Interference by Organic Signals in Highly-time Resolved Nitrate Measurements by Low Mass Resolution Aerosol Mass Spectrometry

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INTRODUCTION

► **Highly time-resolved measurements of nitrate in ambient aerosols were conducted by an Aerodyne Quadrupole Aerosol Mass Spectrometer (Q-AMS or simply AMS) and a Particle-into-Liquid Sampler with Ion Chromatography (PILS) from field intensives at two sites; an urban site in New York City (Queens College; QC) for wintertime (January 22 to February 5, 2004) and a rural site in southwestern New York State (Pinnacle State Park; PSP) for summertime (July 20 to August 4, 2004).**

► **In this study, we report that in rural atmospheres the inorganic nitrate signal from Q-AMS may contain significant interferences from organic signals. Analysis of the QC data indicates a good agreement between the PILS-nitrate and AMS-nitrate measurements (R^2 = 0.94; linear regression slope = 1.05). In addition, the *m/z* 30 and *m/z* 46 (two dominant ion fragments in nitrate mass spectrum) signals tightly correlate at QC (R^2 = 0.98) and have an average ratio similar to that determined in the laboratory for NH_4NO_3 (*m/z* 30 / *m/z* 46 = 2.4). In contrast, at the PSP site the correlation between PILS- and AMS-nitrate was poor (R^2 = 0.34), the AMS reported nitrate values were substantially higher, and the *m/z* 30 to *m/z* 46 ratios were generally much larger than 2.4. These observations, together with evaluations by aerosol phase ion balance, indicate that the AMS *m/z* 30 signals at PSP have been strongly influenced by organic compounds that also produce signals at *m/z* 30, e.g., organic nitrates (NO^+), oxygenated organics (CH_2O^+), hydrocarbon-like organics ($C_2H_6^+$), and nitrogen-containing organic compounds (CH_4N^+).**

SITE DESCRIPTION

Pinnacle State Park (PSP)
- Rural Site
- Data Collection from July 20 through August 4 in 2004
- Low population density rural village of Addison, New York
- Surrounded by parklands, and forested areas

Queens College (QC)
- Urban Site
- Data Collection from January 22 through February 5 in 2004
- High population density section of New York City
- North is the Long Island Expressway (I-495)
- West is the Van Wyck Expressway (I-678)

SITE MAP

Characteristics of the instruments

Table 1. Site description and characteristics of the semicontinuous instruments

PSP	Classification (Rural), Latitude (42.09°N), Longitude (77.21°W), Elevation (505 m)						
Instrument	Denuder	Inlet Heights (m)	Inlet Flowrate (LPM)	Sampling Flowrate (LPM)	Size Separator	Time Resolution	Detector
AMS	N/A	5	10	0.4	Cyclone	10 min	Mass Spectrometry
PILS-IC	Na_2CO_3 and Citric Acid / Carbon monolith	5	16.7	16.7	Cyclone	15 min	Ion Chromatography
SUNSET	Charcoal-impregnated strips	5	8	8	Cyclone	60 min	NDIR
QC	**Classification (Urban), Latitude (40.74°N), Longitude (73.82°W), Elevation (25 m)**						
Instrument	Denuder	Inlet Heights (m)	Inlet Flowrate (LPM)	Sampling Flowrate (LPM)	Size Separator	Time Resolution	Detector
AMS	N/A	5	10	0.4	Cyclone	10 min	Mass Spectrometry
PILS-IC	Na_2CO_3 and Citric Acid / Carbon monolith	5	16.7	16.7	Cyclone	15 min	Ion Chromatography
SUNSET	Charcoal-impregnated strips	5	8	8	Cyclone	60 min	NDIR

FIGURE 1

► **T**ime series traces for the hourly averaged AMS-nitrate (colored by the mole equivalent ratio of ammonium to sum of nitrate and sulfate from PILS) & PILS-nitrate measurement (gray line)

► **T**he pairwise correlation scatterplots between the hourly averaged AMS-nitrate and PILS-nitrate

► **T**ime-of-day average of fine particulate PILS-nitrate & AMS-nitrate (the cross symbols inside of the box represent the mean value, the boundaries of the box represent the 25th percentile and the 75th percentile, the line within the box indicates the median, and whiskers above and below the box indicate the 90th and 10th percentiles, respectively).

Mole equivalent ratio = $[NH_4^+]/18$ / ($2*[SO_4^{2-}]/96 + [NO_3^-]/62$)

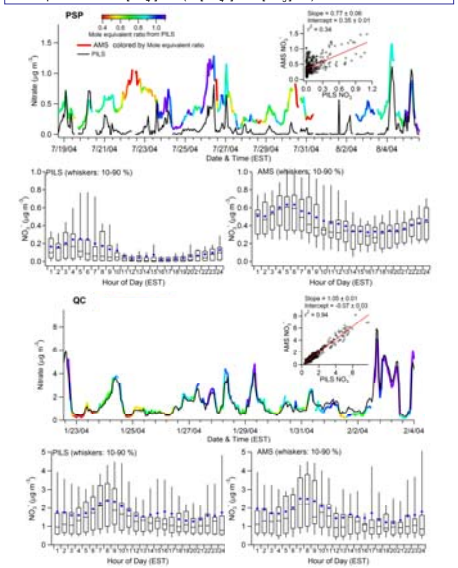


FIGURE 2

► **T**he pairwise correlation scatterplots between the hourly averaged AMS-ammonium and PILS-ammonium and the hourly averaged AMS-sulfate and PILS-sulfate at the PSP (filled circles) and QC (open circles) sites.

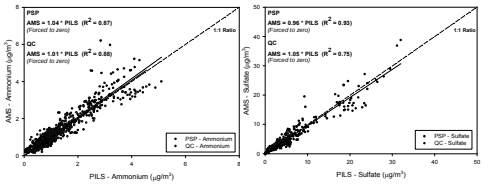


FIGURE 3

► **T**he pairwise correlation scatterplots between PILS-nitrate and each of the hourly averaged mass fragments of *m/z* 30 (filled circles) & *m/z* 46 (open circles) for AMS-nitrate for the PSP and QC sites.

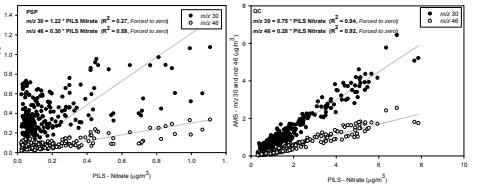
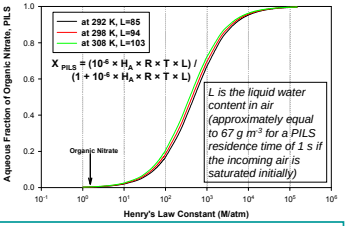


FIGURE 4

► **D**oes the PILS-IC capture and/or detect organic nitrate particles as nitrate ions?

► **A**queous fraction at equilibrium of PILS plotted as function of the Henry's law constant.

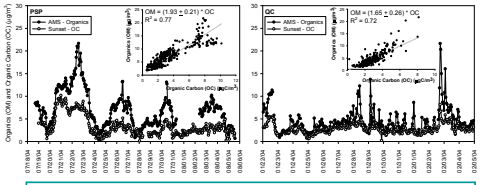


We have shown that the Henry's Law solubilities of organic nitrate are small, and that the hydrolysis of these compounds contributes negligibly to solubility. We used the following equation from Frenzel et al. [2000]:

$$-d\,C_{liquid} / dt = C_{liquid} F_{air} / [H_A \times R \times T \times V_{liquid}] + C_{liquid} \times k_h$$

FIGURE 5

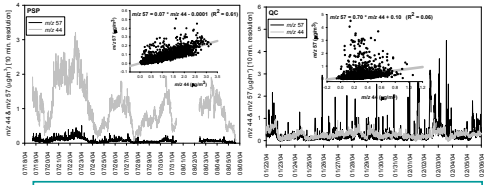
► **T**he time series traces for the hourly averaged AMS-organics (filled circles) and organic carbon (open circles) by SUNSET for OM/OC ratio estimates deployed at the PSP site and QC site



► **P**SP has a higher OM/OC ratio, which is consistent with a greater SOA contribution.

FIGURE 6

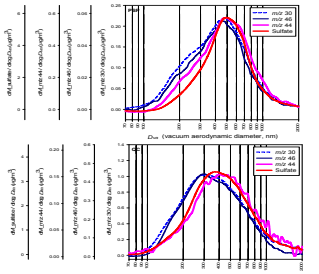
► **T**he time series traces and pairwise correlation scatterplots between the 10 minute resolution mass fragments of *m/z* 44 & *m/z* 57 for AMS-nitrate



► **P**SP is strongly impacted by OOA, **Q**C is strongly impacted by HOA.

FIGURE 7

► **T**he average size distributions of *m/z* 30 (black line), *m/z* 46 (blue line), *m/z* 44 (pink line), and sulfate (red line) deployed at the PSP and QC sites.



► **P**SP summertime particles – uniform, sulfate dominated, and well aged

► **Q**C wintertime particles – dynamic and smaller "fresh" nitrate together with larger sulfate & organics.

FIGURE 8

► **E**stimate the "excess" m/z 30 signal attributable to organic-linked *m/z* 30 and/or organic-linked nitrate using the following equation:

$$\Delta m/z\ 30 = m/z\ 30_{\ measured} - 2.4 \times m/z\ 46_{\ measured}$$

► **T**he pairwise correlation scatterplots between the hourly averaged mass fragments of *m/z* 30 & *m/z* 46 at the PSP site, *m/z* 30 & *m/z* 46 at the QC site, and *m/z* 30 & *m/z* 44 at the PSP site (colored by the ratio of PILS-nitrate to AMS-nitrate).

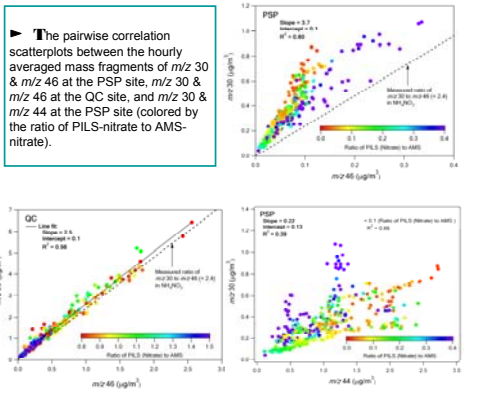
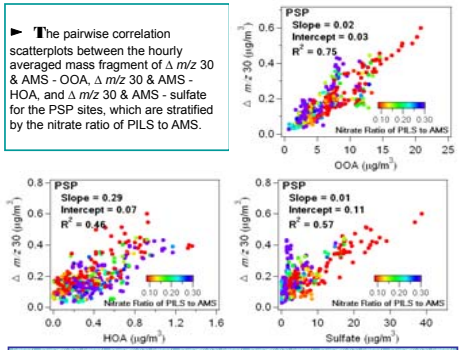


FIGURE 9

► **H**ow does "excess *m/z* 30" vary with OOA, HOA, and sulfate?

► **T**he pairwise correlation scatterplots between the hourly averaged mass fragment of Δ *m/z* 30 & AMS - OOA, Δ *m/z* 30 & AMS - HOA, and Δ *m/z* 30 & AMS - sulfate for the PSP sites, which are stratified by the nitrate ratio of PILS to AMS.



CONCLUSIONS AND SUGGESTIONS

We have found and reported evidence of interference at a rural location in the *m/z* 30 mass fragment measured by the Quadrupole Aerosol Mass Spectrometer and commonly ascribed to nitrate.

Together with the ion balance analysis that shows unreasonably high levels of AMS-nitrate in the relatively acidic particles at the PSP site, evidence suggests that the AMS-nitrate signal at this site (which is mostly *m/z* 30 & *m/z* 46) is not purely from inorganic nitrate and is likely impacted by organic compounds that also produce signals at *m/z* 30.

Nitrate signal at *m/z* 30 is estimated based on *m/z* 46 signals:

$$frag\_nitrate[30] = frag\_nitrate[46] \times f_r$$

where frag_nitrate[46] equals *m/z* 46 signal and f_r is the *m/z* 30 to 46 ratio determined for NH_4NO_3. (At QC f_r = 2.5 and in the laboratory f_r = 2.4.)

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