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Semi-continuous $PM_{2.5}$ inorganic composition measurements during the Pittsburgh Air Quality Study

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Abstract

A method for semi-continuous (10 min time resolution) $PM_{2.5}$ nitrate and sulfate measurements, based on the humidified impaction with flash volatilization design of Stolzenburg and Hering (Environ. Sci. Technol. 34 (2000) 907), was evaluated during the Pittsburgh Air Quality Study (PAQS) from July 2001 to August 2002. The semi-continuous measurements were corrected for several operating parameters. The overall corrections were less than 10% on average, but could be quite large for individual 10 min measurements. These corrections resulted in an improvement in the agreement of the measurements with the filter-based measurements, with a major axis regression relationship of $y = 0.83x + 0.20\,\mu g\,m^{-3}$ and R^2 of 0.84 for nitrate and $y = 0.71x + 0.42\,\mu g\,m^{-3}$ and R^2 of 0.83 for sulfate. The corrected semi-continuous measurements were calibrated over the entire year using collocated denuder/filter-pack-based measurements. These calibrated semi-continuous measurements are used in conjunction with temporally resolved gas-phase measurements of total (gas- and aerosol-phase) nitrate and meteorological measurements to investigate short-term phenomena at the Pittsburgh Supersite. The gas-to-particle partitioning of nitrate varied daily and seasonally, with a majority of the nitrate in the particle phase at night and during the winter months.

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1. Introduction

Filter-based methods have traditionally been used to characterize water-soluble inorganic ions in $PM_{2.5}$ and PM_{10}. These filter methods typically involve the offline analysis of particle samples collected onto substrates by inertial impaction or filtration; The particles are then extracted from the substrate in water and the extract is analyzed by ion chromatography (IC) for the major inorganic PM components (Chow, 1995). Filter measurements are often performed daily, or at intervals of a few hours during intensive field studies. Inherent drawbacks to using filter-based methods for the measurement of inorganic aerosols include losses of volatile or reactive components from the substrate (Hering et al., 1988; Koutrakis et al., 1992; Suh et al., 1994; Hering and Cass, 1999; Babich et al., 2000; Pang et al., 2001), detection limit problems for high time temporal resolution measurements, and high labor costs.

In light of the above limitations of conventional filter-based methods, several alternate methods for temporally resolved inorganics measurements have been developed. Some methods bypass the filters and filter sampler used in the conventional method by collecting the particles directly into a liquid medium (Buhr et al., 1995;

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Khlystov et al., 1995; Liu and Dasgupta, 1996; Karlsson et al., 1997; Ito et al., 1998; Weber et al., 2001). These methods avoid the collection and extraction steps and their associated problems, although they typically employ a similar analytical technique, IC. Flame photometry has been used to perform in situ quantification of sulfate concentrations by Mueller and Collins (1980), D'Ottavio et al. (1981), Allen et al. (1984), and Lippmann et al. (2000). Another approach uses an aerodynamic particle time-of-flight to select the particle size range, followed by thermal vaporization and analysis using molecular mass spectrometry (Kolb et al., 2000). Other instruments perform single-particle composition analysis using mass spectrometry (McKeown et al., 1991; Carson et al., 1995; Marijinissen et al., 1988; Liu et al., 1999; Middlebrook et al., 2001; Prather et al., 1994). Single particle mass spectrometry measurements are generally not quantitative, although they provide valuable single-particle composition information.

We report here on an alternate method for temporally resolved inorganic aerosol measurement, that uses bulk collection followed by in situ analysis using a standard gas analyzer (Hering and Stolzenburg, 1998). Recently, Rupprecht and Patashnick (R&P) commercialized this instrument design for semi-continuous $PM_{2.5}$ nitrate (R&P model 8400N) and $PM_{2.5}$ sulfate (R&P model 8400S) (Meyer et al., 2000). These commercialized versions of the Hering and Stolzenburg (1998) instrument are the subject of this work.

While the above semi-continuous instruments offer one to two orders of magnitude of improvement in time-resolution over the conventional filter-based techniques, their precision and accuracy relative to conventional methods has not been widely investigated over long time periods. Watson et al. (1998) used these instruments to collect high time-resolution $PM_{2.5}$ nitrate and sulfate measurements across California during the California Regional PM Air Quality Study (CRPAQS). Watson et al. (2000) collected high time-resolution $PM_{2.5}$ nitrate and sulfate measurements at the Fresno Supersite. Watson and Chow (2002) used these measurements to investigate a wintertime $PM_{2.5}$ episode at the site. Hering et al. (2001) investigated differences in short-term variability in ground and aloft nitrate measurements collected at the rural Angiola CRPAQS site. Hering et al. (2003) used high time-resolution $PM_{2.5}$ sulfate measurements that were collected at Big Bend National Park to estimate light extinction coefficients. Several intercomparisons of the prototype instruments relative to standard methods have demonstrated the accuracy of the prototype systems (Hering and Stolzenburg, 1998; Stolzenburg and Hering; 2000; Liu et al., 2000). However, issues raised during the current intercomparison suggest that the commercialized versions of these instruments need to be investigated as well, and under various conditions.

In this work, the performance of the semi-continuous instruments is evaluated relative to 24 h integrated measurements collected using a conventional filter-based sampler and analyzed using IC. Comparisons were also performed relative to measurements collected using another temporally resolved semi-continuous method, the Khlystov et al. (1995) steam sampler, and analyzed using IC. The R&P semi-continuous nitrate and sulfate instruments operated from July 2001 to August 2002, the steam sampler operated from July 2001 to March 2002, and the filter sampler operated from July 2001 to March 2002. The objectives of this paper are (1) to evaluate the accuracy of the semi-continuous measurements relative to the standard filter-based measurements, (2) to evaluate the correction and calibration techniques used to improve their accuracy, and (3) to discuss temporally resolved variations in nitrate and sulfate measured at the PAQS Supersite.

2. Ambient inorganic PM and gas measurements

The central site was located in Schenley Park, a 456 acre wooded park in the greater Pittsburgh area, approximately 6 km from the downtown area and 500 m from the nearest heavily traveled street.

2.1. Semi-continuous inorganic PM and gas measurements

Semi-continuous nitrate and sulfate aerosol concentrations were measured on a 10 min basis using Rupprecht and Patashnick (R&P) instrument models 8400N and 8400S, respectively. The R&P instrument model 8400N follows a two-step process to measure $PM_{2.5}$ nitrate (Stolzenburg and Hering, 2000). In the first step, the ambient $PM_{2.5}$ is sampled through a sharp-cut cyclone, denuder, and humidifier and impacted for 8 min on a Nichrome® flash strip that is mounted in an integrated collection and vaporization (ICV) cell. The sharp-cut cyclone, denuder, and humidifier remove larger particles and vapors and increase the collection efficiency of the remaining particles; particle collection is most efficient for particles above 0.1 μm. In the second step, the collected ambient $PM_{2.5}$ is analyzed using a standard high-sensitivity NO_x gas analyzer. A flow path to the gas analyzer is established using a carrier gas of purified nitrogen, which also serves to purge the ICV cell of ambient gases. The baseline response of the gas analyzer is recorded. Then the collected particles are thermally vaporized in place, catalytically reducing the nitrate to NO_x. The evolved gas is drawn into the carrier gas stream and delivered to the gas analyzer for analysis. The R&P instrument model 8400S is similar in design and operation, except that platinum flash strips are used to collect the $PM_{2.5}$, purified air is used as the carrier gas, and a high-sensitivity SO_2 gas analyzer is used to measure the evolved gas. For both instruments, the instrument output is an ambient concentration calculated as the difference between the integrated areas under the evolved gas response curve and the baseline, adjusted for theoretical conversion efficiency, sample flow rate and gas analyzer flow rate.

During routine operation, the instrument offset, actual conversion efficiency, gas analyzer efficiency, sample flow rate, and reaction cell vacuum were measured to assess the performance of the semi-continuous instruments. The instrument offset was measured on a biweekly basis during PAQS by placing a HEPA filter on the inlet of the instrument, and collecting and averaging three consecutive 10 min measurements. The instrument offset for the whole study was $0.18 \pm 0.15\,\mu g\,m^{-3}$ (average ± one standard deviation) for the nitrate instrument and $0.30 \pm 0.16\,\mu g\,m^{-3}$ for the sulfate instrument. An evaluation of the daily variability over a 2 week period indicated that the instrument offset varied as much daily as it did biweekly.

The conversion efficiency was also quantified on a biweekly basis by performing aqueous standard calibrations. Conversion efficiency is a measure of the ability of the instrument to convert a microliter aliquot of a standard solution of ammonium nitrate to NO_x or ammonium sulfate to SO_2. The aliquot of the standard solution is applied directly to the flash strip using a syringe. Three duplicate measurements were made at five points over the working range of the instruments ($0–28\,\mu g\,m^{-3}$ for nitrate, and $0–29.4\,\mu g\,m^{-3}$ for sulfate). The study average conversion efficiency was 0.85 ± 0.08 for the nitrate and 0.65 ± 0.07 for the sulfate instrument; typical correlation coefficients of the relationships were greater than 0.99. An evaluation of the daily variability of the conversion efficiency over a 2 week period indicated that like the instrument offset, the conversion efficiency varied as much daily as it did biweekly.

Gas analyzer efficiency was measured daily (nitrate) and every 4 days (sulfate) at PAQS. The gas analyzer efficiency is a measure of the accuracy of the gas analyzer and is determined by sequentially routing two calibration gases through the ICV cell to the gas analyzer. Purified nitrogen (nitrate) or air (sulfate) is sent to the gas analyzer first. A calibration gas mixture of 5080 ppbv NO in nitrogen (nitrate) or 790 ppbv SO_2 in air (sulfate) is sent to the gas analyzer second. The gas analyzer efficiency was calculated as the ratio of the instrument response to calibration gas divided by the actual concentration of the calibration gas. The study average gas analyzer efficiency was stable at 0.99 ± 0.04 for the nitrate instrument and 0.99 ± 0.06 for the sulfate instrument.

The actual sample flow rate was measured on a monthly basis to quantify drift in the flow calibration using a certified flow standard. The study average ratio of the actual sample flow rate to the instrument indicated sample flow rate was 0.91 ± 0.15 for the nitrate instrument and 1.21 ± 0.21 for the sulfate instrument.

The nitrate gas analyzer reaction cell vacuum was recorded on a 10 min time basis to monitor deviations from the vacuum setpoint as a result of variable or declining pump performance. Vacuum deviations affect the accuracy of the semi-continuous measurements as well as the accuracy of the instrument offset, conversion efficiency and gas analyzer efficiency measurements. Kirby and Hering (2001) showed that $PM_{2.5}$ nitrate measurements made during the CRPAQS field campaign decreased by 13% for every inch of Hg that the vacuum in the gas analyzer reaction cell increased from its setpoint.

Total ($PM_{2.5}$ and gas) nitrate measurements were also made on a 1–2 h basis using the steam sampler developed by Khlystov et al. (1995) with analysis by IC. The steam sampler inlet included a Teflon-coated $PM_{2.5}$ cyclone and a Teflon-coated 20 cm length 1-in ID aluminum pipe maintained at ambient conditions. Losses of total nitrate in the inlet were evaluated and found to be negligible. The steam sampler draws 16.7 LPM of ambient air through the inlet and mixes it with $2\,g\,min^{-1}$ of steam, supersaturating the sample air with water vapor. The supersaturation causes a rapid growth of water droplets on the particles. At the same time, condensing water dissolves water soluble gases present in the sample air. The droplets and the condensed water, containing dissolved aerosol species and gases, are collected using two cyclones in series and automatically delivered into vials for offline analysis of major inorganic ions by IC.

2.2. *Filter-based inorganic measurements*

Measurements of total ($PM_{2.5}$ and gas) and $PM_{2.5}$ nitrate, and $PM_{2.5}$ sulfate were also made on a 4, 6, or 24 h time basis using a denuder- filter-based collection system and IC analysis (Chow, 1995). The filter-based sampler had two parallel lines, one with a $PM_{2.5}$ cyclone and filter pack and one with a denuder upstream of the $PM_{2.5}$ cyclone and filter pack. The filter packs contained a PTFE Teflon filter (Whatman Cat. No. 7592-104), a nylon filter (Whatman Cat. No. 7410-004), and a backup Cellulose-fiber filter (Whatman Cat. No. 1441-047) in series. Ambient air was drawn through both lines at a flow rate of 16.7 LPM. $PM_{2.5}$ sulfate and nitrate measurements were determined from the analysis of the Teflon filter and the Teflon and nylon filters, respectively, while inorganic gas-phase measurements were determined by difference of the same filters on the two parallel lines. Measurements of gas-phase and aerosol nitrate using this configuration have minimal artifacts and will therefore provide a basis for comparison for the semi-continuous method evaluation.

3. Corrections to semi-continuous ambient PM measurements

The raw semi-continuous measurements were corrected for sampling blanks (instrument offset) and analytical system calibrations (conversion efficiency). Corrections were also applied to the 10 min ambient nitrate and sulfate measurements to account for a software error, and correct for gas analyzer efficiency, vacuum drift, and sample flow rate drift.

3.1. Raw semi-continuous measurements

The output of the semi-continuous instruments is an ambient nitrate or sulfate measurement that is calculated as

$$C_i^* = 1000\,\frac{\left(\int C_{\mathrm{s},i}\,\mathrm{d}t - \int C_{\mathrm{b},i}\,\mathrm{d}t\right)}{t_{\mathrm{s},i}\;ef_{\mathrm{c},i}}\,\frac{\mathrm{MW}_i}{V}\,\frac{Q_{\mathrm{c},i}}{Q_{\mathrm{s},i}}, \tag{1}$$

where i is nitrate or sulfate, C_i^* the raw semi-continuous measurement corrected for the manufacturer software error in $\mu\mathrm{g\,m^{-3}}$, $C_{\mathrm{s},i}$ is the gas-phase concentration of NO_x or SO_2 measured by the gas analyzer after the sample has been flash volatilized in ppb, $C_{\mathrm{b},i}$ is the background gas-phase concentration of NO_x or SO_2 measured by the gas analyzer in ppb, t is the duration of the flash response measured by the gas analyzer in seconds, MW_i is molecular weight of nitrate ($62.01\,\mathrm{g\,mol^{-1}}$) or sulfate ($96.06\,\mathrm{g\,mol^{-1}}$), V is the molar volume of the carrier gas ($0.0224\,\mathrm{m^3\,mol^{-1}}$), $Q_{\mathrm{c},i}$ is the carrier gas flow rate in $\mathrm{l\,min^{-1}}$, $Q_{\mathrm{s},i}$ is the instrument indicated sample flow rate that is impinged on the flash strip in $\mathrm{l\,min^{-1}}$, $t_{\mathrm{s},i}$ is the total sample duration in seconds, and $\mathrm{ef}_{\mathrm{c},i}$ is the theoretical conversion efficiency (from zero to one) of the instrument to reduce aerosol nitrates to NO_x or sulfates to SO_2; Values of 0.82 and 0.69 were determined from factory calibrations of the nitrate and sulfate instruments, respectively, and were programmed into the instrument software by the manufacturer.

3.2. Software error correction

A correction was applied to the raw ambient measurements to account for an error in 8400S and 8400N software versions prior to 0.703. Version 0.702 was used during the study. The software error correction was 3% for nitrate and 11% for sulfate.

3.3. Instrument offset correction

Biweekly instrument offset measurements were used to assign a single instrument offset value to all times between the offset measurements. The resultant offset values were averaged over a rolling 30 day period by

$$C_{\mathrm{o},i}(\tau) = \frac{\sum_{\tau-15\mathrm{days}}^{\tau+15\mathrm{days}} C_{\mathrm{o},i,\mathrm{assigned}}(\tau)}{N}, \tag{2}$$

where $C_{\mathrm{o},i}$ is the averaged instrument offset measurement at date τ, i is nitrate or sulfate, $C_{\mathrm{o},i,\mathrm{assigned}}$ is the instrument offset for nitrate or sulfate measured prior to date τ, τ is the Julian date, and N is the number of offset values averaged together over the rolling 30 day period centered at date τ. This averaging procedure was used to incorporate daily variability into the biweekly instrument offset measurements, as shown in Fig. 1. Averaged 10 min instrument offset measurements were subtracted from the software corrected ambient measurements. The instrument offset correction ranged from 1% to 92% (18% on average) for nitrate and 0.1% to 53% (9% on average) for sulfate.

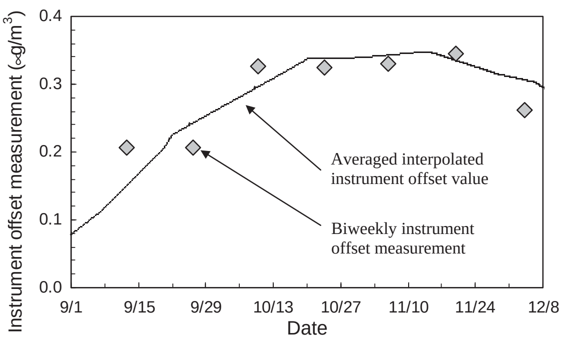

Fig. 1. Sulfate biweekly instrument offset measurements for the fall of 2001 and averaged instrument offset values used to adjust the ambient measurements, which were continuous and smoothed relative to the biweekly offset measurements.

3.4. Conversion efficiency correction

The raw semi-continuous measurements are calculated by the instrument software using the factory measured (‘theoretical’) conversion efficiencies. Deviations from the theoretical conversion efficiency were accounted for during data correction. The software corrected ambient measurements were multiplied by the theoretical conversion efficiency and divided by the actual measured conversion efficiency. Biweekly conversion efficiency measurements were used to assign a single conversion efficiency value to all times between the efficiency measurements. The resultant efficiency values were averaged over a rolling 30 day period. The conversion efficiency correction ranged from −38% to 16% (−4% on average) for nitrate and −32% to 36% (−7% on average) for sulfate.

3.5. Gas analyzer efficiency correction

The gas analyzer efficiency is assumed to be unity in the raw semi-continuous measurement calculation.

Deviations in the gas analyzer efficiency from unity were corrected for by dividing the nitrate and sulfate measurements by the actual gas analyzer efficiency. To account for slowly drifting efficiencies, gas analyzer efficiency measurements made daily or every 4 days were used to assign a single gas analyzer efficiency value to all times between the efficiency measurements. The resultant efficiency values were averaged over a rolling 2 day period (nitrate) or 8 day period (sulfate). The gas analyzer efficiency correction ranged from −19% to 4% (−1% on average) for nitrate and −4% to 18% (1% on average) for sulfate.

3.6. Sample flow drift correction

Semi-continuous measurements were also corrected for discrepancies between the measured sample flow rate and the indicated (by the instrument) sample flow rate. The sample flow rate correction ranged from −12% to 18% (−3% on average) for nitrate and −90% to 98% (−6% on average) for sulfate.

3.7. Gas analyzer vacuum drift correction

Differences between the NO_x gas analyzer reaction cell vacuum and the vacuum setpoint of 5.0 in Hg affected the semi-continuous nitrate measurements, and the nitrate instrument offset, conversion efficiency and gas analyzer efficiency measurements. These discrepancies were corrected by multiplying the software corrected ambient measurement, conversion efficiency or gas analyzer efficiency measurements by the linear relationship proposed by Kirby and Hering (2001). The reaction cell vacuum correction ranged from −24% to 5% (−1% on average) for the semi-continuous nitrate measurements.

3.8. Corrected semi-continuous measurements

The final corrected semi-continuous sulfate measurement was calculated from the raw semi-continuous measurement as

$$C_S = (C_S^* - C_{o,S})\,\frac{ef_{c,S}}{ef'_{c,S}}\,\frac{1}{ef_{ga,S}}\,\frac{Q_{s,S}}{Q'_{s,S}}, \tag{3}$$

where C_S is the corrected semi-continuous sulfate measurement in $\mu g\,m^{-3}$, C_S^* is the raw semi-continuous measurement corrected for the manufacturer software error in $\mu g\,m^{-3}$, $C_{o,S}$ is the averaged instrument offset measurement in $\mu g\,m^{-3}$, $ef_{c,S}$ is the theoretical conversion efficiency, $ef'_{c,S}$ is the actual conversion efficiency, averaged, and corrected for gas analyzer efficiency, $ef_{ga,S}$ is the averaged actual gas analyzer efficiency, $Q_{s,S}$ is the instrument indicated sample flow rate in LPM, and $Q'_{s,S}$ is the actual sample flow rate in LPM. The overall correction to the semi-continuous sulfate measurements was −1% on average but ranged from −90% to 100% for individual points.

The final corrected semi-continuous nitrate measurement was calculated from the raw semi-continuous measurement as

$$C_N = (C_N^* - C_{o,N})\,\frac{ef_{c,N}}{ef'_{c,N}}\,\frac{1}{ef_{ga,N}}\,\frac{Q_{s,N}}{Q'_{s,N}} \times [1 + 0.13\,(V_N - 5.0)], \tag{4}$$

where C_N is the corrected semi-continuous nitrate measurement in $\mu g\,m^{-3}$, C_N^* is the raw semi-continuous measurement corrected for the manufacturer software error in $\mu g\,m^{-3}$, $C_{o,N}$ is the averaged instrument offset measurement in $\mu g\,m^{-3}$, $ef_{c,N}$ is the theoretical conversion efficiency, $ef'_{c,N}$ is the actual conversion efficiency, averaged, and corrected for gas analyzer efficiency and reaction cell vacuum drift, $ef_{ga,N}$ is the actual gas analyzer efficiency, averaged, and corrected for reaction cell vacuum drift, $Q_{s,N}$ is the instrument indicated sample flow rate in LPM, $Q'_{s,N}$ is the actual sample flow rate in LPM, and V_N is the nitrate instrument gas analyzer reaction cell vacuum in inch Hg. The overall correction to the semi-continuous nitrate measurements was 8% on average but ranged from −62% to 93% for individual points.

4. Field comparison with filter-based measurements

The 10 min measurements were averaged on a 24 h basis for comparison against the daily filter-based measurements. These 24 h averages were considered valid when more than 75% of the possible 10 min measurements were available. Data recovery for the 24 h average semi-continuous sulfate measurements was greater than 90% for all of the study months except November 2001, and for the nitrate was greater than 80% for all months except August 2002. Data loss was associated with vacuum pump failures or excessive flash strip breakages within a single month.

With only the software error correction and the typical ambient PM corrections, the semi-continuous measurements were found to be nonlinear (sulfate) or moderately correlated (nitrate) underpredictions of the true inorganic concentrations measured using the filter-based method, as shown in Fig. 2. With all of the corrections, the semi-continuous $PM_{2.5}$ nitrate and sulfate measurements were found to correlate linearly and reasonably with the filter-based measurements, as shown in Fig. 3. However, the relationship of $y = 0.83x + 0.20\,\mu g\,m^{-3}$ for nitrate and $y = 0.71x + 0.42\,\mu g\,m^{-3}$ for sulfate indicated that there was still a systematic bias in the measurements. The non-unity slope in these relationships could be due to incomplete collection of particles after humidification on the flash

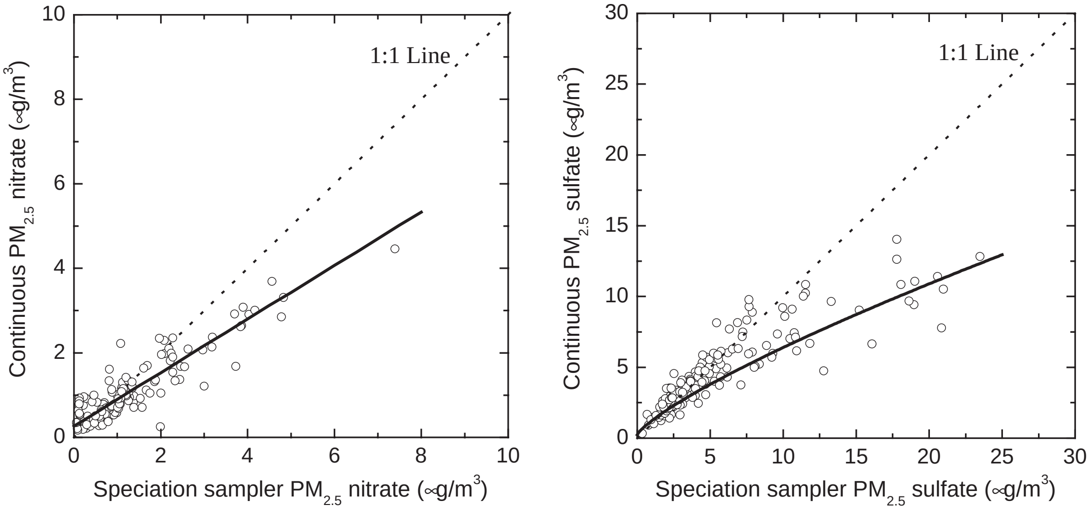

Fig. 2. Comparison of the daily averages of the instrument reported (raw measurements) semi-continuous nitrate and sulfate with the corresponding values of the filter-based speciation sampler from July 2001 to March 2002. The linear correlation (black line), $y = 0.63x + 0.27\,\mu g\,m^{-3}$ with $R^2 = 0.82$, was obtained for nitrate. The nonlinear correlation (black line), $y = x^{0.79} + 0.23\mu g\,m^{-3}$ with $R^2 = 0.86$, was obtained for sulfate. Also shown are the 1:1 lines (dashed lines).

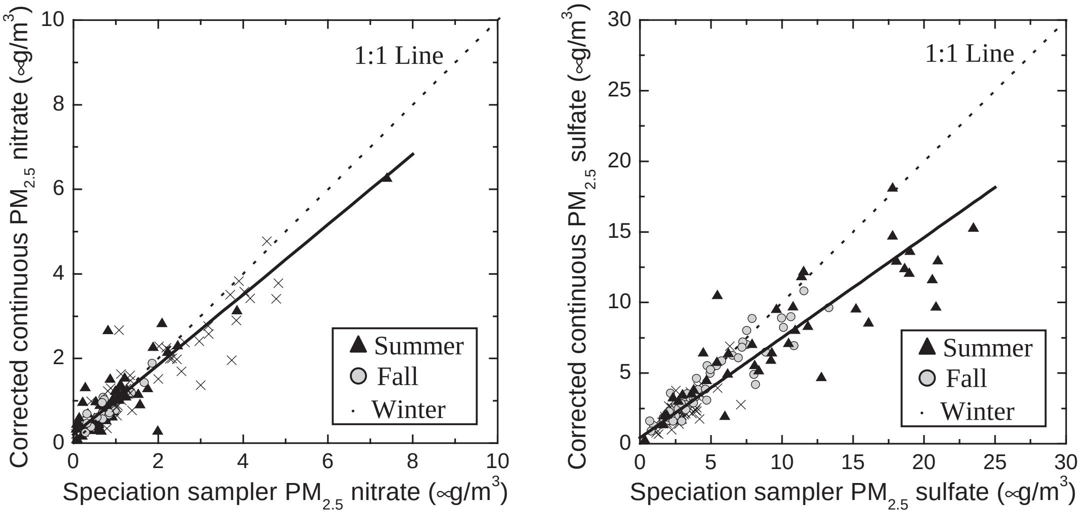

Fig. 3. Comparison of the daily averages of the corrected semi-continuous nitrate and sulfate with the corresponding values of the filter-based speciation sampler from July 2001 to March 2002. The linear correlation (black line), $y = 0.83x + 0.20\,\mu g\,m^{-3}$ with $R^2 = 0.84$, was obtained for nitrate, and the linear correlation (black line), $y = 0.71x + 0.42\,\mu g\,m^{-3}$ with $R^2 = 0.83$, was obtained for sulfate. Also shown are the 1:1 lines (dashed lines).

strip or incomplete conversion of the various chemical forms of nitrate and sulfate to NO_x and SO_2. The non-zero offset indicates a positive measurement artifact possibly due to organonitrates and organosulfates.

The apparent bias in the semi-continuous measurements can be reduced by calibrating the measurements against collocated filter-based measurements. The validity of this approach is based on two key assumptions: (1) individual points used to compute an average semi-continuous measurement have randomly distributed error, and (2) filter-based measurements should serve as the standard for evaluating the performance of the semi-continuous measurement methods. The first assumption is reasonable given that temporally resolved measurements of semi-continuous nitrate were consistent with independent temporally resolved measurements

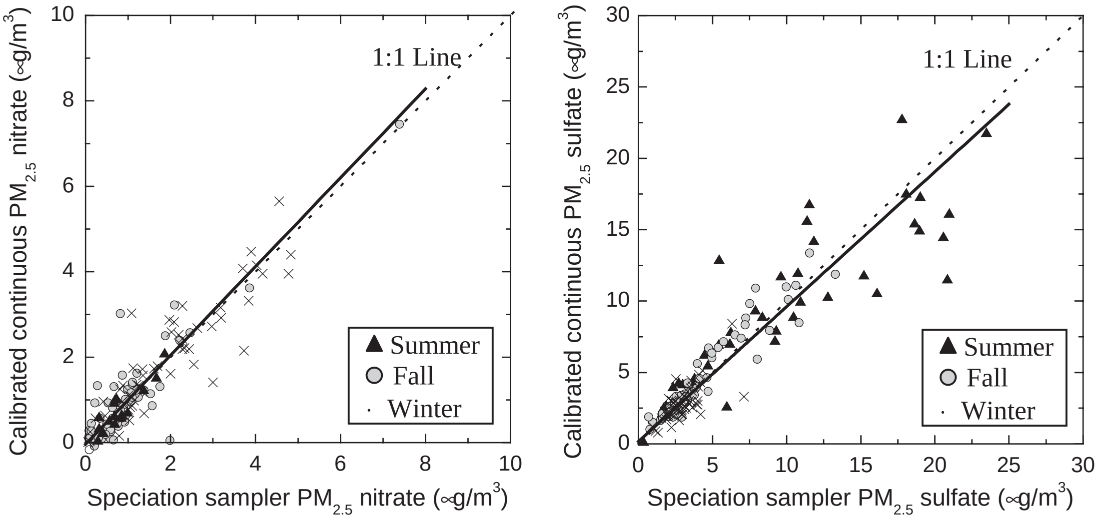

Fig. 4. Final comparison of the daily averages of the calibrated semi-continuous nitrate and sulfate with the corresponding values of the filter-based speciation sampler from July 2001 to March 2002. The linear correlation (black line), $y = 1.04x - 0.04\,\mu g\,m^{-3}$ with $R^2 = 0.83$, was obtained for nitrate, and the linear correlation (black line), $y = 0.94x + 0.17\,\mu g\,m^{-3}$ with $R^2 = 0.84$, was obtained for sulfate. Also shown are the 1:1 lines (dashed lines).

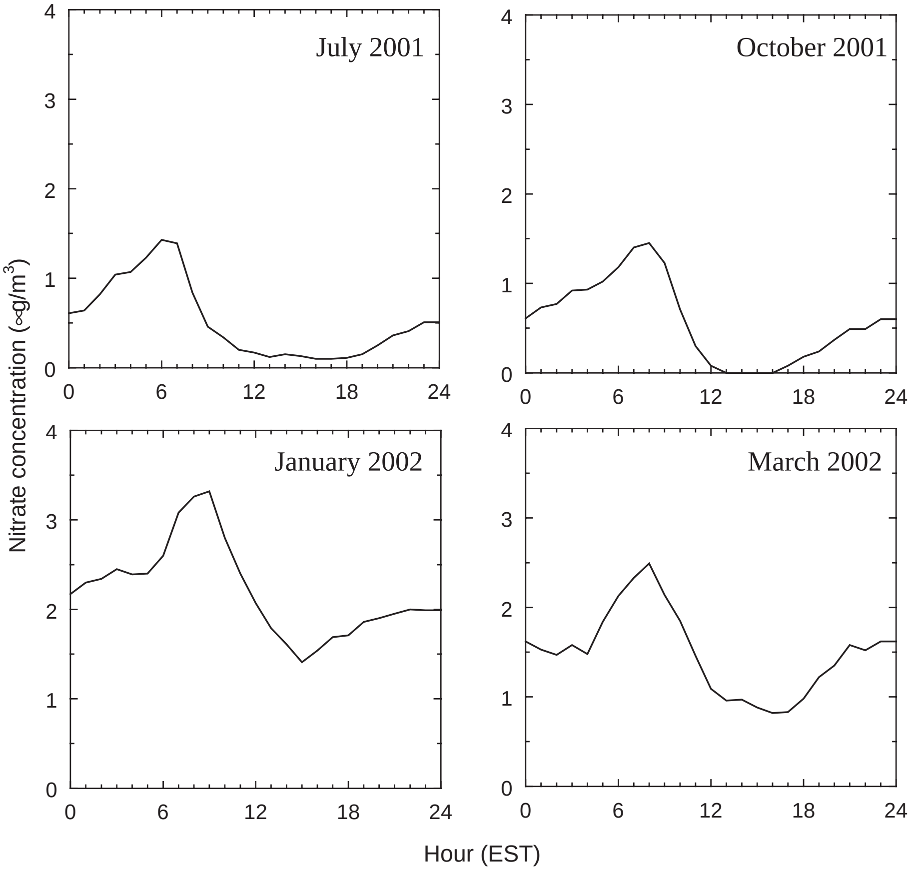

Fig. 5. Average diurnal $PM_{2.5}$ nitrate monthly profiles for July 2001, October 2001, January 2002, and March 2002.

of UV radiation and total nitrate. The second assumption is justified by the design of the filter-based sampler used in this study that minimized volatilization losses of nitrate from the filters.

Major axis regression was performed to account for measurement error in both measurements. In general, regressions were performed on 24 h filter-based measurements and 24 h averages of the semi-continuous measurements. In July 2001 and January 2002, 4 and 6 h filter-based measurements were available. During these intensive periods, regressions were performed on the 4–6 h filter-based measurements and identical averages of the semi-continuous measurements basis. A robust Huber's method (Meier and Zund, 2000) was used to identify gross outliers prior to regression when more than two measurements were available. High time-resolution concentrations were obtained by calibrating the 1 h semi-continuous concentrations using the corrected 24 h averages. The final relationship of $y = 1.04x - 0.04\,\mu\mathrm{g\,m^{-3}}$ for nitrate and $y = 0.94x + 0.17\,\mu\mathrm{g\,m^{-3}}$ for sulfate indicated that the use of this calibration procedure resulted in a more accurate

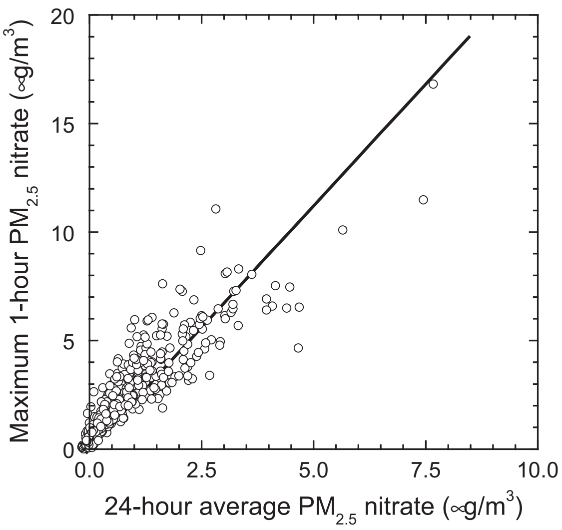

Fig. 6. The linear correlation of the 24-h average nitrate and the maximum daily 1-h average nitrate for all points from July 2001 to August 2002: $y = 2.24x\,\mu\mathrm{g\,m^{-3}}$ with $R^2 = 0.77$.

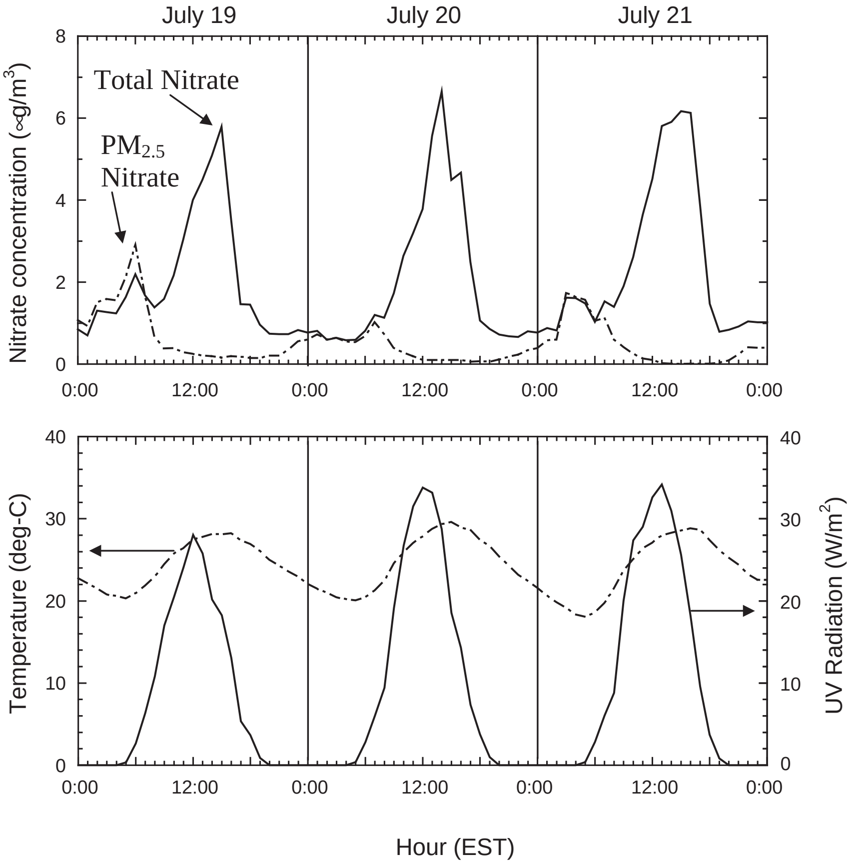

Fig. 7. Diurnal gas-to-particle partitioning of nitrate at PAQS for three consecutive days in July 2001. Also shown are hourly averaged temperature and ultraviolet (UV) radiation measurements made on the same days.

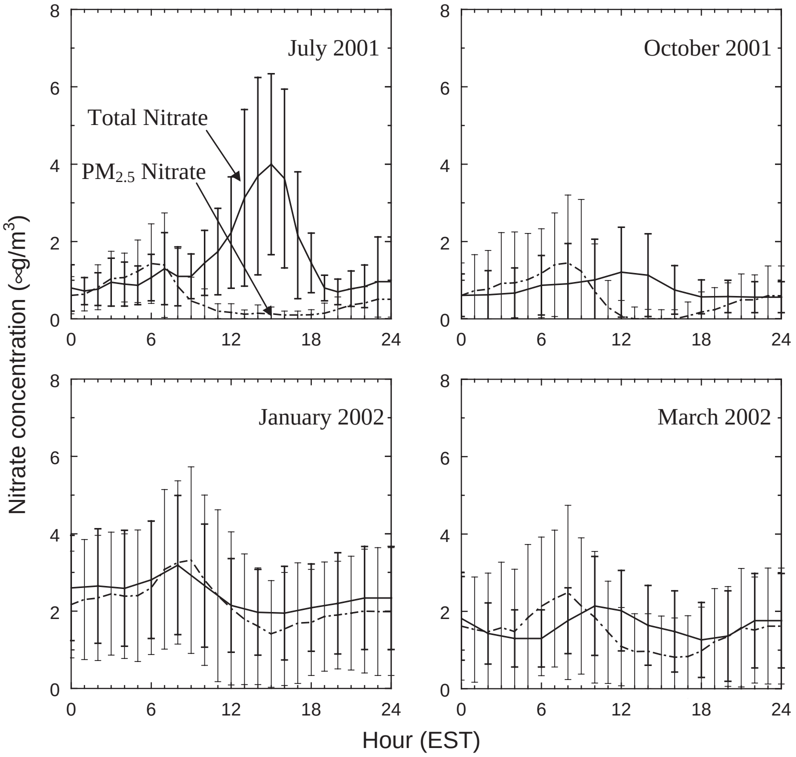

Fig. 8. Average diurnal gas-to-particle partitioning of nitrate for July 2001, October 2001, January 2002, and March 2002. Also shown is the standard deviation of the hourly measurements used to compute both monthly average diurnal profiles. $PM_{2.5}$ nitrate diurnal profiles were computed from the final corrected nitrate semi-continuous measurements. Total ($PM_{2.5}$ + Gas) nitrate diurnal profiles were computed from the steam sampler 1- to 2-h measurements.

temporally resolved data set. Fig. 4 shows these final results.

5. Temporally resolved nitrate observations

Average diurnal $PM_{2.5}$ nitrate profiles were computed for each month in the study from the 1 h averages of the final semi-continuous concentrations; profiles for selected months are shown in Fig. 5. The profiles exhibit a strong diurnal pattern, with the maximum nitrate observed in the early morning a little before sunrise and minimum nitrate observed a couple hours before sunset. The time of the maximum and minimum nitrate shifted on a seasonal basis, consistent with changes in the ultraviolet radiation and temperature. The magnitudes of the maximum and minimum nitrate also changed on a seasonal basis and were greatest during the winter months. The minimum $PM_{2.5}$ nitrate concentration during the winter months was non-zero and correlated with lower ambient temperatures measured at PAQS. Despite shifts in the position and magnitude of the maximum and minimum nitrate concentrations, the same general profile shape is observed regardless of season. This consistency is also present on a daily basis. The linear correlation of the 24 h average nitrate and the maximum daily 1 h average nitrate over the study period is shown in Fig. 6. Days that did not follow this consistent pattern are also indicated in Fig. 6 and were typically associated with a dramatic change in the air mass.

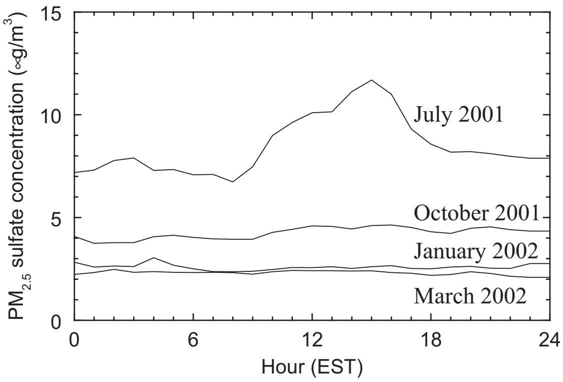

Fig. 9. Average diurnal $PM_{2.5}$ sulfate profiles for July 2001, October 2001, January 2002, and March 2002.

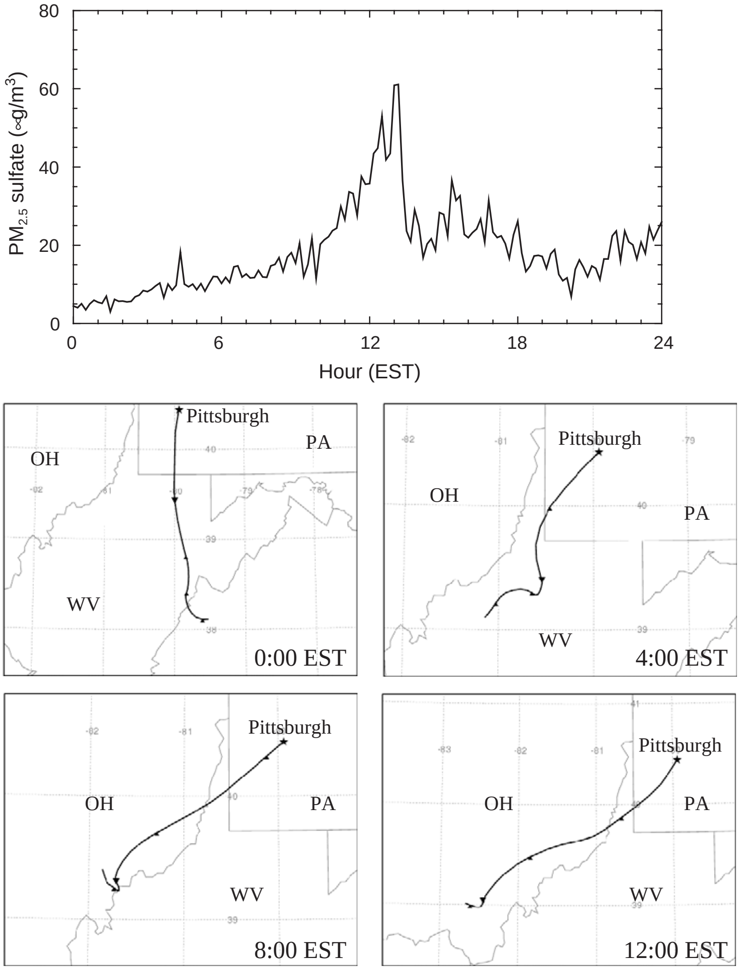

Fig. 10. 1-h average sulfate concentrations are shown for July 26, 2002. Also shown are 24-h back trajectories modeled using HYSPLIT to end at the PAQS Supersite at 0:00, 4:00, 8:00, 12:00, 14:00, 18:00, and 20:00. Triangles indicate 6-h of transport time.

The daily gas-to-particle partitioning of nitrate followed a consistent diurnal pattern as well, as shown in Fig. 7 for three consecutive days in July 2001. During the summer nights most of the nitrate was in the particle phase, while during the daytime practically all the nitrate existed in the gas phase as nitric acid vapor. Specific features of the diurnal gas-to-particle partitioning of nitrate varied seasonally, as shown in Fig. 8. During the winter almost all the nitrate was in the particle phase throughout the day. The fall and spring showed intermediate behavior, with almost all of the nitrate in the particle phase during the night and some nitrate in the gas phase during the day. At night, the nitrate is mostly in the particle phase because of the lower temperature and higher relative humidity (RH). As the sun rises and the atmosphere warms, nitrate is transferred to the gas phase. As the atmosphere continues to warm and the RH continues to decrease, the nitrate partitions almost completely to the gas phase. As the sun sets, some nitric acid vapor is partitioned back into the particle phase and some nitric acid vapor is lost by dry deposition and transport away from the city of Pittsburgh. These diurnal variations were not clear from integrated filter based measurements (even on a 6 h basis).

6. Temporally resolved sulfate observations

Average diurnal $PM_{2.5}$ sulfate profiles were computed for each month in the study from the 1 h averages of the final sulfate measurements; profiles for selected months are shown in Fig. 9. During the summer months, the profiles exhibit a characteristic diurnal pattern, with maximum sulfate observed a couple hours before sunset. In fall, winter, and spring, the profiles on average do not exhibit a diurnal pattern. Fig. 10 shows sulfate concentrations and 24 h back-trajectories to the PAQS

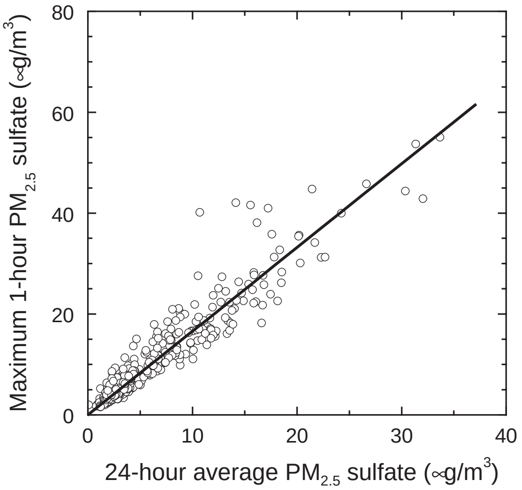

Fig. 11. The linear correlation of the 24-h average sulfate and the maximum daily 1-h average sulfate for all points from July 2001 to August 2002: $y = 1.66x\,\mu g\,m^{-3}$ with $R^2 = 0.89$.

Supersite on July 26, 2002. Over 12 h the sulfate concentration increases from $4\,\mu g\,m^{-3}$ to more than $60\,\mu g\,m^{-3}$ and then drops to less than $20\,\mu g\,m^{-3}$. The initial increase in concentration occurred as the wind direction shifted from southerly to southwesterly and the wind speeds increased. The decrease in concentration occurred after a front passed and the wind speed dramatically decreased at noon. For the remainder of the day, the sulfate concentrations are quite variable and decrease as the result of a short rain event at 16:00.

The average $PM_{2.5}$ sulfate concentrations were highest during the summer months at PAQS. The 24 h average sulfate concentrations are well correlated with the maximum daily 1 h average sulfate over the study period (Fig. 11). Days that did not follow this consistent pattern are also indicated in this figure and were typically associated with rain events or a change in the air mass that resulted in a reduction of sulfate over a short period of time.

7. Conclusions

With only the software error correction and the typical ambient PM corrections (instrument offset and actual conversion efficiency), the semi-continuous measurements were nonlinear (sulfate) or underpredictions (nitrate) of the true inorganic concentrations measured using the filter-based method. To improve the accuracy of the continuous measurements, the instrument reported semi-continuous measurements were also corrected for gas analyzer efficiency, drift in reaction cell pressure (nitrate only), and drift in sample flow rate. The overall corrections were small on average (less than 10% for most corrections), but were quite large for individual 10 minute measurements (varied from -89% to 100%). The corrected semi-continuous $PM_{2.5}$ nitrate and sulfate measurements correlated linearly and reasonably with the filter-based measurements, although a strong systematic bias was still apparent in the measurements. This bias could be due to incomplete collection of particles, lower than expected conversion of particles to the corresponding gases, and the presence of a positive measurement artifact. The bias was minimized by calibrating the semi-continuous concentrations using collocated filter-based measurements. Once corrected and calibrated, the final semi-continuous inorganic measurements allowed two orders of magnitude increase in time resolution.

The final semi-continuous measurements were used to characterize short-term variations in $PM_{2.5}$ inorganic measurements in the Pittsburgh region. When used in conjunction with temporally resolved steam sampler and meteorological measurements, several short-term phenomena were revealed that were not clear from the integrated filter-based measurements. Nitrate followed a consistent diurnal pattern throughout the study period, with maximum nitrate observed in the early morning and minimum nitrate observed in the late afternoon. The time of the maximum and minimum nitrate shifted with seasonal changes in ambient temperature and UV radiation. The maximum nitrate concentration was observed during the winter months when the minimum nitrate concentration was non-zero.

A majority of the nitrate was partitioned into the particle phase at night and into the gas phase during the day. Features of the diurnal patterns and the degree of gas-to-particle partitioning of the nitrate shifted seasonally with temperature, relative humidity, and ultraviolet radiation. During the summer, a majority of the nitrate partitioned into the gas phase during the day, while during winter, little if any nitrate partitioned into the gas phase. Fall and spring showed intermediate degrees of partitioning.

Sulfate concentrations varied diurnally only during the summer, consistent with the gas-phase photochemical production during the day. During the summer, maximum sulfate was observed a couple hours before sunset. During the fall, winter, and spring, sulfate concentrations were relatively stable over the course of a day.

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