We greatly value the careful reading and the detailed comments provided by the referees. The responses to the comments of the referees in our direct reply (shown below) and within the revised manuscript (see marked copy) are provided. The pages and lines indicated below correspond to those in the marked copy.

Response to Referee 1 (Referees' comments are italicized)

1. Referee comment: "*These observational data sets should be very useful for the researchers who are interested in the topic of aerosol acidity and organic acid partitioning (especially there are several observations still without reasonable explanations, such as the partitioning of formic and acetic acids). Thus, if possible, I suggest these valuable observational data can be made available/accessible to the research community. In fact, the journal says that "Authors are required to provide a statement on how their underlying research data can be accessed. This must be placed as the section "Data availability" at the end of the manuscript before the acknowledgements. Please see the manuscript composition for the correct sequence. If the data are not publicly accessible, a detailed explanation of why this is the case is required. The best way to provide access to data is by depositing them (as well as related metadata) in reliable public data repositories, assigning digital object identifiers, and properly citing data sets as individual contributions.*"

Author response: The data is made available upon request:

Page 27 line 841: "Data can be accessed by request (rweber@eas.gatech.edu)."

2. Referee comment: "*Section 2.2, Lines 262-263: the unit of Haq+ should be mole kg-1 and, given the Equation 1, the pH definition is based on molality rather than molarity.*"

Author response: The referee is correct in stating that the pH definition is based on molality rather than molarity, as recommended by IUPAC. However, most thermodynamic equilibrium models (e.g., ISORROPIA-II, E-AIM) report species in terms of concentration per volume of air (e.g., µg m^{-3}, µmol m^{-3}). In addition, the particle pH can be calculated in terms of molarity, using the concentrations of species expressed in terms of molarity (mol L^{-1}) and concentrations per volume of air (e.g., µg m^{-3}) as shown in previous studies. To remove any confusion, the following changes have been made to the manuscript:

Page 9 line 276: "The pH of an aqueous solution is defined as the negative logarithm of the hydronium ion (H_3O^+) activity on a molality basis (www.goldbook.iupac.org/html/P/P04524.html, last access: 6 July 2018):

$$pH = -\log_{10}[a(H^+)] = -\log_{10}[m(H^+)\gamma_m(H^+)/m^\theta] \qquad (1a)$$

where $a(H^+)$ is the hydronium ion activity in an aqueous solution, $m(H^+)$ is the hydronium ion molality, $\gamma_m(H^+)$ is the molality-based hydronium ion activity coefficient, and m^θ is the standard molality (1 mol kg^{-1}). For simplicity, H_3O^+ is denoted here as H^+ even though we recognize that the unhydrated hydrogen ion is rare in aqueous solutions. Since most thermodynamic equilibrium models (e.g., ISORROPIA-II, E-AIM) report species in terms of concentration per volume of air (e.g., µg m^{-3}, µmol m^{-3}), the particle pH can be calculated as:

$$pH = -\log_{10}\gamma_{H^+}H^+_{aq} = -\log_{10}\frac{1000\gamma_{H^+}H^+_{air}}{W_i + W_o} \cong -\log_{10}\frac{1000\gamma_{H^+}H^+_{air}}{W_i} \qquad \text{(1b)}$$

where γ_{H^+} is the molarity-based hydronium ion activity coefficient (assumed to be 1), H^+_{aq} (mole L^{-1}) is the molar concentration of hydronium ions in particle water (i.e., pH is calculated in terms of molarity), H^+_{air} (µg m^{-3}) is the hydronium ion concentration per volume of air, and W_i and W_o (µg m^{-3}) are the bulk particle water concentrations associated with inorganic and organic species per volume of air, respectively. In equation 1b, the molecular weight of H^+ is taken as 1 g $mole^{-1}$, and 1000 is the factor needed for unit conversion of g L^{-1} to µg m^{-3}."

3. Referee comment: "*Section 3.3, Lines 424-425: it is mentioned that "diurnal variation in particle pH is driven by Wi". Can the authors provide a quantitative analysis to show the relationship in the pH and Wi diurnal variations? I feel the Wi may not be the dominant factor that affects the diurnal variation of pH.*"

Author response: The referee is correct in stating that W_i is not the dominant factor that affects the diurnal variation of particle pH. Further analysis of the diurnal profiles of W_i and H^+_{air} reveals that their maximum/minimum ratios are comparable (6.5 and 5.3, respectively). This indicates that the diurnal variation of particle is driven by both W_i and H^+_{air}. This information has been added to the revised manuscript:

Page 15 line 475: "PM_1 pH varied by approximately 1.4 units throughout the day. W_i has an average value of 1.6 ± 1.7 µg m^{-3}. PM_1 W_i and pH showed similar diurnal profiles, with both peaking in the mid-morning and reaching their minima in the mid-afternoon. These diurnal trends are consistent with those previously reported by Guo et al. (2015) for PM_1 measured during the summer and winter in different parts of the southeastern U.S. Also shown in Fig. 3b is the diurnal profile of H^+_{air}, which peaked in the mid-afternoon. The W_i and H^+_{air} maximum/minimum ratios are comparable (6.5 and 5.3, respectively), thus indicating that the diurnal variation in particle pH is driven by both W_i and H^+_{air}."

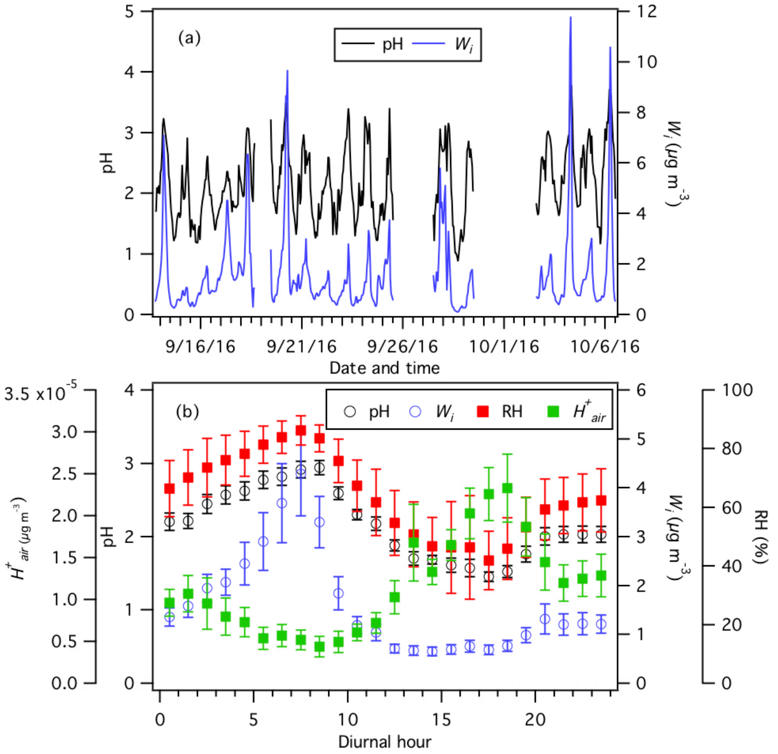

Figure 3: (a) Time series and (b) diurnal profiles of ISORROPIA-predicted PM_1 pH and W_i. The diurnal profiles of RH and ISORROPIA-predicted H^+_{air} are also shown in panel (b). Dates and times displayed are local time. All the data shown here represent averages in 1-hour intervals. Error bars shown in panel (b) are the standard errors.

4. Referee comment: "*Section 3.3, Lines 429-439: the average pH of this study is 2.2, which is 0.3 pH unit higher than PM1 pH in CalNex. The NH3 level in this study is four times compared to CalNex. A 0.6 pH unit difference is expected from the relationship of 1 pH unit increase ~ 10 times increase in NH3. This manuscript attributes this 0.3 unit difference to much higher levels of sulfate and nitrate in CalNex. I think this statement is not well justified since the ambient temperature and RH in these two campaigns are also different. I suggest to provide a more thorough analysis on this pH difference or remove these sentences from the manuscript.*"

Author response: The referee is correct in stating that meteorological differences, specifically ambient RH and temperature, in this study vs. the CalNex campaign may also contribute to the 0.3 pH unit difference. As such, we have revised the manuscript to be more circumspect about the role of PM_1 NO_3^- mass concentrations in the CalNex campaign causing the 0.3 pH unit difference:

Page 16 line 498: "This may be due, in part, to PM_1 SO_4^{2-} and NO_3^- mass concentrations at CalNex being approximately 2 times and 18 times larger than those of this study, respectively. Aerosol inorganic SO_4^{2-} and NO_3^- species are hygroscopic species. The much higher NO_3^- mass concentrations in the CalNex campaign (due, in part, to high NO_x emissions) increased particle W_i substantially, which diluted H^+ and raised particle pH, resulting in more gas-to-particle partitioning of NO_3^-, and eventually leading to pH levels similar to those observed in this study. This type of feedback does not happen in the southeastern U.S. where non-volatile SO_4^{2-} dominates the uptake of particle water. It is also possible that the higher RH and lower

temperatures during the CalNex campaign (relative to this study) contributed to high particle W_i, which diluted H^+ and raised particle pH levels similar to those observed in this study."

5. Referee comment: "*Section 3.4: On the diurnal variations of organic acids. Several factors (such as emission sources and photochemical production) are provided to explain the diurnal variations of the gas-phase and particle-phase organic acids. The authors seem to ignore the role of phase partitioning on the diurnal variations of the organic acids. If the organic acids are in a gas-particle equilibrium, no matter how they are formed, they would be re-partitioned between these two phases depending on the pH value and the aerosol water mass.*"

Author response: The referee is correct in stating that gas-particle partitioning of organic acids can also contribute to the observed diurnal variations of the organic acids. As such, this possibility has been added to the revised manuscript:

Page 19 line 603: "Some of these gas-phase organic acids may also be formed in the particle phase during organic aerosol photochemical aging, with subsequent volatilization into the gas phase. The gas-particle partitioning of organic acids likely depends on thermodynamic conditions, which are controlled by particle pH and W_i and meteorological conditions as will be shown in section 3.5."

6. Referee comment: "*Section 3.5, Lines 605-608: an increase from 81% to 89% is expected from the S curve analysis, and what are the corresponding values (εC2O4(2-)) for the observations? Do the observations support the S curve analysis?*"

Author response: Although the measured $\varepsilon(C_2O_4^{2-})$ values are generally consistent with the calculated S curve, the measured $\varepsilon(C_2O_4^{2-})$ data at particle pH 2.2 and 2.5 is not clear enough to give definite values to support S curve analysis due to data scatter. For example, the averages (± standard deviation) of the measured $\varepsilon(C_2O_4^{2-})$ at pH 2.2 and pH 2.5 are similar (78 ± 3 % and 79 ± 3 %, respectively) because of the scatter. Therefore, we emphasize in the revised manuscript that the S curve can be used to gain a qualitative understanding of how high NH_3 events at the site affect oxalic acid gas-particle partitioning:

Page 22 line 704: "Since the measured $\varepsilon(C_2O_4^{2-})$ are in general agreement with the analytically calculated S curve (Fig. 7), we can use the S curve to understand qualitatively how high NH_3 events at the site affect oxalic acid gas-particle partitioning. Here we define high NH_3 events as periods where the NH_3 concentration was higher than 13.3 ppb (which is the average NH_3 concentration + 1 standard deviation). As discussed in section 3.3, the PM_1 pH during high NH_3 events is 2.5 ± 0.6, which is slightly higher than the average PM_1 pH of 2.2 ± 0.6. Based on the S curve calculated using the average temperature and W_i values, $\varepsilon(C_2O_4^{2-})$ increases from 81 % to 89 % when particle pH increases from 2.2 to 2.5. While this result indicates that high NH_3 concentrations can raise the particle pH sufficiently such that it can promote gas-to-particle partitioning of oxalic acid, this is not always the case. Specifically, increasing the particle pH from -2 (or lower) to 1 will not result in a significant increase in $\varepsilon(C_2O_4^{2-})$. Therefore, whether or not particle pH, and consequently oxalic acid gas-particle partitioning, is sensitive to NH_3 concentration depends strongly on particle pH values."

7. Referee comment: "*Section 3.5, Lines 618-620: it reads from Figure S12 that there is a negative bias of εC2O4(2-) during the daytime and a positive bias during the nighttime. Can the authors provide a more quantitative analysis for the diurnal variations of εC2O4(2-)?*"

Author response: Note that Fig. S12 in the original manuscript is now Fig. S13 in the revised manuscript. First, we view this change in partitioning resulting from changes in temperature and particle W_i as a shift, not a bias. Second, the purpose of Fig. S13 is to show that the S curve will change during the transition from day to night as a result of changes in meteorological conditions and particle W_i. Ambient RH and temperatures are higher and lower at night, respectively. Particle W_i will increase as a result of these changes in RH and temperature during the transition from day to night. These changes in the meteorological conditions and particle W_i will generally result in a higher fraction of oxalic acid partitioning to the particle phase for particle pH in this study. Since this shift is non-linear (i.e., see changes in S curve shape), we feel the best way to show the changes is graphically, as done in Fig. S13. It is not possible to provide a more quantitative analysis of $\varepsilon(C_2O_4^{2-})$.

8. Referee comment: "*Section 3.5, Lines 625-627: I do not think the statement that "S curves can be used to estimate activity coefficients based on gas-particle partitioning data xxx" can be derived from the data analysis in this section. For example, in Equation 4, the relation- ship between εC2O4(2-) and pH depends on three activity coefficients: those of H+, C2H2O4, and C2HO4-, and this relationship is nonlinear. In this case, it seems unlikely to obtain a reasonable value for any activity coefficient.*"

Author response: We agree with the referee's point. Therefore, we have removed the above-mentioned statement in the revised manuscript.

<u>Response to Referee 2 (Referees' comments are italicized)</u>

1. Referee comment: "*Line 17-40: I feel that the authors described mostly the summary of the results in the abstract. I strongly recommend highlighting important findings of the study in this section.*"

Author response: We respectfully disagree with the referee's comment that the abstract is mostly a summary of the results. There are five important findings of this study, and they have been highlighted in the abstract:

1) Despite the high NH_3 concentrations (average 8.1 ± 5.2 ppb), PM_1 were highly acidic with pH values ranging from 0.9 to 3.8, and an average pH of 2.2 ± 0.6.

2) The measured molar fraction of oxalic acid in the particle phase (i.e., particle-phase oxalic acid molar concentration divided by the total oxalic acid molar concentration) ranged between 47 and 90 % for PM_1 pH 1.2 to 3.4.

3) The measured oxalic acid gas-particle partitioning ratios were in good agreement with their corresponding thermodynamic predictions, calculated based on oxalic acid's physicochemical properties, ambient temperature, particle water and pH.

4) The measured formic and acetic acid gas-particle partitioning ratios did not agree with their corresponding thermodynamic predictions.

5) Our study suggests that while higher NH_3 concentrations may lead to higher organic aerosol mass concentrations due to increased gas-to-particle partitioning of some organic acids, this effect is minor since organic acids comprised a small fraction of the overall aerosol mass.

2. Referee comment: "*Line 22: Define "SOA".*"

Author response: This is defined in the revised manuscript.

3. Referee comment: "*Line 26 and 27: What do authors mean by "study average". I think it is enough to write only "average" in the entire manuscript.*"

Author response: We have replaced "study average" with "average" in the revised manuscript.

4. Referee comment: "*Line 32 and 33: I suggest to move the sentence "particle-phase. .. ..molar concentration" in the methods or results and discussion section.*"

Author response: The co-editor previously requested that the above-mentioned sentence be added to the abstract to prevent any confusion. Therefore, we will keep the sentence in.

5. Referee comment: "*Line 42-47: There are specific salts produced by the reaction of ammonia with sulfuric acid and nitric acid based on the meteorological conditions. I suggest the authors to briefly explain these points in the introduction.*"

Author response: As requested, we have added a brief explanation on how the formation of specific salts in the particle phase is dependent on environmental conditions in the revised manuscript:

Page 2 line 48: "The formation of particle-phase ammonium sulfate and nitrate salts in the aerosol phase depends on the thermodynamic states of their precursors and the environmental conditions, which can consequently affect aerosol pH. For example, Guo et al. (2017b) showed that for Southeast U.S. summertime conditions, as aerosol pH increases, the relative fractions of SO_4^{2-} and HSO_4^- increases and decreases, respectively."

References:

Guo, H., Nenes, A., and Weber, R. J.: The underappreciated role of nonvolatile cations on aerosol ammonium-sulfate molar ratios, Atmos. Chem. Phys. Discuss., 2017, 1-19, 10.5194/acp-2017-737, 2017b.

6. Referee comment: "*Line 53-55: Although the references have been provided to back up the sentence, I suggest to at least briefly describe how ammonia is produced by industrial and vehicular emission.*"

Author response: As requested, we have added a brief description of how NH_3 is produced from industrial and vehicular emissions:

Page 2 line 58: "The primary source of NH_3 in urban areas are industrial emissions (e.g., NH_3 synthesis, manufacture of ammonium nitrate and urea, fluid and thermal catalytic cracking processes in petroleum refinery), though vehicular emissions can be a significant NH_3 source in some heavily populated cities (Reis et al., 2009; Lamarque et al., 2010; Yao et

al., 2013; Sun et al., 2017). Vehicular NH_3 emissions are thought to be produced primarily from the reaction of nitrogen oxide with hydrogen in the presence of carbon monoxide in three-way catalysts of gasoline light duty vehicles (Barbier-Jr and Duprez, 1994; Whittington et al., 1995; Livingston et al., 2009; Suarez-Bertoa et al., 2014).”

References:

Barbier-Jr, J., and Duprez, D.: Steam Effects in 3-way catalysis, Applied Catalysis B-Environmental, 4, 105-140, 10.1016/0926-3373(94)80046-4, 1994.

Whittington, B. I., Jiang, C. J., and Trimm, D. L.: Vehicle exhaust catalysis: I. The relative importance of catalytic oxidation, steam reforming and water-gas shift reactions, Catalysis Today, 26, 41-45, 10.1016/0920-5861(95)00093-u, 1995.

Livingston, C., Rieger, P., and Winer, A.: Ammonia emissions from a representative in-use fleet of light and medium-duty vehicles in the California South Coast Air Basin, Atmospheric Environment, 43, 3326-3333, 10.1016/j.atmosenv.2009.04.009, 2009.

Reis, S., Pinder, R. W., Zhang, M., Lijie, G., and Sutton, M. A.: Reactive nitrogen in atmospheric emission inventories, Atmos. Chem. Phys., 9, 7657-7677, 10.5194/acp-9-7657-2009, 2009.

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Yao, X. H., Hu, Q. J., Zhang, L. M., Evans, G. J., Godri, K. J., and Ng, A. C.: Is vehicular emission a significant contributor to ammonia in the urban atmosphere?, Atmospheric Environment, 80, 499-506, 10.1016/j.atmosenv.2013.08.028, 2013.

Suarez-Bertoa, R., Zardini, A. A., and Astorga, C.: Ammonia exhaust emissions from spark ignition vehicles over the New European Driving Cycle, Atmospheric Environment, 97, 43-53, 10.1016/j.atmosenv.2014.07.050, 2014.

7. Referee comment: “*Line 322 and 323: Authors found that ammonia concentration decreased at 14:00 about 1 hour before temperature decreased. Did you measure the boundary layer height during the campaign as mentioned that the decrease in ammonia concentration was because of the change in the boundary layer height?*”

Author response: The boundary layer height was not measured during the study. The decrease in NH_3 concentration was hypothesized to be due to changes in the boundary layer height. As such, we have revised the manuscript to be more circumspect about changes in the boundary layer being the cause of the decrease in NH_3 concentration:

Page 12 line 351: "NH_3 decreased at 14:30, approximately 1 hour before temperature decreased, and may be due to changes in the boundary layer height. However, this hypothesis cannot be tested since the boundary layer height was not measured during the study."

8. Referee comment: "*Line 368-370: This study found that PILS and filter-based measurements of sulfate is two times lower than that of HR-TOF-AMS measurement. The similar results are also observed for nitrate and ammonium. I suggest clarifying the reason behind this in the revised manuscript.*"

Author response: Disagreements between the HR-ToF-AMS and PILS and filter-based measurements are due to our application of composition-dependent collection efficiency (CDCE) values to the raw HR-ToF-AMS data. In our previous manuscript, we calculated CDCE values using the CDCE parameterization method proposed by Middlebrook et al. (2012), which derives CE values based largely on aerosol inorganic species concentrations and the relative humidity in the sampling line. Under our sampling conditions, the Middlebrook parameterization method estimated CDCE values of 0.44 to 0.55 (average of 0.45). However, the application of these CDCE values to the raw HR-ToF-AMS data resulted in the SO_4^{2-}, NO_3^- and NH_4^+ measurements being higher than the PILS and filter-based measurements. This is likely due to organics dominating the aerosol composition during the study (average of 74.2 ± 7.9 % of the non-refractory PM_1 mass concentration). Lee et al. (2015) suggested that a high organic mass fraction may hinder the complete efflorescence of aerosols when they are passed through the drier prior to delivery into the HR-ToF-AMS, reducing the particle bounce and increasing the CE value. As described in our previous manuscript, the CDCE-corrected HR-ToF-AMS measurements had to be scaled by a constant factor of 0.5 in order for them to agree with the PILS and filter-based measurements. It should be noted a previous ambient study also reported poor agreement between the CDCE-corrected HR-ToF-AMS measurements and parallel aerosol composition measurements due to high organic aerosol mass concentrations (see Lee et al. (2015)).

For these reasons, we applied a constant CE value of 0.9 to the raw HR-ToF-AMS data. This CE value was determined from comparisons of the raw HR-ToF-AMS data with PILS measurements. To remove any confusion, the following changes have been made to the manuscript:

Page 6 line 187: "Composition-dependent collection efficiency (CDCE) values of 0.44 to 0.55 were determined using the procedure detailed by Middlebrook et al. (2012), where CDCE values are derived based largely on aerosol inorganic species concentrations and the relative humidity in the sampling line. In addition, a constant collection efficiency (CE) value of 0.9 was determined from the comparison of raw HR-ToF-AMS SO_4^{2-} data with other particulate SO_4^{2-} measurements performed during the study. Comparisons of aerosol mass concentrations obtained from the application of CDCE values (i.e., 0.44 to 0.55) vs. a constant CE value (i.e., 0.9) to the raw HR-ToF-AMS data are discussed in section 3.2."

Page 13 line 389: "The aerosol inorganic chemical composition was measured by several instruments during this study. The HR-ToF-AMS, PILS-IC and PILS-HPIC measured the composition of PM_1, while a filter-based particle composition monitor measured the composition of $PM_{2.5}$. Comparisons of aerosol SO_4^{2-}, NO_3^- and NH_4^+ mass concentrations obtained from the application of CDCE values to the raw HR-ToF-AMS data are compared to those measured by the other three instruments in Fig. S6. NH_4^+ measurements by the PILS-IC are not available for comparison due to denuder breakthrough that occurred

during the study.

SO_4^{2-} measurements by the various instruments are generally well correlated with each other, with R^2 values ranging from 0.64 to 0.92. Although PM_1 SO_4^{2-} measurements by the two PILS systems show good agreement with each other, HR-ToF-AMS CDCE-applied SO_4^{2-} measurements are approximately two times higher than the PILS and filter measurements. Similar systematic differences are also observed for NO_3^- and NH_4^+ measurements. NO_3^- and NH_4^+ measurements by the four instruments are moderately correlated (R^2 = 0.54 to 0.79 and R^2 = 0.94, respectively). NO_3^- measurements by the PILS and filter systems are mostly similar; however, HR-ToF-AMS CDCE-applied PM_1 NO_3^- and NH_4^+ measurements are approximately three times and two times higher than the PILS and filter measurements. One possible reason is that the calculated CDCE is lower due to organics dominating the aerosol composition during the study (average of 74.2 ± 7.9 % of the non-refractory PM_1 mass concentration). Lee et al. (2015) suggested that a high organic mass fraction may impede the complete efflorescence of aerosols when they are passed through the drier prior to delivery into the HR-ToF-AMS, thus reducing the particle bounce and increasing the CE value. Hence, we estimated HR-ToF-AMS PM_1 mass concentrations that would be consistent with PILS and filter measurements by multiplying all the raw HR-ToF-AMS data by a constant CE value of 0.9, which was obtained from comparisons of the raw HR-ToF-AMS SO_4^{2-} data with PILS-IC and PILS-HPIC SO_4^{2-} measurements. The constant CE-applied HR-ToF-AMS data is used in all our subsequent analyses.

Figure S6 caption: "Aerosol (panels a to d) SO_4^{2-}, (panels e to h) NO_3^-, and (i) NH_4^+ comparisons between HR-ToF-AMS, PILS-IC, PILS-HPIC and filters for the entire field study. CDCE values were applied to the raw HR-ToF-AMS data to obtain the mass concentrations shown here (see main text for details). For comparisons between the HR-ToF-AMS, PILS-IC and PILS-HPIC data (panels c, d, g and h), the measurements are averaged over 1 hour intervals. For comparisons with filter data (panels a, b, e, f and i), the HR-ToF-AMS, PILS-IC and PILS-HPIC data are averaged over 24 hour intervals. Orthogonal regression fits are shown. Uncertainties in the fits are 1 standard deviation."

References:

Lee, B. P., Li, Y. J., Yu, J. Z., Louie, P. K. K., and Chan, C. K.: Characteristics of submicron particulate matter at the urban roadside in downtown Hong Kong-Overview of 4 months of continuous high-resolution aerosol mass spectrometer measurements, Journal of Geophysical Research-Atmospheres, 120, 7040-7058, 10.1002/2015jd023311, 2015.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, Aerosol Science and Technology, 46, 258-271, 10.1080/02786826.2011.620041, 2012.

9. Referee comment: "*Line 386-398: This is an exciting result that the organic aerosol mass concentration was higher at nighttime. This result probably indicated the unique atmospheric processing of organic aerosols in the nighttime. Nevertheless, I did not find any discussion on the formation mechanisms of organic aerosols at nighttime. I suggest discussing this point in the revised version.*"

Author response: As requested, we have added some discussion on the possible nighttime formation mechanisms of organic aerosols in the revised manuscript:

Page 14 line 420: "Organic aerosol mass concentration was slightly higher at night, which is likely caused by changes in the boundary layer height, emission sources and SOA formation processes (Xu et al., 2015b). Previous studies have shown that nighttime SOA production in the Southeastern U.S. is largely attributed to nitrate radical oxidation and ozonolysis of monoterpenes, which are abundant at night (Pye et al., 2015; Xu et al., 2015a; Xu et al., 2015b; Lee et al., 2016; Zhang et al., 2018). Specifically, the nitrate radical oxidation of some monoterpenes (e.g., β-pinene) could form low volatility organic nitrates that are condensable and could contribute substantially to the nocturnal organic aerosol mass (Boyd et al., 2015; Boyd et al., 2017; Ng et al., 2017)."

References:

Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I., and Ng, N. L.: Secondary organic aerosol formation from the beta-pinene+NO3 system: effect of humidity and peroxy radical fate, Atmos. Chem. Phys., 15, 7497-7522, 10.5194/acp-15-7497-2015, 2015.

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Ng, N. L., Brown, S. S., Archibald, A. T., Atlas, E., Cohen, R. C., Crowley, J. N., Day, D. A., Donahue, N. M., Fry, J. L., Fuchs, H., Griffin, R. J., Guzman, M. I., Herrmann, H., Hodzic, A., Iinuma, Y., Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., Mao, J. Q., McLaren, R., Mutzel, A., Osthoff, H. D., Ouyang, B., Picquet-Varrault, B., Platt, U., Pye, H. O. T., Rudich, Y., Schwantes, R. H., Shiraiwa, M., Stutz, J., Thornton, J. A., Tilgner, A., Williams, B. J., and Zaveri, R. A.: Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol, Atmos. Chem. Phys., 17, 2103-2162, 10.5194/acp-17-2103-2017, 2017.

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10. Referee comment: "*Line 395-399: Authors found that nitrate concentration increased after sunset and peaked at sunrise due to the formation of organic nitrates from the nighttime chemistry of nitrate and increased gas to particle partitioning of organic and inorganic nitrates due to the decrease in temperature. I do not agree to include the sentence that the result of organic nitrates will be discussed in a future publication. The conclusion stated in lines 396 and 397 does not make sense without the data of organic nitrates.*"

Author response: We agree with the referee that organic nitrate data is needed to explicitly explain the observed diurnal profile of NO_3^- mass concentration This information has been added to the revised manuscript:

Page 14 line 432: The NO_3^- mass concentration measured by the HR-ToF-AMS is the nitrate functional group ($-ONO_2$) present on organic and inorganic nitrates. Hence, the diurnal profile of the NO_3^- mass concentration in Fig. 2 has contributions from both organic and inorganic nitrates. The mass concentrations of organic and inorganic nitrates increased after sunset and peaked at sunrise (Fig. S7), likely due to the formation of organic nitrates from nighttime NO_3 chemistry and increased gas-to-particle partitioning of organic and inorganic nitrates as temperature decreased (Xu et al., 2015a; Xu et al., 2015b). Quantification and characterization of organic nitrates based on HR-ToF-AMS and PILS-IC PM_1 NO_3^- measurements will be discussed in a future publication.

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Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S.-H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, Proceedings of the National Academy of Sciences of the United States of America, 112, 37-42, 10.1073/pnas.1417609112, 2015a.

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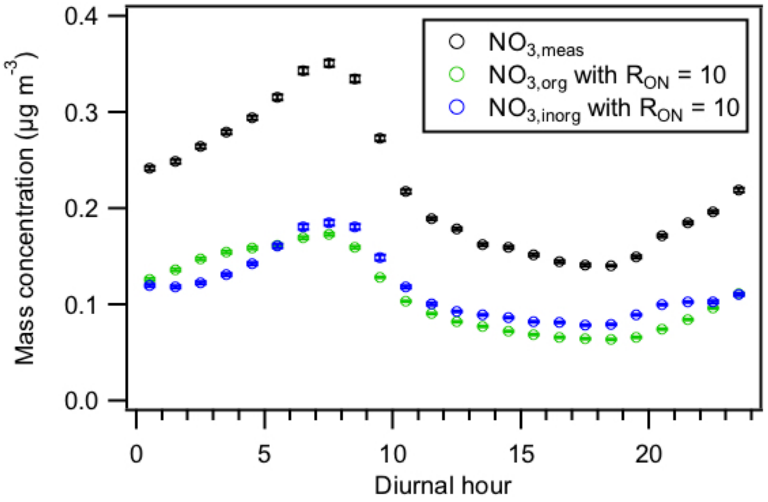

Figure S7: Diurnal profiles of the total nitrate functionality contributed by organic and inorganic nitrates ($NO_{3,meas}$), and the nitrate functionality solely from organic nitrates ($NO_{3,org}$) and inorganic nitrates ($NO_{3,inorg}$). $NO_{3,org}$ and $NO_{3,inorg}$ are estimated using the NO^+/NO_2^+ ratio method as described by Farmer et al. (2010) and Xu et al. (2015). Similar to Xu et al. (2015), we used a R_{ON} (defined here as the NO^+/NO_2^+ ratio for organic nitrates) value of 10 to calculate $NO_{3,org}$ and $NO_{3,inorg}$. All the data shown here represent averages in 1-hour intervals. Error bars shown are the standard errors.

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Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J., and Jimenez, J. L.: Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry, Proceedings of the National Academy of Sciences of the United States of America, 107, 6670-6675, 10.1073/pnas.0912340107, 2010.

Xu, L., Suresh, S., Guo, H., Weber, R. J., and Ng, N. L.: Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates, Atmos. Chem. Phys., 15, 7307-7336, 10.5194/acp-15-7307-2015, 2015.

11. Referee comment: "*Line 405: Which temperature and relative humidity data were used for ISORROPIA-II model inputs? Is it fixed temperature and RH values or temperature and RH observed during the campaign?*"

Author response: Temperature and RH values measured during the campaign was used for ISORROPIA-II model inputs. This is clarified in the revised manuscript:

Page 15 line 460: "CIMS HNO_3 and NH_3 data, CE-corrected HR-ToF-AMS PM_1 SO_4^{2-} and NH_4^+ data, PILS-IC PM_1 NO_3^- and non-volatile cation (Cl^-, Na^+, Ca^{2+}, K^+ and Mg^{2+}) data, measured temperature and RH are used as ISORROPIA-II model inputs to predict PM_1 W_i and pH from 13 September to 6 October."

12. Referee comment: "*Line 433 and 435: What do authors mean by highly hygroscopic? Are that sulfate and nitrate alone contribute more to the hygroscopicity of aerosol particles or their salts play a role in the hygroscopic behavior of aerosol particles?*"

Author response: We meant to write that aerosol inorganic sulfate and nitrate are hygroscopic species (i.e., their salts contribute to the hygroscopic behavior of aerosols). This is corrected in the revised manuscript:

Page 16 line 499: "Aerosol inorganic SO_4^{2-} and NO_3^- species are hygroscopic species."

13. Referee comment: "*Line 518-520: Which type of biogenic volatile organic compound precursors elevated at high temperature and produced a high amount of organic acids during warm and sunny days? Can you give some examples?*"

Author response: Isoprene, which is the dominant BVOC in Yorkville, is one example of a BVOC precursor that is elevated at high temperature. We showed in a previous paper that the concentration of isoprene is moderately correlated with those of formic and acetic acids ($R^2 = 0.42$ and 0.40, respectively), which are known products of isoprene photooxidation (Nah et al., 2018). As requested, this information has been added into the revised manuscript:

Page 19 line 600: "For example, isoprene, which is the dominant BVOC in Yorkville, has a somewhat similar diurnal profile as the organic acids. In addition, the concentration of isoprene is moderately correlated with those of formic and acetic acids (Fig. S10 of Nah et al., 2018), which are known products of isoprene photooxidation."

References:

Nah, T., Ji, Y., Tanner, D. J., Guo, H., Sullivan, A. P., Ng, N. L., Weber, R. J., and Huey, L. G.: Real-time measurements of gas-phase organic acids using SF6- chemical ionization mass spectrometry, Atmos. Meas. Tech. Discuss., 2018, 1-40, 10.5194/amt-2018-46, 2018.

14. Referee comment: "*Line 539-542: Glutarate is a higher homologous diacid of oxalate that has almost similar sources and formation processes. What is the reason that oxalate as well as malonate and succinate peaked in the mid to late afternoon but glutarate peaked on the mid-morning? I do not agree with the authors explanation that they have different biogenic volatile organic compound precursors or different production mechanisms. What about the photodegradation of glutarate to lower carbon number diacids during the afternoon?*"

Author response: The referee is correct in stating that the photodegradation of particle-phase glutaric acid may result in the formation of its successive homologues (i.e., oxalic, malonic and succinic acids) via C-C bond cleavage. Therefore, differences in the diurnal profiles of particle-phase oxalate, malonate, succinate and glutarate may also be due, in part, to organic aerosol photochemical aging. This information has been added to the revised manuscript:

Page 20 line 628: "Particle-phase oxalate, malonate and succinate peaked in the mid- to late afternoon, while glutarate generally peaked in the mid-morning. This suggests that while the production of these organic acids is photochemically-driven, they may have different BVOC precursors and/or different photochemical production pathways. In addition, since oxalic (C_2), malonic (C_3), succinic (C_4) and glutaric (C_5) acids belong to the same homologous series of organic diacids, it is possible that the photochemical aging of particle-phase glutaric acid resulted in the formation of its successive homologues via the cleavage of C-C bonds. Hence, organic aerosol photochemical aging may also have contributed to the diurnal profiles of particle-phase oxalate, malonate, succinate and glutarate."

<u>Additional revisions</u>

1. We corrected the units of the duty cycles for the SF_6-CIMS and NH_3-CIMS:

Page 6 line 166: "The detection limits for HNO_3, SO_2 and the various organic acids measured by the SF_6-CIMS ranged from 1 to 60 ppt for 2.5 min integration periods, which corresponded to the length of a background measurement with a ~4 % duty cycle for each *m/z* (Table S1)."

Page 6 line 170: "The detection limit for NH_3 measured by the NH_3-CIMS was 1 ppb for 2.3 min integration periods, which corresponded to the length of a background measurement with a ~29 % duty cycle for the NH_4^+ ion."

2. We added another possible explanation for the disagreement between measured and modeled $\varepsilon(HCOO^-)$ and $\varepsilon(CH_3CO_2^-)$ in the revised manuscript:

Page 25 line 791: "In addition, formic and acetic acids may not be internally mixed with most of the other PM_1 aerosol components (e.g., SO_4^{2-}, NO_3^-, NH_4^+, CH_3CO_2H), and thus are not associated with acidic aerosols, as assumed above. They may instead be associated with aerosols largely composed of non-volatile cations and have a pH closer to neutral. More research is needed to explain this disagreement."

Characterization of Aerosol Composition, Aerosol Acidity and Organic Acid Partitioning at an Agriculture-Intensive Rural Southeastern U.S. Site

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Abstract

The implementation of stringent emission regulations has resulted in the decline of anthropogenic pollutants including sulfur dioxide (SO_2), nitrogen oxides (NO_x) and carbon monoxide (CO). In contrast, ammonia (NH_3) emissions are largely unregulated, with emissions projected to increase in the future. We present real-time aerosol and gas measurements from a field study conducted in an agricultural-intensive region in the southeastern U.S. during the fall of 2016 to investigate how NH_3 affects particle acidity and secondary organic aerosol (SOA) formation via the gas-particle partitioning of semi-volatile organic acids. Particle water and pH were determined using the ISORROPIA-II thermodynamic model and validated by comparing predicted inorganic HNO_3-NO_3^- and NH_3-NH_4^+ gas-particle partitioning ratios with measured values. Our results showed that despite the high NH_3 concentrations (average 8.1 ± 5.2 ppb), PM_1 were highly acidic with pH values ranging from 0.9 to 3.8, and an average pH of 2.2 ± 0.6. PM_1 pH varied by approximately 1.4 units diurnally. Formic and acetic acids were the most abundant gas-phase organic acids, and oxalate was the most abundant particle-phase water-soluble organic acid anion. Measured particle-phase water-soluble organic acids were on average 6 % of the total non-refractory PM_1 organic aerosol mass. The measured molar fraction of oxalic acid in the particle phase (i.e., particle-phase oxalic acid molar concentration divided by the total oxalic acid molar concentration) ranged between 47 and 90 % for PM_1 pH 1.2 to 3.4. The measured oxalic acid gas-particle partitioning ratios were in good agreement with their corresponding thermodynamic predictions, calculated based on oxalic acid's physicochemical properties, ambient temperature, particle water and pH. In contrast, gas-particle partitioning of formic and acetic acids were not well predicted for reasons

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currently unknown. For this study, higher NH_3 concentrations relative to what has been measured in the region in previous studies had minor effects on PM_1 organic acids and their influence on the overall organic aerosol and PM_1 mass concentrations.

1. Introduction

Ammonia (NH_3) is the most abundant basic gas in the troposphere and plays an important role in many atmospheric processes. It is a major neutralizer of atmospheric acidic species, reacting readily with sulfuric acid (H_2SO_4) and nitric acid (HNO_3) to form ammonium sulfate and nitrate salts (e.g., $(NH_4)_2SO_4$, and other forms such as NH_4HSO_4, $(NH_4)_3H(SO_4)_2$, and NH_4NO_3), which are often the main inorganic components of atmospheric aerosols. The formation of particle-phase ammonium sulfate and nitrate salts in the aerosol phase depends on the thermodynamic states of their precursors and the environmental conditions, which can consequently affect aerosol pH. For example, Guo et al. (2017b) showed that for Southeast U.S. summertime conditions, as aerosol pH increases, the relative fractions of SO_4^{2-} and HSO_4^{-} increases and decreases, respectively. Wet and dry deposition are the principle NH_3 sinks (Dentener and Crutzen, 1994). NH_3 is spatially heterogeneous, with the highest concentrations typically found near emission sources (Seinfeld and Pandis, 2016). The dominant NH_3 sources in rural areas are agricultural in nature, and include the application of fertilizers and volatilization of livestock waste (Reis et al., 2009; Ellis et al., 2013; Van Damme et al., 2014). Biomass burning, either from wildfires or from controlled burning during land-clearing operations, is also a significant source of NH_3 in rural environments. The primary source of NH_3 in urban areas are industrial emissions (e.g., NH_3 synthesis, manufacture of ammonium nitrate and urea, fluid and thermal catalytic cracking processes in petroleum refinery), though vehicular emissions can be a significant NH_3 source in some heavily populated cities (Reis et al., 2009; Lamarque et al., 2010; Yao et al., 2013; Sun et al., 2017). Vehicular NH_3 emissions are thought to be produced primarily from the reaction of nitrogen oxide with hydrogen in the presence of carbon monoxide in three-way catalysts of gasoline light duty vehicles (Barbier-Jr and Duprez, 1994; Whittington et al., 1995; Livingston et al., 2009; Suarez-Bertoa et al., 2014).

In the US, implementation of stringent emission controls on traditional anthropogenic air pollutants, such as sulfur dioxide (SO_2), nitrogen oxides (NO_x) and carbon monoxide (CO), have led to steady decreases in their emissions, and consequently their concentrations (Blanchard et al., 2013b; Xing et al., 2013). In contrast, NH_3 emissions are largely unregulated, and are projected to increase due to increased agricultural operations to feed a growing world population (Reis et al., 2009; Ellis et al., 2013). Satellite observations showed that gas-phase NH_3 concentrations have increased substantially in US agricultural areas from 2002 to 2014 (Warner et al., 2017). More wildfires from a changing climate, or from controlled burning for land clearing for agricultural use, may also lead to increased NH_3 emissions (Reis et al., 2009; Pechony and Shindell, 2010; Warner et al., 2016). These trends suggest that NH_3 could play an increasingly important role in atmospheric chemistry.

Previous laboratory studies have shown that NH_3 can influence secondary organic aerosol (SOA) formation and processing. For example, NH_3 increases SOA mass yields in the α-pinene ozonolysis system, and is hypothesized to be due to the formation of ammonium salts from the reaction of NH_3 with organic acids (Na et al., 2007). The heterogeneous uptake of NH_3 by SOA can also lead to the formation of particulate organonitrogen compounds, a class of brown carbon species that can reduce visibility and impact climate (Laskin et al., 2010; Updyke et al., 2012; Lee et al., 2013; Laskin et al., 2015).

The southeastern U.S. is a natural outdoor laboratory for studying the effects of biogenic-anthropogenic interactions on atmospheric aerosol formation and processing. Subtropical vegetation composed mainly of mixed conifer and deciduous forests emit large quantities of biogenic volatile organic compounds (BVOCs) that can act as precursors for SOA formation (Blanchard et al., 2011; Guenther et al., 2012; Blanchard et al., 2013a). Large urban centers and small towns are surrounded by large expanses of forests and widespread rural areas with agricultural activities. Scattered within the southeastern U.S. are also coal-burning power plants and industrial facilities. Anthropogenic activities in this region emit large concentrations of VOCs, SO_2, NO_x, CO, NH_3 and aerosols (Blanchard et al., 2013c). Similar to other parts of the U.S., SO_2, CO and NO_x concentrations have decreased steadily in the southeastern U.S. due to the implementation of emission controls (Blanchard et al., 2013b). In contrast, gas-phase NH_3 concentrations have increased in the southeastern U.S. over the same time period (Saylor et al., 2015). These factors make the southeastern U.S. an intriguing place to study the influence of NH_3 on atmospheric aerosol chemistry.

We performed aerosol and gas measurements during a field study conducted in Yorkville, Georgia, U.S., in the fall of 2016, with the goal of understanding how NH_3 affects aerosol acidity and SOA formation. The field site is surrounded by forest and agricultural land, affording an opportunity to make ambient observations in an area impacted by local emissions of BVOCs and NH_3. In this paper, we present gas and aerosol composition measurements that includes a suite of organic acids. The thermodynamic equilibrium model, ISORROPIA-II, is used to calculate particle water and pH based on measured inorganic aerosol and gas composition (Nenes et al., 1998; Fountoukis and Nenes, 2007), and these predictions are compared to observed gas-particle partitioning of NH_3, HNO_3 and organic acids. Together, these measurements are used to determine how aerosol acidity affects the mass concentration of particle-phase organic acids at this site.

2. Methods

2.1. Field site

Aerosol and gas measurements were conducted at the Yorkville, Georgia (33.929 N, 85.046 W) SouthEastern Aerosol Research and Characterization (SEARCH) field site from mid-August to mid-October 2016. This is one of the sampling sites for the Southeastern Center for Air Pollution and Epidemiology (SCAPE) study where aerosol characterization measurements were conducted in the summer and winter of 2012 (Xu et al., 2015a; Xu et al., 2015b). A detailed description of the field site can be found in Hansen et al. (2003) . This rural site is situated in a mixed forest-agriculture area approximately 55 km northwest and generally upwind of Atlanta. The immediate surrounding area is used for cattle grazing and poultry concentrated animal feeding operations (CAFOs) (Fig. S1). There are no major roads near the field site and nearby traffic emissions were negligible. A large coal-fired power plant (Plant Bowen) is situated approximately 25 km north of the site. Hence, the field site is impacted mainly by BVOC and NH_3 emissions, with occasional spikes in SO_2 and minimal influence from urban anthropogenic pollutants such as HNO_3, O_3, NO_x and CO (Fig. S2). The sampling period was characterized by moderate temperatures (24.0 °C average, 32.6 °C max, 9.5 °C min) and high relative humidities (68.9 % RH average, 100 % RH max, 21.6 % RH min). Meteorological data are shown in Fig. S3. Data reported are displayed in eastern daylight time (EDT).

2.2. Instrumentation

Instruments were housed in a temperature controlled (~20 °C) trailer during the field study. Gas-phase HNO_3, SO_2 and organic acids (formic, acetic, oxalic, butyric, glycolic, propionic, valeric, malonic and succinic acids) were measured by a custom-built chemical ionization mass spectrometer (CIMS) using sulfur hexafluoride ions (SF_6^-) as reagent ions. SO_2 and HNO_3 were detected as fluoride adducts ($F_2SO_2^-$ and $NO_3^- \cdot HF$, respectively) while the organic acids (HX) were detected primarily as conjugated anions (X^-) by the quadrupole mass spectrometer (Huey et al., 1995; Huey et al., 2004; Nah et al., 2018). This CIMS is referred hereafter as the SF_6-CIMS. Gas-phase NH_3 was measured by an additional custom-built CIMS using protonated ethanol clusters ($(C_2H_5OH)_n^+$) as reagent ions. NH_3 was detected primarily as NH_4^+ ions by the quadrupole mass spectrometer (Nowak et al., 2002; Yu and Lee, 2012; You et al., 2014a). This CIMS is referred hereafter as the NH_3-CIMS.

Since HNO_3, NH_3 and organic acids may condense on surfaces, both SF_6-CIMS and NH_3-CIMS used inlet configurations that minimized wall interactions (Huey et al., 2004; Nowak et al., 2006). Each CIMS was connected to an inlet (a 7.6 cm ID aluminum pipe) that protruded beyond the trailer's wall by ~40 cm into the ambient air. Both inlets were ~2 m above the ground. A donut-shaped ring was attached to the ambient sampling port of each pipe to curtail the influence of crosswinds on the pipe's flow dynamics. Both rings were wrapped with a fine wire mesh to prevent ingestion of insects. A flow of ~2800 L min^{-1} was maintained in each pipe using regenerative blowers (AMETEK Windjammer 116637-03). Part of this flow (7 L min^{-1} for the SF_6-CIMS and 4.6 L min^{-1} for the NH_3-CIMS) was sampled through a custom-made three-way PFA Teflon valve, which connected the pipe's center to the CIMS sampling orifice and could be switched automatically between ambient and background measurements.

Background measurements were performed every 25 min for 4 min for both the SF_6-CIMS and NH_3-CIMS. During each background measurement, the sampled air flow was passed through an activated charcoal scrubber (Sigma Aldrich) that removed SO_2, HNO_3 and organic acids prior to delivery into the SF_6-CIMS, and through a silicon phosphate scrubber (Perma Pure Inc.) that removed NH_3 prior to delivery into the NH_3-CIMS. > 99 % of the targeted species were removed during background measurements for both the SF_6-CIMS and NH_3-CIMS. Standard addition calibrations were performed every 5 h for the SF_6-CIMS using the outputs of a 1.12 ppm $^{34}SO_2$ gas cylinder (Scott-Marrin Inc.) and a formic or acetic acid permeation device (VICI Metronics). Calibrations for the other gases measured by the SF_6-CIMS were performed in post-field laboratory work, details of which can be found in Nah et al. (2018) and SI section S1. Standard addition calibrations were performed hourly for the NH_3-CIMS using the output of a NH_3 permeation device (KIN-TEK). The outputs of the formic and acetic acid permeation devices were measured periodically by scrubbing the output of the permeation tube in deionized water, followed by ion chromatography analysis for formate and acetate. The emission rate of the NH_3 permeation device was measured using UV optical absorption (Neuman et al., 2003).

The detection limits for species measured by the SF_6-CIMS and NH_3-CIMS were approximated from 3 times the standard deviation values (3σ) of the ion signals measured during background mode. The detection limits for HNO_3, SO_2 and the various organic acids measured by the SF_6-CIMS ranged from 1 to 60 ppt for 2.5 min integration periods, which corresponded to the length of a background measurement with a ~4 % duty cycle for each *m/z* (Table S1). Measurement uncertainties for the concentrations of HNO_3, SO_2 and the various organic acids originate mainly from calibration measurements, and were between 12 and 25 % (Table S1). The detection limit for NH_3 measured by the NH_3-CIMS was 1 ppb for 2.3 min integration periods, which corresponded to the length of a background measurement with a ~29 % duty cycle for the NH_4^+ ion. Measurement uncertainties for NH_3 concentrations were 13 %.

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A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc.) was used to measure the elemental composition of ambient non-refractory PM_1 (particles with aerodynamic diameters < 1 µm). Ambient air was sampled at 16.7 L min^{-1} though a URG PM_1 cyclone and then through a nafion dryer prior to delivery into the HR-ToF-AMS. Aerosols were dried to RH < 20 % to eliminate the influence of RH on the HR-ToF-AMS's particle collection efficiency. A detailed description of the HR-ToF-AMS can be found in the literature (DeCarlo et al., 2006; Canagaratna et al., 2007; Canagaratna et al., 2015). Briefly, the aerodynamic lens of the HR-ToF-AMS focused the dried submicron aerosols into a narrow beam. The aerosols were then impacted onto a heated tungsten surface (~600 °C) where they were flash vaporized. The resulting vapors were ionized by electron impact ionization (70 eV), and the ions were detected by a time-of-flight mass spectrometer. Gas-phase interferences were accounted for by subtracting the signals obtained during daily measurements of filtered, particle-free sampling air. Ionization efficiency calibrations were performed weekly using 300 nm ammonium nitrate and ammonium sulfate particles. Composition-dependent collection efficiency (CDCE) values of 0.44 to 0.55 were determined using the procedure detailed by Middlebrook et al. (2012), where CDCE

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values are derived based largely on aerosol inorganic species concentrations and the relative humidity in the sampling line. In addition, a constant collection efficiency (CE) value of 0.9 was determined from the comparison of raw HR-ToF-AMS SO_4^{2-} data with other particulate SO_4^{2-} measurements performed during the study. Comparisons of aerosol mass concentrations obtained from the application of CDCE values (i.e., 0.44 to 0.55) vs. a constant CE value (i.e., 0.9) to the raw HR-ToF-AMS data are discussed in section 3.2. Uncertainties in HR-ToF-AMS measurements were estimated to be approximately 25 % (Canagaratna et al., 2007).

Particle-phase water-soluble organic acids, inorganic cations and anions were measured using two Particle-into-Liquid Sampler (PILS) systems coupled to ion chromatographs (ICs) (Orsini et al., 2003). Each PILS sampled ambient air at nominally 16.7 L min^{-1} through a URG PM_1 cyclone. Before PILS1, which was used to measure water-soluble inorganic cation and anions, two long (24 cm) URG glass annular denuders coated with sodium carbonate and phosphorous acid were used to remove acidic and basic gases. Before PILS2, which measured water-soluble organic acids, a 28 cm parallel plate carbon denuder (Sunset Lab) was used to remove organic gases (Eatough et al., 1993). In each PILS, aerosols were mixed with water vapor at ~100 °C generated from heated ultrapure deionized water (Weber et al., 2001; Orsini et al., 2003). The resulting droplets were impacted onto a plate, with the resulting liquid sample analyzed by ICs. Each IC system was calibrated at the beginning and end of the study using five multi-compound standards in order to create calibration curves. Periodically, a HEPA filter (Pall Life Sciences) was placed on the inlet to determine the background in near real-time. The measurement uncertainty for each IC system was about 10 %.

PILS1 was connected to two Dionex ICS-1500 ICs (Thermo Fisher Scientific) to measure the water-soluble inorganic ions. These two IC systems include an isocratic pump, self-regenerating anion or cation suppressor, and conductivity detector. This system will be referred hereafter as the PILS-IC. Anions were separated using a Dionex IonPac AS15 guard and analytical column (4 x 250 mm, Thermo Fisher Scientific) employing an eluent of 38 mM sodium hydroxide at a flow rate of 1.5 mL min^{-1}. Cations were separated using a Dionex IonPac CS12A guard and analytical column (4 x 250 mm, Thermo Fisher Scientific) employing an eluent of 18 mM methanesulfonic acid at a flow rate of 1 mL min^{-1}. A new chromatogram was obtained every 30 min with a sample loop fill time (i.e., ambient sample integration time) of 20 min. The limit of detection for the various anions and cations was approximately 0.01 μg m^{-3}.

PILS2 was coupled to a Dionex ICS-4000 capillary high-pressure ion chromatography (HPIC) system to measure the water-soluble organic acids. The HPIC includes an eluent generator, isocratic pump, degausser, suppressor, carbonate removal device, and conductivity detector. This system will be referred hereafter as the PILS-HPIC. The organic acids were separated using a Dionex AS11-HC-4μm capillary guard and analytical column (0.4 x 250mm, Thermo Fisher Scientific), which used a potassium hydroxide gradient separation method at a flow rate of 0.015 mL min^{-1}. A new chromatogram was obtained every 60 min with a sample loop fill time of 2 min. The limit of detection for the various organic acids was approximately 0.001 μg m^{-3}.

Particle- and gas-phase water-soluble organic carbon ($WSOC_p$ and $WSOC_g$, respectively) were measured using two Sievers 900 series total organic carbon (TOC) analyzers (GE Analytical Instruments), as described by Sullivan et al. (2004). For $WSOC_p$ measurements, ambient air was sampled at 15.2 L min^{-1} through a URG PM_1 cyclone and a parallel plate carbon denuder into a PILS coupled to the first TOC analyzer. For $WSOC_g$ measurements, ambient air was sampled at 20 L min^{-1} through a Teflon filter (45 mm diameter, 2.0 μm pore size, Pall Life Sciences) to remove particles in the air stream. This filter was changed every 3 to 4 days. The particle-free air was then directed to a MIST chamber filled with ultrapure deionized water, which scrubbed the soluble gases at an air flow rate of 20 L min^{-1}. Soluble gases with Henry's law constants greater than 10^3 mole L^{-1} atm^{-1} were scrubbed into deionized water in the MIST chamber (Spaulding et al., 2002). The resulting MIST chamber liquid sample was analyzed by the second TOC analyzer. The TOC analyzers converted the organic carbon in the liquid samples to carbon dioxide using UV radiation and chemical oxidation. The carbon dioxide formed was then measured by conductivity. The amount of organic carbon in the liquid samples is proportional to the measured increase in conductivity of the dissolved carbon dioxide. Each $WSOC_p$ and $WSOC_g$ measurement lasted 4 min. Background $WSOC_p$ and $WSOC_g$ measurements were performed for 45 min every 12 h by stopping the sample air flow and rinsing the system with deionized water. Both TOC analyzers were calibrated at the beginning and end of the study using varying concentrations of sucrose solutions to create calibration curves (as specified by the instrument manual). The limit of detections for $WSOC_p$ and $WSOC_g$ were 0.2 and 0.4 μgC m^{-3}, respectively. The measurement uncertainties for $WSOC_p$ and $WSOC_g$ were estimated to be 10 % based on uncertainties in the TOC analyzer, sample air and liquid flows.

A suite of instruments operated by the SEARCH network provided supporting gas and aerosol measurements (Hansen et al., 2003; Edgerton et al., 2005, 2006). O_3 was measured by a UV absorption instrument (Thermo Fisher Scientific) with a temporal resolution of 1 min. NO and NO_x were measured by a chemiluminescence instrument (Thermo Fisher Scientific) with a temporal resolution of 1 min. NO_2 was obtained from the difference between NO and NO_x. CO was measured by a non-dispersive infrared absorption instrument (Thermo Fisher Scientific) with a temporal resolution of 1 min. NH_3 was measured by a denuder-based instrument (ARA) with a temporal resolution of 5 min. Comparisons of measurements by the NH_3-CIMS and denuder-based instrument will be presented in section 3.1. A filter-based particle composition monitor (ARA) provided 24 h-integrated $PM_{2.5}$ measurements of particle mass and major inorganic ions measured offline by ion chromatography. Organic carbon (OC) and elemental carbon (EC) in $PM_{2.5}$ were measured by a OCEC Analyzer (Sunset Labs) with a temporal resolution of 1 h. This analyzer determined OC by thermal optical transmittance. VOCs were measured by a gas chromatography-flame ionization detector (GC-FID, Agilent Technologies) with a temporal resolution of 1h.

2.2. Particle pH and water calculation

The thermodynamic equilibrium model ISORROPIA-II was used to determine the phase state and composition of an NH_4^+-SO_4^{2-}-NO_3^--Cl^--Na^+-Ca^{2+}-K^+-Mg^{2+}-water inorganic aerosol in equilibrium with its corresponding gas-phase species (Fountoukis and Nenes, 2007; Nenes et al., 1998). This approach was used in previous studies to determine particle water and pH in different parts of the world (Guo et al., 2015; Bougiatioti et al., 2016; Guo et al., 2016; Weber et al., 2016; Guo et al., 2017a; Guo et al., 2017c; Shi et al., 2017). The pH of an aqueous solution is defined as the negative logarithm of the hydronium ion (H_3O^+) activity on a molality basis (www.goldbook.iupac.org/html/P/P04524.html, last access: 6 July 2018):

$$pH = -\log_{10}[a(H^+)] = -\log_{10}\left[m(H^+)\gamma_m(H^+)/m^\theta\right] \qquad (1a)$$

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where $a(H^+)$ is the hydronium ion activity in an aqueous solution, $m(H^+)$ is the hydronium ion molality, $\gamma_m(H^+)$ is the molality-based hydronium ion activity coefficient, and m^θ is the standard molality (1 mol kg^{-1}). For simplicity, H_3O^+ is denoted here as H^+ even though we recognize that

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the unhydrated hydrogen ion is rare in aqueous solutions. Since most thermodynamic equilibrium models (e.g., ISORROPIA-II, E-AIM) report species in terms of concentration per volume of air (e.g., µg m^{-3}, µmol m^{-3}), the particle pH can be calculated as:

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$$pH = -\log_{10} \gamma_{H^+} H^+_{aq} = -\log_{10} \frac{1000 \gamma_{H^+} H^+_{air}}{W_i + W_o} \cong -\log_{10} \frac{1000 \gamma_{H^+} H^+_{air}}{W_i} \qquad (1b)$$

where γ_{H^+} is the molarity-based hydronium ion activity coefficient (assumed to be 1), H^+_{aq} (mole L^{-1}) is the molar concentration of hydronium ions in particle water (i.e., pH is calculated in terms of molarity), H^+_{air} (µg m^{-3}) is the hydronium ion concentration per volume of air, and W_i and W_o (µg m^{-3}) are the bulk particle water concentrations associated with inorganic and organic species per volume of air, respectively. In equation 1b, the molecular weight of H^+ is taken as 1 g $mole^{-1}$, and 1000 is the factor needed for unit conversion of g L^{-1} to µg m^{-3}. H^+_{air} and W_i are outputs of the ISORROPIA-II model. Previous studies have shown that particle pH values predicted using only W_i are reasonably accurate since the sensitivity of particle pH to the effects of W_o is small (Guo et al., 2015). For the southeastern U.S., Guo et al. (2015) reported that particle pH values predicted using only W_i were systematically 0.15 to 0.23 units lower than those predicted using W_i + W_o during the 2013 Southern Oxidant Aerosol Study (SOAS) and SCAPE campaigns. Given this small deviation and that organic aerosol hygroscopicity was not measured in this field study, we report particle pH only considering W_i.

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ISORROPIA-II was run in "forward" mode, which assumes that aerosols are "metastable" with no solid precipitates, to predict particle pH and the partitioning of semi-volatile compounds. In "forward" mode, the model calculates the gas-particle equilibrium partitioning concentrations based on the input of the total concentration of a species (i.e., gas + particle). In "reverse" mode, the model calculates the gas-particle equilibrium partitioning concentrations based on the input of only the particle-phase concentration of a species. We used "forward" mode because the "reverse" mode is sensitive to measurement errors, which often result in large model biases in the predicted particle pH (Hennigan et al., 2015). The measured particle-phase inorganic NH_4^+, SO_4^{2-} and NO_3^- concentrations and gas-phase HNO_3 and NH_3 concentrations were used as model inputs. The "metastable" assumption is reasonable since the high RH (average RH 68.9 %) observed during the study indicated that the aerosols had likely deliquesced. We excluded data for periods where the RH was above 95 % since the exponential growth in particle liquid water with RH introduces large pH uncertainties (Malm and Day, 2001; Guo et al., 2015).

In using ISORROPIA-II to predict particle pH and the partitioning of semi-volatile compounds, we also assumed that the aerosols are internally mixed and that the particle pH does not change with particle size (i.e., the overall particle pH is characterized by the particle's bulk properties). As long as some small fraction of sulfate is mixed with various aerosol components, (e.g., non-volatile cations), the assumption that aerosols are completely internally mixed has a small effect on the predicted pH (Guo et al., 2017b). However, the presence of multiple organic and inorganic species in ambient aerosols may lead to multiple phases within the particle (i.e., phase separation). Consequently, this may result in the unequal distribution of inorganic species among different phases, each with its own water activity and inorganic concentration. Previous studies have shown that liquid-liquid and solid-liquid phase separations may occur for mixed organic and inorganic aerosols at low RH and organic aerosol oxygen-to-carbon atomic ratios (O/C) (Bertram et al., 2011; Song et al., 2012; You et al., 2013; You et al., 2014b; You and Bertram, 2015). Phase separations were always observed at O/C ≤ 0.5, while no phase separation was observed at O/C ≥ 0.8. The probability for the occurrence of phase separation decreased at higher RH for 0.5 < O/C < 0.8. The average O/C for this field study is 0.69 ± 0.06. Organic acids were not included in the calculation of particle pH. This is reasonable since their total mass concentration was small compared to the total inorganic mass concentration. The average ratio of the organic acid mass concentration to the inorganic mass concentration is 0.25. Furthermore, Song et al. (2018) showed that including organic acid mass concentrations in thermodynamic model calculations had minor effects on particle pH if the system is in equilibrium. The validity of these assumptions and the resulting thermodynamic model predictions will be evaluated by comparing the predicted gas-particle partitioning ratios of semi-volatile inorganic compounds with measured values in section 3.3.

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3. Results and Discussion

3.1. NH_3 observations

Continuous measurements of NH_3 were made using the NH_3-CIMS from 13 September to 12 October. Figures 1a and 1b show the time series and average diurnal profile of NH_3,

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respectively. NH_3 concentrations ranged from 0.7 to 39.0 ppb (0.5 to 28.5 µg m^{-3}), and exhibited consistent diurnal cycles. NH_3 was generally higher in the late mornings and early afternoons. Concentrations started to increase at 07:30, which coincided with an increase in temperature at sunrise (Fig. S3). Possible reasons for the morning increase include volatilization of particulate ammonium and animal waste, entrainment from the residual layer where NH_3 may not have been depleted, evaporation of dew or fog that contained dissolved NH_3, and emission from plant stomata (Ellis et al., 2011). NH_3 decreased at 14:30, approximately 1 hour before temperature decreased, and may be due to changes in the boundary layer height. However, this hypothesis cannot be tested since the boundary layer height was not measured during the study. The diurnal plot does not account for dilution as the boundary layer expanded, and only indicates that if emissions were solely from the surface and lower concentrations aloft, these NH_3 sources were of significant magnitude.

The average NH_3 concentration measured by the NH_3-CIMS is 8.1 ± 5.2 ppb. This is approximately 2 times higher than the average NH_3 concentration (3.8 ± 2.9 ppb) measured by the denuder-based instrument operated by the SEARCH network over the same time period (Fig. S4). Differences in NH_3 concentrations measured by the two instruments may be due to positive and negative sampling artifacts caused by differences in sampling inlets (e.g., inlet length and location), frequency of calibration and background measurements, and (in the case of the denuder-based instrument) possible sample contamination during chemical analysis. Discussions on how differences in measured NH_3 concentrations affect PM_1 pH predictions will be presented in section 3.3. Nevertheless, there is a record of NH_3 concentrations measured by the denuder-based instrument at this site since 2008. Just prior to, and during this study, NH_3 concentrations are generally the highest observed since 2011 (Fig. S5). These elevated NH_3 concentrations may be due to sporadic biomass burning episodes caused by elevated temperatures and widespread drought across the southeastern U.S. in 2016 (Park Williams et al., 2017; Case and Zavodsky, 2018).

The NH_3-CIMS measurements are examined with the meteorological data to gain insights on the primary NH_3 sources during the sampling period. To account for wind speed, the 1-hour averaged NH_3 concentrations are first multiplied by their corresponding 1-hour averaged wind speeds. These normalized NH_3 concentrations are then used to construct a wind direction polar plot showing the average normalized NH_3 concentration per 10 degrees bin (Fig. 1c). The wind direction polar plot shows that the normalized NH_3 is approximately 2 times greater than the average when air masses are transported from the south-east, the general direction of the poultry CAFOs located approximately 2 km from the field site (Fig. S1), which are known for high NH_3 emissions. This conclusion is reaffirmed by NH_3 measurements by the SEARCH network's denuder-based instrument.

NH_3 concentrations measured by the two instruments in this study are substantially higher than those measured in three recent field studies conducted in the continental U.S.: 2010 California Nexus (CalNex) study, 2013 Southeast Nexus (SENEX) study and 2013 SOAS study (see Table 1). The differences in NH_3 may be attributed to differences in land use, proximity to CAFOs and meteorological conditions. The high NH_3 concentrations in this study allow us to make ambient observations of the effect of NH_3 on particle acidity and the gas-particle partitioning of semi-volatile inorganic and organic compounds, and compare them with previous studies.

3.2. PM_1 composition

The aerosol inorganic chemical composition was measured by several instruments during this study. The HR-ToF-AMS, PILS-IC and PILS-HPIC measured the composition of PM_1, while a filter-based particle composition monitor measured the composition of $PM_{2.5}$. Comparisons of aerosol SO_4^{2-}, NO_3^- and NH_4^+ mass concentrations obtained from the application of CDCE values to the raw HR-ToF-AMS data are compared to those measured by the other three instruments in Fig. S6. NH_4^+ measurements by the PILS-IC are not available for comparison due to denuder breakthrough that occurred during the study.

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SO_4^{2-} measurements by the various instruments are generally well correlated with each other, with R^2 values ranging from 0.64 to 0.92. Although PM_1 SO_4^{2-} measurements by the two PILS systems show good agreement with each other, HR-ToF-AMS CDCE-applied SO_4^{2-} measurements are approximately two times higher than the PILS and filter measurements. Similar systematic differences are also observed for NO_3^- and NH_4^+ measurements. NO_3^- and NH_4^+ measurements by the four instruments are moderately correlated (R^2 = 0.54 to 0.79 and R^2 = 0.94, respectively). NO_3^- measurements by the PILS and filter systems are mostly similar; however, HR-ToF-AMS CDCE-applied PM_1 NO_3^- and NH_4^+ measurements are approximately three times and two times higher than the PILS and filter measurements. One possible reason is that the calculated CDCE is lower due to organics dominating the aerosol composition during the study (average of 74.2 ± 7.9 % of the non-refractory PM_1 mass concentration). Lee et al. (2015) suggested that a high organic mass fraction may impede the complete efflorescence of aerosols when they are passed through the drier prior to delivery into the HR-ToF-AMS, thus reducing the particle bounce and increasing the CE value. Hence, we estimated HR-ToF-AMS PM_1 mass concentrations that would be consistent with PILS and filter measurements by multiplying all the raw HR-ToF-AMS data by a constant CE value of 0.9, which was obtained from comparisons of the raw HR-ToF-AMS SO_4^{2-} data with PILS-IC and PILS-HPIC SO_4^{2-} measurements. The constant CE-applied HR-ToF-AMS data is used in all our subsequent analyses.

Figure 2 shows the time series and average diurnal profiles of non-refractory PM_1 species. The average non-refractory PM_1 organics, SO_4^{2-}, NO_3^- and NH_4^+ mass concentrations are 5.0 ± 2.3, 1.6 ± 0.4, 0.2 ± 0.1 and 0.4 ± 0.2 μg m^{-3}, respectively. Organics are the dominant non-refractory PM_1 species, accounting for 74.2 ± 7.9 % of the non-refractory PM_1 mass concentration during the field study. Organic aerosol mass concentration was slightly higher at night, which is likely caused by changes in the boundary layer height, emission sources and SOA formation processes (Xu et al., 2015b). Previous studies have shown that nighttime SOA production in the Southeastern U.S. is largely attributed to nitrate radical oxidation and ozonolysis of monoterpenes, which are abundant at night (Pye et al., 2015; Xu et al., 2015a; Xu et al., 2015b; Lee et al., 2016; Zhang et al., 2018). Specifically, the nitrate radical oxidation of some monoterpenes (e.g., β-pinene) could form low volatility organic nitrates that are condensable and could contribute substantially to the nocturnal organic aerosol mass (Boyd et al., 2015; Boyd et al., 2017; Ng et al., 2017). Apportionment of organic aerosol sources will be discussed in an upcoming publication. SO_4^{2-} is the second most abundant non-refractory PM_1 species (16.3 ± 5.7 % mass fraction), followed by NH_4^+ (5.9 ± 2 % mass fraction) and NO_3^- (3.6 ± 2.2 % mass fraction). SO_4^{2-} mass concentration peaked in the afternoon due to enhanced SO_2 photooxidation (Weber et al., 2003). The NO_3^- mass concentration measured by the HR-ToF-AMS is the nitrate functional group ($-ONO_2$) present on organic and inorganic nitrates. Hence, the diurnal profile of the NO_3^- mass concentration in Fig. 2 has contributions from both organic and inorganic nitrates. The mass concentrations of organic and inorganic nitrates increased after sunset and peaked at sunrise (Fig. S7), likely due to the formation of organic nitrates from nighttime NO_3 chemistry and increased

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3.3. PM$_1$ pH predictions

CIMS HNO$_3$ and NH$_3$ data, HR-ToF-AMS PM$_1$ SO$_4^{2-}$ and NH$_4^+$ data, PILS-IC PM$_1$ NO$_3^-$ and non-volatile cation (Cl$^-$, Na$^+$, Ca^{2+}, K$^+$ and Mg^{2+}) data, measured temperature and RH are used as ISORROPIA-II model inputs to predict PM$_1$ W_i and pH from 13 September to 6 October. Figure 3 shows the time series and average diurnal profiles of ISORROPIA-predicted PM$_1$ W_i and pH. PM$_1$ are highly acidic with pH values ranging from 0.9 to 3.8, and an average pH of 2.2 ± 0.6. The average PM$_1$ pH was 2.5 ± 0.6 during periods where the NH$_3$ concentration was higher than 13.3 ppb (i.e., average NH$_3$ concentration + 1 standard deviation = 8.1 + 5.2 = 13.3 ppb). The PM$_1$ pH values in this study are generally similar to those reported by Guo et al. (2015) at the same field site during winter 2012. Our observation that PM$_1$ are acidic despite the high NH$_3$ concentrations in this study is consistent with previous studies showing that particle pH has weak sensitivities to wide NH$_3$ and SO$_4^{2-}$ mass concentration ranges due to pH buffering caused by the partitioning of NH$_3$ between the gas and particle phases (Weber et al., 2016; Guo et al., 2017c). This weak particle pH sensitivity also explains the small changes in PM$_1$ pH values (about 10 % lower, Fig. S8) when NH$_3$ measurements by the SEARCH network denuder-based instrument are used in ISORROPIA-II calculations (instead of NH$_3$-CIMS measurements).

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PM$_1$ pH varied by approximately 1.4 units throughout the day. W_i has an average value of 1.6 ± 1.7 µg m^{-3}. PM$_1$ W_i and pH showed similar diurnal profiles, with both peaking in the mid-morning and reaching their minima in the mid-afternoon. These diurnal trends are consistent with those previously reported by Guo et al. (2015) for PM$_1$ measured during the summer and winter in different parts of the southeastern U.S. Also shown in Fig. 3b is the diurnal profile of H^+_{air}, which peaked in the mid-afternoon. The W_i and H^+_{air} maximum/minimum ratios are comparable (6.5 and

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5.3, respectively), thus indicating that the diurnal variation in particle pH is driven by both W_i and H^+_{air}.

The average PM_1 pH for this study is about 1 unit higher than those for the SENEX and SOAS campaigns (Table 1), and is likely due to the much higher abundance of NH_3 in this study. The average NH_3 mass concentration in this study is approximately 49 times and 15 times higher than those in the SENEX and SOAS campaigns, respectively. The average PM_1 pH for this study is similar to that for the CalNex campaign even though the average NH_3 mass concentration in this study is only approximately 4 times higher than that in the CalNex campaign (Guo et al., 2017a). This may be due, in part, to PM_1 SO_4^{2-} and NO_3^- mass concentrations at CalNex being approximately 2 times and 18 times larger than those of this study, respectively. Aerosol inorganic SO_4^{2-} and NO_3^- species are hygroscopic species. The much higher NO_3^- mass concentrations in the CalNex campaign (due, in part, to high NO_x emissions) increased particle W_i substantially, which diluted H^+ and raised particle pH, resulting in more gas-to-particle partitioning of NO_3^-, and eventually leading to pH levels similar to those observed in this study. This type of feedback does not happen in the southeastern U.S. where non-volatile SO_4^{2-} dominates the uptake of particle water. It is also possible that the higher RH and lower temperatures during the CalNex campaign (relative to this study) contributed to high particle W_i, which diluted H^+ and raised particle pH levels similar to those observed in this study.

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The validity of this study's thermodynamic model predictions is evaluated by comparing the predicted gas-particle partitioning ratios of semi-volatile inorganic compounds (i.e., NO_3^- and NH_4^+) with measured values (Fig. S9). CIMS HNO_3 and NH_3 data, PILS-IC NO_3^- and HR-ToF-AMS NH_4^+ data are used in this comparison. $\varepsilon(NO_3^-)$ and $\varepsilon(NH_4^+)$ are defined as the particle-phase molar concentration divided by the total molar concentration (gas + particle), i.e., $\varepsilon(NO_3^-) = NO_3^- / (HNO_3 + NO_3^-)$ and $\varepsilon(NH_4^+) = NH_4^+ / (NH_3 + NH_4^+)$. Predicted NH_3, NH_4^+ and $\varepsilon(NH_4^+)$ values are generally within 10 % of and are highly correlated ($R^2 = 0.96$ to 0.99) with measured values (Fig. S9). While predicted HNO_3 values generally agreed with measurements, substantial scatter can be seen between the predicted and measured values for NO_3^- and $\varepsilon(NO_3^-)$. This scatter can be attributed, at least in part, to uncertainties brought about by the low PM_1 NO_3^- mass concentrations and effects of coarse mode cations (e.g., Na^+, Ca^{2+}, K^+ and Mg^{2+}) on fine mode HNO_3-NO_3^- gas-particle equilibrium (i.e., HNO_3 can partition to both fine and coarse modes, thereby affecting fine

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mode NO_3^- concentrations; no such effect occurs for NH_3-NH_4^+ gas-particle equilibrium). In general, the overall good agreement between model predictions and measurements indicated that our assumptions that aerosols are metastable (i.e., aerosols are supersaturated aqueous droplets) with no phase separation for the thermodynamic calculations are reasonable for the conditions of this study, and do not affect model predictions.

The molar fractions of NO_3^- and NH_4^+ in the particle phase (i.e., $\varepsilon(NO_3^-)$ and $\varepsilon(NH_4^+)$) measured in this study are compared with those measured during the CalNex, SENEX and SOAS campaigns. Figure 4 shows the measured $\varepsilon(NO_3^-)$ and $\varepsilon(NH_4^+)$ values as a function of their ISORROPIA-predicted particle pH for the various field studies. For each field study, only a subset of the data is chosen for this comparison ($1 \leq W_i \leq 4$ μg m^{-3} and 15 °C ≤ temperature ≤ 25 °C) to reduce the effects of variability of W_i and temperature on gas-particle partitioning for comparison with the calculated S (or sigmoidal) curves, which are calculated based on W_i = 2.5 μg m^{-3} and temperature = 20 °C. The S curves for HNO_3-NO_3^- and NH_3-NH_4^+ partitioning as a function of particle pH are also plotted as solid lines. The S curves are calculated based on the solubility and dissociation of NO_3^- and NH_4^+ species in water:

$$\varepsilon(NO_3^-) = \frac{H^*_{HNO_3} RTW_i \times 0.987 \times 10^{-14}}{\gamma_{H^+}\gamma_{NO_3^-} 10^{-pH} + H^*_{HNO_3} RTW_i \times 0.987 \times 10^{-14}} \tag{2}$$

$$\varepsilon(NH_4^+) = \frac{\dfrac{\gamma_{H^+} 10^{-pH}}{\gamma_{NH_4^+}} H^*_{NH_3} RTW_i \times 0.987 \times 10^{-14}}{1 + \dfrac{\gamma_{H^+} 10^{-pH}}{\gamma_{NH_4^+}} H^*_{NH_3} RTW_i \times 0.987 \times 10^{-14}} \tag{3}$$

where $H^*_{HNO_3}$ and $H^*_{NH_3}$ (mole^2 kg^{-2} atm^{-1}) are equilibrium constants and are the products of the Henry's law constant and the dissociation constant of HNO_3 and NH_3, respectively, R is the gas constant (8.314 m^3 Pa K^{-1} mol^{-1}), T is temperature (K), and γ_i's are activity coefficients. $H^*_{HNO_3}$ and $H^*_{NH_3}$ values at 20 °C are calculated using equations found in Clegg and Brimblecombe (1990) and Clegg et al. (1998), respectively. Activity coefficients predicted by ISORROPIA-II are $\gamma_{H^+-NO_3^-} = \sqrt{\gamma_{H^+}\gamma_{NO_3^-}} = 0.28$, $\gamma_{H^+} = 1$ and $\gamma_{NH_4^+} = 1$. Derivations of the analytically calculated S curves for $\varepsilon(NO_3^-)$ and $\varepsilon(NH_4^+)$ in equations 2 and 3 can be found in Guo et al. (2017a). As shown in Fig. 4, the measured $\varepsilon(NO_3^-)$ and $\varepsilon(NH_4^+)$ values for the four field studies all generally converged on the calculated S curves. The higher particle pH values in this study and the CalNex campaign relative to those for the SENEX and SOAS campaigns resulted in less NH_3 and more HNO_3 partitioned to the particle phase, as predicted by these simple analytical expressions. A similar analysis will be performed for the organic acids in section 3.5.

3.4. WSOC and water-soluble organic acids

The time series and average diurnal profiles of $WSOC_g$ and $WSOC_p$ are shown in Fig. S10. The average $WSOC_g$ mass concentration (3.6 ± 2.7 μgC m^{-3}) is roughly four times higher than that of $WSOC_p$ (1.0 ± 0.6 μgC m^{-3}). The diurnal profile of $WSOC_p$ is somewhat flat, likely due to various organic aerosol sources having different water solubility and diurnal cycles, and compensating each other throughout the day (Xu et al., 2015b; Xu et al., 2017). In contrast, $WSOC_g$ displayed strong diurnal variations. $WSOC_g$ increased at 07:30, which coincided with the sharp increase in solar irradiance (Fig. S3). $WSOC_g$ decreased at 21:30, approximately 2 hours after sunset. Also shown in Fig. S10 are the time series and average diurnal profile of the mass fraction of total WSOC in the particle phase, i.e., $F_p = WSOC_p / (WSOC_p + WSOC_g)$. The peak F_p coincided with the minima of $WSOC_g$ at 07:30.

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The average $WSOC_g$ and $WSOC_p$ (3.6 ± 2.7 μgC m^{-3} and 1.0 ± 0.6 μgC m^{-3}) are slightly lower than those measured during the SOAS campaign (SOAS $WSOC_g$ = 4.9 μgC m^{-3} and $WSOC_p$ = 1.7 μgC m^{-3}) (Xu et al., 2017). While the diurnal profiles of $WSOC_p$ in both studies are flat, the diurnal profiles of $WSOC_g$ measured in the two studies are different. $WSOC_g$ measured in the SOAS study decreased at sunset, while $WSOC_g$ measured in this study decreased 2 hours after sunset. Differences in $WSOC_g$ diurnal profiles in the two studies are likely due to differences in emission sources as a result of different sampling periods (SOAS was in early summer and this study was in early fall), land use and/or land cover. The ratio of $WSOC_p$ to OC for this study was estimated at 30 %, but this comparison is imprecise because $WSOC_p$ was PM_1 and OC was $PM_{2.5}$ (refer to Fig. S11 and SI section S2).

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Figure 5 shows the time series of particle- and gas-phase concentrations of formic, acetic, oxalic, malonic, succinic, glutaric and maleic acids. Their diurnal profiles are shown in Fig. 6. Gas-phase measurements of glutaric and maleic acids are not available. Gas-phase measurements of butyric, glycolic, propionic and valeric acids were also measured during the study and have been presented in Nah et al. (2018), but will not be discussed here since their particle-phase measurements are not available.

Assuming that all the measured organic acids are completely water-soluble, 30 % of the $WSOC_g$ is comprised of these organic acids (Nah et al., 2018). Formic and acetic acids are the most abundant gas-phase organic acids, with averages of 2.2 ± 1.6 and 1.9 ± 1.3 μg m^{-3}, respectively. The average carbon mass fraction of $WSOC_g$ comprised of formic and acetic acids are 7 and 13 %, respectively. All the gas-phase organic acids displayed strong and consistent diurnal cycles, with higher concentrations being measured during warm and sunny days. Their concentrations start to increase at sunrise (at 07:30), building to a peak between 15:30 and 19:30, then decrease overnight.

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Nah et al. (2018) previously showed that the measured gas-phase organic acids during the study, including oxalic acid, likely have the same or similar sources. Poor correlations between gas-phase organic acid concentrations and those of anthropogenic pollutants (HNO_3, SO_2, CO and O_3) indicated that these organic acids are not due to anthropogenic emissions, and are likely biogenic in nature. Biogenic emissions of gas-phase organic acids and/or their BVOC precursors are elevated at high temperatures, resulting in higher organic acid concentrations during warm and sunny days. For example, isoprene, which is the dominant BVOC in Yorkville, has a somewhat similar diurnal profile as the organic acids. In addition, the concentration of isoprene is moderately correlated with those of formic and acetic acids (Fig. S10 of Nah et al., 2018), which are known products of isoprene photooxidation. Some of these gas-phase organic acids may also be formed in the particle phase during organic aerosol photochemical aging, with subsequent volatilization into the gas phase. The gas-particle partitioning of organic acids likely depends on thermodynamic conditions, which are controlled by particle pH and W_i and meteorological conditions as will be shown in section 3.5.

The measured particle-phase water-soluble organic acids contributed on average 6 % to the HR-ToF-AMS-measured organic aerosol mass concentration. The average carbon mass fraction of $WSOC_p$ comprised of these organic acids is 4 %. Previous studies have shown that particle-phase organic acids found in rural environments are oxidation products of gas-phase aliphatic monocarboxylic acids, which are formed in the photochemical oxidation of biogenic unsaturated fatty acids and other BVOC precursors (Kawamura and Gagosian, 1987; Kawamura and Ikushima,

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1993; Kerminen et al., 2000; Kawamura and Bikkina, 2016). These particle-phase organic acids can also be produced during the multiphase photochemical aging of ambient organic aerosols (Ervens et al., 2004; Lim et al., 2005; Sorooshian et al., 2007; Sorooshian et al., 2010).

Oxalate is the most abundant measured particle-phase water-soluble organic acid anion (contributing on average 26 % to the total particle-phase organic acid mass concentration), with mass concentrations ranging from 0.01 to 0.34 μg m^{-3} and a average of 0.07 ± 0.05 μg m^{-3}. Acetate (average of 0.06 ± 0.03 μg m^{-3}) and formate (average of 0.05 ± 0.03 μg m^{-3}) are the second and third most abundant measured particle-phase water-soluble organic acid anions, respectively. Particle-phase formate, acetate and maleate showed weak diurnal variations, and may be due, in part, to various emission sources having different diurnal cycles and compensating each other throughout the day. Particle-phase oxalate, malonate and succinate peaked in the mid- to late afternoon, while glutarate generally peaked in the mid-morning. This suggests that while the production of these organic acids is photochemically-driven, they may have different BVOC precursors and/or different photochemical production pathways. In addition, since oxalic (C_2), malonic (C_3), succinic (C_4) and glutaric (C_5) acids belong to the same homologous series of organic diacids, it is possible that the photochemical aging of particle-phase glutaric acid resulted in the formation of its successive homologues via the cleavage of C-C bonds. Hence, organic aerosol photochemical aging may also have contributed to the diurnal profiles of particle-phase oxalate, malonate, succinate and glutarate.

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3.5. Gas-particle partitioning of organic acids

The online and simultaneous measurements of gas- and particle-phase organic acid mass concentrations provided the opportunity to study gas-particle partitioning behavior of semi-volatile organic compounds with respect to particle pH, as is more commonly done with semi-volatile inorganic species (see section 3.3). Since formic, acetic and oxalic acids are the three most abundant measured organic acids present in the gas and particle phases, we focus on the gas-particle partitioning behaviors of these three organic acids. The average molar fractions (± 1 standard deviation) of formic, acetic and oxalic acid in the particle phase (i.e., $\varepsilon(HCOO^-)$, $\varepsilon(CH_3CO_2^-)$ and $\varepsilon(C_2O_4^{2-})$) are 3.6 ± 3.6 %, 5.8 ± 5.0 % and 73.7 ± 9.8 %, respectively. The uncertainties of these ratios for formic, acetic and oxalic acids are 16, 16 and 17 %, respectively,

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which are obtained from the propagation of their SF_6-CIMS and PILS-HPIC measurement uncertainties.

3.5.1. Oxalic acid

To investigate the factors affecting oxalic acid gas-particle partitioning, the equation for the S curve describing the dependence of oxalic acid gas-particle partitioning (i.e., $\varepsilon(C_2O_4^{2-})$ = $C_2O_4^{2-}$ / ($C_2H_2O_4$ + $C_2O_4^{2-}$)) on particle pH is derived. As shown in SI section S3, the analytically calculated S curve for $\varepsilon(C_2O_4^{2-})$ can be simplified to:

$$\varepsilon(C_2O_4^{2-}) \cong \frac{H_{C_2H_2O_4} W_i RT\left(\frac{\gamma_{H^+}\gamma_{C_2HO_4^-}}{\gamma_{C_2H_2O_4}}10^{-pH}+K_{a1}\right)\times 0.987\times 10^{-14}}{\gamma_{H^+}\gamma_{C_2HO_4^-}10^{-pH}+H_{C_2H_2O_4} W_i RT\left(\frac{\gamma_{H^+}\gamma_{C_2HO_4^-}}{\gamma_{C_2H_2O_4}}10^{-pH}+K_{a1}\right)\times 0.987\times 10^{-14}} \quad (4)$$

where $H_{C_2H_2O_4}$ (mole L^{-1} atm^{-1}) is the Henry's law constant for oxalic acid, K_{a1} (mole L^{-1}) is the first acid dissociation constant for oxalic acid, R is the gas constant (8.314 m^3 Pa K^{-1} mol^{-1}), T is temperature (K), and γ_i's are activity coefficients. We used the web version of AIOMFAC (www.aiomfac.caltech.edu) (Zuend et al., 2008; Zuend et al., 2011; Zuend et al., 2012) to compute an average $\gamma_{C_2H_2O_4}$ value of 0.0492. Since AIOMFAC does not predict $\gamma_{H^+}\gamma_{C_2HO_4^-}$, we assumed that $\gamma_{H^+}\gamma_{C_2HO_4^-} = \gamma_{H^+}\gamma_{NO_3^-}$, and used the ISORROPIA-predicted $\gamma_{H^+}\gamma_{NO_3^-}$ value of 0.07. We used the average of $H_{C_2H_2O_4}$ values provided by Clegg et al. (1996), Compernolle and Muller (2014) and Saxena and Hildemann (1996) (6.11×10^8 mole L^{-1} atm^{-1} at 25 °C), and accounted for the effect of temperature using equation 19 in Sander (2015). Although K_{a1} also depends on temperature, we used the K_{a1} value at 25 °C (5.62×10^{-2} mole L^{-1}, (Haynes, 2014)) for all the oxalic acid S curve calculations since equations that compute K_{a1} values for pure aqueous oxalic acid solutions at different temperatures are not available in the literature. In addition, the temperatures observed in this study were close to 25 °C (study-average temperature = 23.4 ± 4.0 °C).

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Different S curves for $\varepsilon(C_2O_4^{2-})$ are calculated using 1-hour average values obtained from the diurnal profiles of temperature and W_i (specifically at 00:30, 06:30 and 12:30). The shape of the S curve changes with the time of day due to the diurnal variations of temperature and W_i (Fig S12 and SI section S3). The S curves for $\varepsilon(C_2O_4^{2-})$ are very different from those of other acids,

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such as ε(NO_3^-) (shown in Fig. 4b). From the S curves for ε($C_2O_4^{2-}$), which are calculated using conditions in this study, some molar fraction of oxalic acid is always expected to be present in the particle phase, even at low particle pH (i.e., the S curve does not go to zero at low pH). In contrast, HNO_3 is expected to be present primarily in the gas phase at low particle pH (i.e., pH < 1) under similar temperature and W_i conditions. This is due primarily to differences in the Henry's law constants for the two acids. H_{HNO_3} (2.57×10^5 mole L^{-1} atm^{-1}) at 23.4 °C is three orders of magnitude smaller than $H_{C_2H_2O_4}$ (7.27×10^8 mole L^{-1} atm^{-1}) (Clegg and Brimblecombe, 1990; Sander, 2015). This means that some undissociated form of oxalate can be found in the particle phase at any pH, and the molar fraction of this form increases with particle W_i (see Fig. S12). Oxalic acid's very high Henry's law constant combined with the W_i conditions in this study ensures that some fraction of the organic acid will be in the particle phase regardless the particle pH.

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Figure 7 compares the measured ε($C_2O_4^{2-}$) vs. ISORROPIA-predicted PM_1 pH to the analytically calculated S curves(s). The S curve is calculated based on the average temperature and W_i from 13 September to 6 October (23.4 ± 4.0 °C and 1.6 ± 1.7 μg m^{-3}, respectively). We also calculated the "upper" and "lower" bounds of this S curve based on one standard deviation from the average temperature and average W_i. Temperature = 27.4 °C and W_i = 0.5 μg m^{-3} are used for calculations of the "lower" bound, while temperature = 19.4 °C and W_i = 3.3 μg m^{-3} are used for calculations of the "upper" bound. For the ambient data, a range in W_i (0.5 to 4 μg m^{-3}) and temperature (15 to 31 °C) is chosen to be close to the analytical calculation. As shown in Fig. 7, the measured ε($C_2O_4^{2-}$) generally converged around the S curve calculated using the average temperature and W_i values. Although there is some scatter, the measured ratios are mostly within the "upper" and "lower" bounds of the S curve.

Since the measured ε($C_2O_4^{2-}$) are in general agreement with the analytically calculated S curve (Fig. 7), we can use the S curve to understand qualitatively how high NH_3 events at the site affect oxalic acid gas-particle partitioning. Here we define high NH_3 events as periods where the NH_3 concentration was higher than 13.3 ppb (which is the average NH_3 concentration + 1 standard deviation). As discussed in section 3.3, the PM_1 pH during high NH_3 events is 2.5 ± 0.6, which is slightly higher than the average PM_1 pH of 2.2 ± 0.6. Based on the S curve calculated using the

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average temperature and W_i values, ε($C_2O_4^{2-}$) increases from 81 % to 89 % when particle pH increases from 2.2 to 2.5. While this result indicates that high NH_3 concentrations can raise the particle pH sufficiently such that it can promote gas-to-particle partitioning of oxalic acid, this is not always the case. Specifically, increasing the particle pH from -2 (or lower) to 1 will not result in a significant increase in ε($C_2O_4^{2-}$). Therefore, whether or not particle pH, and consequently oxalic acid gas-particle partitioning, is sensitive to NH_3 concentration depends strongly on particle pH values.

We also examined how well the analytically calculated S curve for ε($C_2O_4^{2-}$) captures diurnal variations of the measured ε($C_2O_4^{2-}$). The ambient data is divided into two 12 hour sets (08:00 to 19:59 and 20:00 to 07:59) based on the diurnal profile of solar irradiance. Two S curves and their corresponding "upper" and "lower" bounds are calculated based on the average temperature and W_i of the two data sets, and are subsequently compared to the ambient data. As shown in Fig. S13, the measured ε($C_2O_4^{2-}$) in both data sets are generally consistent with predicted values.

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A number of inferences can be drawn from the overall good agreement between the predicted and measured molar fractions of oxalic acid in the particle phase in Figs. 7 and S13. Our assumptions regarding the activity coefficients, Henry's law constant and acid dissociation constants used in the S curve calculations of ε($C_2O_4^{2-}$) are reasonable for the conditions of this study (or are at least self-consistent). Analytically calculated S curves are a simple way of exploring how the gas-particle partitioning of semi-volatile inorganic and organic compounds in the atmosphere are affected by the compound's physicochemical properties (e.g., Henry's law constants and acid dissociation constants), temperature, W_i and pH. Overall, these results indicate that particle-phase oxalate is in equilibrium with gas-phase oxalic acid, and that particle pH can influence particle-phase oxalate concentrations. It also showed that particle-phase oxalate can be found over a broad pH range, and that the presence of oxalate does not necessarily provide insights of the particle pH. Because of its high Henry's law constant, particle-phase oxalate can be found in aerosols even at extremely low pH values (i.e., the flat region in Fig. 7), although our data cannot be used to test this since ambient particle pH values in this study are too high.

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3.5.2 Formic and acetic acids

Similar comparisons between the predicted and measured ε(HCOO$^-$) and ε(CH$_3$CO$_2^-$) can also be made. Derivation of the equations for S curves describing the dependence of formic and acetic acid gas-particle partitioning (i.e., ε(HCOO$^-$) = HCOO$^-$ / (HCOOH + HCOO$^-$) and ε(CH$_3$CO$_2^-$) = CH$_3$CO$_2^-$ / (CH$_3$CO$_2$H + CH$_3$CO$_2^-$), respectively) on particle pH are similar to that of HNO$_3$ since they are monoprotic acids:

$$\varepsilon(HCOO^-) = \frac{H_{HCOOH}W_iRT\left(\frac{\gamma_{H^+}\gamma_{HCOO^-}}{\gamma_{HCOOH}}10^{-pH}+K_{a1}\right)\times 0.987\times 10^{-14}}{\gamma_{H^+}\gamma_{HCOO^-}10^{-pH}+H_{HCOOH}W_iRT\left(\frac{\gamma_{H^+}\gamma_{HCOO^-}}{\gamma_{HCOOH}}10^{-pH}+K_{a1}\right)\times 0.987\times 10^{-14}} \quad (5)$$

$$\varepsilon(CH_3CO_2^-) = \frac{H_{CH_3CO_2H}W_iRT\left(\frac{\gamma_{H^+}\gamma_{CH_3CO_2^-}}{\gamma_{CH_3CO_2H}}10^{-pH}+K_{a1}\right)\times 0.987\times 10^{-14}}{\gamma_{H^+}\gamma_{CH_3CO_2^-}10^{-pH}+H_{CH_3CO_2H}W_iRT\left(\frac{\gamma_{H^+}\gamma_{CH_3CO_2^-}}{\gamma_{CH_3CO_2H}}10^{-pH}+K_{a1}\right)\times 0.987\times 10^{-14}} \quad (6)$$

where H_{HCOOH} and $H_{CH_3CO_2H}$ (mole L^{-1} atm^{-1}) are the Henry's law constants for formic and acetic acid, K_{a1}'s (mole L^{-1}) are the first acid dissociation constants, *R* is the gas constant (8.314 m^3 Pa K^{-1} mol^{-1}), *T* is temperature (K), and γ_i's are activity coefficients. We used the web version of AIOMFAC (www.aiomfac.caltech.edu) (Zuend et al., 2008; Zuend et al., 2011; Zuend et al., 2012) to compute average γ_{HCOOH} and γ_{CH_3COOH} values of 0.334 and 2.150, respectively. Similar to the case of oxalic acid, we assumed that $\gamma_{H^+}\gamma_{HCOO^-}$ = $\gamma_{H^+}\gamma_{CH_3COO^-}$ = $\gamma_{H^+}\gamma_{NO_3^-}$, and used the ISORROPIA-predicted $\gamma_{H^+}\gamma_{NO_3^-}$ value of 0.07. Temperature-dependent H_{HCOOH} and $H_{CH_3CO_2H}$ values are obtained from Sander (2015) using the same methodology employed to determine temperature-dependent $H_{C_2H_2O_4}$ values. We used K_{a1} values at 25 °C (1.78 x 10^{-4} mole L^{-1} for formic acid, and 1.75 x 10^{-5} mole L^{-1} for acetic acid (Haynes, 2014)) for the S curve calculations.

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S curves for ε(HCOO$^-$) and ε(CH$_3$CO$_2^-$) calculated based on temperature = 23.4 °C and W_i = 1.6 μg m^{-3} can be seen in Fig. 8. Practically no formic or acetic acids are predicted to partition to the particle phase (relative to oxalic acid) for the range of PM$_1$ pH calculated in this study. This is due to significant differences in the Henry's law constants and acid dissociation constants for the three organic acids. H_{HCOOH} and $H_{CH_3CO_2H}$ (9540 and 5370 mole L^{-1} atm^{-1}, respectively) at 23.4 °C are substantially smaller than $H_{C_2H_2O_4}$ (7.27 x 10^8 mole L^{-1} atm^{-1}) (Sander, 2015). The K_{a1} values for formic and acetic acids (1.78 x 10^{-4} and 1.75 x 10^{-5} mole L^{-1}, respectively) are also considerably smaller than the K_{a1} value for oxalic acid (5.62 x 10^{-2} mole L^{-1}) (Haynes, 2014). Note that H_{HNO_3} is between that of $H_{C_2H_2O_4}$ and those of H_{HCOOH} and $H_{CH_3CO_2H}$ (compare Fig. 4b with Figs. 7 and 8).

As shown in Fig. 8, higher than expected levels of formate and acetate are observed in the particle phase. This has also been reported in previous studies (Liu et al., 2012). Laboratory tests showed that the disagreement cannot be explained by positive biases in the particle-phase formate and acetate PILS-HPIC measurements resulting from less than 100 % gas removal by the carbon denuder. The measured denuder efficiency for formic acid was ≥ 99.97% (SI section S4). The possibility that formic and acetic acid dimers in the aqueous phase (Schrier et al., 1964; Gilson et al., 1997; Chen et al., 2008) may result in higher than predicted molar fractions of formate and acetate in the particle phase was explored, but also could not explain the observed gas-particle partitioning of these acids (SI section S5). The disagreement could be due to incorrect Henry's law constants for formic and acetic acids. However, the Henry's law constants for formic and acetic acid would have to be ~10^4 times and ~3×10^5 times larger than their literature values, respectively, in order for their S curves to match our measured molar fractions of formic and acetic acid in the particle phase. In addition, formic and acetic acids may not be internally mixed with most of the other PM_1 aerosol components (e.g., SO_4^{2-}, NO_3^-, NH_4^+, CH_3CO_2H), and thus are not associated with acidic aerosols, as assumed above. They may instead be associated with aerosols largely composed of non-volatile cations and have a pH closer to neutral. More research is needed to explain this disagreement.

4. Summary

Gas- and particle-phase measurements were conducted in Yorkville, Georgia (a rural field site) during fall 2016. The goal of the field study was to understand how NH_3 affects particle acidity, and consequently SOA formation through the gas-particle partitioning of semi-volatile inorganic and organic compounds. Since it is a rural site surrounded by forest, agricultural land and CAFOs, this study provided an opportunity for ambient observations in an area impacted by high local emissions of BVOCs and NH_3.

NH_3 concentrations measured by the NH_3-CIMS ranged from 0.7 to 39.0 ppb (average 8.1 ± 5.2 ppb), which were substantially higher than typical levels in the southeastern U.S.. PM_1 inorganic chemical composition, gas-phase HNO_3 and NH_3 concentrations, temperature and RH

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were used as model inputs in the ISORROPIA-II thermodynamic model to calculate PM_1 pH and W_i. PM_1 pH ranged from 0.9 to 3.8, with an average pH of 2.2 ± 0.6. The measured and predicted HNO_3-NO_3^- and NH_3-NH_4^+ gas-particle partitioning ratios were in good agreement. The measured gas-phase organic acids were estimated to contribute 30 % of the overall $WSOC_g$ on a carbon mass basis, whereas measured particle-phase organic acids comprised 6 % of the total organic aerosol mass concentration and 4 % of the overall $WSOC_p$ on a carbon mass basis. Formic and acetic acids were the most abundant gas-phase organic acids, with averages of 2.2 ± 1.6 and 1.9 ± 1.3 µg m^{-3}, respectively. Oxalate was the most abundant particle-phase water-soluble organic acid anion, with a average of 0.07 ± 0.05 µg m^{-3}. Measured oxalic acid gas-particle partitioning ratios generally agreed with analytical predictions, which were based on oxalic acid's physicochemical properties (specifically, its Henry's law constants, acid dissociation constants and activity coefficients), temperature, W_i and particle pH. The partitioning of oxalic acid to the particle phase is highly sensitive to temperature and W_i. In contrast, the partitioning of formic and acetic acids to the particle phase were higher than predicted for reasons currently unknown.

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Although past air regulations have resulted in decreased sulfate, nitrate and ammonium aerosol mass concentrations across the U.S., our study suggests that the current limited regulation of NH_3 emissions may result in some increase in the organic aerosol mass concentration due to increased gas-to-particle partitioning of some organic acids. However, in this study, the effect was small since the organic acids comprised a small fraction of the overall organic aerosol mass.

5. Acknowledgements

The authors thank Eric Edgerton (Atmospheric Research and Analysis, Inc.) for providing SEARCH network measurements and meteorological data.

6. Funding

This publication was developed under U.S. Environmental Protection Agency (EPA) STAR Grant R835882 awarded to Georgia Institute of Technology. It has not been formally reviewed by the EPA. The views expressed in this document are solely those of the authors and do not necessarily reflect those of the EPA. EPA does not endorse any products or commercial services mentioned in this publication.

7. Competing financial interests

The authors declare no competing financial interests.

8. Data availability

Data can be accessed by request (rweber@eas.gatech.edu).

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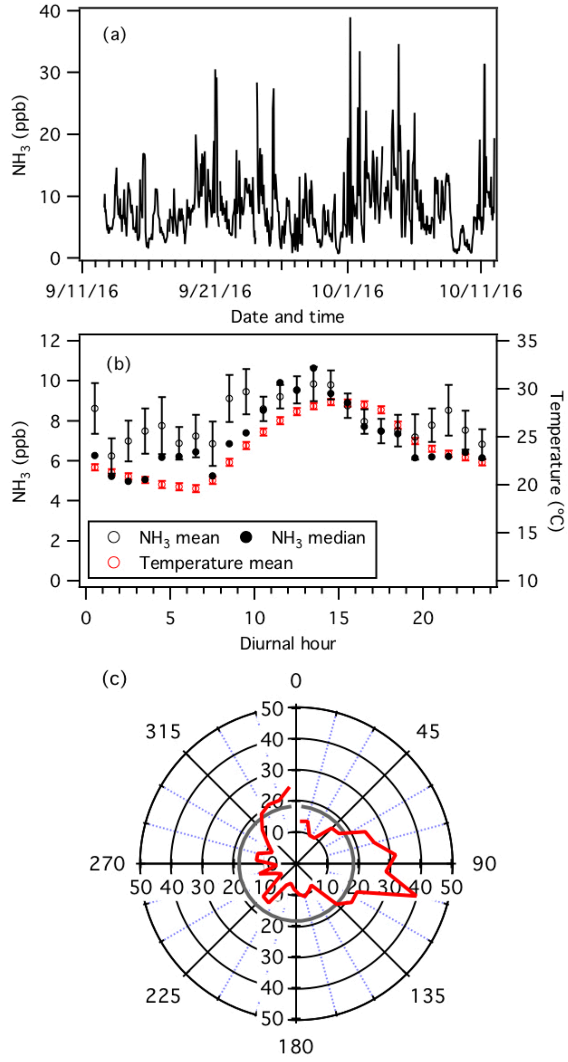

Figure 1: Measurements by the NH$_3$-CIMS during the second half of the study. (a) Time series of NH$_3$ concentration. The data is displayed as 1-hour averages. (b) Diurnal profiles of NH$_3$ concentration (mean and median) and temperature. Error bars shown are the standard errors. Dates and times displayed are local time. All the concentrations represent averages in 1-hour intervals

and the standard errors are plotted as error bars. (c) Average NH_3 concentration normalized to wind speed (i.e., NH_3 concentration (ppb) x wind speed (m s^{-1})) in each 10 degrees bin (red line). The average normalized NH_3 concentration is shown as a grey line.

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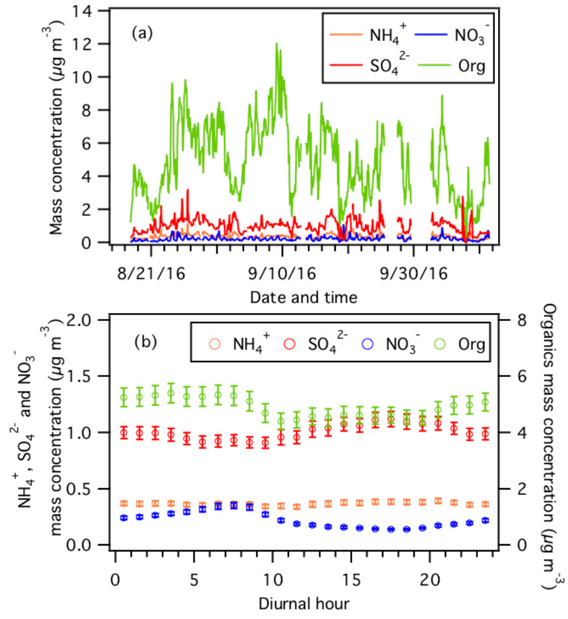

Figure 2: (a) Time series and (b) diurnal profiles of non-refractory PM_1 species measured by the AMS. Error bars shown in panel (b) are the standard errors. Dates and times displayed are local time. All the mass concentrations shown here are obtained from scaling the raw data by 0.5. Refer to the text for details.

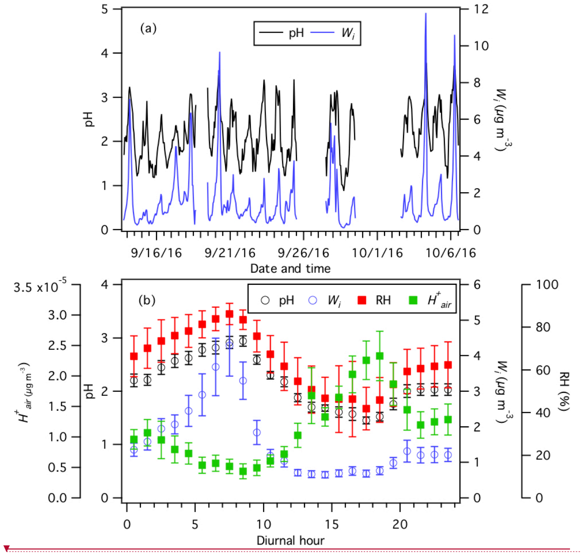

Figure 3: (a) Time series and (b) diurnal profiles of ISORROPIA-predicted PM$_1$ pH and W_i. The diurnal profiles of RH and ISORROPIA-predicted H^+_{air} are also shown in panel (b). Dates and times displayed are local time. All the data shown here represent averages in 1-hour intervals. Error bars shown in panel (b) are the standard errors.

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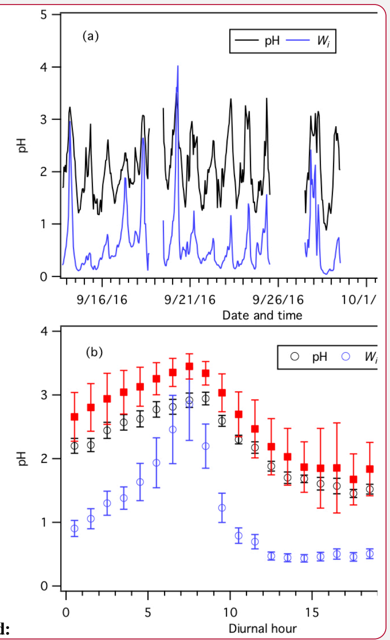

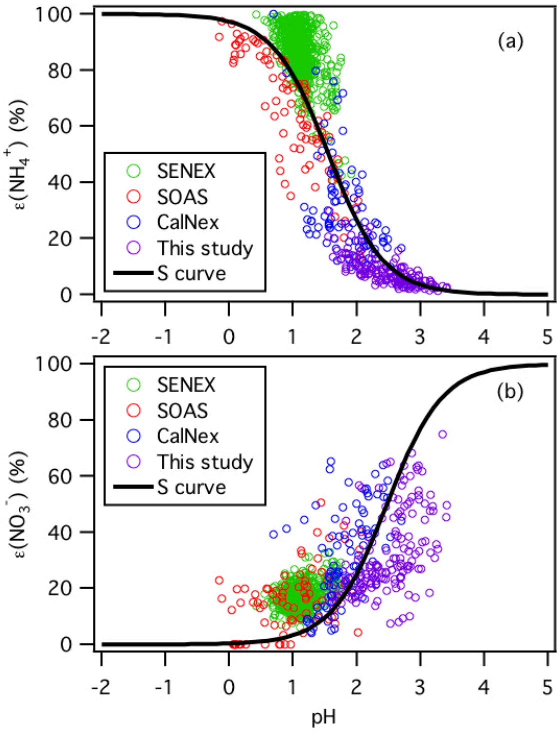

Figure 4: Analytically calculated S curves of ε(NH_4^+) and ε(NO_3^-) and ambient data plotted against ISORROPIA-predicted particle pH for this study, SENEX, SOAS and CalNex. For the ambient datasets, a narrow range of W_i (1 to 4 μg m^{-3}) and temperature (15 to 25 °C) are selected to be close to the analytical calculation input (i.e., W_i = 2.5 μg m^{-3} and temperature = 20 °C). Similar to Guo et al. (2017a), $\gamma_{NH_4^+} = 1$ and $\gamma_{H^+-NO_3^-} = \sqrt{\gamma_{H^+}\gamma_{NO_3^-}} = 0.28$ are used for the analytically calculated S curves.

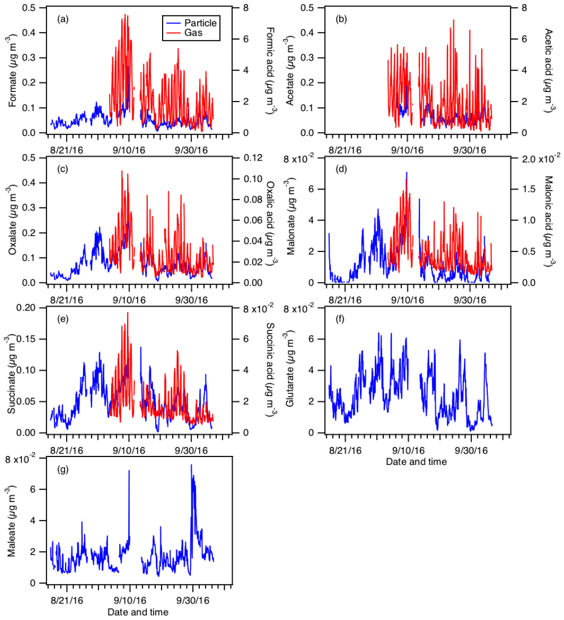

Figure 5: Particle- and gas-phase measurements of (a) formic, (b) acetic, (c) oxalic, (d) malonic, (e) succinic, (f) glutaric, and (g) maleic acids. Particle-phase measurements are shown on the left y axes, while gas-phase measurements are shown on the right y axes. Dates and times displayed are local time. Gas-phase measurements of glutaric and maleic acids are not available.

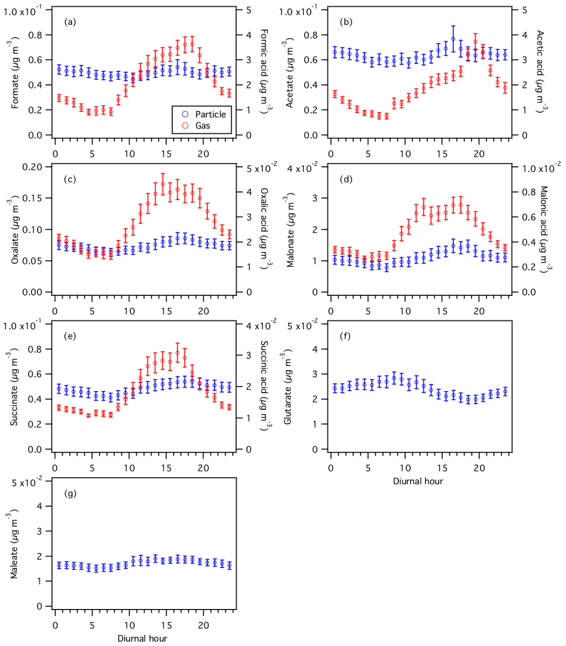

Figure 6: Diurnal profiles of particle- and gas-phase (a) formic, (b) acetic, (c) oxalic, (d) malonic, (e) succinic, (f) glutaric, and (g) maleic acids. Particle-phase measurements are shown on the left y axes, while gas-phase measurements are shown on the right y axes. All the data shown here represent averages in 1-hour intervals. Error bars shown are the standard errors.

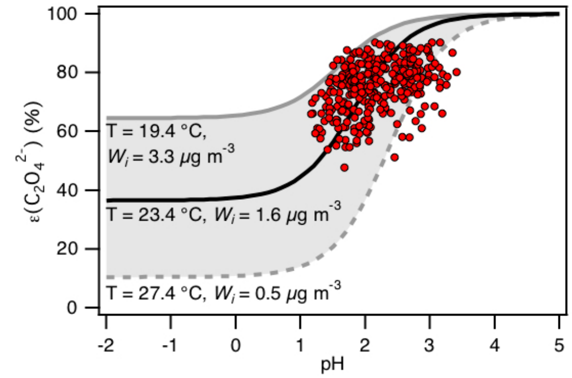

Figure 7: Analytically calculated S curve of $\varepsilon(C_2O_4^{2-})$ and ambient data from 13 September to 6 October 2016 plotted against ISORROPIA-predicted particle pH. For the ambient data, a range in W_i (0.5 to 4 μg m^{-3}) and temperature (15 to 31 °C) are chosen to be close to the analytically calculated outputs. For the analytically calculated S curves, we used $\gamma_{C_2H_2O_4}$ = 0.0492 (AIOMFAC predicted). We also assumed that $\gamma_{H^+}\gamma_{C_2HO_4^-} = \gamma_{H^+}\gamma_{NO_3^-}$, and used the ISORROPIA-predicted $\gamma_{H^+-NO_3^-} = \sqrt{\gamma_{H^+}\gamma_{NO_3^-}}$ = 0.265. The black line is the S curve calculated using the selected time period's average temperature (23.4 ± 4.0 °C) and W_i (1.6 ± 1.7 μg m^{-3}). The grey lines are S curves calculated using one standard deviation from the average temperature and W_i (i.e., temperature = 27.4 °C and W_i = 0.5 μg m^{-3} for dotted grey line, temperature = 19.4 °C and W_i = 3.3 μg m^{-3} for solid grey line).

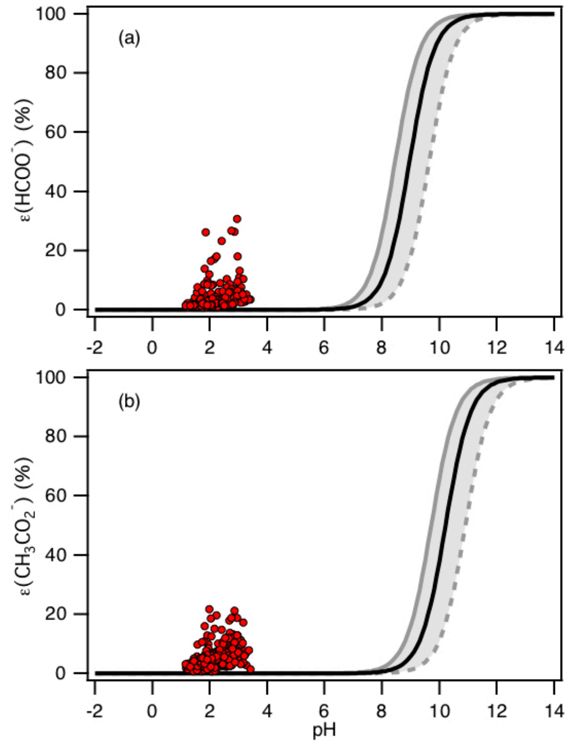

Figure 8: Analytically calculated S curves of ε($HCOO^-$) and ε($CH_3CO_2^-$) (solid black lines) and ambient data from 13 September to 6 October 2016 plotted against ISORROPIA-predicted particle pH (shown in panels (a) and (b), respectively). For the ambient data, a narrow range in W_i (0.5 to 4 µg m^{-3}) and RH (20 to 90 %) is chosen to be close to the analytically calculated outputs. For the analytically calculated S curves, we used γ_{HCOOH} = 0.334 and γ_{CH_3COOH} = 2.150 (AIOMFAC predicted). We also assumed that $\gamma_{H^+}\gamma_{HCOO^-}$ = $\gamma_{H^+}\gamma_{CH_3COO^-}$ = $\gamma_{H^+}\gamma_{NO_3^-}$, and used the ISORROPIA-predicted $\gamma_{H^+-NO_3^-} = \sqrt{\gamma_{H^+}\gamma_{NO_3^-}}$ = 0.265. The black lines are S curves calculated using the selected time period's average temperature (23.4 ± 4.0 °C) and W_i (1.6 ± 1.7 µg m^{-3}). The grey lines are S curves calculated using one standard deviation from the average temperature and W_i (i.e., temperature = 27.4 °C and W_i = 0.5 µg m^{-3} for dotted grey line, temperature = 19.4 °C and W_i = 3.3 µg m^{-3} for solid grey line).

Table 1: Comparisons between different field campaigns for particle pH, major inorganic ions and gases and meteorological conditions. All pH values were calculated using ISORROPIA-II run in forward mode. These statistics were previously compiled by Guo et al. (2017a). Campaign acronyms used here stand for the California Research at the Nexus of Air Quality and Climate Change (CalNex), Southern Oxidant and Aerosol Study (SOAS), and Southeastern Nexus of Air Quality and Climate (SENEX).

Campaign	CalNex		SOAS	SENEX	This study
Type	Ground		Ground	Aircraft	Ground
PM cut size	PM_1	$PM_{2.5}$[a]	PM_1&$PM_{2.5}$[b]	PM_1	PM_1
Year	2010		2013	2013	2016
Season	(Early Summer)		Summer	Summer	Fall
Region/Location	SW US		SE US	SE US	SE US
SO_4^{2-}, μg m^{-3}	2.86 ± 1.70	1.88 ± 0.69	1.73 ± 1.21	2.05 ± 0.80	1.6 ± 0.4
NO_3^-, μg m^{-3}	3.58 ± 3.65	3.74 ± 1.53	0.08 ± 0.08	0.28 ± 0.09	0.20 ± 0.10
HNO_3, μg m^{-3}	6.65 ± 7.03	4.45 ± 3.59	0.36 ± 0.14	1.35 ± 0.66	0.50 ± 0.26
$\varepsilon(NO_3^-)$	39 ± 16 %	51 ± 18 %	22 ± 16 %	18 ± 6 %	26 ± 15 %
Total NO_3^-, μg m^{-3}	10.22 ± 9.74	8.19 ± 3.89	0.45 ± 0.26	1.63 ± 0.70	0.70 ± 0.28
NH_4^+, μg m^{-3}	2.06 ± 1.67	1.79 ± 0.65	0.46 ± 0.34	1.06 ± 0.25	0.40 ± 0.20
NH_3, μg m^{-3}	1.37 ± 0.90	0.75 ± 0.61	0.39 ± 0.25	0.12 ± 0.19	5.79 ± 3.67
$\varepsilon(NH_4^+)$	55 ± 25%	71 ± 19%	50 ± 25%	92 ± 11%	7 ± 5 %
Total NH_4^+, μg m^{-3}	3.44 ± 1.81	2.54 ± 0.89	0.78 ± 0.50	1.17 ± 0.81	6.19 ± 3.68
Na^+, μg m^{-3}	\	0.77 ± 0.39	0.03 ± 0.07	\	\
Cl^-, μgm^{-3}	\	0.64 ± 0.48	0.02 ± 0.03	\	0.01 ± 0.01
RH, %	79 ± 17	87 ± 9	74 ± 16	72 ± 9	69 ± 18
T, °C	18 ± 4	18 ± 3	25 ± 3	22 ± 3	24 ± 4
W_i, μg m^{-3}	13.9 ± 18.1	29.8 ± 20.7	5.1 ± 3.8	3.2 ± 2.8	1.6 ± 1.7
pH	1.9 ± 0.5	2.7 ± 0.3	0.9 ± 0.6	1.1 ± 0.4	2.2 ± 0.6
Reference	(Guo et al., 2017a)		(Guo et al., 2015)	(Xu et al., 2016)	This study

[a] Only during the last week of CalNex.

[b] $PM_{2.5}$ was sampled in the first half and PM_1 sampled in the second half of the study. Various parameters were similar in both cases. Crustal components were higher, but are overall generally in low concentrations so the differences had minor effects. For example, $PM_{2.5}$ Na^+ was 0.06 ± 0.09 μg m^{-3} and PM_1 Na^+ was 0.01 ± 0.01 μg m^{-3}.

Characterization of Aerosol Composition, Aerosol Acidity and Organic Acid Partitioning at an Agriculture-Intensive Rural Southeastern U.S. Site

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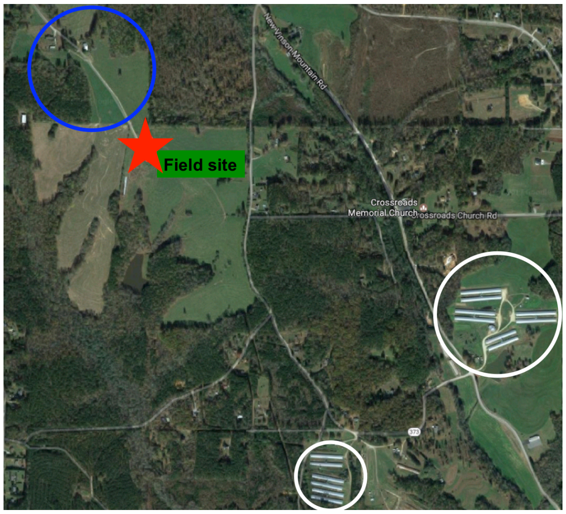

Figure S1: Map of the Yorkville field site (marked by the red diamond) and its surrounding areas (from Google Maps). Locations of nearby cattle-grazing pastures (north-west direction) and poultry CAFOs (south-east direction) are marked by the blue and white circles, respectively.

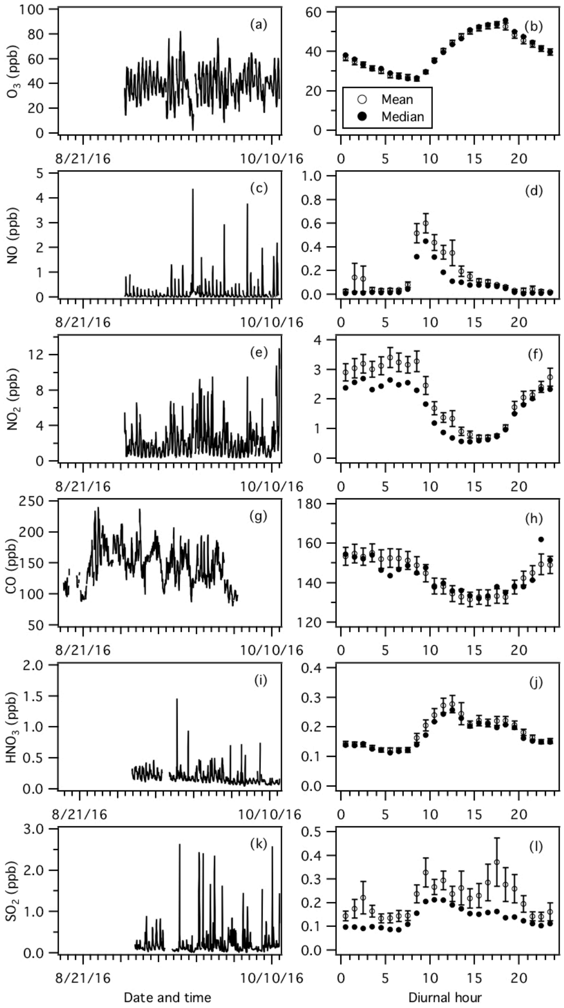

Figure S2: Time series and diurnal profiles of (a and b) O_3, (c and d) NO, (e and f) NO_2, (g and h) CO, (i and j) HNO_3, and (k and l) SO_2. Dates and times displayed are local time. All the concentrations represent averages in 1-hour intervals and the standard errors are plotted as error bars. O_3, NO, NO_2 and CO measurements were provided by the SEARCH network. HNO_3 and SO_2 were measured by the SF_6-CIMS.

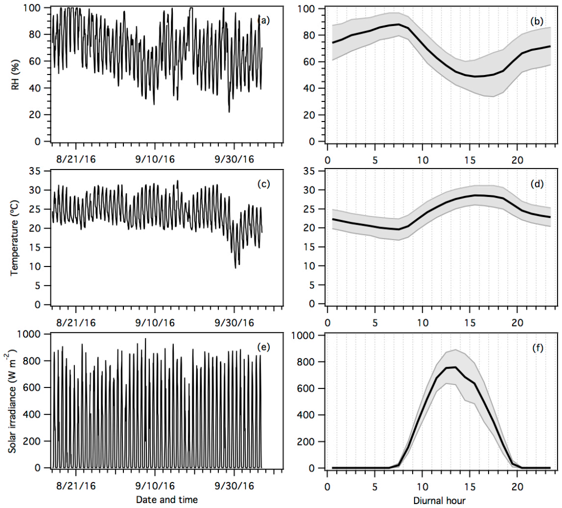

Figure S3: Time series and diurnal profiles of (a and b) RH, (c and d) temperature, and (e and f) solar irradiance. Dates and times displayed are local time. In panels b, d and f, the lines within the shaded area represents the average values. The upper and lower boundaries of the shaded areas mark one standard deviation. RH, temperature and solar irradiance measurements were provided by the SEARCH network.

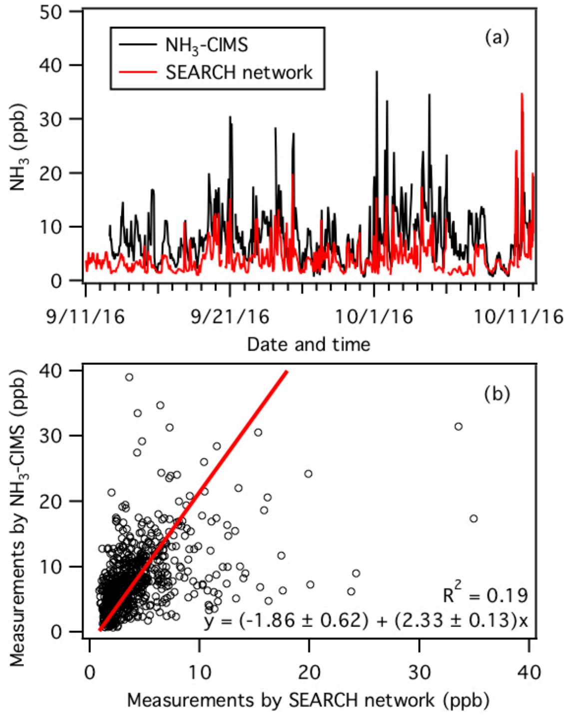

Figure S4: (a) Time series of NH_3 concentrations measured by the NH_3-CIMS and denuder-based instrument operated by the SEARCH network. (b) Comparison of NH_3 concentrations measured by the NH_3-CIMS and denuder-based instrument. The red line is the orthogonal distance regression fit to the data. All the data are displayed as 1-hour averages.

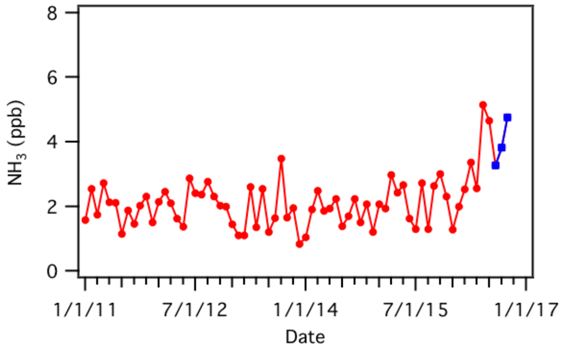

Figure S5: Monthly-averaged NH_3 concentrations at the Yorkville SEARCH monitoring site for 2011 to 2016. These measurements were made using the denuder-based instrument operated by the SEARCH network. Concentrations measured during this study (mid-August to mid-October 2016) are shown in blue.

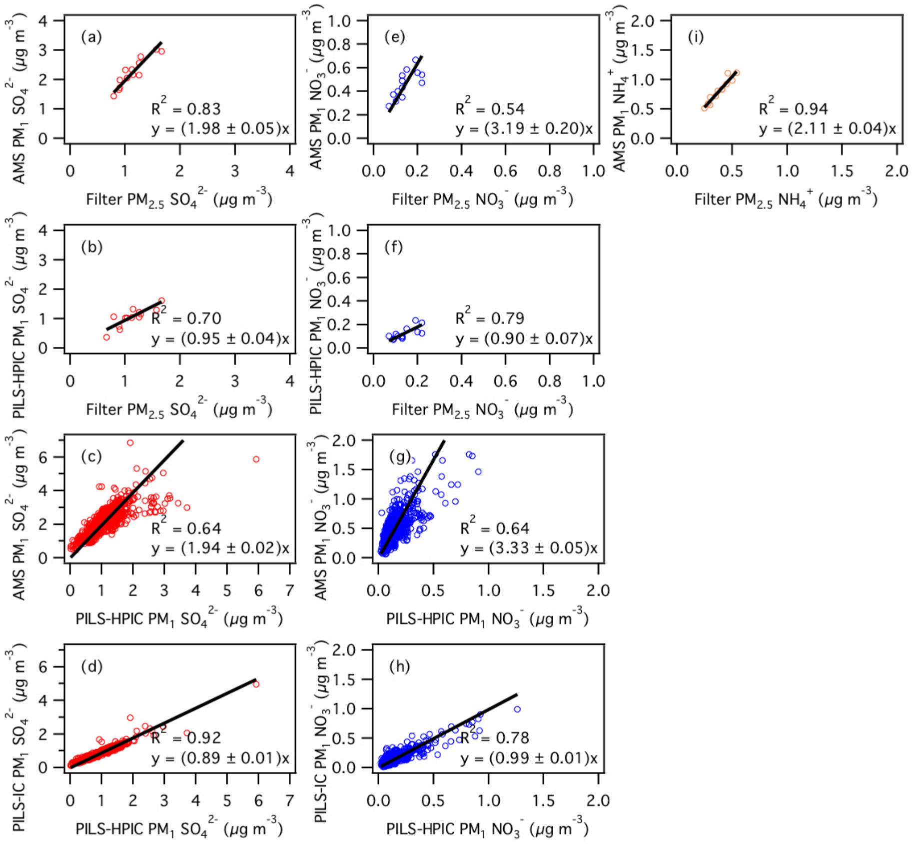

Figure S6: Aerosol (panels a to d) SO_4^{2-}, (panels e to h) NO_3^-, and (i) NH_4^+ comparisons between HR-ToF-AMS, PILS-IC, PILS-HPIC and filters for the entire field study. CDCE values were applied to the raw HR-ToF-AMS data to obtain the mass concentrations shown here (see main text for details). For comparisons between the HR-ToF-AMS, PILS-IC and PILS-HPIC data (panels c, d, g and h), the measurements are averaged over 1 hour intervals. For comparisons with filter data (panels a, b, e, f and i), the HR-ToF-AMS, PILS-IC and PILS-HPIC data are averaged over 24 hour intervals. Orthogonal regression fits are shown. Uncertainties in the fits are 1 standard deviation.

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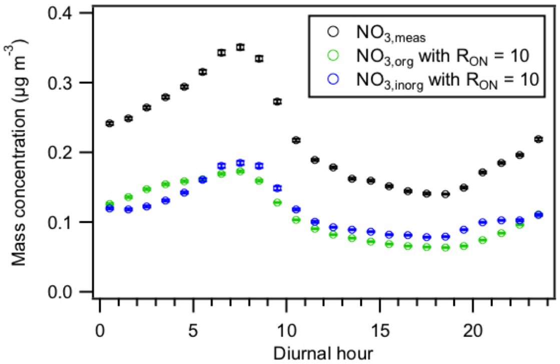

Figure S7: Diurnal profiles of the total nitrate functionality contributed by organic and inorganic nitrates ($NO_{3,meas}$), and the nitrate functionality solely from organic nitrates ($NO_{3,org}$) and inorganic nitrates ($NO_{3,inorg}$). $NO_{3,org}$ and $NO_{3,inorg}$ are estimated using the NO^+/NO_2^+ ratio method as described by Farmer et al. (2010) and Xu et al. (2015). Similar to Xu et al. (2015), we used a R_{ON} (defined here as the NO^+/NO_2^+ ratio for organic nitrates) value of 10 to calculate $NO_{3,org}$ and $NO_{3,inorg}$. All the data shown here represent averages in 1-hour intervals. Error bars shown are the standard errors.

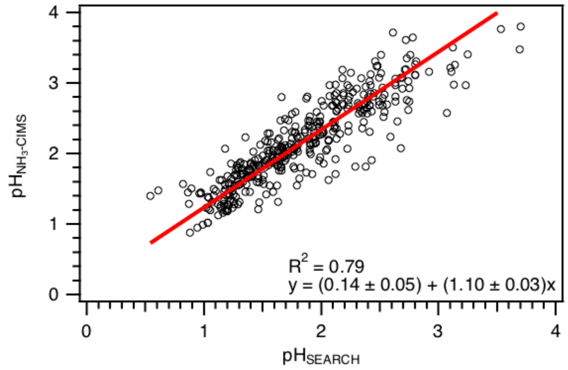

Figure S8: Comparison of predicted PM_1 pH values determined using NH_3-CIMS and SEARCH network's NH_3 measurements as ISORROPIA-II model inputs. The other model inputs are the same. The linear fit is obtained by orthogonal distance regression.

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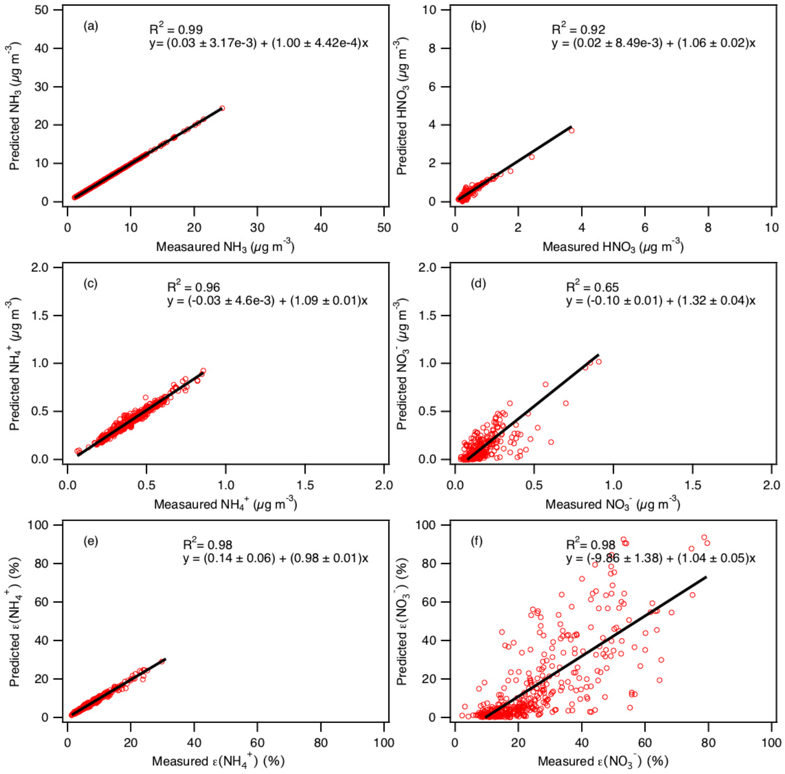

Figure S9: Comparisons of predicted and measured (a) NH_3, (b) HNO_3, (c) NH_4^+, (d) NO_3^-, (e) ε(NH_4^+), and (f) ε(NO_3^-). Orthogonal regression fits are shown. Uncertainties in the fits are 1 standard deviation.

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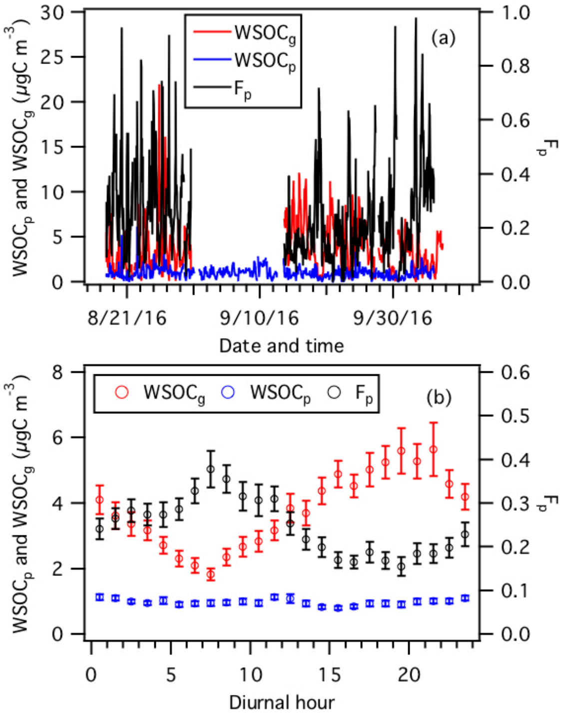

Figure S10: (a) Time series and (b) diurnal profiles of WSOC$_g$, WSOC$_p$ and F$_p$. Dates and times displayed are local time. All the data shown here represent averages in 1-hour intervals. Error bars shown in panel (b) are the standard errors. F$_p$ = WSOC$_p$ / (WSOC$_p$ + WSOC$_g$).

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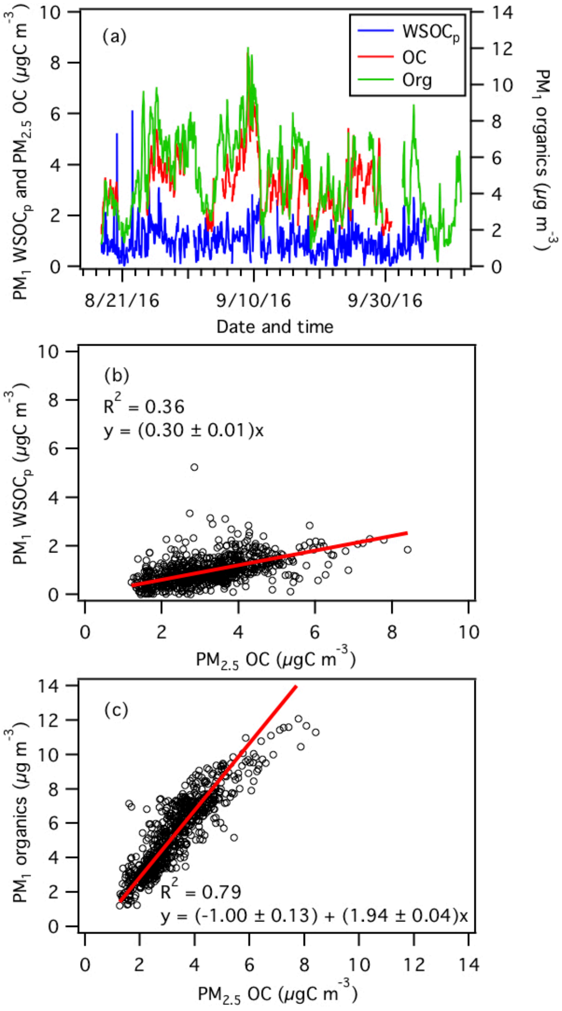

Figure S11: (a) Time series of HR-ToF-AMS organics, WSOC$_p$ and OC. (b) Linear regression correlation between WSOC$_p$ and OC. (c) Linear regression correlation between HR-ToF-AMS organics and OC. All the data shown here represent averages in 1-hour intervals. Note that OC measurements are PM$_{2.5}$, while WSOC$_p$ and HR-ToF-AMS organics measurements are PM$_1$. Linear fits are obtained by orthogonal distance regression.

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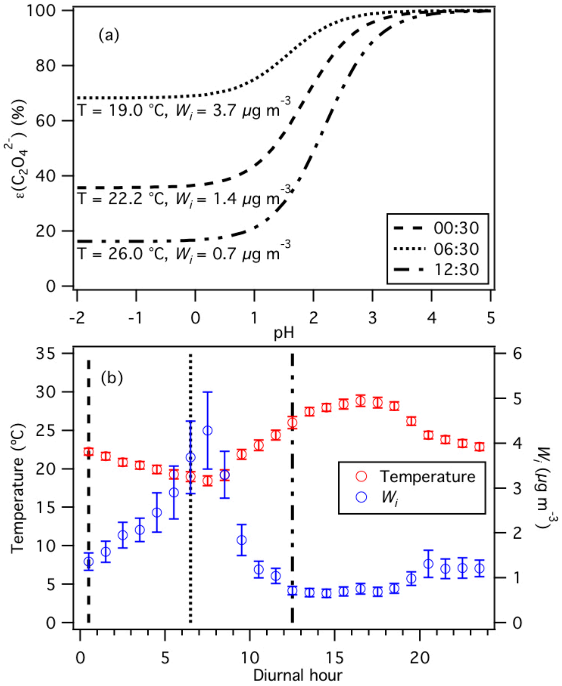

Figure S12: (a) Analytically calculated S curves of $\varepsilon(C_2O_4^{2-})$ at different times of the day: 00:30, 06:30 and 12:30. These S curves are calculated using values obtained from (b) the diurnal profiles of temperature and W_i. The set of 1-hour average temperatures and W_i at diurnal hours 00:30, 06:30 and 12:30 is used to calculate each S curve shown in panel (a). Similar to Fig. 7, we used $\gamma_{C_2H_2O_4}$ = 0.0492 (AIOMFAC predicted) and assumed that $\gamma_{H^+-NO_3^-} = \sqrt{\gamma_{H^+}\gamma_{NO_3^-}} = \sqrt{\gamma_{H^+}\gamma_{C_2HO_4^-}}$ = 0.265 (ISORROPIA-II predicted) to generate these S curves.

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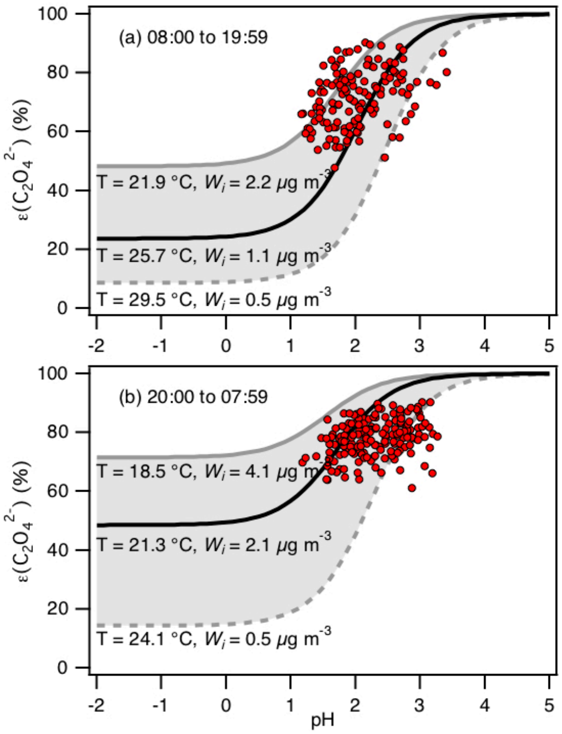

Figure S13: Analytically calculated S curve of ε($C_2O_4^{2-}$) and ambient data from 13 September to 6 October 2016 plotted against ISORROPIA-predicted particle pH. For the ambient data, a narrow range in W_i (0.5 to 4 μg m^{-3}) and RH (20 to 90 %) is chosen to be close to the analytically calculated outputs. We divided the ambient data into two sets: panel (a) 08:00 to 19:59, and panel (b) 20:00 to 07:59. For both analytically calculated S curves, we used $\gamma_{C_2H_2O_4}$ = 0.0492 (AIOMFAC predicted). We also assumed that $\gamma_{H^+}\gamma_{C_2HO_4^-} = \gamma_{H^+}\gamma_{NO_3^-}$, and used the ISORROPIA-predicted $\gamma_{H^+-NO_3^-} = \sqrt{\gamma_{H^+}\gamma_{NO_3^-}}$ = 0.265. In panel (a), we used the average temperature and W_i (25.7 ± 3.8 °C and 1.1 ± 1.1 μg m^{-3}) for the data between 08:00 to 19:59 to calculate the S curve (black line). In panel (b), we used the average temperature and W_i (21.3 ± 2.8 °C and 2.1 ± 2.0 μg m^{-3}) for the data between 20:00 to 07:59 to calculate the S curve (black line). Grey lines in both panels are S curves calculated using one standard deviation from the average temperature and W_i for the two

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datasets. In panel (a), the dotted grey line is the S curve calculated using 29.5 °C and 0.5 µg m^{-3} while the solid grey line is the S curve calculated using 21.9 °C and 2.2 µg m^{-3}. In panel (b), the dotted grey line is the S curve calculated using 24.1 °C and 0.5 µg m^{-3} while the solid grey line is the S curve calculated using 18.5 °C and 4.1 µg m^{-3}.

Table S1: List of gas-phase acids measured by SF_6-CIMS, and their measurement uncertainties and detection limits.

Acid	Measurement uncertainty (%)	Detection limits (ppb)[a]
Nitric acid	13	0.20
Formic acid	12	0.03
Acetic acid	12	0.06
Oxalic acid	14	1×10^{-3}
Butyric acid	14	0.03
Glycolic acid	22	2×10^{-3}
Propionic acid	14	6×10^{-3}
Valeric acid	22	0.01
Malonic acid	25	7×10^{-4}
Succinic acid	25	3×10^{-3}

[a] Detection limits are approximated from 3 times the standard deviation values (3σ) of the ion signals measured during background mode. Shown here are the average detection limits of the organic acids for 2.5 min integration periods which corresponds to the length of a background measurement at a 0.04 s duty cycle for each mass.

S1. SF_6-CIMS calibration of gas-phase HNO_3 and organic acids

Detailed descriptions of post-field laboratory calibrations of HNO_3, oxalic, butyric, glycolic, propionic, valeric, malonic and succinic acids can be found in Nah et al. (2018). The response of the CIMS acid signals were measured relative to the sensitivity of $^{34}SO_2$ in these calibration measurements.

The HNO_3 calibration source was a permeation tube (KIN-TEK) whose emission rate was measured using UV optical absorption (Neuman et al., 2003). Solid or liquid samples of oxalic (Sigma Aldrich, ≥ 99 %), butyric (Sigma Aldrich, ≥ 99 %), glycolic (Sigma Aldrich, 99 %), propionic (Sigma Aldrich, ≥ 99.5 %), valeric (Sigma Aldrich, ≥ 99 %), malonic (Sigma Aldrich, ≥ 99.5 %) and succinic (Sigma Aldrich, 99 %) acids were used in calibration measurements. The acid sample was placed in a glass impinger, which was immersed in a water bath at a fixed temperature to provide a constant vapor pressure. For oxalic, butyric, glycolic, propionic and valeric acids, the water bath temperature was set to 0 ˚C. For malonic and succinic acids, the water bath temperature was set to 40 ˚C in order to generate large enough gas phase concentrations for calibration. 6 to 10 mL min^{-1} of nitrogen gas (N_2) was passed over the organic acid in the glass impinger. This organic acid air stream was diluted with different N_2 flows (1 to 5 L min^{-1}) to obtain different mixing ratios of the organic acid. We calculated the mixing ratios based on the acid's emission rate from the impinger or the acid's vapor pressure. Emission rates of gas-phase oxalic, malonic and succinic acids from the impinger were measured by scrubbing the output of the impinger in deionized water, followed by ion chromatography analysis. We measured the vapor pressures of butyric and propionic acids at 0 ˚C using a capacitance manometer (MKS Instruments). We estimated the vapor pressures of glycolic and valeric acids at 0 ˚C using their literature vapor pressures at 25 ˚C and enthalpies of vaporization (Daubert and Danner, 1989; Lide, 1995; Acree and Chickos, 2010).

S2. $WSOC_p$ and OC

We estimated the water-soluble fraction of OC by comparing the $WSOC_p$ and OC measurements. The time series of organics, $WSOC_p$ and OC are shown in Fig. S11a. As shown in Fig. S11b, $WSOC_p$ is moderately correlated with OC at the site. The orthogonal distance regression fit suggests that 30 % of the OC is water-soluble (estimated measurement uncertainty of 19 %),

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which is significantly smaller than the fraction (61 %) measured during the SOAS study (Xu et al., 2017). This difference may be due, in part, to the $WSOC_p$/OC ratio for this study being under-estimated. $WSOC_p$ are PM_1 measurements while OC are $PM_{2.5}$ measurements. This is in contrast to the SOAS study where both $WSOC_p$ and OC are $PM_{2.5}$ measurements. PM_1 organics mass concentration is highly correlated with OC and has an orthogonal distance regression slope of 1.94 (Fig. S9c), which is similar to the value (1.92) reported for the SOAS study (Xu et al., 2017).

S3. $C_2H_2O_4$- $C_2O_4^{2-}$ partitioning

Here, we show the detailed derivation of equation (4) in that paper. Equilibrium between gaseous $C_2H_2O_4$ and particle-phase $C_2O_4^{2-}$ involves the dissolution of $C_2H_2O_4$ into the aqueous phase (assuming particles are liquids), followed by dissociation of the dissolved $C_2H_2O_4$:

$$C_2H_2O_4(\mathrm{g}) \leftrightarrow C_2H_2O_4(\mathrm{aq}) \quad H_{C_2H_2O_4}$$

$$C_2H_2O_4(\mathrm{aq}) \leftrightarrow C_2HO_4^-(\mathrm{aq}) + H^+(\mathrm{aq}) \quad K_{a1}$$

$$C_2HO_4^-(\mathrm{aq}) \leftrightarrow C_2O_4^{2-}(\mathrm{aq}) + H^+(\mathrm{aq}) \quad K_{a2}$$

for which the reaction equilibriums are expressed as follows:

$$H_{C_2H_2O_4} = \gamma_{C_2H_2O_4}[C_2H_2O_4]/p_{C_2H_2O_4} \tag{1}$$

$$K_{a1} = \frac{\gamma_{H^+}[H^+]\gamma_{C_2HO_4^-}[C_2HO_4^-]}{\gamma_{C_2H_2O_4}[C_2H_2O_4]} \tag{2}$$

$$K_{a2} = \frac{\gamma_{H^+}[H^+]\gamma_{C_2O_4^{2-}}[C_2O_4^{2-}]}{\gamma_{C_2HO_4^-}[C_2HO_4^-]} \tag{3}$$

where $H_{C_2H_2O_4}$ (mole L^{-1} atm^{-1}) is the Henry's law constant for oxalic acid, K_{a1} and K_{a2} (mole L^{-1}) are the first and second acid dissociation constants for oxalic acid, $p_{C_2H_2O_4}$ (atm) is the partial pressure of oxalic acid in the atmosphere, and γ_i's are activity coefficients. In equations (1) to (3), [x] represents aqueous concentrations (mole L^{-1}).

The total dissolved $C_2H_2O_4$ or particle-phase oxalate ($C_2O_4^{\mathrm{T}}$) can be expressed as:

$$[C_2HO_4^{\mathrm{T}}] = [C_2H_2O_4] + [C_2HO_4^-] + [C_2O_4^{2-}] \tag{4}$$

Using equations (1) to (3), [$C_2O_4^{\mathrm{T}}$] can be expressed as:

$$[C_2O_4^{\mathrm{T}}] = H_{C_2H_2O_4} p_{C_2H_2O_4} \left(\frac{1}{\gamma_{C_2H_2O_4}} + \frac{K_{a1}}{\gamma_{H^+}\gamma_{C_2HO_4^-}[H^+]} + \frac{K_{a1}K_{a2}}{\gamma_{H^+}\gamma_{H^+}\gamma_{C_2O_4^{2-}}[H^+]^2} \right) \tag{5}$$

The ideal gas law gives:

$$c(C_2H_2O_4) = \frac{p_{C_2H_2O_4}}{RT} \tag{6}$$

where R is the gas constant, T is temperature, and c(x) represents concentration per volume of air (mole m^{-3}). The particle-phase fraction of oxalate can then be expressed as:

$$\varepsilon(C_2O_4^{2-}) = \frac{c(C_2O_4^{\mathrm{T}})}{c(C_2H_2O_4) + c(C_2O_4^{\mathrm{T}})} = \frac{[C_2HO_4^{\mathrm{T}}]W_i}{c(C_2H_2O_4) + [C_2HO_4^{\mathrm{T}}]W_i} \tag{7}$$

where W_i is the particle liquid water content associated with inorganic species (μg m^{-3}; mass per volume of air). Note that the particle liquid water content associated with organic species is not considered in this case, but it can be included. Alternatively, the measured particle water can be used.

By putting equations (5) and (6) into equation (7), ε($C_2O_4^{2-}$) can be expressed as:

$$\varepsilon(C_2O_4^{2-}) = \frac{H_{C_2H_2O_4} W_i RT \left(\frac{1}{\gamma_{C_2H_2O_4}} + \frac{K_{a1}}{\gamma_{H^+}\gamma_{C_2HO_4^-}[H^+]} + \frac{K_{a1}K_{a2}}{\gamma_{H^+}\gamma_{H^+}\gamma_{C_2O_4^{2-}}[H^+]^2} \right)}{1 + H_{C_2H_2O_4} W_i RT \left(\frac{1}{\gamma_{C_2H_2O_4}} + \frac{K_{a1}}{\gamma_{H^+}\gamma_{C_2HO_4^-}[H^+]} + \frac{K_{a1}K_{a2}}{\gamma_{H^+}\gamma_{H^+}\gamma_{C_2O_4^{2-}}[H^+]^2} \right)} \tag{8}$$

At 298 K, K_{a1} = 5.62 x 10^{-2} mole L^{-1} and K_{a2} = 1.55 x 10^{-4} mole L^{-1} (Haynes, 2014). Assuming that γ_{H^+} = 1, $K_{a1}K_{a2} \ll \gamma_{H^+}\gamma_{H^+}\gamma_{C_2O_4^{2-}}[H^+]^2$ for the conditions of our study. Hence, equation (8) can be simplified to:

$$\varepsilon(C_2O_4^{2-}) \cong \frac{H_{C_2H_2O_4} W_i RT \left(\frac{\gamma_{H^+}\gamma_{C_2HO_4^-}}{\gamma_{C_2H_2O_4}}[H^+] + K_{a1} \right)}{\gamma_{H^+}\gamma_{C_2HO_4^-}[H^+] + H_{C_2H_2O_4} W_i RT \left(\frac{\gamma_{H^+}\gamma_{C_2HO_4^-}}{\gamma_{C_2H_2O_4}}[H^+] + K_{a1} \right)} \tag{9}$$

After accounting for the SI units and substituting $[H^+] = 10^{-pH}$, equation (9) becomes:

$$\varepsilon(C_2O_4^{2-}) \cong \frac{H_{C_2H_2O_4}W_iRT\left(\frac{\gamma_{H^+}\gamma_{C_2HO_4^-}}{\gamma_{C_2H_2O_4}}10^{-pH}+K_{a1}\right)\times 0.987\times 10^{-14}}{\gamma_{H^+}\gamma_{C_2HO_4^-}10^{-pH}+H_{C_2H_2O_4}W_iRT\left(\frac{\gamma_{H^+}\gamma_{C_2HO_4^-}}{\gamma_{C_2H_2O_4}}10^{-pH}+K_{a1}\right)\times 0.987\times 10^{-14}} \qquad (10)$$

Note that 0.987 x 10^{-14} comes from using R = 8.314 m^3 Pa K^{-1} mol^{-1}, and hence needing to convert 1 atm to 1 Pa and 1 L to 1 µg. We used the average of $H_{C_2H_2O_4}$ values provided by Clegg et al. (1996), Compernolle and Muller (2014) and Saxena and Hildemann (1996) (6.11 x 10^8 mole L^{-1} atm^{-1} at 25 °C), and accounted for the effect of temperature using equation 19 in Sander (2015). Although K_{a1} also depends on temperature, the K_{a1} value at 25 °C (5.62 x 10^{-2}, (Haynes, 2014)) is used for all the oxalic acid S curve calculations in this paper since equations that determine temperature-dependent K_{a1} values are not available. In addition, the temperatures observed in this study are close to 25 °C.

Figure S12 provides a conceptual picture of how the relationship between ε($C_2O_4^{2-}$) and particle pH can change based on the time of the day. Different S curves for ε($C_2O_4^{2-}$) are calculated using equation (10) and 1-hour average values obtained from the diurnal profiles of temperature and W_i (specifically at 00:30, 06:30 and 12:30). The S curves are shown to differ substantially due to the diurnal variations of temperature and W_i. For example, a decrease in temperature and an increase in W_i from 00:30 to 06:30 will result in the S curve shifting to the left, which indicates that a substantially higher fraction of gas-phase oxalic acid will partition to the particle phase for a given particle pH at 06:30 compared to at 00:30. Higher W_i also increases the fraction of oxalate that partitions to the particle phase due solely to solubility, as seen from the plateau regions at low pH in Fig. S12. Conversely, an increase in temperature and a decrease in W_i from 06:30 to 12:30 will result in a considerably lower fraction of gas-phase oxalic acid partitioning to the particle phase for a given particle pH at 12:30 compared to at 06:30.

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S4. PILS-HPIC denuder efficiency

Post-field laboratory experiments were performed to determine if disagreements between the measured and predicted molar fractions of formic and acetic acid in the particle phase were due to positive biases in particle-phase PILS-HPIC measurements as a result of less than 100 % gas removal denuder efficiency and uptake of gases in the PILS liquid system. While experiments were done solely with formic acid, similar results are expected for acetic acid. In these experiments, liquid formic acid (Sigma Aldrich, ≥ 99 %) was diluted with ultrapure deionized water and placed in a bubbler. A flow of 18 mL min^{-1} of N_2 was passed through the formic acid in the bubbler. This formic acid air stream was then passed through a nafion dryer and diluted with 52 L min^{-1} of N_2. Two experiments were performed. In the first experiment, the diluted formic acid air flow was introduced directly into the PILS, which was connected to a Metrohm 761 Compact IC (Metrohm AG). In the second experiment, the diluted formic acid air flow was passed through a 28 cm parallel plate carbon denuder (Sunset Lab) prior to introduction into the PILS-IC system.

Our experiments showed that the IC detected formate when the diluted formic acid air flow was introduced directly into the PILS-IC system. IC analysis revealed that the gas-phase formic acid concentration was ~75 µg m^{-3}. However, no formate was detected above the limit of detection (0.02 µg m^{-3}) when the diluted formic acid air flow was passed through the carbon denuder prior to introduction into the PILS-IC system. These measurements indicated that the carbon denuder has a ≥ 99.97 % formic acid gas removal efficiency. Hence, these experiments indicate that the carbon denuder removes the formic acid gas completely. We conclude that disagreements between the measured and predicted molar fractions of formic and acetic acid in the particle phase were not due to positive biases in particle-phase formate and acetate PILS-HPIC measurements as a result of less than 100 % gas removal denuder efficiency.

S5. Particle-phase formic and acetic acid dimers

Previous studies have shown that formic and acetic acid dimers may form in the aqueous phase (Schrier et al., 1964; Gilson et al., 1997; Chen et al., 2008). If the aforementioned acid dimers are present in aerosols, equilibrium between gas-phase formic/acetic acid (denoted as HA) and particle-phase formate/acetate (denoted as A$^-$) will differ from that predicted assuming no dimers existed, as done in the main text.

The dissolution of HA into the aqueous phase (assuming particles are liquids), followed by the formation of particle-phase dimers (denoted as ((HA)$_2$) and dissociation of the dissolved HA:

$$HA\ (\mathrm{g}) \leftrightarrow HA\ (\mathrm{aq}) \quad H_{HA}$$

$$HA\ (\mathrm{aq}) \leftrightarrow (HA)_2\ (\mathrm{aq}) \quad K_{dim}$$

$$HA\ (\text{aq}) \leftrightarrow A^-\ (\text{aq}) + H^+(\text{aq}) \quad K_{a1}$$

for which the reaction equilibriums are expressed as follows:

$$H_{HA} = \gamma_{HA}[HA]/p_{HA} \tag{11}$$

$$K_{dim} = \frac{[(HA)_2]}{[HA]^2} \tag{12}$$

$$K_{a1} = \frac{\gamma_{A^-}[A^-]\gamma_{H^+}[H^+]}{\gamma_{HA}[HA]} \tag{13}$$

where H_{HA} (mole L^{-1} atm^{-1}) is the Henry's law constant for formic or acetic acid, K_{a1} (mole L^{-1}) is the first acid dissociation constants for formic or acetic acid, p_{HA} (atm) is the partial pressure of formic or acetic acid in the atmosphere, K_{dim} (L $mole^{-1}$) is the dimerization constant, and γ_i's are activity coefficients. In equations (11) to (13), [x] represents aqueous concentrations (mole L^{-1}).

The total dissolved formate or acetate (A^T) can be expressed as:

$$[A^T] = [HA] + [A^-] + [(HA)_2] \tag{14}$$

Using equations (11) to (13), $[A^T]$ can be expressed as:

$$[A^T] = H_{HA}p_{HA}\left(\frac{1}{\gamma_{HA}} + \frac{K_{a1}}{\gamma_{H^+}\gamma_{A^-}[H^+]} + \frac{K_{dim}H_{HA}p_{HA}}{\gamma_{HA}\gamma_{HA}}\right) \tag{15}$$

The ideal gas law gives:

$$c(HA) = \frac{p_{HA}}{RT} \tag{16}$$

where R is the gas constant, T is temperature, and c(x) represents concentration per volume of air (mole m^{-3}). The particle-phase fraction of formate or acetate can then be expressed as:

$$\varepsilon(A^-) = \frac{c(A^T)}{c(HA)+c(A^T)} = \frac{[A^T]W_i}{c(HA)+[A^T]W_i} \tag{17}$$

where W_i is the particle liquid water content associated with inorganic species (μg m^{-3}; mass per volume of air). Particle liquid water content associated with organic species is not considered in this case, but it can be included. Alternatively, the measured particle water can be used.

By putting equations (15) and (16) into equation (17), and accounting for the SI units, $\varepsilon(A^-)$ can ultimately be expressed as:

$$\varepsilon(A^-) = \frac{H_{H_{HA}} W_i RT\left(\frac{1}{\gamma_{HA}} + \frac{K_{a1}}{\gamma_{H^+}\gamma_{A^-}10^{-pH}} + \frac{K_{dim} H_{HA} p_{HA}}{\gamma_{HA}\gamma_{HA}}\right) \times 0.987 \times 10^{-14}}{1 + H_{H_{HA}} W_i RT\left(\frac{1}{\gamma_{HA}} + \frac{K_{a1}}{\gamma_{H^+}\gamma_{A^-}10^{-pH}} + \frac{K_{dim} H_{HA} p_{HA}}{\gamma_{HA}\gamma_{HA}}\right) \times 0.987 \times 10^{-14}} \quad (18)$$

At 298 K, K_{a1} values are 1.78 x 10^{-4} mole L^{-1} and 1.75 x 10^{-5} mole L^{-1} for formic and acetic acid, respectively (Haynes, 2014). K_{dim} values are 0.56 L $mole^{-1}$ and 0.92 L $mole^{-1}$ for formic and acetic acid, respectively (Chen et al., 2008). Temperature-dependent H_{HA} values for formic and acetic acid can be obtained from Sander (2015). p_{HA} can be calculated from the measured gas-phase formic or acetic acid concentrations (μg m^{-3}) and the ideal gas law. We used the web version of AIOMFAC (www.aiomfac.caltech.edu) (Zuend et al., 2008; Zuend et al., 2011; Zuend et al., 2012) to compute study-averaged γ_{HA} values of 0.334 and 2.150 for formic and acetic acid, respectively. We assumed that $\gamma_{H^+}\gamma_{A^-} = \gamma_{H^+}\gamma_{NO_3^-} = 0.07$ for both formic and acetic acid.

Comparison of S curves generated from equation (18) and those generated from equations (5) and (6) in the main text (which assumed that no dimers existed) showed that accounting for the presence of acid dimers increased predicted $\varepsilon(A^-)$ values by less than 1 % for particle pH 0.9 to 3.8 (i.e., pH values in this study). S curves generated by equation (18) also do not match our measured molar fractions of formic and acetic acid in the particle phase. This analysis shows that the molar fractions of formic and acetic acid in the particle phase do not change substantially when the presence of particle-phase acid dimers is accounted for due to the somewhat low H_{HA} values for formic and acetic acid. Hence, disagreements between the measured and predicted molar fractions of formic and acetic acid in the particle phase are not due to the presence of particle-phase formic and acetic acid dimers.

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