Modeling the diurnal variation of nitrate during the Pittsburgh Air Quality Study

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[1]   A thermodynamic model, the Gibbs Free-Energy Minimization model (GFEMN), was used to simulate the partitioning of $PM_{2.5}$ nitrate aerosol and nitric acid using highly time-resolved inorganic measurements collected at the Pittsburgh Air Quality Study during July 2001 and January 2002. Model results were evaluated using independent, high time resolution measurements of aerosol nitrate. The mean observed concentration in July was $0.6 \ \mu g/m^3$ and $2.1 \ \mu g/m^3$ in January. Model predictions were in agreement with the observations within $0.5 \ \mu g/m^3$ on average, with measurement uncertainties often accounting for these discrepancies. The simulations were run assuming particles were liquid in July for all relative humidities (RHs) and solid below 60% RH in January. For both seasons the assumed physical state did not influence considerably the overall agreement with observations. The assumption of particle mixing state did appear to influence model error; however, assuming that particles were externally mixed during low RH periods in July improved agreement significantly. The exceptional sensitivity of predicted aerosol nitrate to ammonia in western Pennsylvania suggests that reductions in $PM_{2.5}$ may be assisted by reductions in ammonia emissions.   *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; *KEYWORDS:* aerosol, nitrate, Pittsburgh Air Quality Study

1.   Introduction

[2]   Fine particles in the atmosphere are composed of sulfate, ammonium, nitrate, elemental carbon, organic material, trace metals, crustal elements, and water [*Seinfeld and Pandis*, 1998]. These aerosols are either primary or secondary in nature, depending on whether they are directly emitted from sources or formed from gas-to-particle conversion processes in the atmosphere. Airborne particulate matter (PM) with aerodynamic diameters less than 2.5 μm has been associated with excess mortality [*Dockery et al.*, 1993] and a key component of global change [*Seinfeld and Pandis*, 1998]. To address these health concerns, EPA has set guidelines on allowable $PM_{2.5}$ levels based on a mass standard. Understanding the partitioning behavior of semi-volatile species between the gas and aerosol phases can help us predict how changes in anthropogenic and biogenic activity will influence formation of aerosols in the atmosphere such that desired goals in particulate matter concentrations can be achieved.

[3]   In the eastern United States, $PM_{2.5}$ particles can be 50% or more inorganic, with sulfate constituting a significant portion of this inorganic fraction [*U.S. Environmental Protection Agency*, 1996]. Because sulfate is an oxidation product of SO_2, current strategies are targeted at reducing SO_2 emissions. However, *West et al.* [1999] have shown that for the eastern United States, reductions in sulfate may not be as effective as it is often assumed in reducing PM mass, as such reductions may lead to the formation of more aerosol nitrate. This behavior is fairly well understood qualitatively: a portion of atmospheric ammonia is bound in ammonium sulfate, and reductions in sulfate concentrations result in more free ammonia available for reaction with nitric acid to produce ammonium nitrate particles. Such nonlinear chemical interactions between gases and particles suggest the need for a careful investigation of alternative PM control strategies. Evaluation and development of mathematical tools to describe such atmospheric interactions will allow us to examine PM response to changes in concentrations of precursor species, as demonstrated in the work of *Ansari and Pandis* [1998].

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[4] One common approach to modeling the partitioning behavior of semivolatile PM components is to assume that the particles are in equilibrium with the gas phase. Several thermodynamic models have been developed for atmospheric simulations [*Bassett and Seinfeld*, 1983; *Saxena et al.*, 1986; *Pilinis and Seinfeld*, 1987; *Wexler and Seinfeld*, 1991; *Kim et al.*, 1993; *Meng et al.*, 1995; *Jacobson et al.*, 1996; *Nenes et al.*, 1999; *Ansari and Pandis*, 1999]. Generally, these equilibrium models assume that particles can be modeled as a "bulk" phase without consideration for the thermodynamic differences of the particle subpopulations across size and time dimensions. Often, data provided as inputs for these thermodynamic simulations are aggregated measurements obtained through filter and denuder-based sampling methods, which have poor size and time resolution.

[5] To examine the thermodynamic predictions of semivolatile inorganics when particles are not assumed to be the same over all size ranges, *Jacobson* [1999] and *Moya et al.* [2002] used a size-resolved chemical equilibrium approach and observed that their model adequately reproduced the size distribution of PM_1 nitrate and ammonium measured in southern California. However, these measurements were available only for 24-hour periods. *Moya et al.* [2001] suggested that in addition to temperature and relative humidity, performance of equilibrium models may be improved by high time resolution measurements.

[6] New semicontinuous instruments at the Pittsburgh Air Quality Study (PAQS) [*Wittig et al.*, 2004a] provided such high time resolution measurements, and this paper will focus on evaluating the performance of a thermodynamic model in predicting nitrate partitioning between the fine particulate matter ($PM_{2.5}$) and the gas phase using these time-resolved data.

2. Experimental Method

[7] Inorganic species concentrations used for thermodynamic modeling were collected with semicontinuous instruments employed during the Pittsburgh Air Quality Study (PAQS). $PM_{2.5}$ sulfate and nitrate aerosol concentrations were measured with Rupprecht and Patashnick (R&P) models 8400S and 8400N, respectively, which provided resolutions as high as 10-minutes. For the purposes of this study, the data were averaged to one and two-hour values. Instrument performance in the PAQS is documented in the work of *Wittig et al.* [2004b]. A steam sampler based on the design of *Khlystov et al.* [1995] was also used to collect $PM_{2.5}$ sulfate, total ($PM_{2.5}$ + gas) nitrate (TN), and total ($PM_{2.5}$ + gas) ammonia (TA) for analysis by ion chromatography for one-hour periods in July 2001 and two-hour periods until the end of PAQS.

[8] Additionally, several filter-based instruments provided reference measurements at the site. A Particle Concentrator Brigham Young University Organic Sampling System (PC-BOSS) [*Eatough et al.*, 1999] provided four and six-hour measurements of $PM_{2.5}$ sulfate and nitrate during July 2001. Another filter-based inorganic speciation sampler at the site supplied four and six-hour measurements in July 2001 and 24-hour measurements from August 2001 to July 2002. This speciation sampler employed multiple filterpacks to collect $PM_{2.5}$ and PM_{10} particles after the air stream was passed through a MgO denuder and citric-acid-coated denuder to remove nitric acid and ammonia gas, respectively. In addition, a separate filterpack was placed upstream of the denuders to measure PM_{10} and gases, and the nitric acid and ammonia concentrations were determined by denuder difference. Each filterpack consisted of a Teflon filter, a nylon filter, and a citric-acid impregnated cellulose fiber filter in series to measure both stable and semivolatile species. Teflon filters were analyzed for sulfate, nitrate, and ammonium, while nylon filters were used to quantify volatilized nitrate. Citric-acid impregnated filters were analyzed for volatilized ammonium. Analysis for all of these species was by ion chromatography using a method similar to that described by *Jaffrezo et al.* [1998]. Furthermore, EPA Speciation Network sites at Hazelwood and Lawrenceville, which were located within a 5-km radius from the main site, provided additional 24-hour filter-based measurements of $PM_{2.5}$ sulfate, nitrate, and ammonium.

[9] Instrument inter-comparisons indicated that filter-based measurements were generally in good agreement with each other, but there appeared to be analytical bias in measurements made by the semicontinuous instruments. Thus the reported concentrations from these instruments were calibrated by regression against the measurements made by the inorganic speciation sampler [*Wittig et al.*, 2004b], which was operated for the entire duration of the study. For 3–5 January 2002, measurements of $PM_{2.5}$ ammonium from Hazelwood and Lawrenceville were used to calibrate the total ammonia of the steam sampler due to possible instrument difficulty and the unavailability of inorganic speciation sampler measurements during that period.

[10] Instrument inter-comparisons also suggested that a measurement error on the order of 15% was present for concentrations of total sulfate (TS) measured with the steam sampler, after bias was removed, and similar errors of similar magnitude are expected for other concentrations measured by the steam sampler. *Solomon et al.* [2001] suggested that the error of the R&P 8400N is around 0.5 $\mu g/m^3$. Though it is more likely that measurement errors are proportional to concentrations, nonetheless this value is considered an estimate of the average error.

[11] The semicontinuous data, after correction, were used for thermodynamic modeling because of their high time resolution. For model inputs, TA and TN measurements were obtained from the steam sampler, and sulfate measurements were averages of the steam sampler and R&P 8400S for July 2001 and from the R&P 8400S alone for January 2002. Independent, corrected semicontinuous measurements of aerosol nitrate from the R&P 8400N were used to evaluate the model's performance in predicting nitrate partitioning.

3. Thermodynamic Modeling

[12] The Gibbs Free-Energy Minimization model (GFEMN) developed by *Ansari and Pandis* [1999] is used to simulate the partitioning of ammonia and nitric acid, and the aerosol water concentration. Inputs into the thermodynamic model include temperature (T) and relative humidity (RH), and concentrations of total ammonia (TA), nitrate (TN), and sulfate (TS). Since sulfuric acid has a very low

vapor pressure at ambient RH, PM$_{2.5}$ sulfate concentrations were used for values of TS.

[13] We assume that: (1) equilibrium is achieved between gas and aerosol phases in the atmosphere, (2) all fine particles are thermodynamically similar and can be modeled as a single mixture, and (3) influence of organics on the thermodynamics of the inorganic PM is negligible. In addition, PM$_{2.5}$ crustal elements were neglected in this study, as their concentrations were very low (<0.2 μg/m^3 in nearly all cases) in Pittsburgh and had little impact on the results. Nitrate associated with coarse-mode particles is not included in the total nitrate, so the TN used as input into the model is the amount available to partition only between fine-mode particles and the gas phase.

[14] An additional input required for the model is whether the aerosols exist in a state of stable or metastable equilibrium (i.e. whether the aerosols lie on the deliquescence or efflorescence branch), which depends on their history of experienced relative humidities [*Ansari and Pandis*, 2000]. Experimental evidence suggests that during the summer of 2001, aerosols almost always contained water even at low relative humidities, while during the following winter the aerosols were dry at RH less than 60% (A. Khlystov et al., Water content of ambient aerosol during the Pittsburgh Air Quality Study, submitted to *Journal of Geophysical Research*, 2004, hereinafter referred to as Khlystov et al., submitted manuscript, 2004). As such, for the base case simulations, July 2001 data were modeled under the assumption that aerosols were always liquid, while for simulations in January 2002 we assume that particles were liquid above and solid below 60% RH. Simulations for both months were repeated under the assumption that aerosols lie on the deliquescence branch and compared against the base case.

[15] An important assumption employed in thermodynamic models is that all particles are identical and internally mixed, meaning that the chemical species predicted to be in the aerosol phase interact with each other in the same particle. If the particle population is comprised of particles of different chemical composition (external mixture), the chemistry of nitrate partitioning can be changed significantly. The sensitivity of the aerosol nitrate concentration to the physical state of particles at low RH [*Ansari and Pandis*, 2000] allows us to investigate the validity of the internal mixture assumption during July. During the summer, the levels of ammonia were often insufficient to fully neutralize the sulfate to form ammonium sulfate, and therefore the particles were often acidic (molar ratios of TA to TS less than 2) on average. However, as described in a later section, there may have been periods when fully neutralized ammonium sulfate particles coexisted with acidic particles in an externally mixed state. If, for instance, both ammonium sulfate and ammonium bisulfate particles coexisted in the atmosphere, it is possible that during periods when the RH was below 40%, ammonium sulfate would be found in its crystallized form whereas ammonium bisulfate would still exist as a liquid. If the particles are externally mixed, there are infinite combinations of particle composition that are consistent with the observed bulk concentrations. Here, we simulate one rather extreme case of external mixing using the following approach. We first run GFEMN with the original quantities of TA, TN, and TS as inputs, assuming
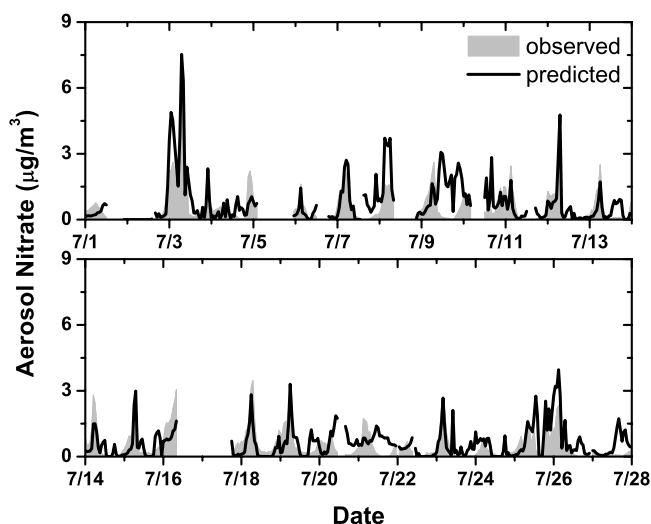

Figure 1. Time series of predicted and observed aerosol nitrate concentrations for July 2001. Missing data either in any of the inputs for the simulation or in the aerosol nitrate measurements are represented by gaps.

that the particles are solid, and calculate the quantity of ammonium sulfate that would form. Then, we remove the ammonium sulfate that has been formed and repeat the simulation with the remaining TN, TS, and TA assuming that the particles are liquid to estimate the amount of acidic aerosol that would form. The sum of aerosol nitrate concentrations associated with each type of particle approximates the total amount of aerosol nitrate that might be found in the aerosol phase if the hypothesized mixing state existed. This approach provides an estimate of a rather extreme case of external mixing in that only two types of particles are considered to exist in the system. The ability of GFEMN to reproduce the observed partitioning behavior in each case is evaluated.

4. Results

[16] The observed concentrations of aerosol nitrate in July were relatively low. The average observed concentration was 0.6 μg/m^3 and reached a maximum of 6 μg/m^3 on the morning of 3 July. The mean observed nitric acid concentration was 3.4 μg/m^3 and 73% of the total nitrate was in the gas phase during July. Aerosol nitrate was observed to consistently peak in the late night and early morning hours when the temperatures were lower and relative humidities higher, but evaporated during the day when temperatures increased, and relative humidity dropped (Figure 1).

[17] Predictions from GFEMN follow the diurnal trend of aerosol nitrate quite well, except during a few daytime periods. During the afternoons of 9, 13, 20, 21, and 27 July, simulations predict that the aerosol nitrate concentrations were rising during the day, when observations indicate that they were close to zero. During these periods, RH was often below 40% and temperatures were generally above 20°C with thermodynamics favoring the existence of nitrate in the gas-phase. In a subsequent section we will test the hypothesis that the ambient aerosols during these periods existed as an external mixture of solid ammonium sulfate particles and

Table 1. Model Performance Against PM$_{2.5}$ Measurements at the PAQS for July 2001 and January 2002

Month	Scenario	Observed, μg/m^3	Predicted, μg/m^3	Mean Bias, μg/m^3	Mean Error, μg/m^3
July 2001	base case	0.56 ± 0.73	0.70 ± 0.89	0.13 ± 0.67	0.46 ± 0.50
	deliquescence		0.32 ± 0.84	−0.25 ± 0.59	0.42 ± 0.49
	external mixture		0.64 ± 0.89	0.07 ± 0.61	0.41 ± 0.46
January 2002	base case	2.09 ± 1.65	2.15 ± 1.89	0.06 ± 0.88	0.64 ± 0.60
	deliquescence		2.06 ± 1.90	−0.03 ± 0.93	0.67 ± 0.64

wet, acidic particles. The model predictions for this month had an absolute error of 0.41 μg/m^3 (Table 1) when the PM during periods with RH below 40% is modeled as an external mixture.

[18] The observed average aerosol nitrate concentration during January 2002 was around 2.1 μg/m^3. As in July, the aerosol nitrate exhibited a diurnal variation with a late night or early morning peak and a minimum in the late afternoon. Figure 2 shows the comparison between predicted and observed aerosol nitrate concentrations for January 2002. In general, there was enough ammonia to neutralize both sulfate and nitrate. During a few periods, for example, 12, 15, 16, 20, and 22 January, the model predicts more aerosol nitrate to be present than observed, though in many of these cases measurement uncertainties may account for the discrepancies. For the period 26 to 28 January, no aerosol nitrate is predicted to form, though observations indicate otherwise. The relative humidity was low during these days, and frequently dropped below 40% during the daytime. The concentrations of ammonia during these periods were such that after neutralizing the sulfate, there was not enough free ammonia remaining to react with the nitric acid vapor to form solid ammonium nitrate particles. Therefore, all of the total nitrate was predicted to remain in the gas phase as nitric acid vapor. Uncertainties and sensitivities of these predictions to measurement error will be discussed in a subsequent section. On average, the model predictions for this month had an absolute error of 0.64 μg/m^3 (Table 1).

4.1. Experimental Uncertainty

[19] Both the predictions and the observations are affected by experimental error. For the predictions, measurement errors in the input variables (TS, TN, TA, T, and RH) affect directly the predicted nitrate. To show how each of these measurement uncertainties can combine to contribute to uncertainties in predictions, a Monte Carlo simulation was performed for two days in July and four days in January. A Latin Hypercube Sampling routine [McKay, 1988] was used considering measurement uncertainties in four of the five input variables (RH, TA, TN, and TS). Normal distributions were chosen for the input distribution of these variables, as uncertainties arising from measurement errors are generally considered to be independent and normally distributed [Ripley and Thompson, 1987] with a mean of zero. A coefficient of variation of 0.15 was assumed for the measured concentrations of TS, TA, and TN, in accordance with our assessment of measurement errors. In addition, a standard deviation of 5% was assumed for RH. To avoid generating artificial correlations among the different input variables and to allow the statistics (e.g., mean and variance) of the output distribution to converge, a sampling size of 200 was selected. Figure 3 shows the predictions with error bars corresponding to the 5th and 95th percentiles of

the simulations' output cumulative distribution function. Combined uncertainties in model inputs can result in uncertain aerosol nitrate concentrations. Furthermore, a standard deviation of 0.5 μg/m^3 was assumed for uncertainty in aerosol nitrate measurements from the R&P 8400N instrument as reported by Solomon et al. [2001], and 200 random samples for aerosol nitrate concentrations were generated for each period. The shaded band in Figure 3 illustrates the range between the 5th and 95th percentiles of the output cumulative distribution function, though concentrations below zero are not shown. In most cases the predictions are within the uncertainties introduced by measurement errors.

4.2. Sensitivity to Assumed Physical State (Solid or Liquid) of Aerosol

[20] In three-dimensional chemical transport models simulating atmospheric aerosol thermodynamics it is often assumed that the aerosol growth follows the deliquescence branch of the hysteresis curve [Nenes et al., 1999]. The error introduced by this assumption can be evaluated by comparing the base-case results (the physical state is an input based on the complementary measurements) to the deliquescence branch predictions.

[21] In the base-case January simulations we assumed that the particles were solid below 60% and aqueous solutions in all other cases, as was observed experimentally (Khlystov et al., submitted manuscript, 2004). The ammonium nitrate deliquescence relative humidity is approxi-
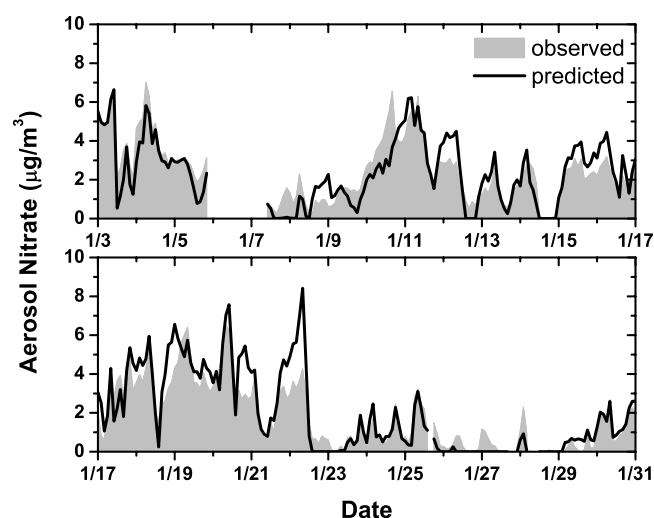

Figure 2. Time series of predicted and observed aerosol nitrate concentrations for January 2002. Missing data either in any of the inputs for the simulation or in the aerosol nitrate measurements are represented by gaps.
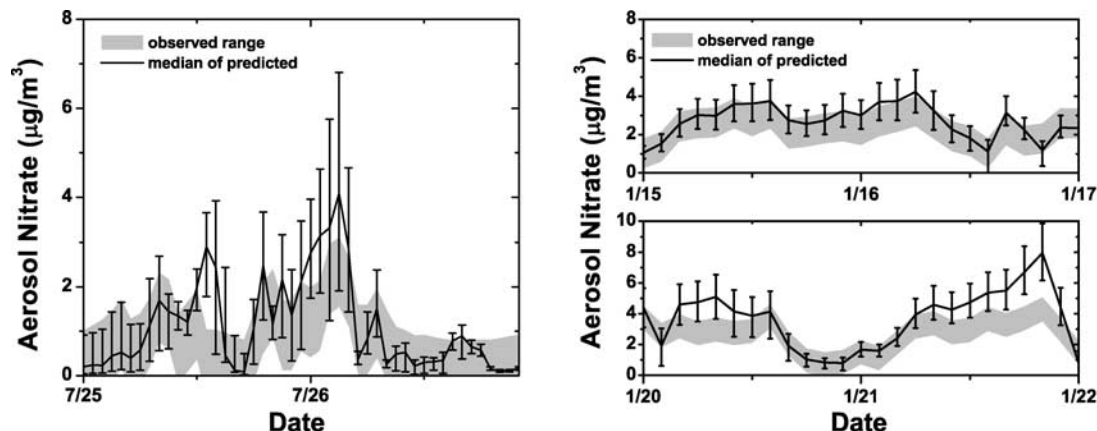
Figure 3. Results from Monte Carlo simulations performed for selected periods in July 2001 and January 2002. Error bars extend to the 5th and 95th percentiles of the cumulative distribution function associated with each prediction. The shaded area bounds the interval between the 5th and 95th percentiles of the observed aerosol nitrate cumulative distribution functions, although concentrations below zero are not shown.

mately 60%, so this choice corresponds approximately to the deliquescence branch of the growth curve of an aerosol containing ammonium nitrate. If deliquescence behavior was assumed for January 2002 with GFEMN calculating the deliquescence RH for each case, particles were predicted to be practically always solid below 66% RH (142 cases), while particles were predicted to be always liquid above 80% RH (79 cases). Out of the 103 remaining cases, the model predicted 57% to be solid, 18% liquid, and 25% a mixture of both. In these instances when the physical state of the particle predicted by deliquescence was different from the base case, the relative difference in mean aerosol nitrate predictions was around 20%. These differences did

not have much impact on the overall agreement of predictions and observations of nitrate partitioning, however. Figure 4 shows the model error, defined as the difference between the predicted and observed concentrations of aerosol nitrate, for the 120 cases when the observed and predicted particle states differed: the overall error between the base case and the deliquescence case simulations is not considerably different (Table 1). This indicates that the model's performance using the deliquescence branch of the growth curve is satisfactory during the winter.

[22] For the base case for July 2001, we assumed that particles were liquid at all relative humidities. If deliquescence behavior was assumed for this month, however,
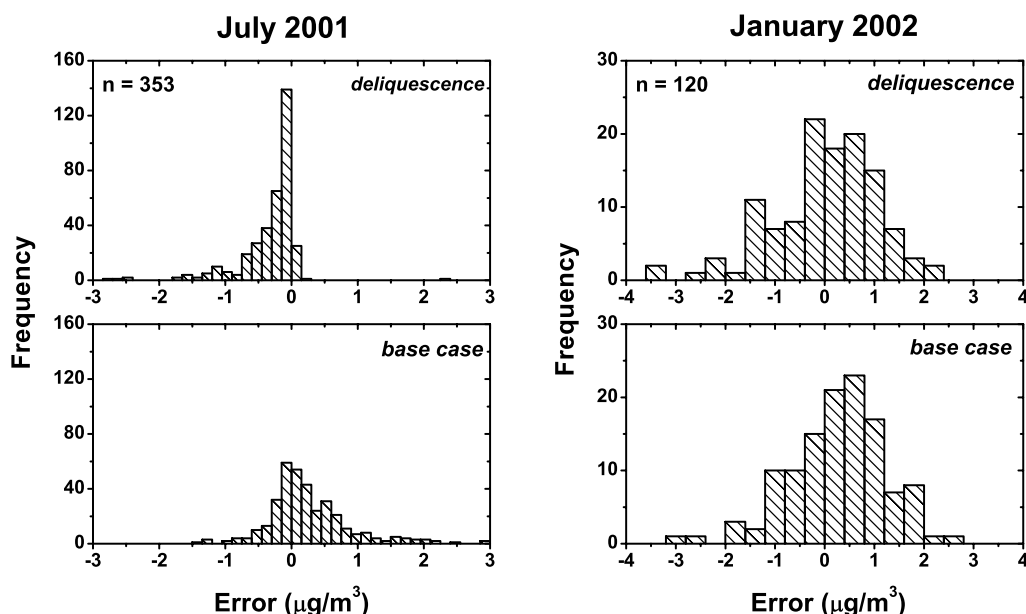

Figure 4. Error distribution assuming different states of particles in July 2001 and January 2002. Errors are calculated as predicted minus observed values of aerosol nitrate. Points included are only those for which the predicted solid or liquid state was different from the one determined based on in situ aerosol water measurements (base case).
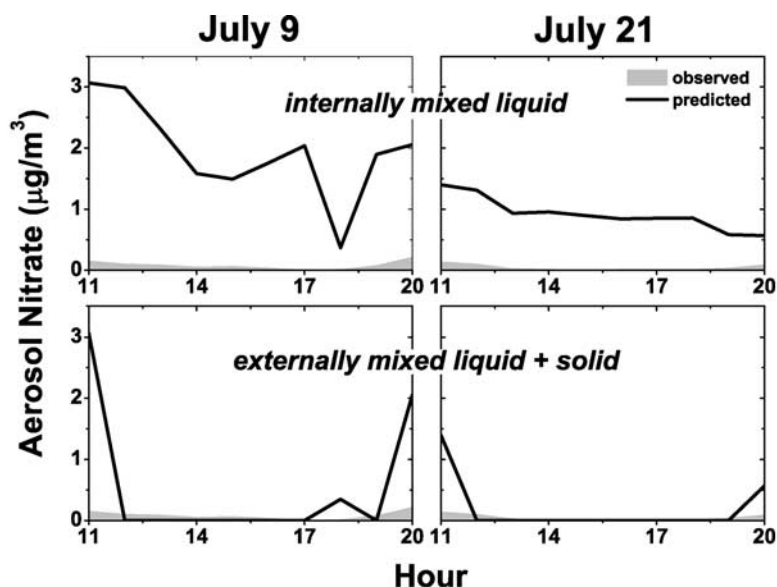
Figure 5. Simulations for 9 and 21 July assuming that particles are (1) internally mixed liquid aerosols, and (2) an external mixture of crystallized ammonium sulfate and wet acidic aerosols when the relative humidity is below 40%.

particles were always predicted to be liquid above 80% RH (127 cases), but below this RH, 15% were predicted to be liquid, 72% solid, and 13% a mixture of both (415 cases altogether). In the instances when the physical state of the particle differed between the deliquescence and base case, the relative mean difference in nitrate predictions was almost a factor of two (Table 1). This is consistent with the results of *Ansari and Pandis* [2000] who suggested that the physical state of the particles affects significantly the aerosol nitrate concentration at low nitrate concentration levels. Figure 4 shows a comparison of the model error for the 353 points when the aerosol is predicted to be solid or a mixture of solid or liquid instead of a pure liquid. The deliquescence case shows a large number of observations have errors close to zero $\mu g/m^3$ with an overall mean of $-0.32 \mu g/m^3$, but a consistent underprediction is observed. This underprediction can be explained by the fact that no nitrate was predicted to be in the aerosol phase in 314 out of the 353 simulations for the deliquescence case, while the same was true for only one instance during the same period when particles were simulated as pure liquid. The spread in the error is greater for the base case, but the distribution of these errors is centered about a mean of 0.25 $\mu g/m^3$.

[23] The assumed physical state affected the relative difference in predictions of aerosol nitrate concentrations during July more so than during January because the nitrate concentrations were generally lower during the summer. Prior knowledge of the physical state of the aerosol was a lot more important for the summer months than in the winter (Table 1).

4.3. Sensitivity to Mixing State (Internal Versus External) During Periods of Acid PM

[24] We examine here the possibility that the discrepancies during the low RH acidity periods in July were due to the existence of an external mixture of acid and neutral particles. The crystallization RH for ammonium sulfate is

40% and the crystallization RH for ammonium bisulfate is much lower. As a result the aerosol could consist of solid neutral particles (ammonium sulfate) and liquid acidic particles (ammonium bisulfate) when the RH dropped below 40%. We first examine the impact of this assumption on the nitrate partitioning on the afternoons of 9 and 21 July, when the disagreement between predicted and observed aerosol nitrate is particularly pronounced in the base case. Figure 5 shows that if the particles are modeled as an internally mixed population, the aerosol nitrate concentration is predicted to be $1-2 \mu g/m^3$ while observations indicate that it is close to zero in the afternoon. However, assuming that the particles are externally mixed and using the algorithm described in the previous section, the predicted aerosol nitrate concentration drops to practically zero, as observed, when the measured RH drops below 40% between noon and 7 pm on these two days. Because the RH threshold below which we simulate the particles as an external mixture is set at 40%, the selection of these periods is very sensitive to measurement errors in RH. Figure 6 shows that if a similar approach is used for the other periods in July in which the measured RH fell below 40%, the performance of the model improves significantly during these times. The premise of hypothesizing the existence of this specific external mixture during these low RH periods is that in the base case, the aerosol nitrate concentrations are overestimated because the particles are liquid and sufficiently neutralized to accommodate a fraction of the total nitrate present in the system. If we assume that one type of particle is neutral but devoid of water and the other is wet but significantly more acidic, the partial pressure product of ammonia and nitric acid vapor required to form ammonium nitrate becomes significantly higher than in the base case and hence results in lower aerosol nitrate concentrations, as we observe. While it is possible that the particles do not exist in one extreme condition or the other but a mix of the two, comparisons with observations suggest that particles
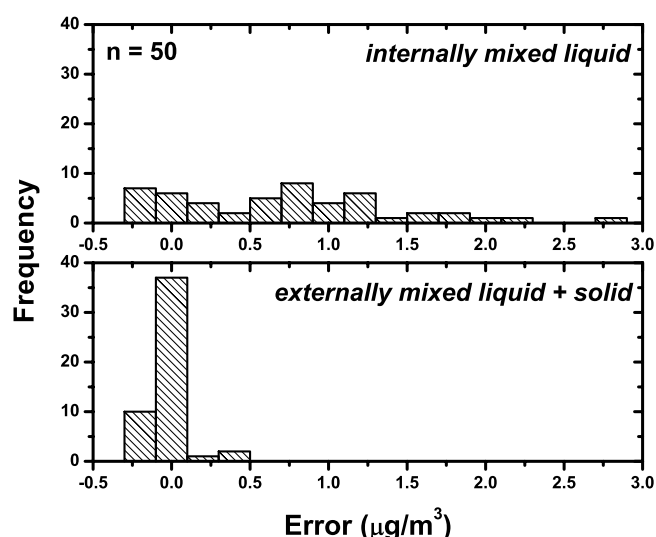
Figure 6. Errors between predictions and observations for periods with RH < 40% assuming different states of particles in July 2001. Errors are calculated as predicted minus observed values of aerosol nitrate.

may be closer to the externally mixed state. This simple algorithm is not suitable for running simulations at higher RHs, however, when both neutral and acidic particles are assumed to be liquid. In these cases, the nitric acid and ammonia can be incorporated into both particle types and the algorithm cannot predict the gas-phase vapor pressures that will satisfy equilibrium conditions with the two particle types simultaneously.

[25] Particles can exist in an externally mixed state if their sources and histories are different. For instance, neutralized particles could be transported into the Ohio River Valley and western Pennsylvania from the ammonia-rich midwestern United States while acidic particles are generated locally. The different types of particles could be mixed together as the nighttime boundary layer vanishes in the morning, or some particles could be formed as a result of cloud processing, while others could be generated through condensation and nucleation. Suitable thermodynamic models and further experimental evidence may reveal more information on the existence of different mixing states.

4.4. Other Sources of Error

[26] Though predictions of nitrate partitioning capture diurnal trends reasonably well, errors in some periods can be high (Table 1) and explanations other than measurement error are needed. As noted previously, many assumptions are invoked when using thermodynamic models. The equilibrium assumption may not be valid if some particles are in the upper size range of $PM_{2.5}$. However, data collected at the PAQS suggest that the geometric mean diameters of $PM_{2.5}$ during the summer were 0.33 μm for ammonium, 0.36 μm for sulfate, and 0.66 μm for nitrate; and during the winter the geometric mean diameters were 0.30 μm for ammonium, 0.31 μm for sulfate, and 0.34 μm for nitrate [*Cabada et al.*, 2004]. As crustal elements are found in low levels in Pittsburgh, salts of nitrate and crustal elements are not expected to be significant. Also, since measurements at

reasonably short timescales were used, it is difficult to explain the observed differences by the averaging of different air masses.

[27] Two additional sources of error remain unaccounted for. Though previous studies have shown that on average, the expected influence of organics on partitioning of semi-volatile inorganics is low [*Koo et al.*, 2003], their impacts on individual cases are still unknown. In addition, the bulk equilibrium approach used in this study can introduce errors, as nitrate does not partition equally into different particles, and modeling them in bulk can introduce errors.

4.5. Sensitivity Analysis

[28] A perturbation analysis was performed to examine the sensitivity of our model to changes in input variables. Such an analysis can strengthen our understanding of the system's chemistry and further elucidate the potential influence of measurement errors. It can also provide a notion of the sensitivity of atmospheric processes to changes in meteorology and chemistry and thus guide our efforts to make preliminary estimates of PM response to changes in concentrations of precursor species. This section will focus primarily on the first objective, but implications for PM control strategies will also be discussed.

[29] The response of the predicted aerosol nitrate concentrations to changes in input parameters depends greatly on the point in the domain space that is examined. *Ansari and Pandis* [1998] proposed a parameter, the gas ratio (GR), that combines three input variables (TA, TS, and TN) to describe different regions of the domain in terms of the amount of free ammonia relative to the amount of total nitrate:

$$GR = \frac{[TA] - 2[TS]}{[TN]}.$$

[30] Table 2 summarizes the characteristics of the different regions of ammonia availability parameterized by GR. Dimensionless sensitivity coefficients can be defined by

$$S_x = \frac{x}{NO_3} \frac{\Delta NO_3}{\Delta x},$$

where NO_3 is the aerosol nitrate concentration and x is an input variable. The sensitivity coefficient can be used to assess the potential impacts of uncertainty in each input variable on the predicted aerosol concentration: S_x is a measure of the relative change in the predicted aerosol nitrate concentration normalized by the relative change in the input variable x when all other input variables are held fixed. Because coarse nitrate is not included in our calculations, we implicitly assume that the small amount of nitrate associated with particles larger than 2.5 μm in the

Table 2. Characterization of GR Regions

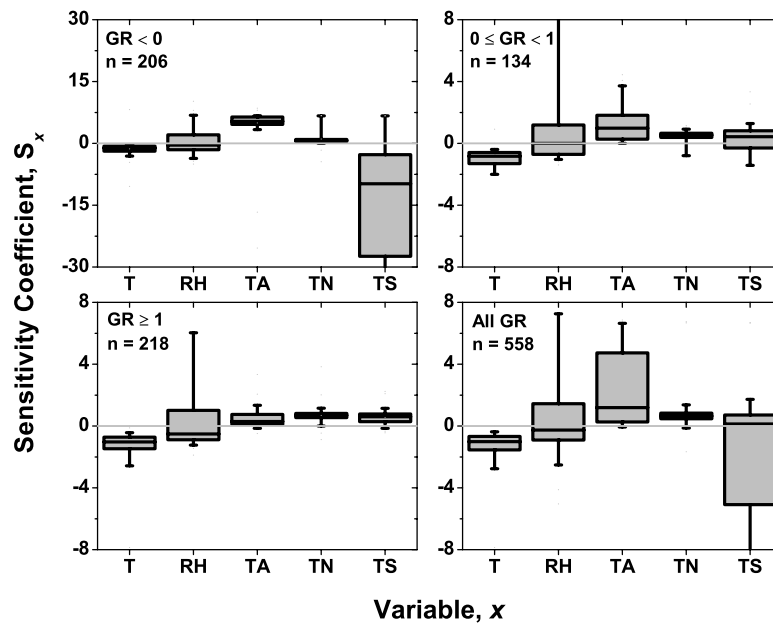| Region Label	Value of GR	Description
Low GR	<0	there is insufficient ammonia to neutralize all of the sulfate to $(NH_4)_2SO$
Moderate GR	≥0 and <1	there is enough ammonia to neutralize all sulfate but not nitrate
High GR	≥1	there is a sufficient quantity of ammonia to neutralize all sulfate and nitrate

Figure 7. Sensitivity coefficients (S_x) of aerosol nitrate in July 2001 in response to model inputs of temperature (−3°C), RH (−5% absolute), and TA, TN, and TS (−15% relative). Separate plots are shown for different regimes of the gas ratio (GR). Shaded boxes cover the interquartile range of S_x, while whiskers extend to the 5th and 95th percentiles of S_x. The black line in the box corresponds to the median.

area [*Cabada et al.*, 2004] will not change during these perturbations. Figures 7 and 8 show values of S_x when the temperature is perturbed by −3°C, RH is perturbed by −5% (absolute), and TA, TN, and TS are perturbed by −15% (relative) for the months of July 2001 and January 2002,

respectively. The response of nitrate is approximately linear over a ±15% range of input concentrations. Overall, the variability in S_x is much larger during the summer, when TA, TN, and TS concentrations spanned a wider range than during the winter.
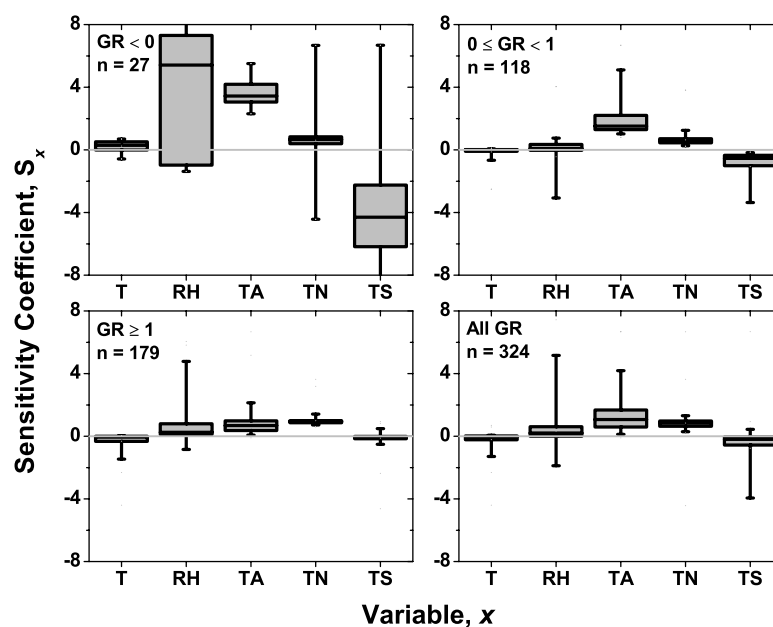

Figure 8. Sensitivity coefficients (S_x) of aerosol nitrate in January 2002 in response to model inputs of temperature (−3°C), RH (−5% absolute), and TA, TN, and TS (−15% relative). Separate plots are shown for different regimes of the gas ratio (GR). Shaded boxes cover the interquartile range of S_x, while whiskers extend to the 5th and 95th percentiles of S_x. The black line in the box corresponds to the median.

[31] During the summer, the sensitivity of nitrate to temperature is relatively small but distinctly negative (median $S_x = -1.01$), because decreasing the temperature lowers the dissociation constant of ammonium nitrate and allows more nitric acid to exist in the aerosol phase. During the winter, nitrate is not as sensitive to this parameter (median $S_x = -0.03$), as most of the nitrate is found in the aerosol phase. The change in nitrate concentrations with respect to RH is on average close to zero (median $S_x = -0.26$ in July and 0.20 in January), but can be significant during certain periods in July 2001 when most particles are liquid, as illustrated by the large variability of S_x for RH (Figure 7). At or near crystallization points, the change in nitrate with respect to RH can be even more significant. Since crystallization is a function of RH, changes in RH by a few percent can change the picture of nitrate partitioning considerably when the predicted aerosol makes a transition from the aqueous to the solid state.

[32] The nitrate response to sulfate can be very large for GRs less than 0 (median $S_x = -9.77$ in July and -4.30 in January), as shown in Figures 7 and 8, because removing sulfate from the system can free up ammonia to react with nitric acid, and adding sulfate can remove ammonia gas and prevent nitrate aerosols from being created. At higher GRs, adding sulfate can actually increase nitrate because sulfates are hygroscopic and increase the water content of aerosols, thus allowing more nitric acid to be pulled into the aerosol phase. Since concentrations of sulfate are generally higher than those of other species, small changes relative to the nominal sulfate can elicit a large response in nitrate, and is reflected in the large values of S_x for this parameter. S_x for TA can be quite large in the case of low and moderate GRs (GR < 0, median $S_x = 5.34$ in July and 3.44 in January; $0 \leq$ GR < 1, median $S_x = 1.05$ in July and 1.52 in January), as the formation of nitrate aerosols is sensitive to the availability of ammonia and perturbation in TA directly changes this quantity. This ammonia-responsive condition is observed 61% of the time in July 2001 and 45% during January 2002. The magnitude of S_x in response to TA can depend quite largely on the sulfate levels if the particles are liquid, as the equilibrium constant of ammonium nitrate is dependent on the ionic strength of the solution, which in turn is influenced by sulfate concentrations [*Ansari and Pandis*, 1998]. As a result, predictions of aerosol nitrate are generally sensitive to measured concentrations of ammonia as well as sulfate, more so during the summer than in the winter. Since aerosol nitrate formation is dependent on the amount of TN in the system, measurement errors in TN can also influence aerosol nitrate predictions. When there is an excess of ammonia, as reflected by higher GRs, much of the nitrate can be found in the aerosol phase. When this occurs, e.g., at night or during the winter, the predicted aerosol nitrate concentrations are more directly influenced by the measured TN. However, the actual sensitivity is also subject to ambient temperatures and relative humidities.

[33] This sensitivity analysis provides insight as to how measurement errors in input variables can affect predictions in nitrate partitioning according to the domain space, but it also suggests implications for $PM_{2.5}$ control strategies. For instance, sulfate reduction is an obvious choice for reducing PM mass since reducing sulfate reduces a large component of $PM_{2.5}$, but this strategy can significantly increase aerosol nitrate concentrations when the formation of nitrate particles is limited by ammonia availability. Our sensitivity analysis shows that aerosol nitrate concentrations are responsive to reductions in ammonia concentrations under such ammonia-limited conditions, which were often observed during July 2001. In these cases, reductions in ammonia may be an additionally effective measure in reducing PM mass.

5. Conclusions

[34] Nitrate partitioning during the Pittsburgh Air Quality Study was simulated using a chemical equilibrium model, GFEMN, for July 2001 and January 2002. The mean observed aerosol nitrate concentrations for July was 0.56 $\mu g/m^3$, while the model predicted 0.64 $\mu g/m^3$, and for January the observed value was 2.09 $\mu g/m^3$ while the mean predicted value was 2.15 $\mu g/m^3$. GFEMN appears to reproduce observed aerosol nitrate concentrations reasonably well, and errors in predictions are about 0.5 $\mu g/m^3$ on average. Monte Carlo simulations indicate that in many cases experimental uncertainties can explain the discrepancy between model predictions and observations.

[35] For moderate relative humidities (60–80%) in January, the agreement between predicted and observed nitrate aerosol concentrations was approximately the same whether the particles were assumed to be in a stable or metastable state. Furthermore, during July, the difference in overall model error between efflorescence branch predictions and deliquescence branch predictions was relatively small.

[36] During periods in July when the relative humidity was low, our modeling results suggest that particles existed not as internally mixed liquids but as an external mixture of crystallized ammonium sulfate and wet, acidic particles. A sensitivity analysis showed that different variables can have varying degrees of influence on the predicted aerosol nitrate, depending on the initial point in the domain space. When temperatures are low and most of the nitrate is in the aerosol phase, as seen in January 2002, errors in temperature measurements do not contribute to model errors as strongly as when the temperatures are higher and nitric acid gas is prevalent. When particles are assumed to be liquid as in July 2001, or when the relative humidity is close to a transition point between solid and liquid aerosol, measurement errors in relative humidity can contribute significantly to model errors for nitrate predictions. Under ammonia-limited conditions when aerosol nitrate formation is a strong function of ammonia availability, the predicted amount of nitrate partitioned into the aerosol phase can be sensitive to measurement errors in both sulfate and ammonia concentrations. This sensitivity has an additional implication that while reducing sulfate is a promising strategy for reducing $PM_{2.5}$ mass, reducing ammonia could also provide additional benefits by inhibiting aerosol nitrate formation for regions where ammonia-limited conditions are frequently observed.

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