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An evaluation of the thermodynamic equilibrium assumption for fine particulate composition: Nitrate and ammonium during the 1999 Atlanta Supersite Experiment

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[1] Data obtained during the 1999 Atlanta Supersite Experiment are used to test the validity of the assumption of thermodynamic equilibrium between fine particulate ($PM_{2.5}$) nitrate (NO_3^-) and ammonium (NH_4^+) and gas-phase nitric acid (HNO_3(g)) and ammonia (NH_3(g)). Equilibrium is tested by first calculating the equilibrium concentrations of HNO_3(g) and NH_3(g) implied by the $PM_{2.5}$ inorganic composition (i.e, Na^+, NH_4^+, Cl^-, NO_3^-, and SO_4^{2-}), temperature, and relative humidity observed at the site. These calculated equilibrium concentrations are then compared to the corresponding observed gas-phase concentrations. The observed $PM_{2.5}$ composition is based on the 5-min averaged measurements of the Georgia Tech PILS [*Weber et al.*, 2001], while the observed HNO_3(g) and NH_3(g) concentrations are based on the measurements of *Edgerton et al.* [2000a] and *Slanina et al.* [2001], respectively. The equilibrium gas-phase concentrations are calculated using the ISORROPIA model of *Nenes et al.* [1998]. Out of the entire Atlanta Supersite database, we were able to identify 272 five-minute intervals with overlapping measurements of $PM_{2.5}$ composition, HNO_3(g) and NH_3(g). Initial calculations using these 272 data points suggest an absence of thermodynamic equilibrium with the calculated equilibrium NH_3(g) generally less than its observed concentration and predicted HNO_3(g) generally greater than the observed concentration. However, relatively small downward adjustments in the measured $PM_{2.5}$ SO_4^{2-} (or apparent acidity) bring the calculated and measured NH_3(g) and HNO_3(g) into agreement. Moreover, with the exception of 31 of the 272 data points with either anomalously low observed concentrations of SO_4^{2-} or NH_3(g), there is a close correspondence between the SO_4^{2-} (or acidity) correction needed for HNO_3 and that needed for NH_3 (slope of 1.04, intercept of $\sim$0, and $r^2 = 0.96$). The average relative corrections required for equilibrium with HNO_3 and NH_3 are -14.1% and -13.7%, respectively; significantly larger than the estimated uncertainty arising from random errors in the measurement. One interpretation of our results is that thermodynamic equilibrium does in fact apply to the inorganic $PM_{2.5}$ composition during the Atlanta Supersite Experiment and either (1) the $PM_{2.5}$ SO_4^{2-} concentration measured by the PILS was systematically overestimated by $\sim$15% or (2) the $PM_{2.5}$ PILS systematically underestimated the concentration of the alkaline components by $\sim$15%; and/or 3. The ISORROPIA model systematically underestimated the pH of the $PM_{2.5}$ encountered during the experiment. *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:* thermodynamic equilibrium, fine particles, nitrate/nitric acid, ammonium/ammonia, acidity

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1. Introduction

[2] Atmospheric aerosols are solid or liquid particles suspended in the gas phase. The particles are composed of water, inorganic salts, carbonaceous materials (e.g., elemental carbon, semivolatile organic compounds), crustal materials (e.g., silicon), and trace metals. Aerosols have adverse impacts on human health (review by *Vedal* [1997]) and affect air quality, visibility, and climate [*Malm et al.*, 1994a, 1994b; *Groblicki et al.*, 1981; *Wigley*, 1989; *Mitchell et al.*, 1995; *Intergovernmental Panel on Climate Change* (*IPCC*), 1996]. The aerosols that are most effective in giving rise to these impacts generally range in diameter 0.1–1.0 microns (μm). In part because of this fact, $PM_{2.5}$ (particulate matter with aerodynamic diameters less than 2.5 μm, also-called fine particles) was designated as a criteria pollutant by the US EPA in 1997.

[3] In the continental boundary layer, inorganic salts are usually found to comprise about 25%–75% of the total $PM_{2.5}$ dry mass, and mainly consist of ammonium (NH_4^+), sulfate (SO_4^{2-}), nitrate (NO_3^-), and small amounts of sodium (Na^+) and chloride (Cl^-) [*Heintzenberg*, 1989; *Malm et al.*, 1994b; *Potukuchi and Wexler*, 1995]. To calculate the inorganic composition of aerosols in air quality models, thermodynamic equilibrium of semivolatile species between the particulate and the gas phases is generally assumed. Since H_2SO_4 has an extremely low vapor pressure, the amount of sulfuric acid in the gas phase under thermodynamic equilibrium is generally predicted to be negligible. Since acidic particles will absorb gas-phase ammonia (NH_3(g)) and nitric acid is more volatile than sulfuric acid, thermodynamic equilibrium models generally predict negligible amounts of NH_3(g) and particulate NO_3^- as long as the $[NH_4^+]$:$[SO_4^{2-}]$ ratio in the particulate phase is less than 2. If excess NH_3(g) remains after the SO_4^{2-} has been neutralized, larger levels of particulate NO_3^- are predicted to form via formation of solid NH_4NO_3(s)

$$NH_3(g) + HNO_3(g) \Leftrightarrow NH_4NO_3(s) \tag{1}$$

or, if the particles have deliquesced, dissolution of gas-phase nitric acid (HNO_3(g))

$$HNO_3(g) \Leftrightarrow H^+(aq) + NO_3^-(aq) \tag{2}$$

where the subscript "aq" is used here to denote a dissolved species in the particulate phase. In addition to the concentrations of NH_3(g) and HNO_3(g), the direction of reactions (1) and (2) depend on the ambient temperature and relative humidity, which affect the equilibrium constant and liquid water content of the particles. Thus under thermodynamic equilibrium, the amount of NH_4^+ and NO_3^- in the particulate phase is a complex function of SO_4^{2-} and other strong acids present in the particles, the relative amounts of NH_3(g) and HNO_3(g) present in the atmosphere, as well as temperature which affects the relevant equilibrium constants and relative humidity which affect the deliquescence of the particles.

[4] The use of thermodynamic equilibrium models to predict inorganic $PM_{2.5}$ composition rests on two basic assumptions: (1) whether thermodynamic equilibrium applies, and (2) whether the models used to describe the equilibrium partitioning between the gas and the particulate phases are sufficiently accurate. The first issue has been addressed theoretically by a number of previous investigations [cf. *Wexler and Seinfeld*, 1991, 1992; *Meng and Seinfeld*, 1996; *Dassios and Pandis*, 1999; *Capaldo et al.*, 2000]. For the most part these investigators estimated the timescale needed to achieve gas-particulate equilibrium and compared this time with the characteristic timescale for variations in the concentrations of volatile and particulate species (i.e., typically a few minutes). If the equilibration time was found to be short compared to the timescale for atmospheric variability, it was concluded that thermodynamic equilibrium would hold. These studies indicated that the timescale for equilibration depends upon the size of the particle. Submicron particles were generally predicted to have relatively short equilibration times and able to reach equilibrium with the gas phase. Supermicron particles, on the other hand, were found to have relatively long equilibration times and thus more likely to exist in non-equilibrium transition states. Since $PM_{2.5}$ contains both submicron and supermicron particles, these studies suggest that thermodynamic equilibrium may or may not be a reasonable approximation for these particles depending upon the degree of accuracy needed and details of the $PM_{2.5}$ size distribution.

[5] The validity of assumptions 1 and 2 have been evaluated empirically by comparing the observed partitioning between the two phases with that predicted by thermodynamic equilibrium models; investigators that focused on the ammonia/nitrate/sulfate system include *Stelson et al.* [1979], *Doyle et al.* [1979], *Stelson and Seinfeld* [1982a, 1982b, 1982c], *Fridlind et al.* [2000], *Fridlind and Jacobson* [2000], and *Moya et al.* [2001]. The results of these studies are somewhat ambiguous; in some cases thermodynamic equilibrium appeared to hold, in other cases it did not, and in still others thermodynamic equilibrium was found to only hold for the smaller particles in the distribution. However, all of the aforementioned studies were based on measurements of PM composition using filter-based techniques with relatively long sampling times (i.e., 6 hours to > 1 day). During such long sampling periods, there can be significant variations in the ambient gas- and particulate-phase composition, as well as the ambient temperature and relative humidity. Since the equilibrium partitioning between the gas and particulate phases of individual parcels of air can generally be quite different from the equilibrium partitioning obtained by mixing these parcels together [*Perdue and Beck*, 1988], the equilibrium predicted on the basis of the average conditions over a sampling periods will not necessarily reproduce the actual partitioning even though equilibrium may apply to each of the individual parcels. This fact along with the susceptibility of filter-based techniques to artifacts [*Chow*, 1995; *Weber et al.*, 2001; *Slanina et al.*, 1992, 2001] raises some question as to the accuracy of these studies.

[6] In this work, measurements of $PM_{2.5}$ composition and HNO_3(g) and NH_3(g) concentrations are used to test the validity of the thermodynamic equilibrium assumption. However, unlike the aforementioned previous studies, the data used in this study were gathered during 1999 Atlanta Supersite Experiment [*Solomon et al.*, 2002]. During this experiment, a suite of techniques was used to measure $PM_{2.5}$ composition on relatively short timescales; the shortest of these being 5 min. (NH_3(g) and HNO_3(g) concentrations were also measured on timescales of up to 15 min.) There are two unique advantages of this data set: (1) the high time resolution of the $PM_{2.5}$ measurements makes it possible to more rigorously test the validity of the thermodynamic equilibrium assumption; and (2) the existence of redundant (and generally consistent) measurements of $PM_{2.5}$ composition by independent techniques lends credence to the validity of the data used [see, e.g., *Weber et al.*, 2002].

2. Experimental Data

[7] The 1999 Atlanta Supersite Experiment was conducted from 3 August to 1 September 1999 at a site in midtown Atlanta (i.e., 4 km NW of downtown). An overview of the experimental objectives, design, and implementation, as well as a description of the instrumentation used during the experiment is provided by *Solomon et al.* [2002] and the papers cited therein. The data applied in this study were collected from 18 August to 1 September 1999. In total we made use of 384 distinct data points based on 5-min averages of the $PM_{2.5}$ concentrations of Na^+, SO_4^{2-}, NH_4^+, NO_3^-, and Cl^-, the gas-phase concentrations of NH_3 and HNO_3, and ambient temperature (T), pressure (p) and relative humidity (RH). (To explore the sensitivity of our results to the data averaging time, we also carried out calculations using 15 and 20 min averaging times; our results were virtually unchanged.)

[8] Of the total 384 data points, 272 had data for all relevant particulate and gaseous species. There were 111 data points that lacked data for NH_3(g) (because of missing data) or particulate NH_4^+ (because the ion concentration was below the detection limit); and 1 data point that lacked data for NO_3^- (because the ion concentration was below the detection limit). The sources of these data are discussed below.

2.1. Inorganic Ion Data

[9] The inorganic $PM_{2.5}$ composition is based on inorganic ion concentrations of Na^+, SO_4^{2-}, NH_4^+, NO_3^-, and Cl^- measured by the Particle Into Liquid Sampler (PILS) with a 5-min sampling period and a 7-min duty cycle. Note, the PILS, which uses ion chromatography to detect and quantify dissolved species, is able, in principle, to detect virtually any dissolved ion in the sampled particles. We only considered concentrations of these 5 ions because these were the only ones consistently identified to be present at significant concentrations. Other data from the Atlanta Supersite Experiment confirm other ionic species (e.g., formate, acetate, Ca^{2+}, Mg^{2+}, K^+) generally only contributed a few percent to the total $PM_{2.5}$ mass [e.g., *Baumann et al.*, 2002].

[10] The experimental methodology and a general discussion of the data gathered by PILS are provided by *Weber et al.* [2001, 2002]. The detection limits for these ions were 0.1ug/m^3. The random error in the measurement of each ion was estimated to be ±8% [*Diamond*, 2002]. It is relevant to note that the PILS instrument was one of four non-filter-based, semicontinuous techniques used during the Atlanta Supersite for quantifying the inorganic $PM_{2.5}$ composition [*Solomon et al.*, 2002]. For the most part the data from these various techniques were consistent with each other (see Table 1 and *Weber et al.* [2002]); however, there are some significant inconsistencies (e.g., $[SO_4^{2-}]$ measurements from the Dasgupta method). We elected to use the data from PILS because it was the only instrument that had simultaneous measurements of $PM_{2.5}$ anions and cations and for which the time intervals of its measurements overlapped with the time intervals of measurements of NH_3(g) and HNO_3(g) at the Supersite; a prerequisite for being able to rigorously evaluate the thermodynamic equilibrium assumption. A brief discussion of how our results and conclusions would have been affected had we been able to use any of these alternate data sets for inorganic $PM_{2.5}$ composition is presented later in this work.

Table 1. Comparison of $[SO_4^{2-}]$ and $[NH_4^+]$ Measured by PILS With Measurements Made by Other Semicontinuous Techniques Used During the Atlanta Supersite Experiment[a]

	Ratio of Means	Ratio of Medians
	$[SO_4^{2-}]$ Measurements	
PILS:ECN[b]	1.03	1.04
PILS:Dasgupta[c]	1.42	1.32
PILS:Hering[d]	1.04	1.02
	$[NH_4^+]$ Measurements	
PILS:ECN[b]	1.16	1.07

[a] Adopted from *Weber et al.* [2002]. For PILS, see *Weber et al.* [2001, 2002] and text.
[b] For ECN, see *Slanina et al.* [2001].
[c] For Dasgupta, see *Simon and Dasgupta* [1995].
[d] For Hering, see *Stolzenburg and Hering* [2000].

2.2. Gas-Phase Data

[11] NH_3(g) concentrations used here are based on the measurements of the ECN SJAC-Aerosol Sampler [*Slanina et al.*, 2001], while the HNO_3(g) concentrations are based on ARA instrument described by *Edgerton et al.* [2000a]. The ECN instrument was operated with a time resolution of 15 min and the ARA instrument was operated with a time resolution of 10 min. The reported detection limits for NH_3(g) and HNO_3(g) are 0.015ppbv, and 0.05ppbv, respectively. The measurement uncertainty was estimated to be approximately ±20% for both instruments (E. Edgerton, private communication, 2002; J. Slanina, private communication, 2001).

[12] These measured NH_3(g) and HNO_3(g) concentrations were parsed into 5-min averages so as to overlap with the 5-min-averaged $PM_{2.5}$ composition data obtained from the PILS. When the time period of an individual NH_3(g) or HNO_3(g) measurement was not coincident with the 5-min periods of the $PM_{2.5}$ measurements, appropriate weighted averages of the gas-phase measurements were used.

2.3. Meteorological Data

[13] Temperature (T), air pressure (p) and relative humidity (RH) were monitored with 1-min time resolution during the experiment by two independently operated sets of meteorological equipment. Information on the measurement

techniques used and the meteorological conditions encountered during the experiment are provided by *Edgerton et al.* [2000b] and St John et al. (unpublished manuscript, 2001). In this study, 5-min averages of T, p, and RH were adopted from a simple average of the data obtained from the two sets of instruments; the 5-min intervals were chosen to overlap with those obtained from the $PM_{2.5}$ data. In the rare cases when data was missing from either set of meteorological equipment, simple linear interpolation was used to fill in the data gaps.

3. Model Calculations

[14] The model ISORROPIA of *Nenes et al.* [1998] is used here to calculate the equilibrium concentrations of HNO_3(g) and NH_3(g) on the basis of the aforementioned observations of the $PM_{2.5}$ composition and meteorological conditions. The model has a number of distinct advantages; these include the facts that: (1) the model is relatively fast and stable; and (2) it considers interactions between two or more salts that can lead to mutual deliquescence. Moreover the model is able to simulate two types of deliquescence case: (1) a so-called "deliquescent branch," where particles are assumed to exist as aqueous solutions at relative humidities above the nominal deliquescence points and as solids below; and (2) an "efflorescent branch," where metastable aqueous solutions are allowed at relative humidities below the nominal deliquescence points. A potential disadvantage of ISORROPIA is its implicit assumption that inorganic ions are internally mixed within $PM_{2.5}$; this may or may not lead to inaccuracies depending upon the actual properties of the $PM_{2.5}$ samples during the Supersite Experiment.

3.1. Standard Method

[15] For our standard Model calculations, the observed $PM_{2.5}$ composition was used to calculate the equilibrium concentrations of HNO_3(g) and NH_3(g) in a straightforward manner:

1. Each set of 5-min averaged observations of $[Na^+]$, $[SO_4^{2-}]$, $[NH_4^+]$, $[NO_3^-]$, and $[Cl^-]$, as well as T and RH was used as input to ISORROPIA;
2. The equilibrium concentrations of HNO_3(g) and NH_3(g) were then calculated for each 5-min data point using ISORROPIA. Calculations were carried out specifying both the deliquescent and efflorescent (i.e., metastable) branches. However, the deliquescent-branch solutions generally yielded unrealistically large HNO_3(g) concentrations and thus only the efflorescent-branch solutions are reported here. (Our results in this regard are similar to those of *Ansari and Pandis* [2000] who found that, under conditions similar to those encountered during the Atlanta Supersite Experiment with relatively low concentrations of $[NO_3^-]$, the deliquescent and efflorescent branches can differ significantly and that only the efflorescent branch was capable of approximating the observations.)
3. The calculated equilibrium concentrations were then compared to the overlapping measured concentrations for HNO_3(g) and NH_3(g).

[16] In addition to the method described above, we carried out sensitivity calculations using an alternate method: (1) instead of specifying the observed $[NH_4^+]$ and $[NO_3^-]$ concentrations in step 1 and calculating equilibrium concentrations of HNO_3(g) and NH_3(g) to compare to the observed gas-phase concentrations, we specified the total amount of ammonia and nitrate in the system based on the sum of the gas- plus particulate-phase observations and then calculated the equilibrium partitioning between the phases and compared these results to the observed partitioning. As discussed later, this other approach yielded essentially the same conclusions.

3.2. Iterative Method

[17] As demonstrated below, the calculated equilibrium HNO_3(g) and NH_3(g) concentrations are quite sensitive to pH. A small change, for example, in the ratio of $[SO_4^{2-}]$ to $[NH_4^+]$ used in the model calculations causes a large change in the resulting concentrations calculated for HNO_3(g) and NH_3(g). To explore this effect in more detail we also adopted an alternate iterative method that independently inferred the "Acidity" of the $PM_{2.5}$ needed to produce an equilibrium HNO_3(g) concentration and an equilibrium NH_3(g) concentration equal to their respective observed concentrations. The steps in this case were:

1. Each set of 5-min averaged observations of $[Na^+]$, $[NH_4^+]$, $[NO_3^-]$, and $[Cl^-]$, as well as T and RH was used as input to ISORROPIA.
2. The secant method was then used to adjust the value for $[SO_4^{2-}]$ input into ISORROPIA for each 5-min data point so that the calculated equilibrium HNO_3(g) matched the observed HNO_3(g) concentration for that data point to within 10%.
3. The required change in "Acidity" for thermodynamic equilibrium (i.e., the difference between the inferred $[SO_4^{2-}]$ and the observed $[SO_4^{2-}]$) was calculated.
4. Steps 1–3 were then repeated for NH_3(g).
5. The results for HNO_3(g) and NH_3(g) were then compared.

[18] It should be noted that the observed concentration of NH_3(g) was not used to calculate $[SO_4^{2-}]$ in step 2 and the observed concentration of HNO_3(g) was not used in step 4. Thus the two sets of results are numerically independent of each other. This suggests that if the two sets of results are consistent with each other, some mechanism must exist that couples $PM_{2.5}$ acidity to both HNO_3(g) and NH_3(g). One such mechanism is that related to the establishment of thermodynamic equilibrium.

4. Results and Analysis

4.1. General Trends in $PM_{2.5}$ Inorganic Composition

[19] The $PM_{2.5}$ concentrations of Na^+, NH_4^+, SO_4^{2-}, and NO_3^- measured by the PILS as a function of time are shown in Figure 1; the measured Cl^- were generally too small to appear in the figure with the scale chosen and are not illustrated. Also illustrated in Figure 1 is the apparent acidity, denoted here by "Acidity" and given by

$$\text{"Acidity"} = \left[SO_4^{2-}\right] + \left[NO_3^-\right] - \left[NH_4^+\right] - \left[Na^+\right] \qquad (3)$$

where [I] is the concentration of species I in the particulate phase in units of $\mu eq/m^3$ of air.

[20] Inspection of Figure 1 reveals that the concentrations of SO_4^{2-} and NH_4^+ generally dominate over those of NO_3^- and Na^+. Moreover, $[NH_4^+]$:$[SO_4^{2-}]$ tends to hover around a value of about 1.2, and, thus for most of the data set

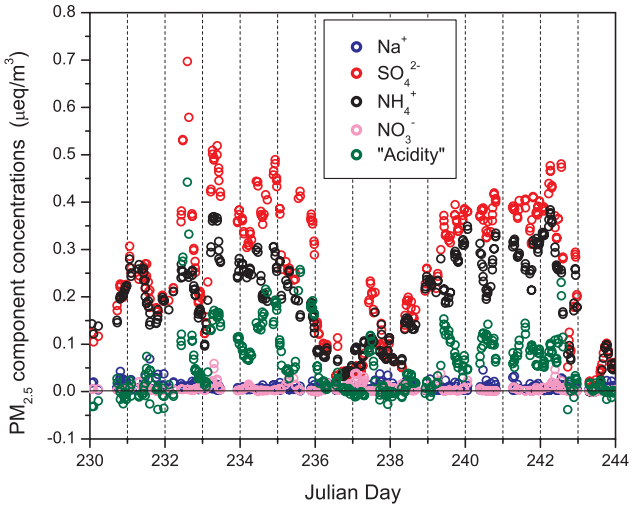

Figure 1. Concentrations of fine particle composition versus Julian day of the measurements from 18 to 31 August 1999 during the Atlanta Supersite Experiment.

"Acidity" > 0. There are three notable intervals, however, when the apparent acidity fell below zero: (1) during the beginning of the sampling period (Julian dates 230–232); (2) about midway through the sampling period (Julian dates 237–239); and (3) near the end of the sampling period (Julian dates 243–244). The later two intervals corresponded to periods of rainfall and were characterized by unusually low $PM_{2.5}$ ratios of SO_4^{2-} mass-to-organic carbon mass; i.e., on a typical day the ratio was generally ~1, but during portions of these rainy periods the ratio was 0.1–0.2 [*Weber et al.*, 2002].

[21] As illustrated in Figure 2, there are significant correlations between $[SO_4^{2-}]$, $[NH_4^+]$, and "Acidity," but no correlations between these three parameters and temperature and humidity. By comparison, $[NO_3^-]$ is uncorrelated with $[SO_4^{2-}]$, $[NH_4^+]$, and "Acidity," but weakly correlated with RH and, to a lesser extent anticorrelated with T (see Figure 3). These results are not surprising. Given the low volatility of sulfate, we would not expect $[SO_4^{2-}]$ to be strongly affected by meteorological factors, and, in as much as sulfate is the major anion, it follows that "Acidity" would be correlated with $[SO_4^{2-}]$. Since acidic particles should tend to react with $NH_3(g)$, it follows that $[NH_4^+]$ would also correlate with $[SO_4^{2-}]$. The correlation of $[NO_3^-]$ with RH probably reflects the greater dissolution of $HNO_3(g)$ onto deliquescent particles as the amount of liquid water on these particles increases with increasing RH. Since RH generally tends to increase with decreasing T, this would also explain the weak anticorrelation of $[NO_3^-]$ with T.

4.2. Results Using Standard Method

[22] A scatterplot comparing observed concentrations of $NH_3(g)$ with model calculated concentrations using the standard method is presented in Figure 4. A similar scatterplot for $HNO_3(g)$ is presented in Figure 5. Inspection of the figures reveals an absence of correlation between the calculated equilibrium concentrations and the observed concentrations for both species. Further note that the measured and calculated concentrations differ by orders of magnitude, and thus the discrepancy far exceeds the esti-

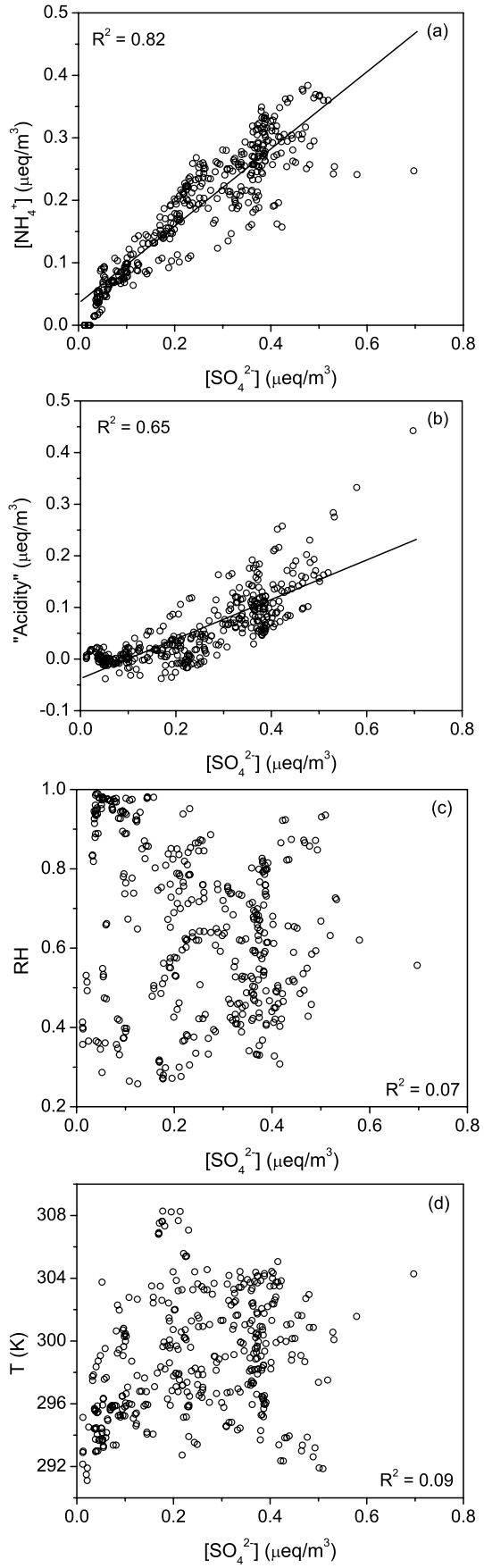

Figure 2. Scatterplots of $[SO_4^{2-}]$ versus (a) $[NH_4^+]$, (b) "Acidity," (c) RH, and (d) T.

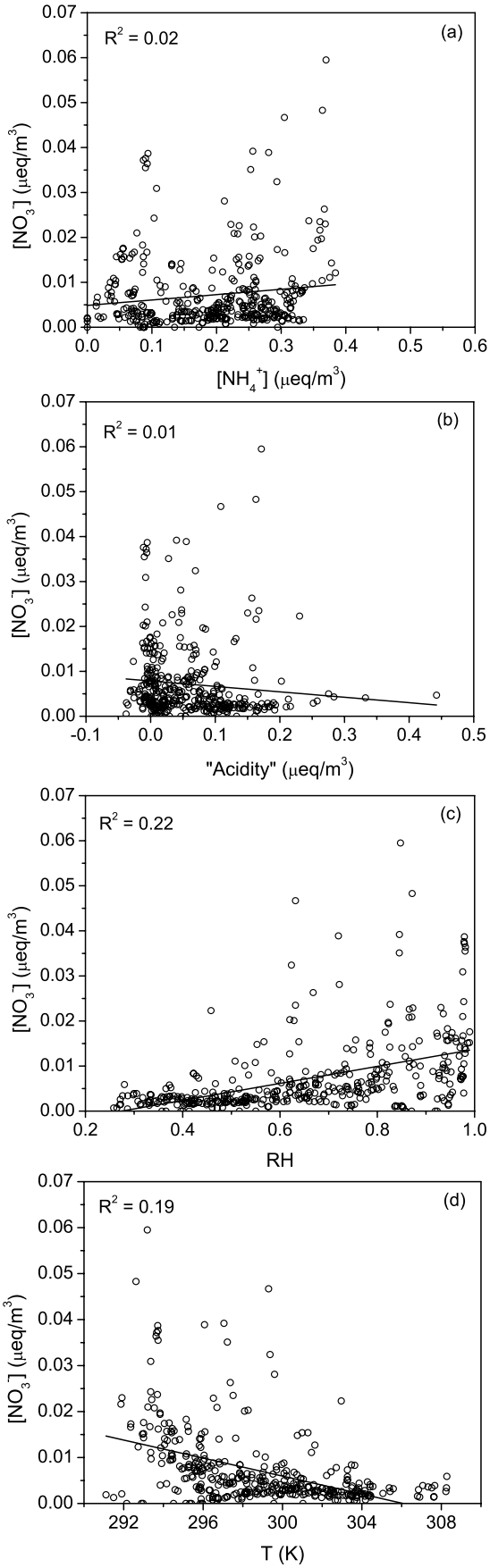

Figure 3. Scatterplots of [NO_3^-] versus (a) [NH_4^+], (b) "Acidity," (c) RH, and (d) T.

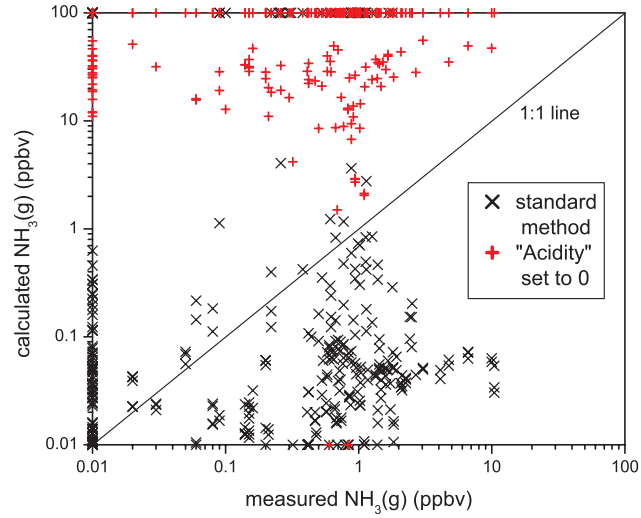

Figure 4. Scatterplot of measured and calculated equilibrium NH_3(g) concentrations.

mated uncertainty in the measurements. This result would appear to suggest that thermodynamic equilibrium does not apply to the data collected during the Atlanta Supersite Experiment and/or ISORROPIA is not able to accurately simulate such a state for the conditions encountered during the experiment. However, as discussed below, a more detailed examination of the results suggests the viability of another interpretation.

[23] Figures 6 and 7 show the dependences of the measured and calculated concentrations of NH_3(g) and HNO_3(g), respectively, on "Acidity." Inspection of the figures reveals the presence of some interesting trends. We find that the calculated NH_3(g) is generally lower than the measured NH_3, suggesting that the observed NH_3(g) is shifted toward the gas phase relative to the calculated equilibrium concentration. On the other hand, the calculated HNO_3(g) is generally larger than the measured concentration, i.e., while the observed NH_3(g) appears to be shifted in favor of the gas phase, the observed HNO_3(g) appears to be shifted toward the particulate phase.

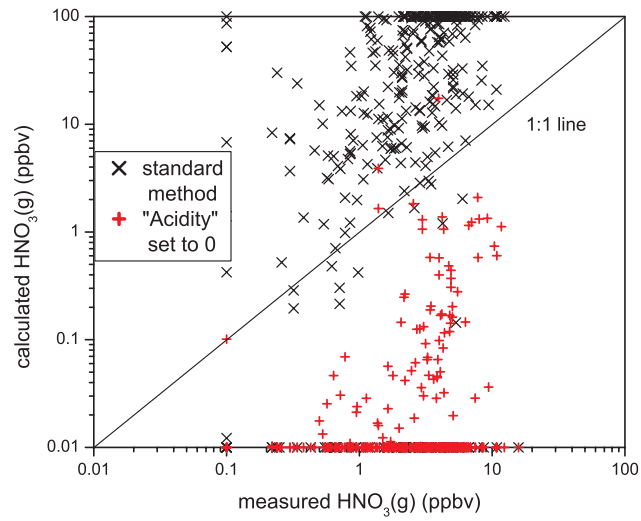

Figure 5. Scatterplot of measured and calculated equilibrium HNO_3(g) concentrations.

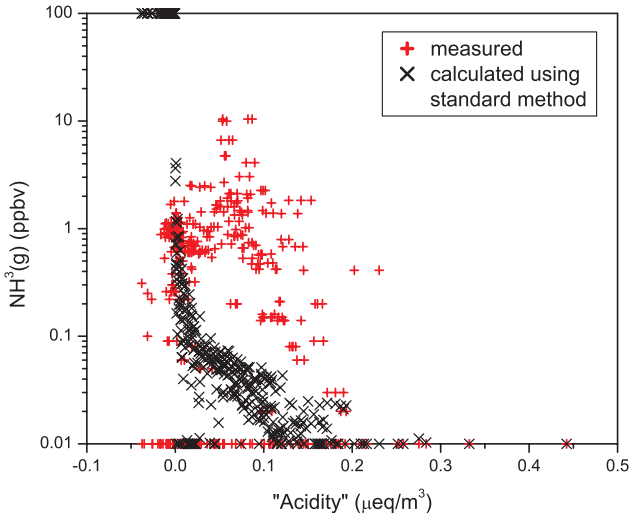

Figure 6. Dependence measured and calculated $NH_3(g)$ concentrations on "Acidity." Note: points with $NH_3(g)$ > 100ppbv are made equal to 100ppbv; points with $NH_3(g)$ < 0.01ppbv are made equal to 0.01ppbv.

[24] The finding of these disequilibria in both the nitrate and ammonium systems seems to be reasonably independent of the method we used to do the calculations. For example, inputting the data as 15- and 20-min averages instead of 5-min averages, yields the same underestimate in $NH_3(g)$ and overestimate in $HNO_3(g)$. When we use the alternate approach for the standard method described in Section 3.1, we overestimate $[NH_4^+]$, underestimate $NH_3(g)$, and both overestimate and underestimate the relatively small values for $[NO_3^-]$. It is also unlikely that the implicit assumption in our calculations of an internal mixture of particles is the source of the discrepancy. For example, *Perdue and Beck* [1988] found that when an external mixture of cloud drops in equilibrium with a collection of trace gases are collected in a bulk sample, the resulting sample will be supersaturated with respect to the existing trace composition. However, in our calculations we found an apparent undersaturation with respect to NH_3.

[25] Despite the quantitative disagreements described above, Figures 6 and 7 indicate a rough qualitative consistency between the observed and model-calculated dependence of the gas-phase concentrations on "Acidity." The measured and the calculated equilibrium $NH_3(g)$ both exhibit a trend toward an anticorrelated with the "Acidity," while a trend toward positive correlation is found in the case of $HNO_3(g)$. It is also interesting to note that the exceptions to the trend of underestimates by the model in $NH_3(g)$ and overestimates in $HNO_3(g)$ generally occur when the "Acidity" is less than zero (i.e., when the PILS measurements suggest that the $PM_{2.5}$ is basic or alkaline). One implication of this result is that the disagreement between the calculated and the measured concentrations is not due to an absence of thermodynamic equilibrium but to an error in the apparent acidity of $PM_{2.5}$ inferred from the inorganic ion concentration measurements of *Weber et al.* [2001]) and/or ISORROPIA. We examine this possibility below.

[26] We first examine what happens if "Acidity" is set to zero. In principle this change could be accomplished via the addition of some cation and/or the reduction in the concentration of one or more of the observed anions. For simplicity we have carried out these calculations by appropriately adjusting the value for $[SO_4^{2-}]$ input into ISORROPIA for each 5-min data point and keeping all other ion concentrations constant. Scatterplots between these newly calculated equilibrium $NH_3(g)$ and $HNO_3(g)$ concentrations (along with the original calculated concentrations) and the measured concentrations are illustrated in Figures 4 and 5, respectively. Note that these newly-calculated $NH_3(g)$ concentrations are generally greater than the observed concentrations (i.e., the points are shifted to the upper side of 1:1 line in Figure 4), and similarly, the newly-calculated equilibrium $HNO_3(g)$ concentrations are generally lower than the observed concentrations (i.e., the points are shifted to the lower side of 1:1 line in Figure 5).

[27] The results described above suggest that for most data points there is some value for "Acidity" between that inferred from the measurements and zero that will yield calculated equilibrium $NH_3(g)$ and $HNO_3(g)$ concentrations that are equal to their observed concentrations. To explore this possibility and its implications in more detail we carried out model calculations using the iterative method as described below.

4.3. Results Using the Iterative Method

[28] For the purposes of this discussion we will use the following nomenclature: (1) "Acidity"$_{obs}$ = the observed apparent acidity; (2) "Acidity"$_{HNO3}$ = the apparent acidity required to obtain agreement with the $HNO_3(g)$ observation; (3) "Acidity"$_{NH3}$ = the apparent acidity required to obtain agreement with the $NH_3(g)$ observation; (4) δ(diff) = the relative inferred "Acidity" difference = ("Acidity"$_{NH3}$ − "Acidity"$_{HNO3}$)/$[SO_4^{2-}]_{obs}$, where $[SO_4^{2-}]_{obs}$ is the observed sulfate concentration in unit of $\mu eq/m^3$.

[29] Figure 8 illustrates the variation of the 3 apparent acidities as a function of their time of observation. In Figure 8a we present the results for all 272 5-min averaged data points for which we had data for all parameters needed for

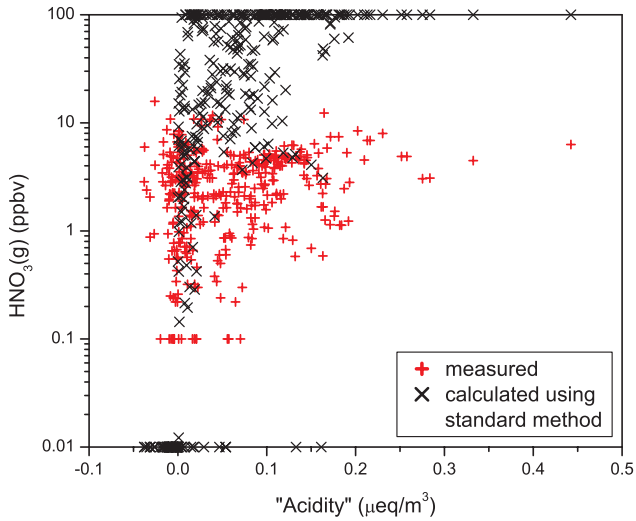

Figure 7. Dependence of measured and calculated $HNO_3(g)$ concentrations on "Acidity." Note: points with $HNO_3(g)$ > 100ppbv are made equal to 100ppbv; points with $HNO_3(g)$ < 0.01ppbv are made equal to 0.01ppbv.

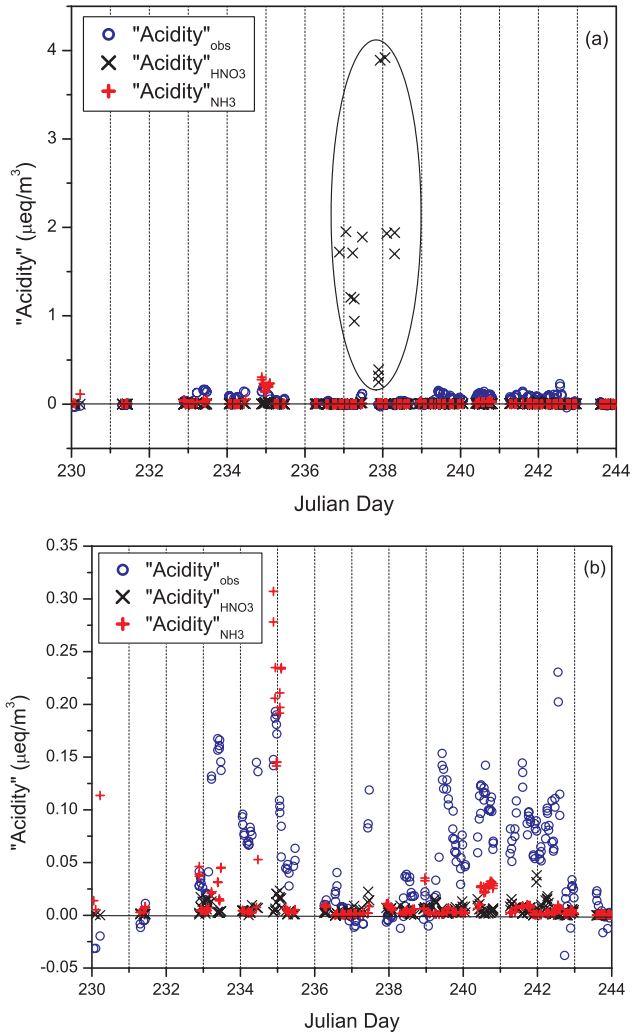

Figure 8. Measured and calculated "Acidity" as a function of Julian Day. (a) All 272 data points included. (b) Same as Figure 8a but with the 15 data points circled in Figure 8a excluded (see section 4.3).

our calculations. Inspection of this figure reveals that while for most of the data points there appears to be a relatively close correspondence between all apparent acidities, there are 15 data points, all occurring during Julian date 237 and 238, when "Acidity"$_{HNO3}$ is found to be much greater than both "Acidity"$_{obs}$ and "Acidity"$_{NH3}$. For reasons that are not immediately obvious these data points are anomalous; for example, the sulfate corrections required to obtain agreement with the HNO_3(g) observations for these 15 data points lie outside the 99.9% confidence intervals of the sulfate corrections required for nitrate equilibrium for the remaining 257 data points. It is also interesting to note that these 15 data points all correspond to a rainy period during the Supersite Experiment when both [SO_4^{2-}] and the ratio of $PM_{2.5}$ [SO_4^{2-}]-to-organic C mass was unusually low (see discussion in Section 4.1). In the discussion that follows, the results from these 15 data points are excluded.

[30] Figure 8b illustrates the apparent acidities as a function of time for the remaining 257 data points. Inspection of this figure, with its expanded scale, reveals two trends: (1) both "Acidity"$_{HNO3}$ and "Acidity"$_{NH3}$ generally tend to be less than "Acidity"$_{obs}$ confirming that a reduction in [SO_4^{2-}] was in fact needed to bring the calculated thermodynamic equilibrium HNO_3(g) and NH_3(g) concentrations into agreement with the observations; and (2) for most of the data points considered here, there is a fairly close correspondence between "Acidity"$_{HNO3}$ and "Acidity"$_{NH3}$. There are 16 data points that contradict this later trend. For these data points, which occur during Julian dates 230, 232, and 234, "Acidity"$_{HNO3}$ is significantly less than "Acidity"$_{NH3}$. For many of these 16 data points, "Acidity"$_{NH3}$ is greater than "Acidity"$_{obs}$. The anomalous behavior of these 16 data points is even more apparent in Figure 9a where we illustrate, δ(diff), the relative difference between "Acidity"$_{HNO3}$ and "Acidity"$_{NH3}$, as a function of time for the aforementioned 257 data points. While the discrepancies between the two inferred apparent acidities obtained for these 16 data points are not nearly as large as that obtained for the 15 data points excluded earlier, they are nevertheless quite significant (i.e., ranging from ~20% to almost 100%). It turns out that all of these points are characterized by

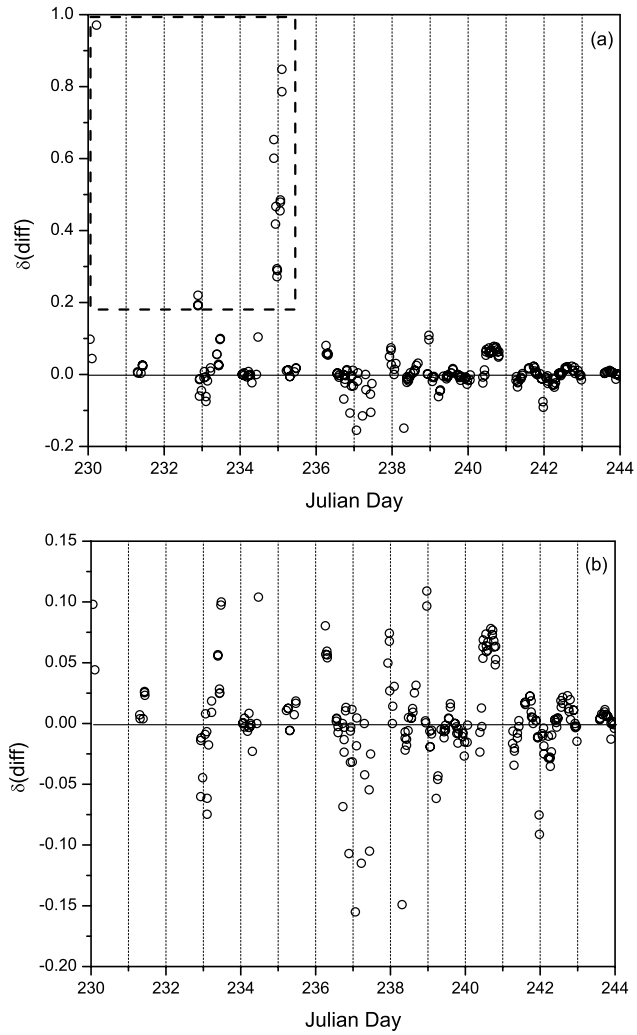

Figure 9. Relative difference in the "Acidity" corrections for NH_3(g) and HNO_3(g) as a function of Julian Day. (a) Results for all 257 data points; (b) Results excluding the 16 data points in the dashed rectangle in Figure 9a (see section 4.3).

extremely low observed concentrations of NH_3(g) (i.e., $\leq$ 0.05ppbv, within a factor of 3 of the stated detection limit).

[31] In Figure 9b we plot δ(diff) as a function of time after excluding both the 16 data points with low observed NH_3(g) concentrations as well as the 15 data points discussed earlier (i.e., a total of 241 data points). Figure 10 illustrates the magnitude in the apparent acidity corrections needed for HNO_3 and NH_3 as a function of time. Note that the corrections in the apparent acidity needed to reproduce the HNO_3(g) and NH_3(g) observations for the 241 data points are relatively small and quite consistent with each other. The average apparent acidity correction needed to reproduce the NH_3(g) and HNO_3(g) observations are -0.046 μeq/m^3 and -0.048 μeq/m^3, or -13.7% and -14.1% of $[SO_4^{2-}]_{obs}$, respectively. The average relative difference in the two corrections is only 0.39% and the standard error of the difference ($\sigma/\sqrt{N-1}$) is 0.24%.

4.4. Implications of Results Using the Iterative Method

[32] The quantitative consistency between the "Acidity"$_{NH3}$ and "Acidity"$_{HNO3}$ suggests that thermodynamic equilibrium did in fact apply during the Atlanta Supersite Experiment. As noted above, the average of the two apparent acidities for the 241 data points agree to within 0.4%. Linear regression between the two relative "Acidity" corrections yields a correlation coefficient of 0.96, a slope of 1.04, and an intercept of -0.0002 (see Figure 11). Given the large number of data points involved in the analysis (241), the probability that this correlation is fortuitous is much less than 0.1%. Since the calculation of "Acidity"$_{NH3}$ was carried out independently of the calculation of "Acidity"$_{HNO3}$, the strong correlation between the two parameters suggests the existence of some mechanism that mutually couples the $PM_{2.5}$ acidity to both the concentration of NH_3(g) and that of HNO_3(g); one such mechanism is that of thermodynamic equilibrium. Thus the data collected during the Atlanta Supersite Experiment are consistent with thermodynamic equilibrium between $PM_{2.5}$ and NH_3(g) and HNO_3(g) on the timescale of 5 min.

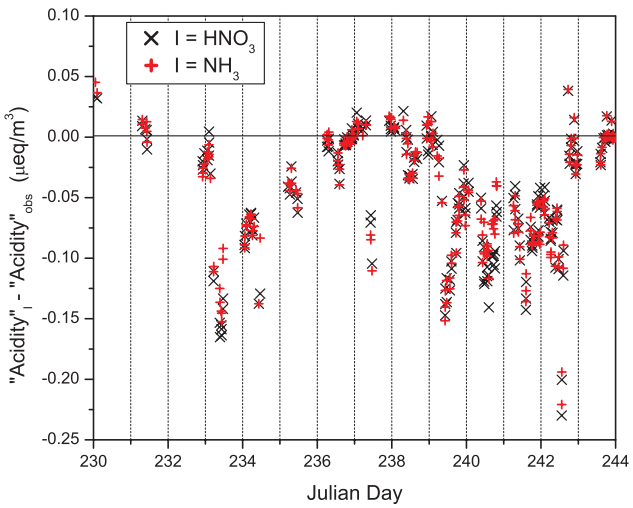

Figure 10. Absolute corrections of "Acidity" for NH_3(g) and HNO_3(g) for the 241 data points (i.e., excluding the 15 low $[SO_4^{2-}]$ data points and the 16 low NH_3(g) data points).

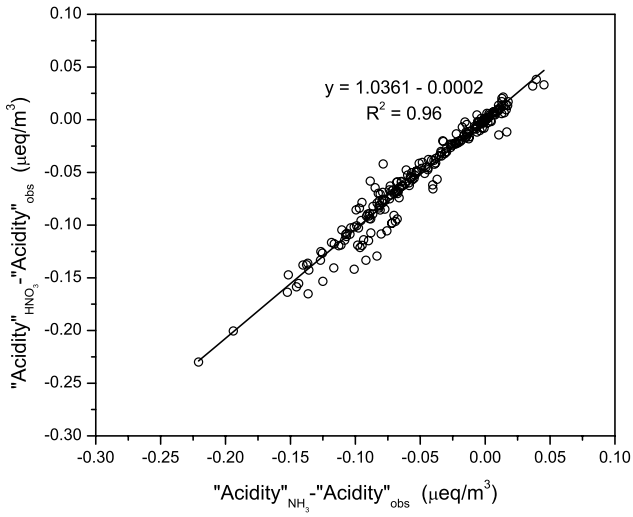

Figure 11. Scatterplot of absolute "Acidity" corrections for HNO_3(g) versus that for NH_3(g) for the 241 data points.

[33] However, if thermodynamic equilibrium did apply during the Supersite Experiment, it follows that some aspect or combination of the input data and model calculations used in our analysis to calculate the $PM_{2.5}$ "Acidity" was in error. One possible source of error is ISORROPIA; the discrepancy between the "Acidity" used in the standard and iterative methods could be due to the model systematically overestimating the acidity of particulate matter encountered during the Supersite Experiment.

[34] Another potential source of error is the PILS measurements. Recall that our calculations suggest that an average relative correction in the apparent acidity of about -14% is needed to make the NH_3(g) and HNO_3(g) observations consistent with thermodynamic equilibrium. On the other hand, the PILS single point measurement random error for each ion is estimated at ±8% [*Diamond*, 2002]. A simple propagation of error analysis suggests the random error in each inferred value of "Acidity" is ~50%. This implies that the approximate average error in "Acidity" for the entire population of 241 data points ($\sigma/\sqrt{N-1}$) is about 3%. Thus the required average -14% adjustment in the calculated "Acidity" is significantly larger than the average uncertainty in the measurements and suggests the existence of a systematic error in the data. This systematic error could arise in two ways: (1) A failure to identify a significant alkaline component in $PM_{2.5}$ (e.g., organic base if any); and/or (2) An error in the concentrations of one or more ions identified by PILS. With regard to the second possibility it is interesting to note that on average the PILS-measured $[SO_4^{2-}]$ was in fact about 20% larger than the $[SO_4^{2-}]$ measured from chemical analysis of 24-hour integrated filter samples [*Weber et al.*, 2002].

[35] However, if the error did in fact arise from the PILS measurements, it is likely that similar errors would have been obtained had we been able to use data from the other semicontinuous instrumentation operating during the Supersite Experiment. Inspection of Table 1 indicates that use of the ECN or Hering $[SO_4^{2-}]$ instead of that of the PILS would decrease the calculated "Acidity" by only a few percent; too small a correction to remove the discrepancy. Use of the ECN $[NH_4^+]$ would further increase the calculated

"Acidity" and thus worsen the discrepancy. Use of the Dasgupta [SO_4^{2-}] would overcompensate and produce a calculated "Acidity" that is too small to yield thermodynamic equilibrium.

5. Conclusion

[36] A thermodynamic equilibrium model, ISORROPIA, was applied to 5-min-averaged measurements of $PM_{2.5}$ inorganic composition and gas-phase concentrations of NH_3 and HNO_3 to determine the viability of the assumption of thermodynamic equilibrium. We found that the partitioning of ammonium/ammonia and nitrate/nitric acid between the particulate and gas phases is highly sensitive to the apparent acidity of the particulate phase. Adjustments in the apparent acidity using [SO_4^{2-}] as a free variable, suggest that the $PM_{2.5}$ acidity required to make the equilibrium NH_3(g) concentration equal to its observed concentration is essentially the same as the acidity required to make the equilibrium HNO_3(g) concentration equal to its observed concentration for ~90% of the data points analyzed here. Moreover, the average correction required to produce this acidity is larger than the estimated random error in the apparent acidity inferred from the measurements. These results suggest that: (1) The data collected during the Atlanta Supersite Experiment are consistent with the assumption of thermodynamic equilibrium on the timescale of 5 min; and (2) ISORROPIA is, for the most part, capable of reproducing the partitioning of inorganic species between particulate and gas phases during the experiment. For this to be the case, however, one or more of the following must apply: (1) The $PM_{2.5}$ SO_4^{2-} concentration measured by the PILS has a systematic overestimate of ~15%; (2) The $PM_{2.5}$ PILS systematically underestimated the concentration of the alkaline components by ~15%; and/or (3) The ISORROPIA model systematically overestimated the acidity of the $PM_{2.5}$ encountered during the experiment.

[37] It should be noted that there were 31 data points (out of a total of 272) that either had inconsistent sulfate corrections or unrealistically large sulfate corrections. These 31 data points were characterized by either anomalously low concentrations of [SO_4^{2-}] or NH_3(g). The inconsistencies in these cases may have been caused by inaccuracies in the data. However, we can not preclude the possibility that physicochemical processes not accounted for in our model calculations were at work in these instances. For example, the low [SO_4^{2-}] cases occurred during rainy periods and were characterized by unusually low ratios of sulfate to organic carbon, and it is possible that the preponderance of organic carbon affected the particle-to-gas partitioning [see, e.g., *Cruz et al.*, 2000]. This is certainly an issue that requires further study.

[38] Another limitation of our work is that it only considered data collected during one summer in Atlanta. For the most part, these data were collected during periods of high temperatures and relative humidities. Investigations during cooler, dryer conditions would no doubt help provide more insight into the general applicability of thermodynamic equilibrium to $PM_{2.5}$.

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