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Highly time resolved fine particle nitrate measurements at the Baltimore Supersite

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Abstract

Nitrate in particles smaller than 2.5 μm was measured at 10-min intervals at the Baltimore Supersite in east Baltimore from 14 February through 30 November 2002, using the R&P 8400N semicontinuous monitor to determine its contributions to fine-particle aerosol mass concentrations. Comparison with 24-h filter-based measurements, revealed a discrepancy of 33% between the 24-h averages derived from the two methods, for most of the 9.5 month study period, despite corrections for conversion efficiency and Reaction Cell Pressure deviations, suggesting a true conversion efficiency of 68%. Estimates of precision in individual 10-min measurements averaged 8.7% and ranged from 6.3% to 23%, excluding uncertainty encompassing dissociation losses. Uncertainties in 24-h averages of the 10-min measurements were generally larger (median of 9.1%) owing to missing or invalid values. The detection limits for 24-h averaged and 10-min concentrations were typically 0.17 and 0.24 $\mu g\,m^{-3}$, respectively, during the study (both after slope correction to achieve agreement with 24-h speciation measurements). Regression slopes were statistically equivalent for all months except February and October (an outlier not understood). Intercepts were generally small and insignificant. Good agreement between the 24-h data sets was achieved after the monthly mean regression slopes were applied to the 10-min data. In February, when flat flash strips were used and instrument compartment/outdoor ambient temperature differences were often severe, the regression slope was statistically larger than the average for the remaining months and the intercept was positive and significant. Results of a nonlinear least squares model used to estimate dissociation losses suggest that the largest errors occurred when concentrations are near the detection limit, instrument-outdoor temperature differences were large, and ambient RH low (<40%), i.e., conditions which most frequently and severely occurred in February and March. In February, dissociation losses as large as 1.65 $\mu g\,m^{-3}$ (100% of the slope-corrected measured value) may have occurred and such losses were predicted to be >30% in 63.5% of the 10-min measurements for that month. However, model predictions for the other months, when new ridged-flash strips were used, suggest that dissociation losses were much less significant, i.e., <15% in >95% of the measurements. Our experience suggests that the semicontinuous monitor can produce reliable 24-average concentrations when instrument-outdoor differences are kept small, an independent measurement is used to correct the data, and are improved when grooved flash strips are used.

Keywords: Nitrate; R&P8400N; Semicontinuous nitrate monitor

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1. Introduction

Atmospheric aerosol particles scatter and absorb light and hence reduce visibility and affect radiative forcing (Seinfeld and Pandis, 1998a; Ramanathan et al., 2001). They are vehicles for the transport of toxic and nutrient materials, control cloud formation, mediate nucleation of condensable products of reactive gas reactions, and have been linked with serious health effects including increased mortality and morbidity from respiratory and cardiovascular diseases (Samet et al., 2000; Pope, 2001; Pope et al., 2002). With few exceptions, protection against the human and environmental effects of aerosol particles and their constituents is achieved by implementing emission and ambient air quality standards based on particle mass. Knowledge of the composition and sources of primary aerosol particles and secondary aerosol particle mass is, therefore, important, to both scientific and regulatory endeavors.

Nitrate is a substantial fraction of aerosol mass in many airsheds, especially, in California (Christoforou et al., 2000). Moreover, particulate nitrate concentrations and their relative contributions to aerosol particle mass are generally increasing as a result of reductions in SO_2 emissions (Wexler and Seinfeld, 1991). Atmospheric nitrate (including particulate nitrate and nitric acid vapor) is of special interest in Maryland, owing to its role in the eutrophication of the Chesapeake Bay, which is, perhaps, the world's most productive estuary (Fisher and Oppenheimer, 1991). For these reasons atmospheric particulate nitrate measurements were an important component of the EPA Supersites Program and, especially, the Baltimore Supersite (BSS) Project. While airborne particulate nitrate has been routinely determined on the basis of 24-h integrated filter-based measurements, more highly time resolved measurements offer the potential for improved understanding of the sources of particulate nitrate and the conditions and processes leading to its occurrence on aerosol particles. Furthermore, a cost savings might be realized through the deployment of semicontinuous monitors which incorporate sampling and analysis in a field instrument, in place of expensive off-line analyses. For these reasons, the evaluation of such technology was another important objective of the EPA Supersites Program. Important considerations are the precision, accuracy (or at least equivalence), completeness of data capture, and ease of operation of semicontinuous monitors for chemical species ("speciation monitors") such as those available for particulate nitrate. Four semicontinuous nitrate monitoring methods are compared by Weber et al. (2003).

In the Baltimore Supersite (BSS) Project, highly time-resolved particulate nitrate measurements were made for more than 9.5 months with the Rupprecht and Patashnik (R&P, 25 corporate circle, Albany, NY), model 8400N monitor, a commercial version of the ADI (Aerosol Dynamics, Inc., Berkeley, CA) semicontinuous nitrate monitor that was evaluated at the Atlanta Supersite (Weber et al., 2003). In both the prototype and commercial instruments, nitrate is determined by measuring NO produced after high-temperature dissociation of particulate nitrate on a metallic substrate. However, as described below, there are differences in substrate composition as well as operational protocols between the two instruments. In Baltimore, nitrate concentrations were also obtained with an integrated 24-h filter technique, which encompasses off-line analysis by ion chromatography provided by the EPA contract laboratory as part of the "Speciation Monitoring Program" (US EPA, 1997). Herein, we discuss the operation and performance of the R&P 8400N in comparison with the 24-h speciation monitor results, including the former's apparent conversion efficiency, baseline blank, method precision and equivalence with the 24-h method. A method of assigning uncertainties to the 10-min measurements and their 24-h averages is also discussed. Lastly, a dissociation expression was used in a least-squares model to estimate losses during periods when the instrument compartment temperature exceeded the ambient air temperature.

2. Experimental methods

2.1. Instruments

Twenty-four hour samples for determinating nitrate in fine particles (i.e., particles with diameters $<2.5\,\mu m$, $PM_{2.5}$) were collected with two Met One Model SASS^{TM} ambient chemical speciation samplers (Met One Instruments, Inc., Grants Pass Oregon) equipped with "sharp-cut" cyclones. Filter holders were located $<1\,m$ from the sampling inlet. Speciation samples for nitrate analyses were collected from midnight to midnight, at ambient outdoor temperature on 47-mm Nylon filters at a flow rate of $6.7\,l\,min^{-1}$, after removal of ambient ammonia and nitric acid using a MgO denuder using the EPA protocol (US EPA, 1997). Beginning and ending flows were checked daily using a primary standard frictionless piston flow measurement device (BIOS^{TM} Dry Cal, BIOS International Corporation, NJ). On the day following collection, the sampling cartridge was removed and placed in a cooler at "ice" temperature and returned to the laboratory where it was stored at $-20\,^{\circ}C$ until shipped in coolers via next-day-service to Research Triangle Institute (RTP, NC) for extraction and analysis by ion chromatography (US EPA, 2000).

Semicontinuous nitrate measurements were made with the R&P 8400N, Ambient Particulate Nitrate Monitor, i.e., a commercial version of the prototype instrument described by Stolzenburg and Hering (2000),

designed to be installed inside a laboratory trailer. In the commercial instrument, nitrate contained in particles with aerodynamic diameters $<2.5\,\mu m$ is collected by impaction on a Nichrome strip after humidification of the aerosol sampling stream using a Nafion tube. Humidification induces nitrate particle growth (Stelson and Seinfeld, 1982; Mozurkewich, 1993; Wexler and Seinfeld, 1991), which improves collection efficiency and eliminates nitrate loss resulting from dissociation of ammonium nitrate, a major form of particulate nitrate. After collection, nitrate is converted to oxide forms (NO + NO_2) by rapid resistive heating of the Nichrome ("flash") strip. Any NO_2 is reduced to NO in a molybdenum convertor and the NO mixing ratio is then determined by chemiluminescence induced by reaction with O_3. Flash volatilization and conversion to NO is achieved in the instrument's "pulse generator" module, while the NO_x analyzer is referred to as the "pulse analyzer." The NO_x laden nitrogen gas stream is defined as the "analyzer" flow ($Q_{analyzer}$). The instrument is shipped with a 2.5-μm "sharp cut" cyclone. A carbon honeycomb denuder, installed at the inlet to the Nafion humidifier removes any nitric acid and ammonia vapor not removed by the intake plumbing. Both the sharp-cut cyclone and the denuder are located inside the instrument compartment.

Ambient air is supplied to the instrument through a 2.5-m long, 1.25-cm ID aluminum tube which penetrates the ceiling immediately above the instrument and extends to a height 5 ft above the roof. Between the instrument and the ceiling, a flexible metal duct insulates the sampling tube and serves as a conduit through which outdoor air is aspirated into the instrument compartment by a small blower in an attempt to maintain the aerosol collector at the outdoor ambient temperature so as to reduce nitrate dissociation losses (Mozurkewich, 1993). To minimize this problem, we insulated the indoor section of the sampling duct with fiberglass insulation covered with aluminum foil and installed 1-in Onethick insulation on the outside walls of the cell compartment. However, the instrument compartment could not be maintained at ambient temperatures during cold weather, owing to substantial heat generated by an online gas chromatograph, sulfate analyzer, and other instruments operating nearby.

2.2. Study site and period of operation

The instruments were deployed at the Baltimore Supersite compound located at 299 Ponca St., 2 km due east of downtown Baltimore (39.2891°, −76.5546°) from February until 30 November 2002. During this period, the Met-One sampler was operated approximately daily during three intensive periods, i.e., March, July and the first two weeks of August, and again in November, and every 3rd day during the other months, resulting in collection of a total of 161 24-h filter samples, 150 of which were used in analyses described herein. The R&P 8400N was used to determine aerosol particulate nitrate, every 10 min, continuously, during the entire study period, except for instrument calibrations and maintenance.

2.3. Corrections and data reduction for the R&P 8400N

As described by Stolzenburg and Hering (2000), the ambient nitrate concentration is proportional to the net time-concentration integral induced by NO_x evolved from the flash strip, i.e.,

$$S = Q_c \times \frac{mw}{v} \int C\,dt, \tag{1}$$

where: S is the nitrate mass (ng), Q_c is the analyzer flow ($L\,s^{-1}$), mw is the molecular weight nitrate ($62.005\,g\,mole^{-1}$), v is the molar volume of an ideal gas at the desired reference conditions, and $\int C\,dt$ is the integrated NO pulse from the analyzer (ppb s).

In the R&P instrument, the sample and baseline signals are integrated for 20 s to determine the "Pulse" and "Baseline" areas, both in ppb s. Both integrals are stored for each analysis cycle (i.e., every 10 min), along with the analyzer flow rate ($Q_{analyzer}$), sampling time, aerosol sampling flow rate, and ambient temperature. As indicated in Eq. (1), nitrate mass collected on the flash strip may be calculated (in units of ng) as the product of the net time-concentration integral, analyzer flow rate, and a factor needed to convert ppb NO to μg of nitrate l^{-1} of analyzer flow gas. As the stoichiometric ratio of nitrate to NO is 1, the factor is simply the ratio of the molecular weight of nitrate ($62.005\,ng\,nmole^{-1}$) divided by the molar volume of analyzer gas referenced to a convenient temperature and pressure. R&P chooses the reference condition of 1 atm and 25 °C, at which the molar volume of any ideal gas is 24.46 l. However, they define this conversion factor as the inverse, i.e., the molar volume divided by the molecular weight of nitrate, and incorporate the analyzer flow in the conversion factor, yielding a conversion factor in ppb s ng^{-1}. The former convention dictates that the conversion factor appears in the denominator of the analytical equation. The latter convention causes the conversion factor to vary with changes in analyzer flow rate. Hence the R&P algorithm calculates the conversion factor for each measurement cycle. The nitrate concentration is simply the nitrate mass divided by the volume of air flowing over the flash strip during the sampling interval. Herein, corrections to ambient temperature were done off-line, with a database application, using data reported by the BSS meteorological station, or by various other instruments. R&P's algorithm incorporates two additional factors. These are a "Theoretical Conversion Efficiency," used to account for the

efficiency of conversion of nitrate collected on the flash strip to NO measured by the detector, and an "Audit correction factor" which accounts for drift in the calibration of the instrument's NO detector. As the chemiluminescence product is collisionally relaxed, the analysis is sensitive to the absolute pressure of gas in the analytical cell (known as the reaction cell, Rcell). In principle, the reaction cell pressure is maintained at 5″ Hg by a regulator connected to the air sampling pump. However, the pump could not maintain this pressure for extended periods, even after installing a second vacuum pump on the "pulse analyzer" module, therefore, Rcell corrections were developed as described below.

Herein, ambient nitrate concentrations were calculated from the raw instrument data using a database application (OSL, Inc., Whitehouse Station, NJ) based on the following formula.

$$\text{nitrateconc} = \frac{(\text{pulse1area} - \text{baselinearea}) \times Q_{\text{analyzer}} \times 60 \times \text{Rcellfactor}_i \times \text{Auditcorrectionfactor}_i}{23.67 \times \text{conveff} \times \text{samplingtime} \times \text{sampleflow} \times (\frac{273.16+\text{ambienttemp}}{298.16})}, \quad (2)$$

where Rcellfactor_i, and $\text{Auditcorrectionfactor}_i$ are dimensionless correction factors determined for each 10-min measurement and conveff is the dimensionless conversion efficiency derived from pipetted standards.

2.3.1. NO calibrations and audits

A cylinder containing 4850 ppbV NO in nitrogen (Air Products, Allentown, PA) was calibrated against a NIST traceable reference NO standard and was used to periodically calibrate the instrument's NO analyzer. The analyzer response was shown to be linear over the operating range. Pure Nitrogen (Scott Marin Co., Riverside, CA) was used as a zero reference gas.

Calibration "audits" were performed between calibrations (at first weekly). Prior to 29 July, the span of the analyzer was shown to decrease dramatically over time (i.e., by as much as 20%) due to deposition of black material derived from rubber o-rings in the ozone line. The optical window was cleaned and the rubber o-rings replaced, and, thereafter, daily audits (with span and zero gas) were run automatically at 2 a.m. The audit (span and zero gas) data were used to correct the apparent analyzer calibration by linear interpolation of the daily audits to all 10 min concentrations collected, according to Eq. (2).

2.3.2. Rcell correction factors

Rcell correction factors were developed for the instrument by observing the NO concentration reported for the span gas while artificially varying the total Rcell pressure between 16.6 and 24.4 kPa (absolute). The Rcell correction factors (1 for Rcellpressure = 16.9 kPa) were calculated from the regression coefficients as follows:

$$\text{Rcellfactor} = \frac{1}{(-0.1177 \times \text{Rcellpressure} + 1.5809)} \quad (3)$$

and were applied to all 10 min measurements and to audit gas and pipetted standards measurements.

2.3.3. Conversion efficiency factor

The system was also calibrated by multipoint injection of aqueous KNO_3 standards ($100\,\text{ng}\,NO_3\,\mu\text{l}^{-1}$, as provided by R&P) onto the flash strip, again in accordance with R&P's operating procedure. This calibration was performed on 17 separate occasions throughout the study period during which time the conversion efficiency for the KNO_3 varied between 84% and 95%, with an average of 90.5±4%, and with no apparent pattern of deviations. We attributed the deviations to precision in pipetting the standard solutions and, therefore, applied the average efficiency of 90.5±4% to the entire dataset.

2.3.4. Instrument blank

Periodic operation of the instrument with the addition of a HEPA filter to the inlet suggested that there was a nonzero signal (equivalent to an average "dynamic" blank of $0.200\pm0.069\,\mu\text{g}\,\text{m}^{-3}$) in the absence of particles in the sampling stream. (Interestingly, the average offset observed in calibration curves developed from pipetting standards was 2.35±1.2 ng, which corresponds to $0.235\pm0.120\,\mu\text{g}\,\text{m}^{-3}$ nitrate, i.e., a similar value.) However, the blank tests were done with a thick HEPA filter, which probably absorbed nitric acid and ammonia. Thus, when fairly clean air was then processed by the denuder and it is likely that, it became a source of nitric acid and ammonia. Moreover, the mean offset from correlating the 24-h speciation monitor data vs. 24-h-averaged RPnitrate data (where only valid, i.e., BSSFlag = 1, data were used) was negligibly small, $-0.035\pm0.037\,\mu\text{g}\,\text{m}^{-3}$, and, thus, there appears to be no offset and, therefore, no "dynamic blank" correction was applied to the data.

2.3.5. Measurement uncertainties

Uncertainties in the measurements were propagated from those in each of the measured terms in Eq. (2), as follows. Uncertainties in the measured flows are ±2%, as reported by the manufacturer. Uncertainty in the conversion efficiency over the measurement period was 4.4% (4/90.5). Rcell correction factors, as derived from the regression (standard error about the regression line), ranged from 0.5% to 0.7% over the range of corrections

experienced and, herein, were taken to be 0.6%. The average of monthly-average uncertainties in the Audit correction factors was ±2.6% after correction for Rcell Factor. Error in the Kelvin temperature (±0.5) was typically less than 0.2%. To estimate uncertainty in the net integrated signal (pulsearea−baselinearea), we assumed that the error in pulse and baseline areas were proportional to their square roots. The relative uncertainty in the net pulse area (δP_{net}) was, thus, taken to be

$$\delta P_{net} = \frac{\sqrt{|\text{pulsearea}| + |\text{baselinearea}|}}{|\text{pulsearea} - \text{baselinearea}|}. \quad (4)$$

R&P's states that the "resolution" of the instrument for 10-min sampling times is $\pm 0.2\,\mu g\,m^{-3}$, which we take to be a measure of the instrument's precision. Instrument precision would be affected mainly by δP_{net} and uncertainties in the flow rate and temperature measurements. Combining these, we obtain a mean precision of 0.094, i.e., consistent with the R&P figure. The total relative uncertainties in the individual 10-min concentrations were computed as the square root of the sums of squares of all the above-mentioned uncertainties. These averaged 8.7% and ranged from 6.3% to 23%.

3. Results and discussion

3.1. Completeness of data capture

During the 9.5-month study period, 97.8% of the possible 41,040 10-min concentrations 41,040 was recorded of only 4.1% of which were flagged invalid. However, for a large number of periods (nearly 40%), the instrument compartment temperature (T_{comp}) exceeded the ambient outdoor temperature by $\geqslant 4\,^{\circ}C$, a condition which is reported to result in dissociation losses (Hering, 2003). This condition was (flagged with BSS code 8) most prevalent in the coldest months of the study period, i.e., February, March, and November, when T_{comp} exceeded $T_{ambient}$ by $\geqslant 4\,^{\circ}C$ in $\geqslant 80\%$ of the measurements.

3.2. Intercomparison of 24-averaged 10-min and integrated 24-h speciation nitrate measurements

To determine the degree of equivalence, integrated 24-h Speciation nitrate concentrations were regressed against 24-h averages of the 10-min measurements. Regressions were made on the entire 9.5-month data set (150 speciation monitor measurements) and on monthly data sets to investigate the temporal behavior of the regression parameters (Figs. 2 and 3). Once the regression parameters were obtained, they were applied to the individual 10-min data to achieve agreement with the 24-h speciation monitor data. New 24-h averages were then computed from the adjusted 10-min data and plotted along with the 24-h integrated speciation monitor data in Figs. 1–3. Outliers were then identified as those points for which the difference between the new 24-h average and 24-h speciation result differed by more than twice (2σ) the relative uncertainty estimated for the former, as described immediately below. Eight outliers were thus identified. These were removed from the analysis, after which, the regression parameters were recomputed to produce the final sets of monthly and all-data regression parameters shown in Figs. 1–3.

Additional uncertainty in estimates for the 24-h averages used in the identification of outliers resulted from, from missing/invalid data (see Table 1). Herein, missing or invalid values were replaced by interpolation and their uncertainties were estimated as the standard deviation of n measurements before and n measurements after the missing data, where n is the number of missing and/or invalid values. Most often, $n = 2$ as a result of the automated audits, however as many as 68 (28 February) consecutive 10-min periods were missing or invalid, generally, due to instrument maintenance. Including these uncertainties, the median uncertainty (expressed as 1σ) in 24-h averages of 10-min measurements for the 9.5-month data set was 9.1%. On 26 July, where 26 consecutive values were interpolated, the concentration was $0.75\,\mu g\,m^{-3}$ and the relative uncertainty in the 24-h average was 28%. This is compared with a value of 16% on 4 July, when the uncertainty was only 17% for the identical concentration. The largest uncertainties corresponded to days for which concentrations were $<0.2\,\mu g\,m^{-3}$ (after correction for slope), for example, 6–8 August, i.e., concentrations near the detection limit (for 24-h average concentrations), which (defined as the value where the measured concentration is twice its uncertainty) was typically $0.17\,\mu g\,m^{-3}$ (after correction for slope), based on the uncertainty analysis.

In calculating 24-h averages, regression analyses were made, first, using only valid data (BSS flag = 1; Fig. 2) and, again, using data for which the Rcell temperature exceeded the ambient temperature by more than $4\,^{\circ}C$ (i.e., BSSFlags 1 and 8, respectively). In all cases, we made no attempt to restore missing or invalid data, and data pairs were used in all regressions, only if $<20\%$ of the 144 10-min measurements were missing (i.e., interpolations were used only to estimate uncertainties in the 24-h averages). As shown Figs. 1–3, R^2 values of the speciation-reconciled data ranged from 0.87 (August) to 0.997 (June) and were >0.91 in all months except August. The slope (1.032 ± 0.140; $R^2 = 0.965$) for October data (not shown) was approximately 30% less than those for the other months. Inspection of our operator logs revealed nothing to explain this difference, either for the R&P 8400N or the speciation monitor, however, we have excluded these from further consideration, herein.

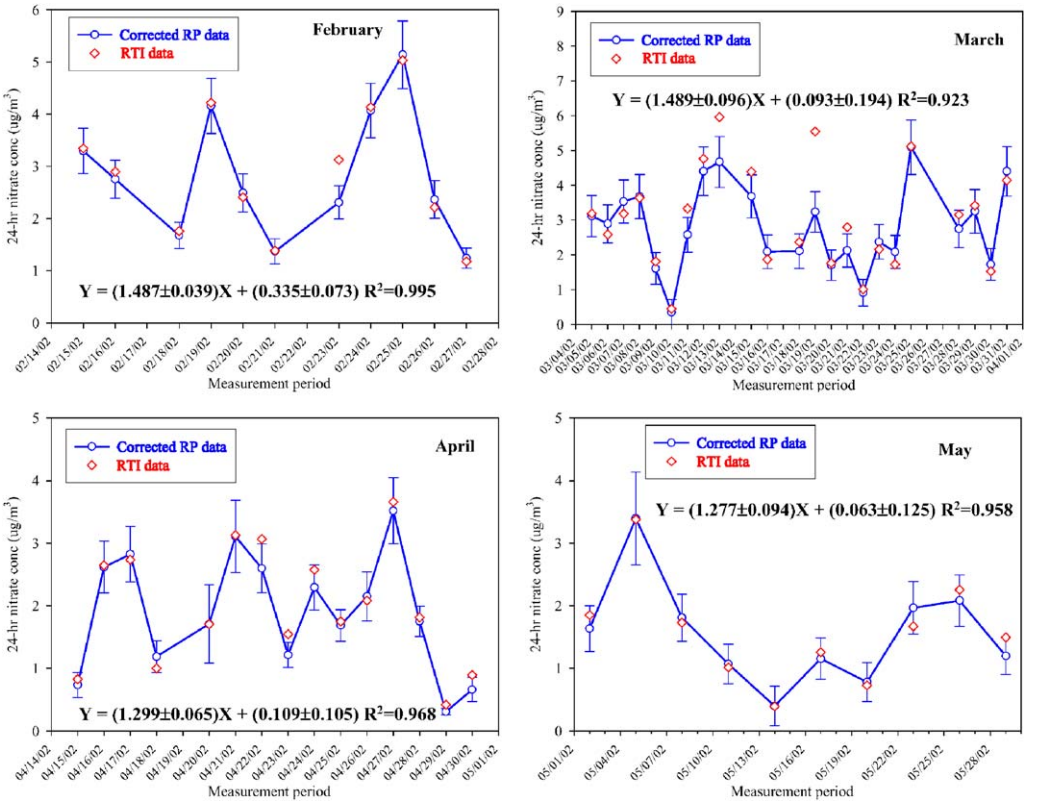

Fig. 1. Plot of 24-h integrated- (◆) and slope-corrected 24-h averages of 10-min nitrate measurements (lines) for February, March, April, and May, 2002. Error bars shown are two standard deviations of uncertainties propagated for the 24-h averages and include estimates of the uncertainty resulting from missing or invalid data. Regression equations are those determined after removal of outliers.

The slope for the correlation between the 24-h speciation monitor data and 24-h-averaged RPnitrate data (where BSSFlag = 1) was 1.27±0.04 and the intercept ($-0.036 \pm 0.035\,\mu g\,m^{-3}$) was negligible. This is comparable, but larger, to the mean relative difference for the prototype instrument, which was reported by Weber et al. (2003), to be 20.7%, which we presume would lead to a slope of 1.207. The difference between these slopes might be attributable to differences in the calibration materials used, i.e., ammonium nitrate in the case of the prototype, and potassium nitrate in the case of the R&P 8400N. The slope for all valid data after removal of the 8 outliers was somewhat larger (1.403±0.03) but the intercept was identical to the previous case. Monthly regression slopes (BSSFlag 1 and 8 data) ranged from 1.177±0.125 (August) to 1.489±0.096 (March). Their weighted average (where weights are 1/one standard error about the line) is 1.36, i.e., in close agreement with the result found for all valid data (where BSSFlag = 1). The uncertainties in the monthly slopes suggest that only the slope for February (1.487±0.04) was significantly different from their average. For the remaining months (March through November), the weighted-average slope was 1.33±0.078, i.e., in excellent agreement with that found for the data where BSSFlag = 1. Intercepts for these months ranged from −0.16±0.17 to 0.109±0.105, but only that for June ($-0.12 \pm 0.03\,\mu g\,m^{-3}$) was significant. Furthermore, the uncertainty-weighted average of the intercepts for March through November, $-0.04\,\mu g\,m^{-3}$, was insignificant, whereas the intercept for February data, $0.335 \pm 0.073\,\mu g\,m^{-3}$, was. For this reason, data for March through November were corrected (herein defined as "speciation-corrected") by multiplying the 10-min data by 1.33, and no intercept was applied. For February, the monthly slope and intercept were applied to correct the data plotted in Figs. 1–3. Note, that the error in the regression correction (0.078/1.33 = 5.9%) is small relative to those captured by error analysis discussed above, as it tends to be driven by the larger values in the data set. Therefore, the best error estimates of the 24-h averages are those described above, which consider missing data.

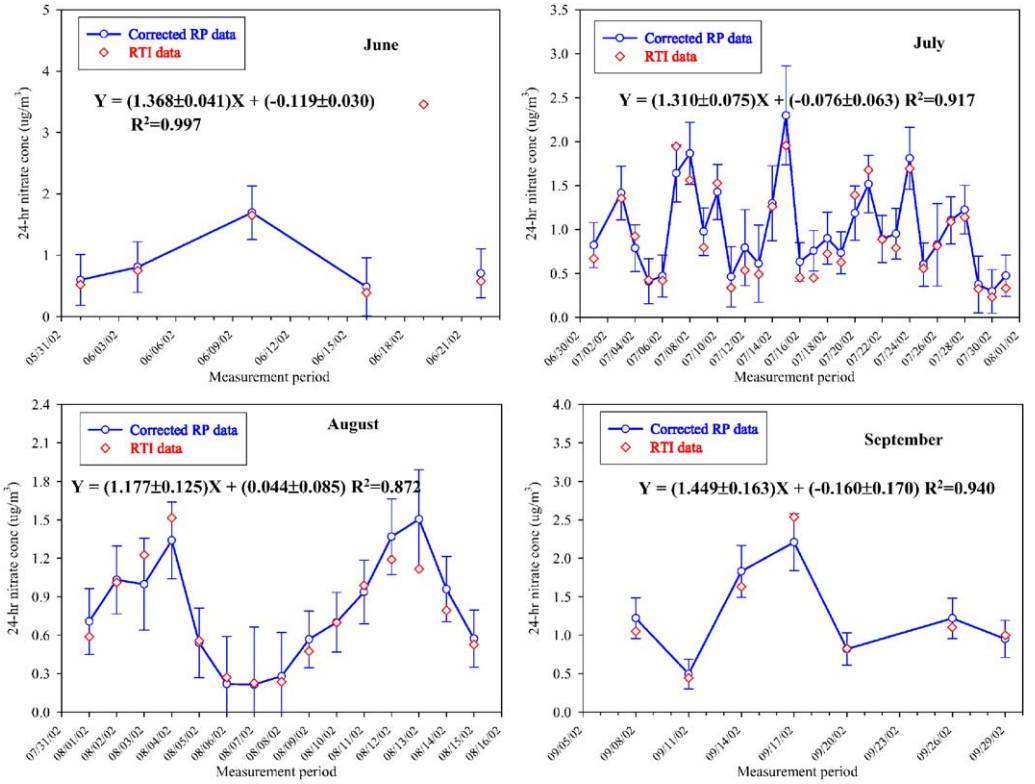

Fig. 2. Plot of 24-h integrated- (◆) and slope-corrected 24-h averages of 10-min nitrate measurements (lines) for June, July, August, and September, 2002. Error bars shown are two standard deviations of uncertainties propagated for the 24-h averages and include estimates of the uncertainty resulting from missing or invalid data. Regression equations are those determined after removal of outliers.

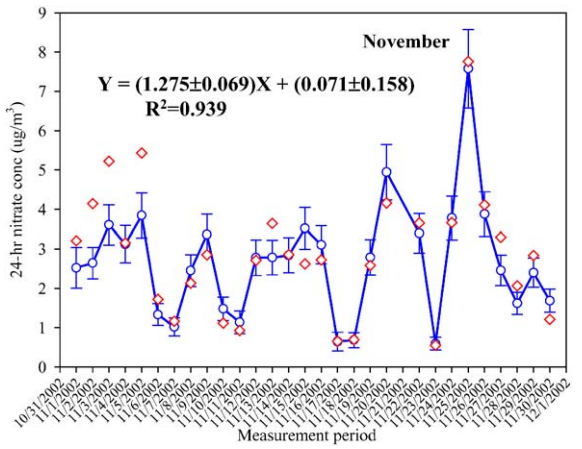

Fig. 3. Plot of 24-h integrated- (◆) and slope-corrected 24-h averages of 10-min nitrate measurements (lines) for November, 2002. Error bars shown are two standard deviations of uncertainties propagated for the 24-h averages and include estimates of the uncertainty resulting from missing or invalid data. The regression equation is that determined after removal of outliers.

According to Hering (2003), the conversion efficiency for ammonium nitrate, the primary form of particulate nitrate, is 10% less than that for KNO_3 and, in the prototype instrument, was a function of flash strip temperature and amount of carbon present. In fact, Hering reports that for stainless steel flash strips (R&P uses NiCr), good efficiencies were not observed until the flash strip was seasoned, which was accompanied by the build up of visible carbon deposits. Thus, the factor 1.33 probably indicates the average difference between the conversion efficiency for ammonium nitrate measured with the R&P 8400N and the potassium nitrate standards, possible matrix effects, and impaction efficiency. As discussed above, we had already applied a theoretical conversion efficiency factor of 0.905 to the data based on the pipetted standards. Therefore, considering the regression-derived factor, the true theoretical conversion efficiency is $1/(1.33)\times 0.905 = 0.68$.

It is tempting to suggest that the larger slope for February is the result of dissociation losses. However, as indicated in Table 1, conditions favoring such losses were at least as prevalent in March as in February, and,

Table 1
Concentrations and various statistics for measurements made at the Baltimore Supersite at Ponca St. in 2002

	Avg R&P ($\mu g\,m^{-3}$)	Avg difference[a] (%)	Tcell exceedances[b] (%)	No. of missing or invalid 10-min measurements[c]	RSD,[d] Auditfactor (after correction for Rcell factor)
February	2.62	0	92	79 (68)	ND
March	2.76	−3.43	78	84 (71)	0.017
April	1.94	−1.82	63	60 (27)	0.034
May	1.49	−1.83	48	12 (12)	0.018
June	1.25	9.25	3.7	11 (3)	0.04
July	1	8.89	0.07	164 (27)	0.031
August	0.83	4.37	0.6	52 (10)	0.029
September	1.19	1.85	0	16 (3)	0.014
October	1.51	—	43	12 (2)	0.023
November	2.9	−0.29	82	69 (10)	0.027
Average					0.026

[a]Difference between 24-h average of 10 min and integrated 24-h measurements of particulate nitrate.
[b]Number of 10-min measurement periods for which the instrument compartment temperature exceeded the ambient outdoor temperature by more than 4 °C.
[c]Number of missing or invalid measurements considered in estimating uncertainties for "speciation-reconciled" 24-h averages. Number in parentheses is the largest continuous block of missing or invalid 10-min measurements.
[d]Relative standard deviation of audit correction factors after correction for Rcell pressure deviations.

in fact, the incidences of conditions favoring extreme dissociation losses, herein defined as $T_{comp} - T_{amb} > 9\,^{\circ}C$ and RH < 40% in March, were nearly twice those occurring in February (such conditions occurred during only one 10-min measurement period in November). Furthermore, this contention is not supported by the March correlation slope, which we would expect to be more comparable to that in February if dissociation losses were the major contributing factor. Rather, we observe that flat flash strips were used in February whereas improved flash strips, of the same material, but incorporating ridges to better dissipate heat, were used in the remainder of the study, and apparently resulted in improved sampling and/or conversion efficiency. Such differences were not observed with pipetted standards. However, the standards simulate neither the true matrix nor the actual impaction process. We conclude, therefore, that the difference in the correlation slope for February and those for the other months is related to the flash strip. Nevertheless, it is useful to further explore the effect of potential dissociation losses as these should have affected the 10-min data.

3.3. Dissociation losses

Herein, dissociation losses are assumed to be confined to the inlet tube, cyclone, and denuder, all of which lie upstream of the Nafion humidifier, and only when the RH is below the particle deliquescence point. Such losses are suppressed in the presence of atmospheric NH_3 and HNO_3 from other sources. However, some, if not all, of the vapor phase NH_3 and HNO_3 is probably lost to the walls of these structures. As mentioned above, conditions conducive to losses occurred most often in February, March, and November.

To estimate the severity of such losses, we constructed a model in which the amount of ammonium nitrate lost between the sampling inlet (at ambient temperature) and flash cell is estimated using its dissociation equilibrium constant. The amount lost is then added back to the measured 10-min nitrate concentrations from which 24-h averages are calculated and the results fit to the 24-h speciation nitrate measurements. Given the uncertainties in the assumptions of the model, we regard the amounts lost to be upper limits.

For the ammonium nitrate dissociation equilibrium,

$$NH_4NO_3(s) NH_3(g) + HNO_3(g) \quad (5)$$

and the equilibrium constant, K_{diss}, is simply

$$P_{NH_3} P_{HNO_3} = K_{diss}. \quad (6)$$

Seinfeld and Pandis (1998b) give K_{diss} (in ppb^2) as a function of temperature, as follows:

$$\ln K_{diss} = 84.6 - \frac{24220}{T} - 6.1 \ln\left(\frac{T}{298}\right). \quad (7)$$

If there is no ammonia or nitric acid in the gas phase other than that which is formed by dissociation, then, given the 1:1 stoichiometry, the ammonium nitrate concentration lost to the gas phase is simply the square root of K_{diss}. Therefore, in the model, the nitrate loss to

dissociation, ΔN_k, was calculated from the difference in vapor pressure of ammonium nitrate at Tamb and Tcell, after applying a gas law factor to convert ppb to $\mu g\,m^{-3}$, i.e.,

$$\Delta N_k = -\frac{M10^{-9}\beta}{RT_{amb_k}}(ppb_{T_{amb}} - ppb_{T_{comp}}) \quad (8)$$

where M is the molecular weight of ammonium nitrate, R is the gas constant, T_{amb_k} and $Tcell_k$ are the ambient aerosol and cell compartment temperatures for the kth 10-min nitrate measurement, and $ppb_{T_{amb}}$ and $ppb_{T_{comp}}$, are the $\sqrt{K_{diss}}$ evaluated at ambient outdoor and the instrument compartment temperatures, respectively. T_{offset} is provided as a threshold below which nitrate losses would be insignificant by replacing T in Eq. (7) for $T_{comp} - T_{offset}$ when calculating $ppb_{T_{comp}}$. The factor β is applied to account for the fact that evaporation may be incomplete, either because part of the ammonium nitrate solid surface is covered by other particulate components, because the equilibrium is suppressed by the presence of ammonia and/or nitric acid, not removed in the inlet plumbing, or because equilibrium conditions are not reached.

The dissociation-loss-corrected 10-min nitrate concentrations, N_k, are calculated as follows.

$$N(k) = (RPnitrate_k - b) * M \quad \text{if } RH_k > RHdel_k \times \xi \text{ or} \quad (9a)$$

$$= (RPnitrate_k - b) * M \quad \text{if } N_{diss} < 0 \quad \text{or} \quad (9b)$$

$$= (RPnitrate_k - b) * M + \Delta N_k \quad \text{if } N_{diss} > 0 \quad (9c)$$

where RH_k is the ambient outdoor relative humidity during collection of the kth sample, $RHdel_k$ is the relative humidity at the deliquescence point at the outdoor aerosol temperature for pure ammonium nitrate particles;

$$\ln(RHdel) = \frac{723.7}{T} + 1.6954$$

(Seinfeld and Pandis, 1998b); (10)

where, M is the slope needed to account for the true conversion efficiency; and, in this model, b is the zero offset reported by the instrument, so it must also be multiplied by the conversion efficiency slope. The factor ξ allows for the fact that the particle might yet be wet below the ammonium nitrate deliquescence point or that its deliquescence might be controlled by other salts, e.g., ammonium sulfate. Eq. (9b) is applied to prevent corrections from being applied when T_{amb} exceeds T_{comp}.

The parameters ξ, β, T_{offset}, M, and b are determined by minimizing Q, i.e., the difference between the 24-h averages of the computed dissociation-loss-corrected concentrations, $N24_i$, and the 24-h integrated Speciation nitrate measurements, $Nspeci_i$, as follows:

$$Q = \frac{\sum \sqrt{(N24_i - Nspeci_i)^2}/\sqrt{\sum \delta_i^2}}{n} \quad (11)$$

where δ_i is the root mean square relative uncertainty calculated for the ith 24-h average and ith 24-h integrated speciation measurement. The former were computed as discussed above, the latter was taken to be 3%, except in the case of outliers (e.g., 23 February, see Table 2), in which case an uncertainty of 100% was used. Lastly, n is the number of 24-h averages used in the model and, thus defined, the expectation value of Q is 1.

3.3.1. February data

The February data were fit, first with all 5 parameters as unknowns (5 parameter model), and then twice, again, i.e., after applying the correlation slopes of 1.487 (case ii) and 1.33 (case iii) to the data. The 1.487 slope

Table 2
Nitrate concentrations, RH, and temperature deviations corresponding to outliers

Date	24-h R&P (slope corrected) ($\mu g\,m^{-3}$)	Avg/Max RH (%)	Avg/Max $T_{comp} - T_{amb}$ (°c)	Comment
23-Feb	2.31	43.8/63.8	9.19/10.31	Expect evap losses
13-Mar	4.67	96.2/98.3	7.84/8.74	Rain
19-Mar	3.24	69.6/89.3	7.76/8.97	Rain after 22:30
2-Nov	2.64	44.3/60.9	6.75/10.86	Expect evap losses
3-Nov	3.61	50.6/82.5	6.52/7.81	Expect evap losses
5-Nov	3.85	72.7/98.7	5.78/6.85	Rain after 18:00
13-Nov	2.78	69.4/87.7	5.93/6.68	Expect evap losses
15-Nov	3.52	63.9/81.3	5.23/6.99	Rain after 21:00

should apply if the conversion/collection efficiency of the older style flash strips used in February was the cause of the poorer agreement with 24-h integrated measurements for that month. If this is not true, then the 1.33 slope would better apply. In both cases (ii) and (iii), the offset (instrument zero blank) was set to zero in accordance with arguments made above. Relative dissociation corrections for each case are reported as the predicted dissociation loss ($\mu g\,m^{-3}$) divided by the slope-corrected nitrate measurement, where the slope is that either found by or used in the model. Note that in Fig. 4, the measurements reported by the instrument in February were corrected using the correlation slope and intercept determined for that month. Thus, it is also useful to compare the concentrations predicted by the model with the correlation corrected results.

Not surprisingly, the best fit ($Q = 0.56$) was obtained when all five parameters were taken to be unknowns, in which case, the slope was 1.448, $\beta = 0.136$, $T_{offset} = 0$, and $\xi = 0.865$. This slope is nearly identical to the correlation slope (1.406) for all valid data after removal of outliers. It is also statistically equivalent to the February correlation slope (1.487±0.039), however, the offset, which in this model corresponds to the instrument zero blank, was $-0.11\,\mu g\,m^{-3}$, (i.e., the correction to the original data is positive because the zero blank should be subtracted). This is consistent with our contention that the instrument blank was zero or at least positive, as discussed above, and indicates that larger dissociation losses should apply.

When the model was rerun (case ii) with the slope and offset forced to 1.487 and $0\,\mu g\,m^{-3}$ (Fig. 4), i.e., the correlation slope and intercept, which we take to account for non-dissociation calibration effects, a comparable, albeit slightly poorer fit ($Q = 0.618$) was obtained with the following parameters: $\beta = 0.145$, $T_{offset} = 0$, and $\xi = 0.955$. In this case, the predicted dissociation losses were often substantial, i.e., the median was $0.33\,\mu g\,m^{-3}$, and the maximum was $1.65\,\mu g\,m^{-3}$. The latter occurred in interval 1248 and amounts to a 149% increase in the nitrate concentration reported by the instrument (i.e., $1.11\,\mu g\,m^{-3}$ before slope correction), and 100% after correction of the reported concentration by the slope factor 1.487. As shown in Fig. 4, this period was characterized by low (<50%) ambient RH and the largest $T_{comp} - T_{amb}$ difference (11.8 °C). Large fractional corrections are also predicted for intervals where the $T_{comp} - T_{amb}$ difference was large (9.1 °C), RH low (38%), and the nitrate concentration reported by the instrument, $0.14\,\mu g\,m^{-3}$, was in the range of the detection limit. Ratios of the model results to the slope-and intercept-corrected results are shown in Fig. 5. Interestingly, 85% of the slope- and intercept-corrected measurements differ from the model results for this case by <10% of the latter. One difference between the model-predicted and the correlation corrected concentrations is that the model applies an additive correction only to intervals when the ambient RH exceeds the ammonium nitrate deliquescence point, while in the latter, the offset is applied to all data. This exacerbates differences for periods near the detection limit.

When rerun with the slope and offset forced to 1.33 and $0\,\mu g\,m^{-3}$, the best fit was somewhat worse ($Q = 0.864$), and corresponded to $T_{offset} = 0$, and $\xi = 0.955$, and understandably, a much larger β of

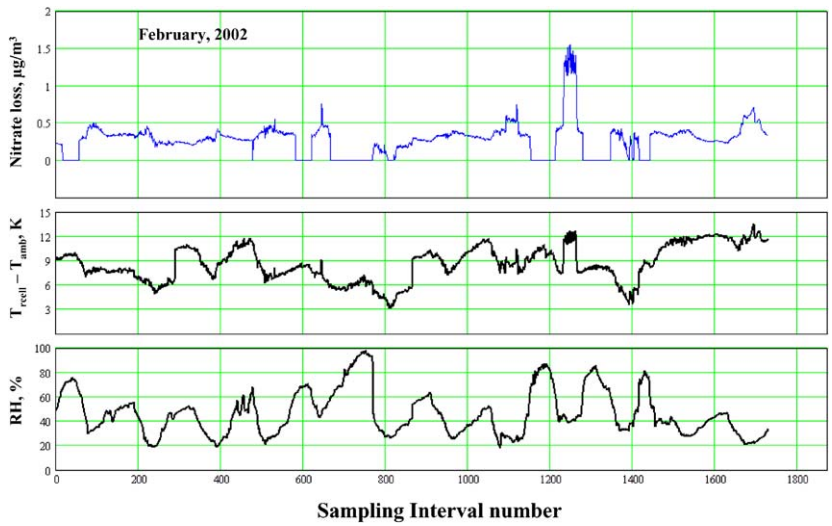

Fig. 4. Predicted dissociation loss (forced slope = 1.487) vs. 10-min sampling interval number (panel A); ambient, compartment temperature, and $T_{amb} - T_{comp}$ differencs (panel B); and ambient relative humidity (panel C) in February, 2002, when flat flash strips were used.

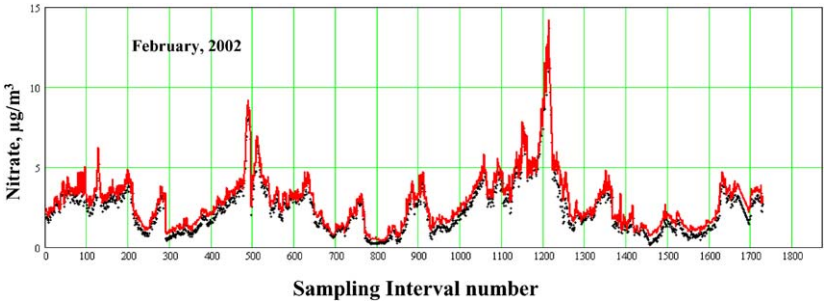

Fig. 5. Model-predicted (solid line) and slope (1.487) corrected (dotted line) nitrate measurements vs. 10-min sampling interval (panel A) in February; and fractional deviation of the former from slope and intercept corrected measurements used in to construct 24-h averages shown for February in Fig. 1.

0.273. As a consequence of the latter most, predicted losses in this case were 1.88-fold greater than in the previous case, e.g., $3.1\,\mu g\,m^{-3}$ for interval 1248 in February. However, for the reasons discussed above, we believe that case (ii) represents the best assessment of the dissociation losses, i.e., closer to $1.65\,\mu g\,m^{-3}$ for February interval 1248.

3.3.2. Other months

For the other months, the model was run with the fixed slope (1.33) and zero intercept. In March, where the incidences of extreme conditions for dissociation losses were twice those occurring in February, but the new, ridged, flash strips were used, $\beta = 0.082$, and predicted dissociation losses were at most $1.2\,\mu g\,m^{-3}$ (57% of the slope corrected measurement), and were $<15\%$ in 72% of the 10-min measurements (87% were $<30\%$). The lower predicted losses for March, despite the higher incidence of severe conditions, is tentatively attributed to the change in flash strip type.

For the months April through November, predicted dissociation losses were $<15\%$ for $>95\%$ of the measurements. Clearly, without more highly time-resolved filter/IC-based nitrate data, the true nature of the 10-min dissociation losses cannot be determined. Such losses were reported to be small (typically $<5\%$) by Stolzenburg and Hering (2000) for the prototype instrument as assessed in laboratory and field experiments. However, $T_{comp} - T_{amb}$ differentials were not reported. The model provides some insight into the magnitude of dissociation losses and suggests that they are small in most cases. Differences between the model and slope- and intercept-corrected 10-min results were large (50%), in most cases when nitrate concentrations were near the detection limit.

In summary, our analysis suggest that (i) the instrument true conversion efficiency for Baltimore aerosol nitrate was 68%, (ii) instrument "blank" was negligible, (iii) average method precision was 8.7% and ranged from 6.3 to 23%, (iv) and dissociation losses were likely small ($<15\%$ of corrected measured values) except in extreme circumstances. Lastly, in most cases, accurate 24-h average nitrate concentrations were obtained after corrections derived from correlations against filter-based speciation measurements.

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