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#### **Special Section:**

Winter INvestigation of Transport, Emissions and Reactivity (WINTER)

#### **Key Points:**

- Highly acidic aerosols (pH = 0.77  $\pm$  0.96) for altitudes up to 5000 m in the northeastern U.S. in wintertime
- Thermodynamically predicted HNO<sub>3</sub>--NO<sub>3</sub><sup>-</sup> partitioning by ISORROPIA-II agrees with observation above 40% RH
- Particle pH should be explicitly determined to accurately assess properties impacted by aerosol acidity, such as HNO<sub>3</sub>-NO<sub>3</sub><sup>-</sup> partitioning

Supporting Information:

Supporting Information S1

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# Fine particle pH and the partitioning of nitric acid during winter in the northeastern United States

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Abstract Particle pH is a critical but poorly constrained quantity that affects many aerosol processes and properties, including aerosol composition, concentrations, and toxicity. We assess PM<sub>1</sub> pH as a function of geographical location and altitude, focusing on the northeastern U.S., based on aircraft measurements from the Wintertime Investigation of Transport, Emissions, and Reactivity campaign (1 February to 15 March 2015). Particle pH and water were predicted with the ISORROPIA-II thermodynamic model and validated by comparing predicted to observed partitioning of inorganic nitrate between the gas and particle phases. Good agreement was found for relative humidity (RH) above 40%; at lower RH observed particle nitrate was higher than predicted, possibly due to organic-inorganic phase separations or nitrate measurement uncertainties associated with low concentrations (nitrate  $< 1 \,\mu g \,m^{-3}$ ). Including refractory ions in the pH calculations did not improve model predictions, suggesting they were externally mixed with PM1 sulfate, nitrate, and ammonium. Sample line volatilization artifacts were found to be minimal. Overall, particle pH for altitudes up to 5000 m ranged between -0.51 and 1.9 (10th and 90th percentiles) with a study mean of  $0.77 \pm 0.96$ , similar to those reported for the southeastern U.S. and eastern Mediterranean. This expansive aircraft data set is used to investigate causes in variability in pH and pH-dependent aerosol components, such as PM<sub>1</sub> nitrate, over a wide range of temperatures (-21 to 19°C), RH (20 to 95%), inorganic gas, and particle concentrations and also provides further evidence that particles with low pH are ubiquitous.

#### 1. Introduction

Fine particles ( $PM_{2.5}$ ) are complex mixtures of organic and inorganic species [*Kanakidou et al.*, 2005; *Zhang et al.*, 2007a] often mixed with significant amounts of liquid water [*Carlton and Turpin*, 2013]. Sulfate, ammonium, and nitrate are typically the most abundant inorganic ions, with lower levels of sodium, chloride, crustal elements, and trace metal cations, depending on location and season [*Cabada et al.*, 2004; *Sardar et al.*, 2005; *Peltier et al.*, 2007a; *Zhang et al.*, 2010; *Fang et al.*, 2015; *Guo et al.*, 2015]. Among the aqueous aerosol species, the hydronium ion ( $H_3O^+$ , hereafter denoted simply as  $H^+$ , but recognizing that the unhydrated hydrogen ion is rare in aqueous solutions) quantified with a logarithmic scale, pH, drives many processes related to particle composition, gas-particle partitioning, and aerosol toxicity.

 $H^+$  catalyzes heterogeneous reactions such as hydration, polymerization, and carbonyl ring opening [*Jang et al.*, 2002] and may play a key role in secondary organic aerosol (SOA) formation. Laboratory chamber studies have shown the production rate of SOA from some biogenic volatile organic compound precursors, such as isoprene and  $\alpha$ -pinene, can be enhanced by strongly acidic particle seeds [*Jang et al.*, 2002; *Gao et al.*, 2004; *linuma et al.*, 2004; *Tolocka et al.*, 2004; *Edney et al.*, 2005; *Czoschke and Jang*, 2006; *Kleindienst et al.*, 2006; *Northcross and Jang*, 2007; *Surratt et al.*, 2007; *Eddingsaas et al.*, 2010; *Surratt et al.*, 2010]. Evidence for enhanced acid-catalyzed SOA formation in the ambient atmosphere has been reported in some studies [*Chu*, 2004; *Lewandowski et al.*, 2007; *Zhang et al.*, 2007b; *Tanner et al.*, 2009; *Pathak et al.*, 2011; *Lin et al.*, 2012; *Budisulistiorini et al.*, 2013], while others have observed no SOA enhancement [*Takahama et al.*, 2006;

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*Peltier et al.*, 2007b; *Karambelas et al.*, 2014]. Possible reasons for a lack of definitive evidence include varying SOA formation precursors and pathways and a range in particle pH, the latter dictating whether acidity is a limiting factor [*Nguyen et al.*, 2014; *Budisulistiorini et al.*, 2015; *Xu et al.*, 2015a]. The use of pH proxies to infer pH (e.g., ion balances and  $NH_4^+/SO_4^{2-}$  molar ratio) can also obscure the role of H<sup>+</sup> since they are not uniquely related to pH (discussed below) [*Pathak et al.*, 2004; *Guo et al.*, 2015; *Hennigan et al.*, 2015; *Weber et al.*, 2016].

In addition to altering the potential SOA pathways, pH affects particle mass concentrations directly through partitioning of both semivolatile weak (e.g., formic, acetic, and oxalic) and strong acids (e.g., nitric and hydrochloric). Low pH drives these acids to the protonated and volatile states and hence into the gas-phase. In the summer, we reported that  $PM_{2.5}$  aerosol pH was consistently low, between 0.5 and 2 in the southeastern U.S. [*Guo et al.*, 2015]. This leads to low concentrations of semivolatile acids in the particle phase. For example, PM<sub>1</sub> inorganic nitrate (NO<sub>3</sub><sup>--</sup>) concentrations were on average 0.08 µg m<sup>-3</sup> in summer in Centerville, AL [*Guo et al.*, 2015], with typical summertime partitioning ratios,  $\varepsilon(NO_3^-) = NO_3^-/(HNO_3 + NO_3^-)$ , of 24±5% (*Hidy et al.* [2014] Table S4). By impacting PM<sub>2.5</sub> mass concentrations, particle pH can affect emission control priorities aimed at meeting air quality standards to protect human health [*Lelieveld et al.*, 2015]. Furthermore, pH-controlled partitioning of these acids and associated ammonium affect deposition patterns of both acids and nitrogen (nitric acid, ammonia) due to large differences in gas and particle deposition rates [*Huebert and Robert*, 1985; *Duyzer*, 1994; *Schrader and Brummer*, 2014], and particle nitrate potentially affects N<sub>2</sub>O<sub>5</sub> heterogeneous reaction rates and NO<sub>x</sub> control [*Wahner et al.*, 1998; *Bertram and Thornton*, 2009; *Wagner et al.*, 2013].

The pH also affects the solubility of trace metals found in aerosols, such as Fe [*Meskhidze et al.*, 2003; *Oakes et al.*, 2012]. Although mainly present as insoluble oxides, lower pH can dissolve these metals and convert them to soluble forms, such as metal sulfates [*Oakes et al.*, 2012] and thereby significantly change the aerosol environmental impacts. For example, on global scales, metal mobility affects nutrient distributions [*Duce and Tindale*, 1991; *Meskhidze et al.*, 2003; *Meskhidze et al.*, 2005; *Nenes et al.*, 2011; *Ito and Xu*, 2014; *Myriokefalitakis et al.*, 2015; *Myriokefalitakis et al.*, 2016] with important impacts on productivity [*Meskhidze et al.*, 2005], carbon sequestration, and oxygen levels in the ocean [*Ito et al.*, 2016], whereas on regional scales soluble transition metals have been linked to aerosol toxicity or aerosol oxidative potential [*Ghio et al.*, 2012; *Verma et al.*, 2014; *Fang et al.*, 2015]. Synergistic adverse health effects have also been observed between ozone and acidic aerosols [*Last*, 1991; *Enami et al.*, 2008] and many epidemiological studies have reported adverse health outcomes associated with strong aerosol acidity [*Koutrakis et al.*, 1988; *Thurston et al.*, 1994; *Dockery et al.*, 1996; *Raizenne et al.*, 2005; *Lelieveld et al.*, 2015].

These broad impacts of particle acidity motivate determining particle pH. Several studies [*Guo et al.*, 2015; *Hennigan et al.*, 2015] evaluated thermodynamic modeling approaches for calculating pH, including ISORROPIA-II [*Nenes et al.*, 1998; *Fountoukis and Nenes*, 2007] and E-AIM (Extended Aerosol Inorganics Model) [*Clegg et al.*, 1998; *Wexler and Clegg*, 2002; *Clegg et al.*, 2003], since an established analytical method that directly determines aerosol pH does not exist. ISORROPIA-II and E-AIM have been shown to give similar results when both gas and particle phase are input (i.e., models run in the "forward mode") [*Hennigan et al.*, 2015]. These thermodynamic models calculate particle hydronium ion concentrations (moles of particle H<sup>+</sup> per volume air,  $H_{air}^+$ ) and liquid water content that is associated with inorganic components ( $W_i$ ), based on particle- and gas-phase inorganic species concentrations and meteorological conditions (relative humidity, RH, and temperature, *T*).  $H_{air}^+$  and  $W_i$  can then be used to calculate particle pH. Accuracy of model pH predictions can be assessed by comparing predicted to measured particioning of semivolatile species (e.g.,  $NH_{3(g)}$ - $NH_4^+$  and  $HNO_{3(g)}$ - $NO_3^-$ ), which can be highly sensitive to pH, *T*, and RH (i.e.,  $W_i$ ) [*Guo et al.*, 2015; *Hennigan et al.*, 2015]. This paper extends our analysis of fine particle pH from the southeastern [*Guo et al.*, 2015] to northeastern U.S. and presents some of the first data on pH as a function of altitude.

#### 2. Methods

The Wintertime Investigation of Transport, Emissions, and Reactivity (WINTER) aircraft study was based out of NASA Langley Research Center (Hampton, VA) and focused mainly on the northeastern U.S. The National Center for Atmospheric Research (NCAR) C-130 aircraft conducted a total of 13 flights from 1 February to 15 March 2015. The payload included a suite of instruments to measure gas and aerosol composition. Here we focus on gas-phase nitric acid and measurements of aerosol inorganic components. Method details are

provided below. Ambient *T*, RH, and aircraft coordinates were provided by the Research Aviation Facility (RAF) as part of the C-130 instrumentation package (http://data.eol.ucar.edu/master\_list/?project=WINTER). Aircraft data are typically reported at a reference temperature and pressure; concentration data, however, are reported here at ambient temperature and pressure because thermodynamic partitioning calculations need to be carried out at ambient conditions.

#### 2.1. Instrumentation

#### 2.1.1. PILS-IC

 $PM_1$  (particles with aerodynamic diameters < 1.0  $\mu$ m at ambient conditions) water-soluble ions were measured with a Particle-Into-Liquid Sampler coupled with Ion Chromatographs (PILS-IC; Metrohm 761 Compact ICs) [Orsini et al., 2003; Hennigan et al., 2006; Sullivan et al., 2006; Peltier et al., 2007a; Liu et al., 2012; Guo et al., 2015]. Ambient aerosol was sampled from a submicron aerosol inlet [Craig et al., 2013a; Craig et al., 2013b; Craig et al., 2014; Moharreri et al., 2014] at a flow rate of 15.0 L min<sup>-1</sup>. Residence time in the inlet and sample lines is estimated at 2 s. Upstream of the PILS-IC, a nonrotating microorifice impactor [Marple et al., 1991] with a 1.0  $\mu$ m cut size (at 1 atm and 273.15 K) restricted measurements to PM<sub>1</sub> to be comparable with the Aerosol Mass Spectrometer (discussed below). Air temperature was measured just prior to the PILS with a calibrated thermocouple, since changes in T (and thus also RH) from ambient can be significant when sampling from aircraft and especially when ambient temperatures are low. Below we show that the particles did not have sufficient time to adjust to these changing conditions so the impactor cut size can be assumed to be for particles sizes under ambient conditions. (Note that the range in ambient pressures encountered in this study have minor effects on cut size; 10th percentile is 0.99 µm). Therefore, no corrections for PILS-IC measured species are made due to the small deviation from nominal cut size. To eliminate gas interferences, phosphoric acid and sodium carbonate-coated honeycomb denuders were installed before the PILS. The liquid transport flow introduced at the top of the PILS impactor was spiked with lithium fluoride (LiF) and measured with the IC to account for sample liquid dilution. The liquid sample collected from the bottom of the PILS impactor was pumped into two ICs with 150 µL sample loops and operated at a chromatographic separation of 3 min for both the anions (chloride, sulfate, and nitrate) and the cation (lithium, ammonium, etc.). A Metrosep A Supp 15-50/4.0 anion column and a C4-50/4.0 cation column (Metrohm USA, Riverside, FL) were operated at an eluent flow rate of 1.05 mL min<sup>-1</sup> and 1.0 mL min<sup>-1</sup>, respectively. Eluents used during this campaign were 12 mM Na<sub>2</sub>CO<sub>3</sub> (sodium carbonate)/8.0 mM NaHCO<sub>3</sub> (sodium bicarbonate) for anion exchange and 2.0 mM dipicolinic acid/3.0 mM HNO<sub>3</sub> for cation exchange. The cation IC (without suppressor) exhibited higher baseline noise during the campaign than the anion IC so lacked sufficient sensitivity for reliable measurements of  $NH_4^+$ . Therefore,  $NH_4^+$  and other ambient cation data from this instrument are not used in the following analysis. For all flights a valve upstream of the PILS diverted sampled air through a High Efficiency Particulate-Free Air (HEPA) filter (Pall Corp.) to provide blank measurements during the first 10 min after takeoff. All data were blank corrected. Limits of detection (LOD) were estimated from the blank measurements (3 × standard deviation (SD) of blanks) as 0.06  $\mu$ g m<sup>-3</sup> (SO<sub>4</sub><sup>2-</sup>),  $0.05 \,\mu g \,m^{-3}$  (NO<sub>3</sub><sup>-</sup>), and  $0.12 \,\mu g \,m^{-3}$  (Cl<sup>-</sup>) for a 3 min sampling time. The relative measurement uncertainty for the anions is estimated to be 20% based on uncertainty propagation of sample air flow, liquid flow variations, and instrument precision, which is based on variability in calibrations with known liquid standards. 2.1.2. AMS

A high-resolution time of flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc., hereafter referred to as "AMS") measured nonrefractory components of PM<sub>1</sub> at a rate of 1 s in total aerosol mass mode. The general operation of the AMS has been described elsewhere [*Jayne et al.*, 2000; *DeCarlo et al.*, 2006; *Canagaratna et al.*, 2007; *Dunlea et al.*, 2009; *Jimenez et al.*, 2009; *Kimmel et al.*, 2011]. Particles were sampled through a NCAR High-Performance Instrumented Airborne Platform for Environmental Research (HIAPER) Modular Inlet (HIMIL) [*Stith et al.*, 2009] at a flow rate of 10 L min<sup>-1</sup>, into a pressure controlled inlet operated at 325 torr [*Bahreini et al.*, 2008], then introduced into the high vacuum region of the mass spectrometer through an aerodynamic focusing lens, and transmitted to a detection chamber where particles impacted on a porous tungsten vaporizer (600°C). Nonrefractory species are flash vaporized and then ionized with 70 eV electron impact ionization. The generated ions are then extracted and analyzed by time-of-flight mass spectrometry. Residence time from the tip of the HIMIL to the vacuum vaporizer was 0.5 s. An estimated collection efficiency based on the algorithm proposed by *Middlebrook et al.* [2012] was applied to all data, and relative ionization efficiencies for sulfate, ammonium, and chloride were determined by multiple in-field

calibrations. Typical detection limits during the WINTER campaign were  $0.02 \,\mu g \, sm^{-3}$  for sulfate,  $0.01 \,\mu g \, sm^{-3}$  for ammonium, and  $0.07 \,\mu g \, sm^{-3}$  for nitrate and chloride for a 1 s sampling interval (sm<sup>-3</sup> refers to standard cubic meters under 1 atm and 273.15 K). Accuracy for AMS detection of inorganic species is estimated at 35% for aircraft operation [*Bahreini et al.*, 2009]. More refractory species, such as NaNO<sub>3</sub> (sodium nitrate) and Na<sub>2</sub>SO<sub>4</sub> (sodium sulfate), are inefficiently detected by the AMS [*Hayes et al.*, 2013]. AMS data are often used to estimate the fractions of inorganic and organic nitrates using the measured NO<sub>2</sub><sup>+</sup>/NO<sup>+</sup> ion ratios in the AMS [*Fry et al.*, 2013]. However, in this study, the presence of particulate nitrite and the likely partial detection of submicron NaNO<sub>3</sub> made that method underdetermined. For that reason, in addition to total measured nitrate, estimates were made of just inorganic nitrate concentrations based on comparisons of the AMS data to the IC-based instruments.

#### 2.1.3. CIMS

One-second HNO<sub>3</sub> concentrations were quantified by a high-resolution time of flight chemical ionization mass spectrometer (CIMS), which used the I<sup>-</sup> reagent ion to selectively detect HNO<sub>3</sub> [*Slusher et al.*, 2004; *Lopez-Hilfiker et al.*, 2012; *Lee et al.*, 2014; *Lopez-Hilfiker et al.*, 2016]. In a heated teflon flow tube at low pressure, iodide ions are produced to selectively cluster with HNO<sub>3</sub> in ambient air. The ions from the flow tube enter a mass spectrometer, where they are detected. The estimated HNO<sub>3</sub> measurement uncertainty is 15%. This includes the accuracy of NO<sub>2</sub> calibration cylinder and in-flight variability of continuous calibration source. Detection limit varies from flight to flight, and more information regarding the CIMS operation can be found in *Lee et al.* [2014] and *Lopez-Hilfiker et al.* [2016].

#### 2.2. pH and Partitioning Calculations

The ISORROPIA-II thermodynamic model [*Fountoukis and Nenes*, 2007] was used to determine the composition and phase state of an  $NH_4^+-SO_4^{2-}-NO_3^-(-CI^--Na^+-Ca^{2+}-K^+-Mg^{2+})$ -water inorganic aerosol in thermodynamic equilibrium with its corresponding gas phase. Using ISORROPIA-II, we have reported on a comprehensive method for pH prediction, validation, and uncertainty analysis based on the 2013 Southern Oxidant and Aerosol Study (SOAS) [*Guo et al.*, 2015; *Weber et al.*, 2016]. Here we follow the same approach. pH is defined as

$$\mathsf{pH} = -\log_{10}\gamma_{H^+}H_{aq}^+ = -\log_{10}\frac{1000\gamma_{H^+}H_{air}^+}{W_i + W_o} \cong -\log_{10}\frac{1000\gamma_{H^+}H_{air}^+}{W_i} \tag{1}$$

where  $\gamma_{H^+}$  is the hydronium ion activity coefficient (assumed = 1),  $H_{aq}^+$  (mole L<sup>-1</sup>) the hydronium ion concentration particle liquid water,  $H_{air}^+$  (µg m<sup>-3</sup>) the hydronium ion concentration per volume of air, and  $W_i$  and  $W_o$  (µg m<sup>-3</sup>) are particle water concentrations associated with inorganic and organic species, respectively. *Guo et al.* [2015] found that pH predicted solely with  $W_i$  is fairly accurate; pH was 0.15–0.23 units systematically lower than pH predicted with total particle water ( $W_i + W_o$ ) ( $R^2 = 0.97$ ). This is likely an upper bound on the error since organic aerosol mass fractions in that study were high (~60%, [*Xu et al.*, 2015b]). A lower contribution from  $W_o$  is expected in WINTER due to lower organic aerosol mass fractions (~40%);  $\Delta$ pH was estimated to be +0.07 units including  $W_o$  with assumed organic hygroscopic parameter  $k_{org}$  as 0.13 [*Cerully et al.*, 2015]. Given this, and that organic aerosol hygroscopicity was not measured, we determine pH only considering  $W_i$  since neglecting  $W_o$  appears to cause only a minor effect on the pH characterization.

The behavior of pure inorganic salts, under variable RH, including deliquescence and efflorescence, are well established both experimentally and theoretically [*Tang*, 1976; *Wexler and Seinfeld*, 1991; *Tang and Munkelwitz*, 1994]. The behavior of mixed inorganic and organic particles is more complex due to possible liquid-liquid or solid-liquid phase separation between organics and inorganics at lower RH and O:C ratio (organic aerosol atomic O:C ratio) conditions [*Bertram et al.*, 2011; *Song et al.*, 2012; *You et al.*, 2013; *You et al.*, 2014; *You and Bertram*, 2015]. Therefore, liquid or solid phases of atmospheric aerosols (deliquescence or efflorescence) depend on the RH and *T* history, and composition. To simplify the simulations, ISORROPIA-II was run assuming particles are "metastable," with no solid precipitates (H<sup>+</sup> is not stable in effloresced aerosol), although we did a sensitivity study assuming solid phases were present. Therefore, we excluded data with RH < 20%, a condition where aerosols are less likely to be in a completely liquid state [*Ansari and Pandis*, 2000; *Malm and Day*, 2001; *Fountoukis and Nenes*, 2007; *Bertram et al.*, 2011]. Furthermore, at such a low RH range, uncertainties in the pH prediction are expected to be high due to highly uncertain activity coefficients associated with highly concentrated solutions [*Fountoukis et al.*, 2009]. Data for RH > 95% were also excluded due to the exponential growth in particle liquid water with RH, which leads to high *W<sub>i</sub>* 

and subsequently large pH uncertainty due to propagation of RH uncertainties [*Malm and Day*, 2001; *Guo et al.*, 2015] and potential issues with inlet transmission losses. Between these extremes, thermodynamic predictions are also assessed for differing RH ranges.

In running ISORROPIA-II to predict pH and semivolatile acid partitioning, it is also assumed that the particles are internally mixed and that pH does not vary with particle size (so that bulk properties represent the overall aerosol pH) and that the ambient aerosols and gases are in thermodynamic equilibrium. For submicron aerosol (PM<sub>1</sub>), equilibrium states are typically achieved within 30 min under ambient conditions [*Dassios and Pandis*, 1999; *Cruz et al.*, 2000; *Fountoukis et al.*, 2009]. The ISORROPIA-II input RH and *T* during the WINTER campaign were as low as 20% and  $-21^{\circ}$ C. Therefore, the timescale of equilibration could be much longer than 30 min [*Zobrist et al.*, 2008; *Tong et al.*, 2011; *Shiraiwa and Seinfeld*, 2012], so thermodynamic calculations may deviate from observed partitioning of inorganic semivolatiles. Also, organic-containing aerosol may become semisolid or glassy at low RH and *T*, which can further increase the equilibration timescale considerably. This potential impact is evaluated below. For conditions during the SOAS study in the southeastern U.S. in summer ( $T=25\pm3^{\circ}$ C and RH=74±16%), *Guo et al.* [2015] found that thermodynamic calculations accurately predicted bulk particle water and ammonia partitioning over the complete *T* (18 to 33°C) and RH (36 to 96%) ranges.

#### 3. Results

#### 3.1. Comparison Between Methods for Measuring Particle Ionic Composition

Several instruments measured aerosol inorganic chemical composition during this study. For PM<sub>1</sub>, along with the PILS-IC and AMS, a second PILS was coupled to a fraction collector and the vials analyzed offline by IC for water-soluble ions and carbohydrates (e.g., levoglucosan). A filter-sampling system was used to collect nominally PM<sub>4</sub> [McNaughton et al., 2007], which were subsequently analyzed for water-soluble ions by IC. (Methods for PILS with fraction collector and the filter sampling system are described in the supporting information [Dibb et al., 1999; Dibb et al., 2000; Sorooshian et al., 2006].) A summary comparing sulfate and nitrate from these various instruments can be found in Figure S1 in the supporting information. Good correlations were found between the various instruments for sulfate, with  $R^2$  between 0.72 and 0.83. However, systematic differences were observed, with orthogonal regression slopes between 1.05 and 1.52. On average, PILS-IC sulfate ( $PM_1$ ) was the lowest and filter sulfate ( $PM_4$ ) the highest. Somewhat similar results were also found for nitrate, with  $R^2$  between 0.65 and 0.87 and slopes between 0.86 and 1.43. The two PILS measurements were most similar. The lowest correlation was observed between filter and both PILS (also for AMS) nitrate, which is likely due to nitrate associated with particles larger than PM<sub>1</sub>. The better agreement with sulfate between these instruments suggests that the coarse fraction is mostly devoid of sulfate (with the exception of periods during Flight 13, which was conducted far offshore). We note that although the size cut is nominally the same (PM<sub>1</sub>) between PILS and AMS, there are differences between the actual cuts as they are imposed by very different physical devices and under different pressure conditions [see, e.g., DeCarlo et al., 2004]. During periods in which larger particles are present, this effect could lead to some measurement differences.

Ammonium data are not compared since PILS-IC cation data were not available. In the subsequent analyses, we estimated an  $NH_4^+$  concentration that would be consistent with the PILS-IC by multiplying the AMS  $NH_4^+$ , merged to PILS time resolution, by a constant factor of 0.7 (the average of PILS-IC/AMS nitrate and sulfate slope; Figure S1).

In the following analyses of fine particle pH we use both the PILS and the AMS data to calculate pH, since each method has distinct advantages and also to test the sensitivity of predicted pH using different methods for measuring ion concentrations. The PILS-IC (or any other IC analysis method) directly measures aerosol inorganic aqueous ion concentrations making the data directly applicable to pH calculations. (Note that in these methods, the extractions result in highly dilute solutions so that ions are completely dissociated and measured by the IC.) The AMS does not specifically measure ionic concentrations, which can potentially raise a number of issues under certain circumstances. First, refractory species that are at least to some degree soluble (e.g., NaCl, NaNO<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, MgSO<sub>4</sub>, KCl, KNO<sub>3</sub>, and K<sub>2</sub>SO<sub>4</sub>) can have a large impact on pH, even at low concentrations, but are not efficiently detected by AMS. However, often these species are mostly found in the supermicron-size fraction and have little influence on PM<sub>1</sub> pH (discussed in more detail in section 3.8).



**Figure 1.** Comparisons of PM<sub>1</sub> pH predicted with aerosol phase input (NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) from the AMS versus PILS-IC anions and scaled AMS NH<sub>4</sub><sup>+</sup>. Gas-phase HNO<sub>3</sub> and ambient RH, *T* input are the same for the two predictions. Orthogonal regression fit is shown.

The AMS also cannot readily distinguish between inorganic and organic forms of nitrate and sulfate. For example, evidence from AMS and PILS data (not shown) indicates that nitrites and organic nitrates are variably present during WINTER and could explain some of the differences in nitrate observed between these instruments, especially when inorganic concentrations are low (Figure S2). Similar interferences could occur for sulfate. Unlike the PILS-IC, the AMS provides higher time resolution and a more precise measurement of the suite of ions, as the same detector is used for anions and cations. These issues are pertinent to this study. Here we analyze the data to utilize the PILS accuracy and AMS precision. We will show that for this study, the AMS precision is more beneficial for assessing factors that influence pH, while the PILS accuracy is important for constraining the absolute value of pH, especially when there are nonvolatile cations present.

#### 3.2. Predicting pH

For the WINTER data set and the full range of RH sampled (20–95%) we first predict pH with ISORROPIA-II using ambient T, RH, HNO<sub>3</sub> and either (*i*) PILS NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and scaled AMS NH<sub>4</sub><sup>+</sup> or (*ii*) AMS NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NH<sub>4</sub><sup>+</sup>. Figure 1 shows that pH from these two data sets are, on average, in agreement, slope = 1.08, but there is substantial scatter  $R^2$  = 0.44. Also, although AMS sulfate and nitrate are systematically 52% and 43% higher than PILS-IC measurement (Figure S1), these differences do not systematically influence the calculated pH since the difference likely applies to all species. We conclude that pH is not highly sensitive to systematic aerosol input differences, even up to 50%, as long as the ion ratios are scaled accordingly.

A potential limitation with the pH prediction with this data is lack of reliable gas-phase ammonia (NH<sub>3</sub>). Not including NH<sub>3</sub> is expected to result in an overestimation of particle acidity because the partitioning of  $NH_3-NH_4^+$  is derived based on only the  $NH_4^+$  mass loadings; this means a fraction of the measured  $NH_4^+$  is partitioned as NH<sub>3</sub> to the gas-phase and releasing more particulate  $H^+$  in the process. NH<sub>3</sub> was measured as part of the WINTER campaign; however, there were known uncertainties with detection limits and artifacts associated with the inlets/sampling system. When included in the thermodynamic model, it resulted in NO<sub>3</sub><sup>-</sup> overpredicted by 65% compared to the measurement and the  $R^2$  of predicted versus measured  $\epsilon$ (NO<sub>3</sub><sup>-</sup>) decreased from 0.70 to 0.40 (the modeling of HNO<sub>3</sub>-NO<sub>3</sub><sup>-</sup> partitioning will be discussed in the next section). Instead, to assess the effect of lack of NH<sub>3</sub> data, we iterated ISORROPIA-II using the predicted NH<sub>3</sub> data to calculate total ammonia  $(NH_3 + NH_4^+)$  as input for the next iteration, until NH<sub>3</sub> predictions converge. A more straightforward method, predicting gas phase NH<sub>3</sub> based on aerosol composition in ISORROPIA-II reverse mode, is not chosen because the prediction is highly sensitive to  $NH_4^+$  input (i.e., 35% instrument uncertainty can cause large errors [Hennigan et al., 2015]). Based on the iteration method, predicted WINTER mean NH<sub>3</sub> concentrations were  $0.10 \,\mu g \,m^{-3}$  (10th percentile =  $0.0 \,\mu g \,m^{-3}$ , and 90th percentile = 0.25  $\mu$ g m<sup>-3</sup>) and most of the ammonia partitions to the particle phase ( $\epsilon$ (NH<sub>4</sub><sup>+</sup>) = 91 ± 22%). Particle pH changed by only approximately 3% (slope = 0.97, and  $R^2$  = 0.81), with a pH systematically ~0.2 pH units (regression intercept) higher for the iterated solution compared to not including  $NH_3$  data. Therefore, not including gas-phase NH<sub>3</sub> in the thermodynamic calculations for this study has a minor effect, and reported pH is not corrected by the iterated NH<sub>3</sub>.

#### 3.3. Verification of the Thermodynamic Model: Comparison of Nitric Acid-Nitrate Partitioning

Validity of thermodynamic model predictions may be assessed by comparing predicted and measured gas partitioning fractions of the semivolatiles. Comparing completely nonvolatile or volatilized components is

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**Figure 2.** Comparisons of predicted and measured HNO<sub>3</sub> (nitric acid), (NO<sub>3</sub><sup>-</sup>) (nitrate), and  $\epsilon$ (NO<sub>3</sub><sup>-</sup>) (particle nitrate fraction of total nitrate) for data from the complete WINTER study: (a–c) PILS-IC anion input with scaled AMS ammonium (NH<sub>4</sub><sup>+</sup>) and (d–f) AMS input. Example error bars (40%) at three selected data points illustrate the uncertainty in measured  $\epsilon$ (NO<sub>3</sub><sup>-</sup>) from combined HNO<sub>3</sub> (15%) and NO<sub>3</sub><sup>-</sup> (35%) uncertainties. Orthogonal regression fits are shown. Average conditions for each RH range are given in Table 1.

not a viable or useful test. The best semivolatile species for evaluation, however, depends on the pH levels of a given study. For example, in SOAS (summer in the southeastern U.S.) the conditions were such that HNO<sub>3</sub> was almost entirely in the gas phase, whereas NH<sub>3</sub> was evenly distributed between phases ( $\epsilon$ (NH<sub>4</sub><sup>+</sup>) = NH<sub>4</sub><sup>+</sup>/(NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>) = 59 ± 16%), making it the better species to test the model [*Guo et al.*, 2015]. In this study (winter in the northeastern U.S.), NH<sub>3</sub> was estimated to be mainly in the particle phase, as discussed above, and HNO<sub>3</sub> was more evenly distributed between particle and gas ( $\epsilon$ (NO<sub>3</sub><sup>-</sup>) = NO<sub>3</sub><sup>-</sup>/(HNO<sub>3</sub> + NO<sub>3</sub><sup>-</sup>) = 31% PILS data and 39% AMS data) making it the better parameter to compare. Using predicted gas-particle partitioning concentrations is a valid test since when operating in "forward mode," ISORROPIA-II calculates the gas-particle equilibrium partitioning concentrations based on the input of total concentration of a species (gas + particle).

A comparison of predicted HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> to measured values is shown in Figure 2. Overall, for the 20– 95% RH data set, the model captures the observed HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup>. Less scatter is seen when ISORROPIA-II is run with the AMS aerosol data, consistent with expectation that it is more precise than the combined PILS anions and AMS NH<sub>4</sub><sup>+</sup> data set (note that including predicted NH<sub>3</sub> results in a better comparison between predicted and PILS-IC measured NO<sub>3</sub><sup>-</sup>, with the  $R^2$  increasing from 0.71 to 0.77; not shown). From Figure 2, ISORROPIA-II predicted HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> are on average within 10% of the measurements and highly correlated. However, there is much more scatter for the  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>) comparison, partly due to propagation of the uncertainties from both HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> measurements needed for the calculation. (Note that individual data below 2 × LOD concentrations were excluded for  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>), due to larger relative uncertainties.) Not all the spread in  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>), however, can be attributed to the impact of measurement errors or noise, as higher discrepancies tend to be associated with lower RH.

Focusing on narrower RH ranges permits a more detailed exploration of the systematic biases. Figure 3 shows the predicted and measured  $HNO_3$  and  $NO_3^-$  concentrations and  $\epsilon(NO_3^-)$  for three RH ranges, 20–40%, 40–60%, and 60–95%. The least discrepancy is found for the 60–95% RH range, and the largest bias is found for 20–40% RH, which also has the lowest total nitrate concentrations (Table 1). The larger discrepancy at lower

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**Figure 3.** Comparisons between predicted and measured HNO<sub>3</sub>, NO<sub>3</sub><sup>-</sup>, and  $\epsilon$ (NO<sub>3</sub><sup>-</sup>) with data from the complete WINTER study (AMS aerosol data only) for different ambient RH ranges: (a–c) 20–40%, (d–f) 40–60%, and (g–i) 60–95%. Orthogonal regression fits are included in most plots. Note that for the concentrations, the axis ranges get smaller with decreasing RH.

RH may be due to a number of factors, including ignoring possible phase separations and measurement limitations. Each factor is considered below.

#### 3.3.1. Phase Separation

Two types of phase separations are possible: solid-liquid and liquid-liquid. Considering just the inorganic phase first, assuming solid salts precipitate from a supersaturated aqueous phase (i.e., ISORROPIA-II runs in stable mode instead of metastable) does not improve the predictions but rather worsens them;  $NO_3^-$  is much

Table 1. Summary of Ambient Temperature and PM<sub>1</sub> Organic Aerosol (OA) Atomic O:C Ratio, OA to Sulfate Mass Ratio, Nitrate Concentrations (All From AMS Data), and Gas-Phase Nitric Acid Concentrations for Data Binned by Ambient RH

RH	<i>T</i> (°C)	O:C	OA:SO42-	$NO_{3}^{-}$ (µg m <sup>-3</sup> )	$HNO_3 \ (\mu g \ m^{-3})$	Total NO <sub>3</sub> <sup><math>-</math></sup> (µg m <sup><math>-3</math></sup> )	Number of Points
20–40%	$0.0 \pm 7.6$	$0.79 \pm 0.20$	$1.36 \pm 0.72$	$\begin{array}{c} 0.37 \pm 0.36 \\ 0.66 \pm 0.79 \\ 1.40 \pm 1.28 \end{array}$	$1.04 \pm 0.71$	1.41 ± 0.75	272
40–60%	-1.6 ± 6.9	$0.76 \pm 0.16$	$1.54 \pm 0.91$		$0.99 \pm 1.04$	1.65 ± 1.65	1192
60–95%	-0.7 ± 5.3	$0.78 \pm 0.11$	$1.75 \pm 0.79$		$2.37 \pm 2.40$	3.77 ± 2.77	902

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more substantially underpredicted by the model as RH decreases (Figure S3 in the supporting information), compared to metastable aerosol calculations. At high RH, there is little difference between the metastable and semisolid assumptions because the inorganic salts (e.g., NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) deliquesce. Overall, we find that running ISORROPIA-II in metastable mode over the 20–95% RH range agrees better with observations (although there are still discrepancies at lower RHs); thus, solid-liquid phase separations of the inorganic species does not appear to explain the  $\epsilon$ (NO<sub>3</sub><sup>-</sup>) discrepancies at low RH.

Organic-inorganic liquid phase separations are also possible. Lab studies show that liquid-liquid phase separation is always observed at aerosol O:C (organic aerosol atomic O:C ratio)  $\leq$  0.5, whereas no phase separations occur for O:C $\geq$ 0.8 [Bertram et al., 2011; Song et al., 2012; You et al., 2013; You et al., 2014]. Although these experiments were performed at temperatures between 17 and 27°C, the results should still be applicable to the WINTER study (minimum T of  $-21^{\circ}$ C), since liquid-liquid phase separation is not a strong function of temperature for temperatures between -29 and 17°C [Schill and Tolbert, 2013; You and Bertram, 2015]. To assess if conditions are conducive to liquid-liquid phase separation, T, O:C, OA:SO<sub>4</sub><sup>2-</sup> (organic-tosulfate aerosol mass ratio), and nitrate mass loadings are contrasted for the three RH ranges (Table 1). Temperatures are similar with only 2°C difference in the means and so likely not a cause for the  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>) bias at low RH (also shown in Figure S4 in the supporting information). The O:C ratios are generally at the upper end of the range where phase separation can occur. Furthermore, for O:C in the "transition regime" (0.5 < 0.C < 0.8), the case here, if  $OA:SO_4^{2-}$  is larger than unity, phase separations are less likely [Bertram et al., 2011]. All OA:  $SO_4^{2-}$  are on average above unity, suggesting no phase separations, but there is a trend with the smallest ratio (1.36 ± 0.72) coinciding with the 20–40% RH bin, which is where the largest  $\epsilon$ (NO<sub>3</sub><sup>-</sup>) bias is seen. Furthermore, in the O:C transition regime, the possibility of liquid-liquid phase separation increases as RH decreases. Thus, the trends are consistent with increasing likelihood of organic-inorganic phase separations at the lower RH range, but the conditions are not such that phase separation is definitively expected at the lowest RH range, as no clear dependence on O:C is observed in Figures 3c, 3f, and 3i.

Organic-inorganic phase separations may lead to measured  $\varepsilon(NO_3^-)$  (or  $NO_3^-$  concentrations) larger than thermodynamic predictions. For example, during a drying event, an organic semisolid liquid coating formed over the inorganic aqueous phase (or possibly an inorganic solid core) containing the ions might inhibit gasparticle equilibrium, lowering the evaporation of semivolatile  $NO_3^-$ . The pH of the separate phases would also differ. The thermodynamic model predicts pH assuming all ions are only in the inorganic aqueous phase. However, if  $NO_3^-$  is miscible in the organic-rich aqueous phase, and the pH higher than the inorganic aqueous phase, measured bulk aerosol  $NO_3^-$  would be higher than the thermodynamic prediction. Whereas the inorganic phase pH was between -1 and 0 (25th and 75th percentiles), we estimate that an organic-rich phase pH of ~3 would increase  $NO_3^-$  concentrations sufficiently to bring predicted  $\varepsilon(NO_3^-)$ into closer agreement with observed. Higher organic-rich phase pH is possible because of the weaker organic acids compared to sulfuric acid. One of the strongest organic acid, formic acid, has a pKa of 3.75 [*Bacarella et al.*, 1955]. *Bougiatioti et al.* [2016] also found that organic-rich aged biomass burning aerosols sampled in the Eastern Mediterranean had pH levels ~3, consistent with strong nitrate partitioning onto the aerosol.

#### 3.3.2. Uncertainties in Measured Inorganic Nitrate at Low Concentrations

Another factor associated with increasing discrepancies between predicted and measured  $\epsilon$ (NO<sub>3</sub><sup>-</sup>) with lower RH is that total nitrate concentrations were also lowest in this RH range (Table 1 and Figure S5). This can lead to discrepancies in two ways. First, at lower concentrations the measurements have larger relative uncertainties. Second, we have used the AMS data for this analysis since it is more precise than the PILS-IC data, but AMS nitrate may also include some contributions from organonitrates. The relative contribution of organonitrates is likely to be higher when inorganic nitrate concentrations are lower, consistent with higher observed nitrate compared to the model at lower RH. Because the PILS-IC only measures inorganic nitrate, we compared the PILS-AMS nitrate measurements for the three RH ranges. No evidence was found for AMS nitrate being systematically higher at lower RH (Figure S2). An attempt was also made to account for the possibility of interferences in AMS-reported nitrate due to other forms of nitrate or to nitrite. On a flight-by-flight basis, AMS inorganic nitrate (inorgNO<sub>3</sub><sup>-</sup>) was estimated by scaling AMS NO<sub>3</sub><sup>-</sup> to PILS-IC NO<sub>3</sub><sup>-</sup> (see Figure S6 comparing AMS inorgNO<sub>3</sub><sup>-</sup> to AMS NO<sub>3</sub><sup>-</sup>). This type of variable scaling factor resulted in thermodynamic-predicted nitrate for all data on

average 24% higher than observed (Figure S7), whereas for AMS total nitrate the slope was 0.99 (Figure 2e). Comparison between predicted and measured  $NO_3^-$  was also more scattered ( $R^2 = 0.88$  for estimated AMS inorgNO\_3^- versus  $R^2 = 0.96$  for AMS total nitrate). Therefore, in the following analysis, we simply use AMS total  $NO_3^-$  instead of estimated AMS inorgNO\_3^-.

#### 3.3.3. Role of Fine Mode Refractory Cations

If the particles are internally mixed and with uniform composition versus particle size, nonvolatile cations such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> can affect pH. These refractory cations have so far not been considered in the thermodynamic calculations. Including them in ISORROPIA-II does not significantly affect pH until the concentrations become significant relative to the anions. For example, when NaCl is less than 50% of the aerosol ionic molar mass (Na<sup>+</sup>-NH<sub>4</sub><sup>+</sup>-SO<sub>4</sub><sup>2-</sup>-NO<sub>3</sub><sup>-</sup>-Cl<sup>-</sup>), including PILS-fraction collector PM<sub>1</sub> Na<sup>+</sup> and Cl<sup>-</sup> data with AMS  $NH_4^+$ ,  $NO_3^-$ ,  $SO_4^{2-}$  in the ISORROPIA-II analysis does not significantly change the particle pH; the mean change in pH is +0.4 units. Although small, this change in pH can be important for the fraction of total nitrate that partitions to the aerosol if in the pH-sensitive region (discussed below in section 3.6). The general small impact from the nonvolatile Na<sup>+</sup> is because the aerosols were acidic enough so that  $H^+$  is a major ion in the system. However, when the NaCl becomes a significant fraction relative to the total ions (mole fraction > 50%), the pH can dramatically increase (Figure S8). This is observed in the ambient data when there was a dramatic drop in PM<sub>1</sub> sulfate and increase in PM<sub>1</sub> Na<sup>+</sup>, resulting in an aerosol of mainly Na<sup>+</sup>-containing salts, where pH can change from nearzero to above 3. For typical WINTER conditions, a sensitivity analysis shows that this transition occurs at Na<sup>+</sup> greater than  $0.5 \,\mu$ g m<sup>-3</sup>, pH exceeds 2–3, and drives nitric acid partitioning to the aerosol (Figure S9). However, including NaCl causes greater deviation between predicted and measured HNO<sub>3</sub>-NO<sub>3</sub><sup>-</sup> partitioning (Figure S10) suggesting that these other cations are likely not internally mixed with the  $PM_1 NH_4^+$ ,  $NO_3^-$ , and  $SO_4^{2-}$ . Therefore, in the remaining analysis, the reported particle pH is calculated without any refractory ions present. The role of coarse-mode salts is discussed below (section 3.8).

In summary, the overall good agreement between the model and measurements of nitric acid partitioning (HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> regression slopes deviate < 5%, and  $R^2 > 0.9$ ) suggests that when RH is greater than 40%, the assumption of a metastable aerosols (i.e., complete aqueous solution) with no phase separation appears reasonable for the conditions of this study. At lower RH, phase separation may occur and could account for the larger observed discrepancies (e.g., enriched nitrate in the organic phase with higher pH compared to the inorganic phase), although measurement uncertainty, size-cut differences, and/or interferences (e.g., organonitrates and nitrites that are part of AMS nitrate) may also explain some of the differences. PM<sub>1</sub> refractory water-soluble ions (e.g., Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup>) were generally either at too low concentrations or not internally mixed with NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> such that they had little influence on bulk PM<sub>1</sub> pH. Overall, the analysis based on the complete WINTER data shows that the predicted pH is accurate at RH > 40%; similar to what we found in the southeastern U.S. (minimum RH was 36%) [*Guo et al.*, 2015].

#### 3.4. Sample Line Heating Effect

During flight, aircraft cabin temperature was maintained at approximately 20°C. Combined with ram air heating, the temperature of sample air was substantially above ambient before it reached the measurement instrumentation. As a result, sampled air RH decreased, resulting in loss of particle water. Heating and loss of particle water lead to potential evaporation of semivolatile components, such as nitrate and ammonium, which would lead to an incorrect calculation of pH. For WINTER, the ambient *T* was on average  $-3.0 \pm 8.6^{\circ}$ C and the measured PILS sample line *T* was typically ~ 24°C higher. Sample line RH was calculated assuming conservation of water vapor under isobaric heating, a good assumption given the short residence time in the tubing (0.5 s for AMS and 2 s for PILS-IC). Heating of air in the sample line lowered the RH to 23% from an ambient average of 75%.

ISORROPIA-II was run with aerosol and gas-phase species at the sample line *T* and RH and compared to predictions from ambient *T* and RH. Table 2 shows that using sample line *T* and RH at the PILS-IC inlet, the nitric acid partitioning is inconsistent with observations. For example, predicted sample line  $\varepsilon(NO_3^-)$  was  $0.2 \pm 0.3\%$ , indicating that all nitrate was in the gas phase, whereas measured  $\varepsilon(NO_3^-)$  was  $31 \pm 23\%$ , and nitrate concentrations were nonzero  $(1.16 \pm 0.88 \,\mu g \,m^{-3})$ . As noted above, using ambient *T* and RH resulted in good agreement between predicted and measured nitric acid partitioning; therefore, we conclude that repartitioning of volatile inorganics did not substantially affect the measurements and attribute this to the limited residence time within the sample lines. Several studies on mass transfer rates indicate that it takes roughly 15 to 30 min for

	An	nbient	Sample line	
	Measured	Simulated	Measured	Simulated
Number of points	323	323	323	323
Т	4 ± 2°C	N/A	21 ± 1°C	N/A
RH	75 ± 11% <sup>b</sup>	N/A	23 ± 3% <sup>b</sup>	N/A
ε(NO <sub>3</sub> <sup>-</sup> )	31 ± 23% <sup>c</sup>	23 ± 22%	31 ± 23% <sup>c</sup>	$0.2 \pm 0.3\%$
$NO_3^{-}$ (µg m <sup>-3</sup> )	1.16 ± 0.88 <sup>c</sup>	$0.87\pm0.88$	1.16 ± 0.88 <sup>c</sup>	$0.01 \pm 0.02$

**Table 2.** Comparisons Between Measurements of  $PM_1$  Nitrate Concentrations to Thermodynamic Simulations Assuming Ambient Conditions (T, RH) and Conditions in the Sample Line<sup>a</sup>

<sup>a</sup>Only periods when both ambient and sample line data were available, and RH was in the 20–95% range are shown (i.e., data are a subset of the WINTER campaign and not a study average). Aerosol data shown in the table are from AMS measurements, and sample line *T* was measured just upstream of PILS-IC. Saturation water vapor pressures were calculated by equation (21) in *Alduchov and Eskridge* [1996] to estimate sample line RH.

 $^{b}$ RH < 20% was excluded.

<sup>c</sup>Measured by instruments inside the C-130 aircraft.

semivolatile components to reach partitioning equilibrium for particles up to 1  $\mu$ m [*Dassios and Pandis*, 1999; *Cruz et al.*, 2000; *Fountoukis et al.*, 2009], which is over 2 orders of magnitude longer than the estimated sampling line residence times of the aerosol instrumentation of this study (0.5–2 s). Note that for a 2 s residence time, an upper limit volatilization loss of ~35% NH<sub>4</sub>NO<sub>3</sub> was estimated with a thermokinetic model for diluted aircraft ambient sample [*Shingler et al.*, 2016]. Since a sheath flow lacking gas-phase HNO<sub>3</sub> causes more NO<sub>3</sub><sup>--</sup> evaporation, these results are not directly applicable to the nondiluted AMS and PILS-IC measurement techniques used in this study. In the following analysis, we ignore any possible artifacts due to changes in aerosol during sampling and use ambient conditions in the thermodynamic calculations.

#### 3.5. pH Geographical and Vertical Distribution

Research flights were conducted mainly in the northeastern U.S., with some flights extending into the southeast (Figure 4). Bulk PM<sub>1</sub> pH was low, with a campaign average of 0.77  $\pm$  0.96 (median of 0.91; 10th percentile of -0.51; 90th percentile of 1.9). Figure 4 shows the geographical distribution of particle pH, particle nitrate, and  $\epsilon$ (NO<sub>3</sub><sup>-</sup>). No clear systematic spatial distribution is observed in any of these parameters. Higher-nitrate plumes, however, were usually observed simultaneously with higher  $\epsilon$ (NO<sub>3</sub><sup>-</sup>), which were recorded in regions of higher particle pH, as expected.

The pH vertical distribution is shown in Figure 5. Most measurements were below 2 km since WINTER focused on the lower atmosphere. The data points above 2 km are more scattered and uncertain due to low-aerosol mass loading. Despite this, as with the geographical distribution, there is no obvious gradient in pH from about 1 to 5 km altitude, but the pH exhibited a broad variation and ranged between -1 and 2 (Figure 5a). 500 m altitude-binned statistics show a uniform pH range of -0.5 to 2 below 3 km and a slightly lower pH range of



**Figure 4.** WINTER all flight geographical distributions of PM<sub>1</sub> particle (a) pH, (b) PILS-IC NO<sub>3</sub><sup>-</sup>, and (c)  $\epsilon$ (NO<sub>3</sub><sup>-</sup>). The particle pH plotted is calculated based on aerosol phase inputs of PILS-IC anions and scaled AMS NH<sub>4</sub><sup>+</sup>.



**Figure 5.** pH as a function of altitude above ground: (a) colored by the nitrate concentration for all WINTER data; (b) 500 mbinned mean and median, and 10th and 90th percentiles. The particle pH plotted is calculated based on aerosol phase inputs of AMS.

-1 to 0.5 above 3 km (Figure 5b). Very little PM<sub>1</sub> nitrate aerosol was observed aloft. Below 1 km altitude, there was a somewhat similar range in pH as aloft, but a wide range in PM<sub>1</sub> nitrate (0–8 µg m<sup>-3</sup>), with notably higher nitrate measured at higher predicted pH. To understand this observed nitrate variability, interactions between nitrate and pH are explored.

#### 3.6. Nitrate Dependency on pH, W<sub>i</sub>, and T

To study factors affecting nitric acid partitioning, and to test the validity of the thermodynamic model, we first investigate a simpler analytical prediction of  $\varepsilon(NO_3^-)$  and compare to measurements and ISORROPIA-II predictions. Equilibrium between HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> can be simplified as

$$HNO_{3(q)} \leftrightarrow NO_3^- + H^+, \ H^*_{HNO_3}$$
<sup>(2)</sup>

where  $H_{HNO_3}^*$  (mole<sup>2</sup> kg<sup>-2</sup> atm<sup>-1</sup>) is the equilibrium constant and is equal to the "conventional" Henry's law constant multiplied by the dissociation constant of nitric acid ( $K_{n1}$ ) [*Clegg and Brimblecombe*, 1990].  $\epsilon$ (NO<sub>3</sub><sup>-1</sup>) can be directly calculated by equation (3):

$$\varepsilon(NO_3^{-}) = \frac{H_{HNO_3}^* RTW_i \times 0.987 \times 10^{-14}}{\gamma_{H^+} \gamma_{NO_3^{-}} H_{aq}^+ + H_{HNO_3}^* RTW_i \times 0.987 \times 10^{-14}}$$
(3)



**Figure 6.** Simulated  $\varepsilon(NO_3^-)$  at  $-20^\circ$ C,  $0^\circ$ C,  $20^\circ$ C, and various particle liquid water levels (1.25, 2.5, 5, and  $10 \,\mu$ g m<sup>-3</sup>) assuming ideal solutions. The WINTER average  $W_i$  was 2.6  $\mu$ g m<sup>-3</sup>; 1.25 and  $10 \,\mu$ g m<sup>-3</sup> are approximately 50% and 400% of the average  $W_i$  levels, respectively. WINTER average temperature was  $-0.4^\circ$ C.

Note that this is similar to the equation (6) in Meskhidze et al. [2003] but includes activity coefficients to account for solution nonideality, and assuming that  $\left(\frac{\gamma_{H^+}\gamma_{NO_3^-}}{\gamma_{HNO_3}}\left[H_{aq}^+\right] + K_{n1}\right) \approx K_{n1}$  where  $\gamma_{\rm HNO_3}$  is the activity coefficient of protonated HNO<sub>3</sub> in the aqueous phase. This equation, plotted in Figure 6 (activity coefficients are assumed equal to 1) for varying temperatures and particle water concentrations, illustrates the relationship between nitric acid partitioning and pH. From Figure 6 it can be seen that for a given  $W_i$  and T, it takes about 4 pH units to go from complete gas-phase to particle-phase partitioning. Dropping T by 20°C shifts the partitioning fraction curve roughly



**Figure 7.** The measured  $\epsilon(NO_3^{-})$  versus predicted pH colored by ambient *T* for all WINTER data (AMS PM<sub>1</sub> data). Data are restricted to particle liquid water content (*W<sub>i</sub>*), predicted by ISORROPIA-II from inorganic aerosol levels, in the range of 1.5 to 5  $\mu$ g m<sup>-3</sup>.

1 pH unit lower, which can result in a considerable shift in nitric acid to the particle phase, if pH and  $W_i$  are constant. Likewise, more nitrate aerosol formation also occurs with increased  $W_i$ ; a factor of 10 increase in  $W_i$  also shifts  $\varepsilon$ (NO<sub>3</sub><sup>--</sup>) to lower pH by approximately one unit. The dependence of nitric acid partitioning on *T* is directly related to the equilibrium constant,  $H^*_{HNO_3}$  which increases by 700% from 20°C to 0°C; the increase is mainly due to changes in the Henry's law constant, thus the vapor pressure of HNO<sub>3</sub>.

WINTER data show evidence for a similar temperature effect on nitric acid partitioning. In Figure 7 measured  $\varepsilon(NO_3^-)$  is plotted versus particle pH, for data over a relatively narrow  $W_i$  range ( $1.5 < W_i < 5 \ \mu g \ m^{-3}$ ). For a given pH between 0 and 2, higher  $\varepsilon(NO_3^-)$  was observed at a lower ambient *T*. There are differences

between the measured  $\varepsilon(NO_3^-)$  of Figure 7 and the analytical prediction of Figure 6. The S curve in Figure 6 tends to shift 1 pH unit higher compared to the observed data (Figure 7) and is due to the ideal solution assumption (unity activity coefficients), whereas ISORROPIA-II calculates multicomponent activity coefficients [*Fountoukis and Nenes*, 2007]. Given that the WINTER mean particle ionic strength was as high as 38 mole L<sup>-1</sup> (based on PILS-IC anions and scaled AMS NH<sub>4</sub><sup>+</sup>), the ideal solution assumption was invalid. ISORROPIA-II predicts that the mean activity coefficient of the  $H^+ - NO_3^-$  ion pair,  $\gamma_{H^+-NO_3^-} = 0.23$ . Given that,  $\gamma_{H^+-NO_3^-} = \sqrt{\gamma_{H^+}\gamma_{NO_3^-}}$ , we have  $\gamma_{H^+}\gamma_{NO_3^-} = 0.06$  [*Meissner and Tester*, 1972; *Pitzer and Mayorga*, 1973; *Meier*, 1982; *Nenes et al.*, 1998]. Introducing this information in equation (3) shifts the  $\varepsilon(NO_3^-)$  curves to lower pH by 1.2 units, much closer to ISORROPIA-II predicted  $\varepsilon(NO_3^-)$ . Although Figure 6 is somewhat inaccurate at identifying the exact pH at which nitric acids shifts between gas and particle phases, it provides the ideal conceptual framework for understanding how semivolatile partitioning is affected by pH, *T*, and RH.

The influence of particle water on nitric acid partitioning is also evident. Figure 8 shows measured AMS  $NO_3^-$  (PILS  $NO_3^-$  shows a similar result but with more scatter) versus particle pH for all WINTER flight data, segregated by predicted  $W_i$ . The figure shows that  $NO_3^-$  concentrations are affected by pH and  $W_i$ ; the latter controls much of the pH variability. These results are consistent with expectations. For example, in Figure 8, at a constant pH, more  $NO_3^-$  is measured at higher  $W_i$ ; whereas at a constant  $W_i$ , more  $NO_3^-$  is measured at higher pH.  $W_i$  depends primarily on RH and the hygroscopic aerosol mass, which in this case mainly consists of ( $NH_4$ )<sub>2</sub>SO<sub>4</sub>,  $NH_4$ HSO<sub>4</sub>, and  $NH_4NO_3$  (i.e., not considering organic aerosol contributions). Nonlinear relationships are observed between  $NO_3^-$  and pH because  $NO_3^-$  constitutes part of the aerosol mass and is highly hygroscopic



**Figure 8.** Measured nitrate versus predicted pH for all WINTER data segregated by predicted inorganic liquid water content ( $W_i$ ) in the ranges of 0–2, 3–4, and >6 µg m<sup>-3</sup>. ISORROPIA-II using AMS data is shown, excluding NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and HNO<sub>3</sub> concentrations that were within 2 × LOD.



**Figure 9.** (a) Predicted  $W_i$  versus AMS sulfate plus nitrate concentrations. Color scale shows RH dependence. (b) Measured NO<sub>3</sub><sup>-/2</sup>SO<sub>4</sub><sup>2-</sup> ratio (mole mole<sup>-1</sup>) versus predicted pH based on AMS data. NO<sub>3</sub><sup>-</sup> or SO<sub>4</sub><sup>2-</sup> dominant zone denotes NO<sub>3</sub><sup>-/2</sup>SO<sub>4</sub><sup>2-</sup> > 1 or < 1. For both plots the complete WINTER data are shown.

[Fountoukis and Nenes, 2007].  $SO_4^{2-}$  is the other major anion with high hygroscopicity in WINTER PM<sub>1</sub>. Since  $W_i$  is predicted by ISORROPIA-II from the inorganic species mass concentrations, one would expect it to be proportional to particle inorganic anion mass ( $NO_3^- + SO_4^{2-}$ ) and RH (mass loadings of the other AMS-measured anion, 0.02 µg m<sup>-3</sup> Cl<sup>-</sup>, were too small to affect  $W_i$ ). Figure 9a shows that at a given RH,  $W_i$  is nearly linearly related to the sum of nitrate and sulfate mass. (A similar graph plotted with the AMS-measured total ions is shown in Figure S11.)

To simplify the relationship between NO<sub>3</sub><sup>-</sup> and pH, which is affected by  $W_i$  (Figure 8), the NO<sub>3</sub><sup>-</sup>/2SO<sub>4</sub><sup>2-</sup> ratio (mole mole<sup>-1</sup>) is plotted against pH (Figure 9b). From this figure it can be seen that when aerosol anionic composition was dominated by nitrate (NO<sub>3</sub><sup>-</sup>/2SO<sub>4</sub><sup>2-</sup> > 1), particle pH was generally above 1, whereas when dominated by sulfate (NO<sub>3</sub><sup>-</sup>/2SO<sub>4</sub><sup>2-</sup> < 1), particle pH was below 2 and could reach as low as -1.5. The relationship between NO<sub>3</sub><sup>-</sup>/2SO<sub>4</sub><sup>2-</sup> versus pH can be explained by the analytical prediction of  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>) given in equation (4). Neglecting nonideality,

$$NO_{3}^{-}/2 SO_{4}^{2-} = \frac{NO_{3, total}}{2 SO_{4}^{2-}} \varepsilon \left(NO_{3}^{-}\right) = \frac{NO_{3, total}}{2 SO_{4}^{2-}} \frac{1}{kH_{aq}^{+} + 1}$$
(4)

where NO<sub>3, total</sub> is the sum of NO<sub>3</sub><sup>-</sup> and HNO<sub>3</sub> (mole m<sup>-3</sup>) and *k* represents  $1/(H_{HNO_3}^* RTW_i \times 0.987 \times 10^{-14})$ . At low pH ( $H_{aq}^+$  high),  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>) is close to zero and NO<sub>3</sub><sup>-</sup>/2SO<sub>4</sub><sup>2-</sup> is very small (i.e., very little nitrate aerosol). At sufficiently high pH ( $H_{aq}^+$  low),  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>) approaches unity; thus, NO<sub>3</sub><sup>-</sup>/2SO<sub>4</sub><sup>2-</sup> is no longer a function of  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>) and is simply equal to  $\frac{NO_3 \cdot total}{2SO_4^{2-}}$  (in this case, NO<sub>3</sub>,  $total \cong NO_3^-$ ). This explains why the NO<sub>3</sub><sup>-</sup>/2SO<sub>4</sub><sup>2-</sup> increases dramatically at higher-pH levels and is expected to asymptotically increase with increasing pH. When  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>) is 1 (i.e., no HNO<sub>3</sub>), it lacks any dependence on pH (equation (4)). At intermediate pH, the NO<sub>3</sub><sup>-</sup>/2SO<sub>4</sub><sup>2-</sup> is driven by both  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>) and  $\frac{NO_3 \cdot total}{2SO_4^{2-}}$ . Since NO<sub>3</sub><sup>-</sup>/2SO<sub>4</sub><sup>2-</sup> is not only driven by pH but also the total amount of nitrate (related to the sources and sinks of HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup>), it is not a very accurate pH proxy (another pH proxy, ion equivalence ratio, will be discussed in section 3.9).

#### 3.7. Low- Versus High-Nitrate Case Studies

Flights 6 and 8 were selected to contrast cases of low nitrate (Flight 6 mean:  $0.15 \pm 0.32 \,\mu g \,m^{-3}$ ) versus highnitrate loadings (Flight 8 mean:  $0.88 \pm 0.82 \,\mu g \,m^{-3}$ ), illustrating the relationships between NO<sub>3</sub><sup>-</sup>, HNO<sub>3</sub>, SO<sub>4</sub><sup>2-</sup>, *W<sub>i</sub>*, *T*, and pH. Flights 6 and 8 covered similar geographical regions of coastal New York, New Jersey, and Delaware (Figure 10). Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) back trajectories suggest that Flight 8 measured outflow from the greater New York City metropolitan area, at some distance off-shore, and Flight 6 encountered outflow from a wider eastern coastal area. Back trajectory plots are shown in the supplementary material (Figure S12).

The time series of measured inorganic species, predicted pH,  $W_{i_r}$  and T are shown in Figure 11. Although plumes of high total nitrate (HNO<sub>3</sub> + NO<sub>3</sub><sup>-</sup>) were intercepted on Flight 6 (flight mean:  $7.1 \pm 3.2 \,\mu g \,m^{-3}$ ), observed NO<sub>3</sub><sup>-</sup> concentrations were low, but HNO<sub>3</sub> concentrations were high (flight mean:  $6.9 \pm 3.0 \,\mu g \,m^{-3}$ ), with measured  $\epsilon$ (NO<sub>3</sub><sup>-</sup>) only  $2 \pm 3\%$ . In contrast, for Flight 8, plumes of high total nitrate were again observed



Figure 10. pH geographical distributions for Flights (a) 6 and (b) 8.

(yellow shaded regions in Figure 11b), but in this case significant concentrations of NO<sub>3</sub><sup>-</sup> were also measured, and  $\epsilon$ (NO<sub>3</sub><sup>-</sup>) varied between 20% and 60%. These differences can be attributed to pH and temperature. In Flight 6, pH was nearly 2 units on average lower ( $-0.2 \pm 0.5$ ) than within plumes of Flight 8 ( $1.5 \pm 0.4$ ). Temperature also played a role. Flight 8 was on average 9°C colder than Flight 6. Thus, the combination of higher pH and lower *T* resulted in substantially more HNO<sub>3</sub> partitioning into the particle-phase during Flight 8.

Note in Figure 11b that the NO<sub>3</sub><sup>-</sup>,  $W_i$  and pH all peaked in the plumes of Flight 8. The cause for these peaks demonstrates the interrelationships between these parameters. Nitrate is highly hygroscopic, so when more HNO<sub>3</sub> partitions to the particle-phase due to high pH, the particle can take up more water (note that RH did not significantly change), this dilutes  $H^+$ , raises the pH, and further enhances HNO<sub>3</sub> to NO<sub>3</sub><sup>-</sup> partitioning. The interactions between NO<sub>3</sub><sup>-</sup>,  $W_i$ , and pH are complex and nonlinear. In the case of Flight 6, the high sulfate



**Figure 11.** WINTER Flights (a) 6 and (b) 8 time series of altitude, measured  $NO_3^-$ ,  $HNO_3$ ,  $\varepsilon(NO_3^-)$ ,  $SO_4^{2-}$ , RH, *T*, and  $NH_4^+/(NO_3^- + 2SO_4^{2-})$  ratio (mole mole<sup>-1</sup>) and predicted *W<sub>i</sub>*, pH. For both plots PILS-IC anions and scaled AMS  $NH_4^+$  were used for the pH calculations. The yellow shaded area in Figure 11b illustrates four high-nitrate plumes.

concentrations led to higher predicted  $W_i$  (Flight 6  $W_i$  = 4.1 ± 2.6 µg m<sup>-3</sup>; Flight 8:  $W_i$  = 0.8 ± 0.7 µg m<sup>-3</sup>), which could potentially raise pH and allow more HNO<sub>3</sub> dissolution; however, this effect did not compensate for the higher  $H^+$  contributed by sulfate, which prevented nitrate aerosol formation.

#### 3.8. Nitric Acid and Coarse Mode Cations

Overall, good agreement has been found between ISORROPIA-II predictions and observations, indicating that PM<sub>1</sub> nitrate was in thermodynamic equilibrium. However, during the study there were at times significant amounts of coarse-mode ions (Na<sup>+</sup>, Cl<sup>-</sup>, etc.), as well as  $NO_3^{-}$ . Here coarse mode refers to particles with aerodynamic diameters between 1 and nominally 4 µm; the difference between the filter (PM<sub>4</sub>) and PILS or AMS  $(PM_1)$  measurements. For the entire WINTER campaign, the  $PM_1/PM_4$  ratios were on average ± SD: (AMS)  $NO_3^{-}82 \pm 83\%$ ,  $SO_4^{2-}79 \pm 26\%$ ,  $CI^{-}13 \pm 36\%$ , and  $NH_4^{+}71 \pm 52\%$ . Other PM<sub>4</sub> ions were also nonnegligible;  $Na^{+} = 0.50 \pm 0.88 \ \mu g \ m^{-3}$ ,  $Cl^{-} = 0.69 \pm 1.60 \ \mu g \ m^{-3}$ ,  $K^{+} = 0.03 \pm 0.05 \ \mu g \ m^{-3}$ ,  $Ca^{2+} = 0.12 \pm 0.12 \ \mu g \ m^{-3}$ , and  $Mg^{2+} = 0.07 \pm 0.11 \,\mu g \,m^{-3}$ . Not surprisingly, sodium and chlorine were the highest since many flights were made over or near coastal regions. The PM<sub>4</sub> Cl<sup>-</sup>/Na<sup>+</sup> molar ratio was 0.7  $\pm$  0.6, indicating that some fraction of the Na<sup>+</sup> had likely combined with acidic species (i.e.,  $SO_4^{2-}$  and  $NO_3^{-}$ ) resulting in depleted Cl<sup>-</sup> [Gard et al., 1998]. Flight 6 provides an example for comparing equilibrium predictions for fine and coarse modes. During Flight 6, the coarse-mode  $NO_3^{-1}$  fraction,  $(PM_4 - PM_1)/PM_4$ , was  $76 \pm 18\%$ , more than 4 times that of the campaign average (18  $\pm$  17%) and higher than the coarse-mode SO<sub>4</sub><sup>2-</sup> and NH<sub>4</sub><sup>+</sup> fractions, 14  $\pm$  19% and  $48 \pm 21\%$ , respectively. A time series of PM<sub>1</sub>, filter PM<sub>4</sub>, and coarse-mode NO<sub>3</sub><sup>-</sup> fraction are shown in Figure S13 in the supporting information. To contrast a thermodynamic analysis on the fine-mode versus coarse-mode ions of Flight 6, we assume internal mixtures within each of the modes and that all the following ions were exclusively in the coarse mode: Na<sup>+</sup>, Cl<sup>-</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup>. For the coarse mode there is largely disagreement between measured and predicted  $\epsilon(NO_3^-)$ ; more than half predicted  $\epsilon(NO_3^-)$  is nearly 100%, whereas observed  $\epsilon$ (NO<sub>3</sub><sup>-</sup>) was between 0 and 20% (Figure S14). In contrast, ISORROPIA-predicted  $\epsilon$ (NO<sub>3</sub><sup>-</sup>) agreed fairly well with predictions for equilibrium with the fine mode (predicted versus measured  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>) regression, y = 0.64x - 0.01, and  $R^2 = 0.90$ ), considering the low  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>) range (all below 20%). In such cases, a small overestimation in HNO<sub>3</sub> leads to amplified underestimation of NO<sub>3</sub><sup>-</sup>, and it is more difficult for the model to accurately predict the smaller mass species (predicted versus measured HNO<sub>3</sub> regression, y = 1.04x - 0.12, and  $R^2 = 1.00$ , and versus NO<sub>3</sub><sup>-</sup> regression, y = 0.63x - 0.06, and  $R^2 = 0.92$ ). The above finemode versus coarse-mode results can be explained by the fine mode reaching equilibrium but not the coarse mode as the latter process is kinetically limited [Dassios and Pandis, 1999; Cruz et al., 2000; Fountoukis et al., 2009]. Both modes compete for nitric acid. In this type of situation, over an extended period of time, the semivolatile fine-mode ammonium nitrate and gas-phase nitric acid will be depleted, impacting fine-mode pH, and accumulate in the coarse mode in a nonvolatile form, such as sodium nitrate or calcium nitrate. However, because this process is slow, fine-mode nitrate can persist and be accurately predicted by assuming thermodynamic equilibrium.

#### 3.9. Ion Equivalence Ratios and Particle pH

Since running a thermodynamic model to predict pH is not necessarily straightforward, other proxies for particle acidity, based directly on measurement data, are often used instead. This includes ion balances,  $NH_4^+$  to  $SO_4^{2-}$  molar ratios, or cation to anion equivalence ratios. We have noted that this can lead to incorrect conclusions about particle pH and its effects, such as formation of nitrate [*Guo et al.*, 2015; *Hennigan et al.*, 2015; *Weber et al.*, 2016]. Given that the thermodynamic calculations for PM<sub>1</sub> were based solely on  $NH_4^+$ ,  $NO_3^-$ , and  $SO_4^{2-}$  and accurately predicted the partitioning concentrations of HNO<sub>3</sub> and  $NO_3^-$ , we compare the  $NH_4^+/(NO_3^- + 2SO_4^{2-})$  equivalence ratio (mole mole<sup>-1</sup>) with the model-predicted pH to assess the utility of this commonly used pH proxy. In Figure 11, time series of the equivalence ratio and pH are plotted for the two case studies, and a direct comparison of the data is shown in Figure 12a. These plots illustrate that although they may appear to track at times in Figure 11, there is not a simple unique relationship between the ratios and pH (Figure 12a). This is also true for the complete WINTER data set, Figure 12b, which shows the equivalence ratio versus pH for all WINTER data (40–95% RH). An equivalence ratio of unity is interpreted as a fully neutralized aerosol, while smaller ratios reflect a higher particle acidity. For this data set, although the ratio shows a general increasing trend with pH, it provides little overall insight on pH. Considering data for pH greater than approximately 1 (the flatter anvil region of the data points); pH can range from approximately 1 to 3,



**Figure 12.** Measured  $NH_4^+/(NO_3^- + 2SO_4^{2-})$  ratio (mole mole<sup>-1</sup>) versus pH for (a) Flight 6 (entire flight) and Flight 8 plumes ( $NO_3^- > 0.5 \,\mu\text{g m}^{-3}$ ) and (b) for the entire WINTER data set. AMS data are used in the two plots.

whereas  $NH_4^+/(NO_3^- + 2SO_4^{2^-})$  always remained near 1, which would be interpreted as a neutral aerosol. For the other cluster of points, the opposite occurs, equivalence ratios span a range from approximately 0.8 to near 0, while pH remains between -1 and 1 indicating that the aerosol is highly acidic at all times. There is a moderate correlation between the equivalence ratio and pH in this range,  $R^2 = 0.32$ , but with near-vertical slope there is little predictive capability. Furthermore, it is often assumed that nitric acid partitions to the particle to form  $NO_3^-$  only after the molar ratios reach 1. Figure 12b shows an increasing trend with  $NO_3^-$  mass concentration, but significant  $NO_3^-$  is found at ratios less than 1, and a lack of sensitivity inhibits accurate  $NO_3^-$  prediction in the flatter anvil region (equivalence ratio > 0.8). These results demonstrate that these forms of particle acidity proxies should be employed with great care when used to infer particle pH and its impacts.

#### 4. Conclusions

Fine particle pH and the partitioning of  $HNO_3$  are characterized over a large geographical region and for altitudes up to 5 km based on an aircraft campaign conducted from 1 February to 15 March 2015 mainly in the northeastern U.S. PM<sub>1</sub> pH was predicted from the thermodynamic model ISORROPIA-II based on a data set spanning a wide range of ambient conditions. The following results were found:

- Although there were differences of up to 50% between instruments measuring inorganic aerosol concentrations, this had a minor effect on overall predicted PM<sub>1</sub> average pH. Generally, systematic errors for all measured ionic species do not have a large effect on predicted pH, although corrections that affect single components do adversely affect predicted pH. This means that thermodynamic calculations can provide an additional constraint for evaluating the consistency of data sets.
- 2. Considering only the PM<sub>1</sub> NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, ISORROPIA-II accurately predicted the partitioning of HNO<sub>3</sub>-NO<sub>3</sub><sup>-</sup> (HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup> regression slopes deviate < 5%, and R<sup>2</sup> > 0.9) over a broad range of RH (40 to 95%), *T* (-21 to 19°C), and component concentrations (1 min average: HNO<sub>3</sub>, 0.05 to 12  $\mu$ gm<sup>-3</sup>; SO<sub>4</sub><sup>2-</sup>, 0.02 to 11  $\mu$ g m<sup>-3</sup>; NO<sub>3</sub><sup>-</sup>, 0.07 to 7.8  $\mu$ g m<sup>-3</sup>; and NH<sub>4</sub><sup>+</sup>, 0.01 to 3.3  $\mu$ gm<sup>-3</sup>). Best agreement was observed at higher RH (60 to 95%), reasonable agreement was found in the 40 to 60% RH range, and significant discrepancies were observed for RH under 40%. The lowest RH range was also associated with the lowest HNO<sub>3</sub>, NO<sub>3</sub><sup>-</sup>, and liquid water content. Discrepancies between observed and measured  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>) could be due to uncertainty in measured species at low concentrations, such as inclusion of organic acids in AMS-measured nitrate, division by small numbers when calculating  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>), and organic-inorganic phase separations. No clear evidence that any effect single affect dominated the discrepancy was found.
- 3. Substantial sample heating in the aircraft aerosol sample line did not appear to produce artifacts because the residence times (0.5–2 s) in sample lines were insufficient to allow alteration of semivolatile aerosol components. This finding is applicable to other aircraft or ground measurements.
- 4.  $PM_1$  aerosol is highly acidic; for altitudes up to 5000 m pH ranged between -0.51 and 1.9 (10th and 90th percentiles) with a study mean of  $0.77 \pm 0.96$ . The pH range is similar to those reported for the

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southeastern U.S. (0.5 to 2 in summer; 1 to 3 in winter) [*Guo et al.*, 2015] and northern Colorado U.S. (2 to 3 in winter) [*Young et al.*, 2013]. These pHs are also similar to those reported in the Mediterranean, which ranged between 0.5 to 2.8 (highest pH was found in biomass burning plumes, which were not investigated here) [*Bougiatioti et al.*, 2016].

- 5. Factors that affect  $\epsilon(NO_3^{-})$  were investigated with ideal solution analytical calculations. A major factor was pH;  $\epsilon(NO_3^{-})$  was sensitive to pH in the range of approximately -1 (all residing in the gas phase) to 3 (all residing in the particle phase). As expected, increases in partitioning to the particle phase were observed at lower temperatures and higher particle liquid water concentrations. Lower temperatures shift the pH at which the transition occurs to lower values allowing  $NO_3^{-}$  at lower pH. High liquid water contents dilute H<sup>+</sup> and raise the pH. These factors are interrelated in complex ways and can only be captured and resolved with a thermodynamic model.
- 6. PM<sub>1</sub> ions other than NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, such as Na<sup>+</sup> and Cl<sup>-</sup>, did not change the predicted pH if included in the thermodynamic calculations (assumed to be internally mixed), for NaCl mole fractions (relative to all input aerosol ions) below 50%. Note that the subtle pH variation (<0.4 units) can be important for HNO<sub>3</sub>-NO<sub>3</sub><sup>-</sup> partitioning when  $\varepsilon$ (NO<sub>3</sub><sup>-</sup>) is close to 50%. At higher NaCl mole fractions (which were rare), pH was substantially increased. However, Na<sup>+</sup> and Cl<sup>-</sup> appear not to be completely internally mixed with NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>, since larger deviation between predicted and measured HNO<sub>3</sub>-NO<sub>3</sub><sup>-</sup> partitioning is introduced.
- Occasionally, coarse-mode (PM<sub>4</sub> PM<sub>1</sub>) cations and nitrate were found to be abundant. Large discrepancies between observed and predicted HNO<sub>3</sub> and coarse-mode NO<sub>3</sub><sup>-</sup> indicate a lack of thermodynamic equilibrium due to kinetic limitations. However, HNO<sub>3</sub> and PM<sub>1</sub> NO<sub>3</sub><sup>-</sup> partitioning was accurately predicted, indicating equilibrium.
- 8. Traditional pH proxies, such as  $NH_4^+/(NO_3^- + 2SO_4^{2^-})$  equivalence ratios, were not uniquely related to pH and  $NO_3^-$ , implying that their utility for predicting impacts of particle acidity on aerosol processes or properties is suspect. The  $NO_3^-/2SO_4^{2^-}$  ratio was more closely related to particle pH in this study but lost sensitivity to pH when relatively low  $NO_3^-/2SO_4^{2^-}$  ratios were present (e.g., 0.3). The same ratio is also sensitive to emissions of  $HNO_3$ , so a universally applicable correlation may not be possible.
- 9. Particle pH should be explicitly determined to accurately assess its effects on aerosol mass, atmospheric processes, and other health and environmental impacts, including the partitioning of nitric acid between the gas and particle phases and sensitivities thereof to errors.

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