thermodynamic model. Volatilized ammonium nitrate was as much as 80% of daily measured PM_{2.5} mass in Fresno during summer. This sampling artifact has significant implications with respect to evaluating emerging standards for PM_{2.5}.

INTRODUCTION

The California Regional Particulate Air Quality Study (CRPAQS) was conducted in central California over 14 months, from December 1999 through February 2001, to determine the causes of elevated levels of PM_{2.5} and PM₁₀ (particles with diameters less than 2.5 and 10 μm , respectively) and to evaluate the means of reducing them with respect to Federal and state air quality regulations [1]. The U.S. Environmental Protection Agency (EPA) has established National Ambient Air Quality Standards (NAAQS) for PM_{2.5} 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 [2].

Aerosol particulate ammonium nitrate (NH₄NO₃) is formed by a reversible reaction between gaseous ammonia (NH₃) and nitric acid (HNO₃). At equilibrium,



This equilibrium is dependent on temperature (T) and relative humidity (RH). Dissociation of NH₄NO₃ increases with increasing T and decreasing RH above its deliquescence RH, which is 62% at 25 °C.

It has long been recognized that NH_4NO_3 is lost through evaporation from filters during sampling [3,4,5]. This has important implications for accurate assessment of $\text{PM}_{2.5}$ under Federal and state regulations, particularly in California, where nitrate (NO_3^-) is a significant component of air particulates [6].

The impact of NO_3^- volatilization on the measurement of $\text{PM}_{2.5}$ mass on Teflon-membrane filters was assessed during the 1986 Caltech study and the 1987 Southern California Air Quality Study (SCAQS) in the Los Angeles Basin [7]. NO_3^- volatilization was greatest during the warm months and during the warmest periods of the day. Volatilized NH_4NO_3 was up to 60% of measured $\text{PM}_{2.5}$ mass. Volatilization was driven by depletion of the gas phase (i.e., denuding of NH_3 or HNO_3 before the particle filter), by an increase in the temperature of the filter substrate relative to the ambient temperature, and by the pressure drop across the sample filter.

Theoretical relationships describing evaporative loss of volatile compounds such as NH_4NO_3 from filter-based and impactor samplers depend mainly on the relative abundances of ambient gaseous HNO_3 and particulate NO_3^- and on the pressure drop through the sampler [8]. Reducing the gas-to-particle ratio by pre-concentrating the particles significantly reduced NH_4NO_3 evaporation in filter-based and impactor samplers [9].

In this paper, the spatial and temporal variations of NH_4NO_3 volatilization during CRPAQS sampling in the SJV 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 study are used to facilitate this analysis.

EXPERIMENTS

Aerosol sampling during CRPAQS was conducted at three urban (Bethel Island, Fresno, and Bakersfield) and two rural (Sierra Nevada Foothills and Angiola) anchor sites (Figure 1). Desert Research Institute (DRI; Reno, NV) sequential filter samplers (SFS) were operated at all five sites. Andersen Instruments (Smyrna, GA) single-channel FRM samplers equipped with Teflon-membrane and quartz-fiber filters and an Andersen Instruments multiple channel RAAS (reference ambient air sampler) speciation sampler were operated at the Fresno Supersite [10]. All samplers were preceded by $\text{PM}_{2.5}$ size-selective inlets: Sensidyne Bendix 240 cyclone for the SFS; AIHL cyclone for the RAAS; and EPA WINS impactor for the FRM [11]. The SFS and RAAS samplers were preceded by aluminum oxide tubular and sodium carbonate-coated glass denuders, respectively, to



Figure 1. Location of CRPAQS anchor sites.

remove gaseous HNO_3 . The RAAS sampler also contained an undenuded channel in which NO_3^- was collected on a quartz-fiber filter.

Non-volatilized NO_3^- was collected on 47-mm front quartz-fiber filters (Pall Sciences, QAT2500-VP, Ann Arbor, MI) in the FRM, RAAS, and SFS samplers. Volatilized NO_3^- was collected on backup nylon-membrane (Pall Sciences, Nylasorb, Ann Arbor, MI) and sodium chloride-impregnated cellulose-fiber filters (Whatman, 31ET, Hillsboro, OR) in nitric acid-denuded channels in the RAAS and SFS samplers, respectively. $\text{PM}_{2.5}$ NO_3^- was analyzed by ion chromatography (IC) [12]. A citric acid-impregnated cellulose-fiber filter (Whatman, 31ET, Hillsboro, OR) following the Teflon filter in the SFS captured ambient NH_3 and NH_3 volatilized from the Teflon filter. The sum of the SFS quartz-filter ammonium and citric-acid impregnated filter ammonia provides the total ammonia equivalent (particle plus gaseous).

Twenty-four-hour samples were collected on the EPA six-day schedule starting on December 2, 1999, at the Fresno, Bakersfield, and Angiola sites, and on December 2, 2000, at the Bethel Island and Sierra Nevada Foothills sites. Daily SFS samples were collected at Fresno and Angiola during a fall 2000 intensive sampling campaign on the following days: 10/14, 10/16–10/20, 10/22–10/24, and 11/2–11/9/2000. A winter intensive study was conducted at all five anchor sites on 12/15–12/18 and 12/26–12/28/2000, and 1/4–1/7 and 1/31–2/3/2001, when SFS samples were collected from 0000–0005, 0005–1000, 1000–1300, 1300–1600, and 1600–2400 PST. HNO_3 and NH_3 were also determined on the same schedule using DRI SGS (sequential gas samplers) [13]. Total NO_3^- (particle NO_3^- plus gaseous HNO_3) was collected on sodium chloride-impregnated cellulose-fiber filters in an undenuded sample stream. Particle NO_3^- was collected on the same filters in an HNO_3 -denuded channel and HNO_3 was determined by the difference between the denuded and undenuded NO_3^- concentrations (i.e., by denuder difference). NH_3 was determined similarly using a citric acid-coated denuder and citric acid-impregnated cellulose-fiber filters. Gaseous HNO_3 was measured continuously in Fresno using a TEI (Franklin, MA) 42C chemiluminescence analyzer with HNO_3 -denuded and undenuded channels [10]. Meteorological measurements of T and RH were available for the Fresno and Bakersfield sites.

RESULTS AND DISCUSSION

There was a linear inverse relationship between 24-hour average temperature (T °C) and RH (%) at the Fresno ($\text{RH} = -1.91 \text{ T} + 91.1$, $r = 0.87$) and Bakersfield ($\text{RH} = -1.77 \text{ T} + 92.5$, $r = 0.85$) sites. Trends were similar at both sites. Given the dependence of the NH_4NO_3 equilibrium on T and RH, this variation should control the distribution of gaseous and particulate NO_3^- and influence NH_4NO_3 sampling artifacts in the SJV. Seasonal averages of non-volatile and volatilized NO_3^- from 24-hour average SFS samples at the Fresno, Angiola, and Bakersfield sites are shown in Figure 2. The highest and lowest total particle nitrate (PNO_3^-) occurred during winter and summer, respectively, at all sites. The volatilized NO_3^- ranged from 3.5% at Angiola during winter to 84% at Fresno during summer. These results are consistent with those observed in previous studies [5,7]. Monthly average ratios of volatilized NO_3^- to PNO_3^- at the Fresno,

Angiola, and Bakersfield sites were highly correlated among sites and also with monthly average temperature. Similar relationships between temperature and ratios of volatilized NO_3^- to PNO_3^- were observed on daily and diurnal scales during the fall and winter intensive studies, respectively.

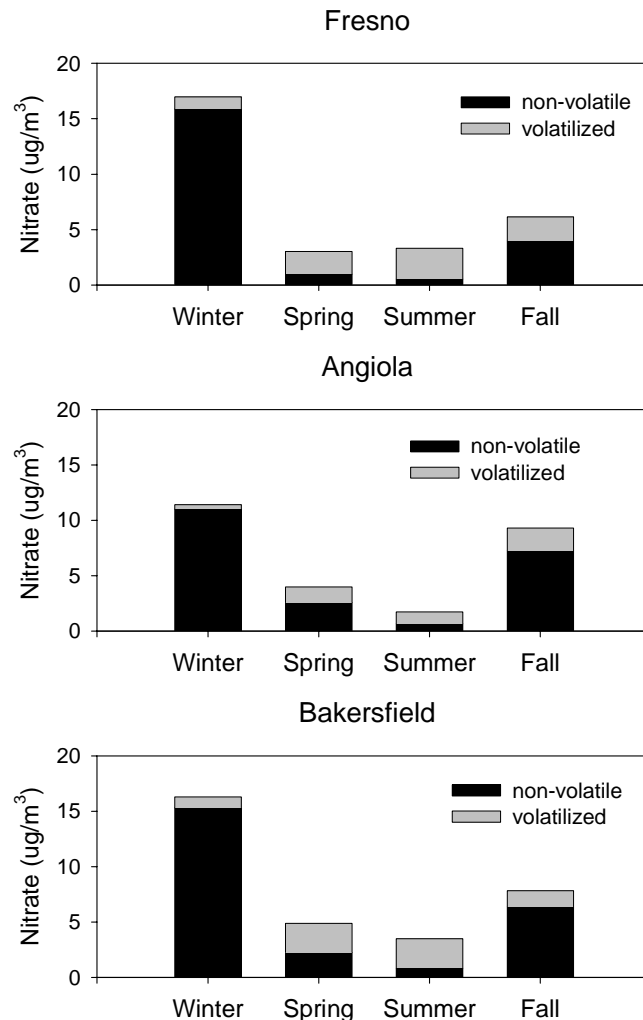


Figure 2. Seasonal average of non-volatilized and volatilized NO_3^- concentrations measured with quartz-fiber front filter and sodium chloride-impregnated cellulose-fiber backup filters, respectively, at the Fresno, Angiola, and Bakersfield sites in California using HNO_3 -denuded SFS samplers for samples acquired from December 2, 1999, to December 2, 2000, with every-sixth-day U.S. Environmental Protection Agency (EPA) sampling schedules: winter = December to February; spring = March to May; summer = June to August; fall = September to November.

Figure 3 compares daily non-volatile NO_3^- on the front quartz-fiber filters in the denuded and undenuded channels of the RAAS sampler in Fresno for warm (May-September) and cold (November-March) months. The largest difference is seen during the warmer months when the average ratio of denuded to undenuded NO_3^- was 0.41 ± 0.21 . These ratios were much higher (denuded to undenuded ratio = 1.08 ± 0.34) during the colder months. Many samples from the colder months reported higher denuded than undenuded

NO_3^- . This may represent some other kind of sampling artifact because the ratio of colder-month denuded to undenuded channel sulfate concentrations, also measured on the front quartz-fiber filters by IC, was 1.21 ± 0.26 , with a correlation of 0.95.

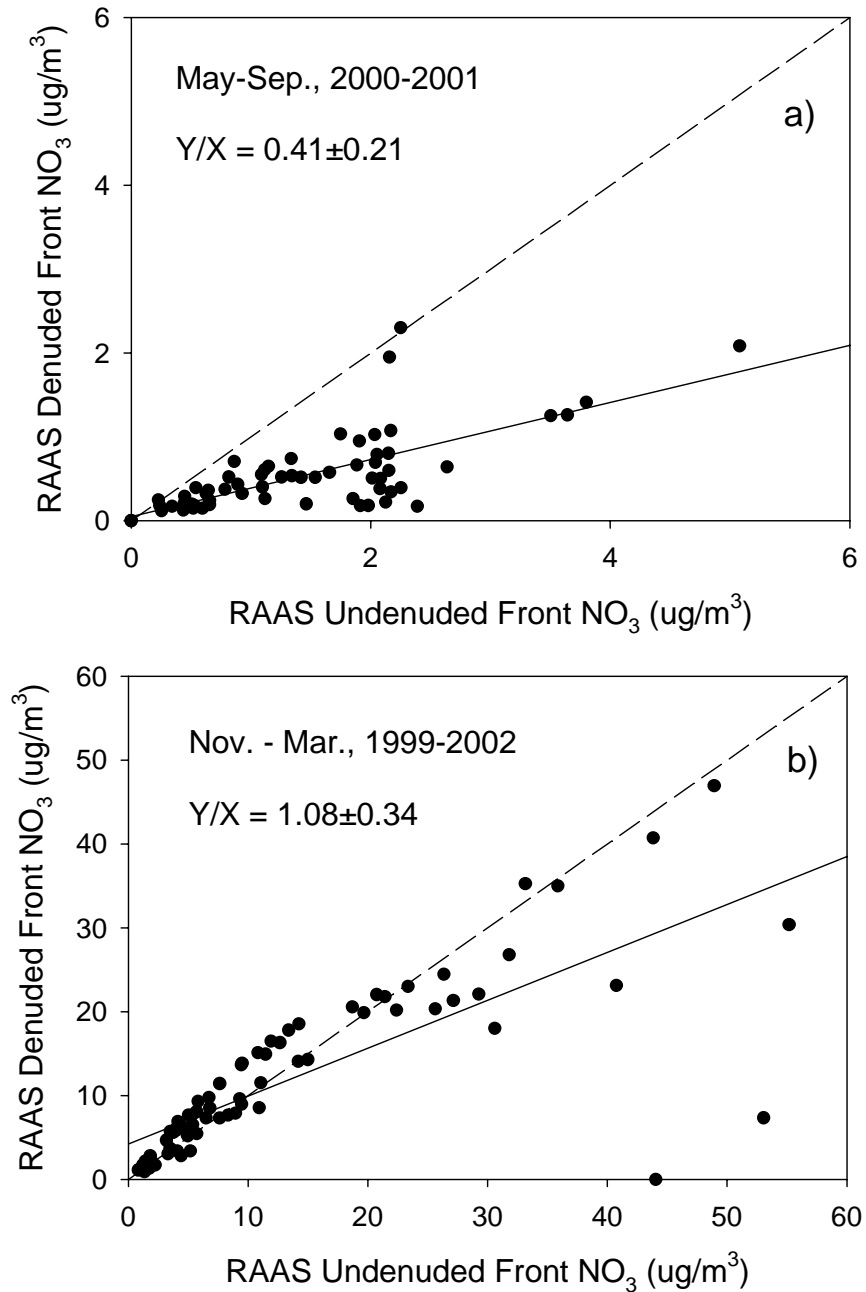


Figure 3. Comparison of daily undenuded and HNO_3 -denuded front quartz-fiber filter non-volatilized NO_3^- from the RAAS sampler in Fresno, CA, for: a) May-September 2000-2001; and b) November-March 1999-2002.

Consistency with Theory

The NH_4NO_3 collection efficiency for filter samplers with and without gas (HNO_3 and NH_3) denuders is related to the pressure drop through the filter and the ratio of ambient gas (e.g., HNO_3) to the sampled particle (NO_3^-) concentration [8]. The effect of the ambient gas-to-particle distribution on NO_3^- volatilization is illustrated by Figure 4, which is based on monthly average RAAS filter and continuous HNO_3 measurements in Fresno. Figure 4a shows that the highest HNO_3 concentrations occurred during the

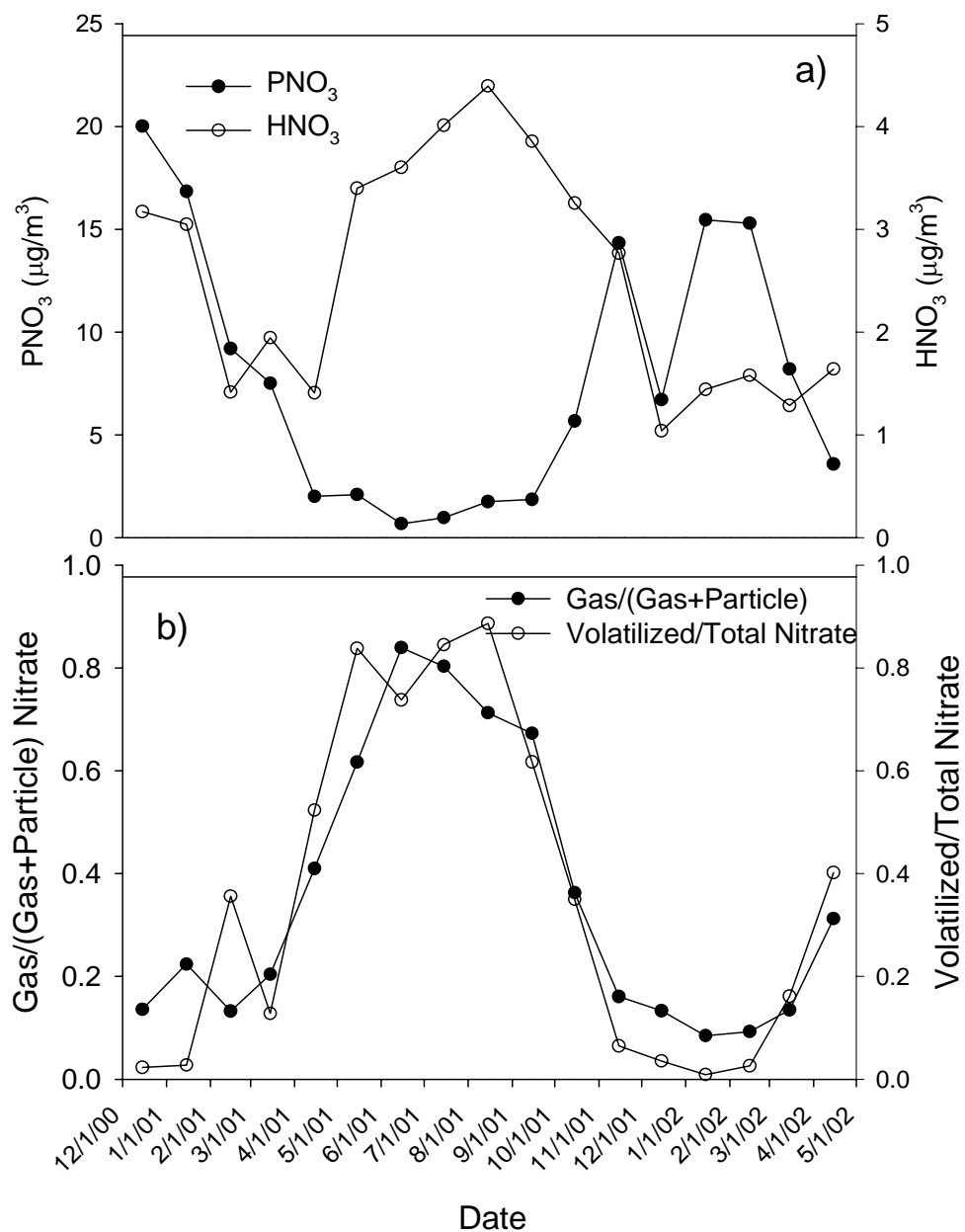


Figure 4. Monthly ratio (a) of RAAS total particle nitrate (PNO_3^-) and HNO_3 in Fresno from December 2000 through April 2002; and (b) monthly ratio of HNO_3 to total nitrate ($\text{HNO}_3 + \text{PNO}_3^-$) and monthly ratio of volatilized NO_3^- to PNO_3^- in Fresno from December 2000 through April 2002.

warmest (and driest) months, when PNO_3^- concentrations were lowest. This follows from the dependence of the gas-particle equilibrium for NH_4NO_3 on T and RH. Figure 4b shows a strong direct relationship (correlation = 0.93) between the fraction of particle NO_3^- volatilized during sampling and the ratio of ambient HNO_3 to total nitrate ($\text{TNO}_3^- = \text{HNO}_3 + \text{PNO}_3^-$). The relationship is nearly one-to-one:

$$\text{Volatilized NO}_3^-/\text{TNO}_3^- = 1.13 [\text{HNO}_3/(\text{HNO}_3 + \text{PNO}_3^-)] - 0.05 \quad (2)$$

For HNO_3 -denuded RAAS filter samples, volatilization of NH_4NO_3 from the quartz-fiber filter simply represents the re-establishment of the HNO_3 – NH_3 equilibrium that existed in the ambient atmosphere.

Nitrate volatilization was estimated with the SCAPE thermodynamic equilibrium model to determine whether closure exists between theory and measurement [14]. This model describes the gas-particle equilibrium for complex aerosol and gas mixtures. The model requires as input Na^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} , CO_3^{2-} , total equivalent NH_3 (particulate ammonium $[\text{NH}_4^+]$ + gaseous NH_3), total equivalent HNO_3 (particulate NO_3^- + gaseous HNO_3), and Cl^- as HCl . Total NH_3 was measured over an annual cycle only in CRPAQS SFS samples. Because HNO_3 was denuded, PNO_3^- is input and the model estimates the retained and volatilized NO_3^- . Calcium ion, Mg^{2+} , and CO_3^{2-} were not measured and are ignored. Twenty-four-hour average chemical concentrations at Fresno and Bakersfield were applied with corresponding hourly average T and RH, and the estimated equilibrium concentrations were used to calculate 24-hour averages.

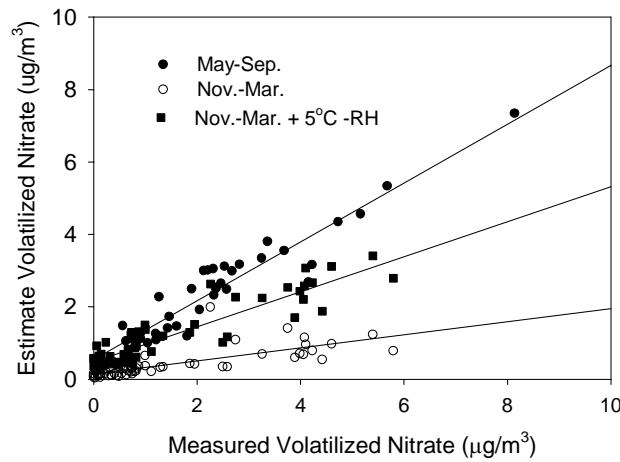


Figure 5. Measured 24-hour average volatilized NO_3^- at Fresno and Bakersfield during CRPAQS compared with volatilized NO_3^- estimated with the SCAPE model for summer (May–September, solid circles), winter (November–March, open circles), and for winter with T raised by 5 °C and RH lowered according to the relationships shown in Figure 3 between the hours of 1000 and 1800 (solid squares).

Measured and estimated volatilized NO_3^- are plotted in Figure 5 for warm (May–Sep.) and cold (Nov.–Mar.) season samples. During the warm season, when NO_3^- volatility is

high, the agreement is quite 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 significantly underestimated. Increasing the temperature of the filter substrate (or of the air passing through it) over the ambient temperature can significantly increase NO_3^- volatilization in denuded and undenuded samples [7]. Underestimation during winter may be related to heating of the sampler plenum during the daylight hours. To test this, the model was rerun with hourly temperatures increased by 5 °C between the hours of 1000 and 1800 local time. The corresponding reduction in RH was estimated using the relationships between RH and T described above. This increased the average estimated cold-season volatilized NO_3^- from 0.41 to 1.21 $\mu\text{g}/\text{m}^3$ and increased the correlation between measured and estimated volatilized NO_3^- from 0.75 to 0.91.

Implications for $\text{PM}_{2.5}$ Standards

The state of California has proposed a 24-hour average standard for $\text{PM}_{2.5}$ of 25 $\mu\text{g}/\text{m}^3$ [15]. NO_3^- volatilization had significant implications for measuring $\text{PM}_{2.5}$ during CRPAQS. Figure 6 presents the daily average ratio of volatilized NH_4NO_3 (AMNIT = 1.29 times volatilized NO_3^-) to $\text{PM}_{2.5}$ mass concentration measured on SFS Teflon-membrane filters (Pall Sciences, R2PJ047, Ann Arbor, MI) along with the corresponding

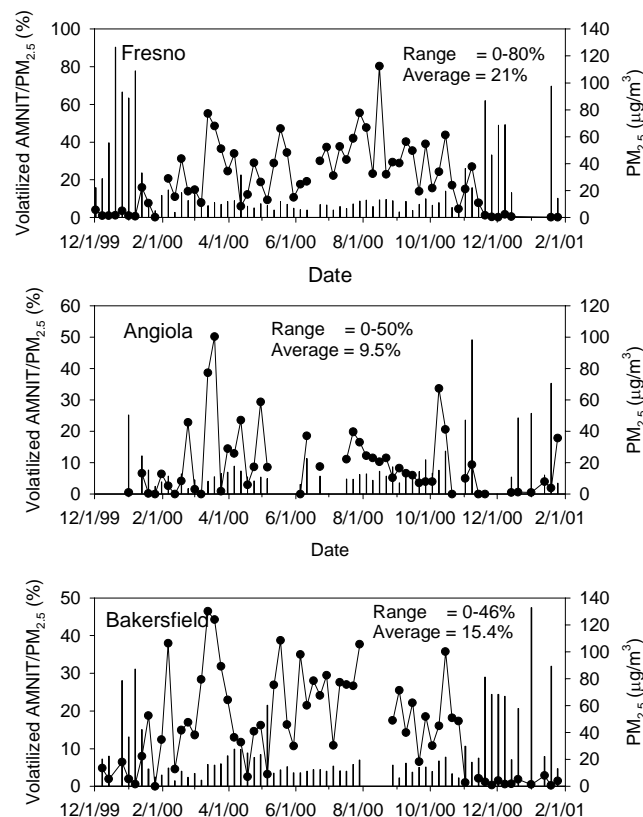


Figure 6. Daily SFS volatilized NH_4NO_3 (AMNIT) as a percentage of $\text{PM}_{2.5}$ measured on SFS Teflon-membrane filters and $\text{PM}_{2.5}$ concentrations (vertical bars) at Fresno, Angiola, and Bakersfield during CRPAQS.

PM_{2.5} concentrations at the Fresno, Angiola, and Bakersfield sites. On average, 21, 9.5, and 15.4% of the measured PM_{2.5} mass was lost through volatilization at Fresno, Angiola, and Bakersfield, respectively. The corresponding maximum daily losses were 80, 50, and 46% at the three sites, respectively. The proposed PM_{2.5} 24-hour standard of 25 µg/m³ was exceeded on 14, 7, and 15 days at Fresno, Angiola, and Bakersfield, respectively. If the PM_{2.5} measurement had included volatilized NH₄NO₃, the proposed standard would have been exceeded on an additional two, two, and five days at the Fresno, Angiola, and Bakersfield sites, respectively, over the 14-month CRPAQS period. While NO₃⁻ evaporative losses are highest during summer, only two of the nine “excess” exceedances occurred during summer months (June, July, or August).

CONCLUSIONS

Volatilization of NH₄NO₃ during aerosol sample collection in SJV was evaluated using measurements from CRPAQS and the Fresno Supersite. On a seasonal basis, the amount of particle NO₃⁻ lost to evaporation during sampling at the Angiola, Fresno, and Bakersfield sites ranged from 3.5 and 6.5%, respectively, during winter, to 61 and 84%, respectively, during summer. The degree of volatilization was correlated with annual, daily, and diurnal variations in ambient temperature, even in winter. However, the relationship between NO₃⁻ volatilization and temperature is indirect. Under hot and dry conditions, the equilibrium between particulate NH₄NO₃ and gaseous HNO₃ and NH₃ is shifted to the gas phase. In Fresno during summer (June–August), 80% of the total NO₃⁻ (the sum of gaseous HNO₃ and particle NO₃⁻) is present as HNO₃. When HNO₃ is denuded from the sample stream, particulate NH₄NO₃ readily evaporates to re-establish the ambient equilibrium. Measured NO₃⁻ volatilization was consistent with that estimated using a detailed thermodynamic equilibrium model. PM_{2.5} mass concentration measured on Teflon-fiber filters was subject to significant negative bias due to evaporation of NH₄NO₃ during sampling. During CRPAQS, 21, 9.5, and 15.4% of PM_{2.5} mass measured in HNO₃-denuded samples by the SFS sampler was lost to evaporation at the Fresno, Angiola, and Bakersfield sites, respectively. Maximum daily losses with respect to PM_{2.5} occurred during spring and summer, and reached 80% in Fresno.

ACKNOWLEDGEMENTS

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