Response to Reviewer

We thank the anonymous reviewer for their helpful comments. The reviewer comments are in black and our responses are in blue and include page and line numbers where changes were made to the accompanying manuscript.

This paper invokes the idea of an organic film over an aqueous aerosol to explain observed low ammonium to sulfate molar ratios, despite excess gas phase ammonia. The paper has substantially changed since the first version, but again these authors chose to analyze aerosol pH effects through the use of molar ratios, which has been shown to be problematic.

The paper now focuses on the observation that both currently used thermodynamic models, ISORROPIA and E-AIM tend to predict higher molar ratios than what is observed. They have added some interesting plots (e.g., Fig 1 is quite nice) and arguments to support the idea that the lower molar ratios may be due to the organic film. Some issues should be considered and clarified in the text prior to publication.

A major issue is clarifying the logic of this hypothesis and its implications. If NH_3 is not in equilibrium with the particle phase, the premise of this work, and given it is the most important fine mode base (in this case, ANS, the only base) it follows that the thermodynamic models cannot be used, as they assume equilibrium. The model predictions are then incorrect, including pH etc. Of coarse it raises the issue how the models do so well predicting actual NH_3/NH_4^+ partitioning over a wide range of ambient conditions, something that should be explained (more on this below). Because this has very large implications, impacting many already published paper, this implication should be very clearly stated in the paper.

A second major point is the authors should explicitly state how the organic film impedes the uptake of NH_3, is it through a low accommodation coefficient, or maybe low solubility of NH_3 in the organic film? A curious thing is that H_2O and NH_3 have nearly identical molar masses making many of their properties similar (diffusivities, etc). How these two molecules could behave so differently when interacting with the film should be directly addressed. More details below.

More Details:

1). A simpler explanation for the model vs measured molar ratio discrepancy could simply be that modeled pH vs observed molar ratios respond differently to treaing the fine mode as a bulk property. When averaged over all sizes, observed molar ratios may be sensitive to this assumption, whereas actual pH less so. It has already been shown that molar ratios and pH are not necessarily related in a simple way. This possible explanation for the molar ratio discrepancy (or this complication when interpreting the data) should be noted in the paper.

We have added on page 3 lines 6-8: “The chemical composition of individual sulfate particles may deviate from the bulk, but it is not clear how such inhomogeneity could explain the observed departure from simple thermodynamics.”

2) Issues with imprecise statements. Eg, in the Abstract, lines 18 to 22 (and other related discussions in the paper, eg first sections of Intro.), regarding ammonia concentrations and molar ratios. The statements are based on the extreme end-members of processes that are asymptotic (E-AIM solution in Fig 1), and the ambient condition is between the two extremes.

We add references to Zhang et al. (2002), Martin et al. (2004), and Yu et al. (2005) to support the statements that the thermodynamic behavior described is observed in a range of environments in the US (page 2 lines 13-14).

Line 29-30 statement that molar ratios decrease with decrease sulfate is incompatible with theory is, I believe, not correct, it is predicted by the model (see more on this below).

We amend the text to refer to Marais et al. (2016) that shows the significant decreasing trend in aerosol acidity predicted by ISORROPIA in response to decreasing sulfate, supporting the statement in the text (page 7 lines 25-26).

3) The authors assert the film will lower the rate of NH3 uptake so that equilibrium is not achieved since the time scales to reach equilibrium become long. This would seem to then invalidate the use of the thermodynamic models in general since the model assumes equilibrium for all semi-volatile species, including water vapor. To argue that an organic film affects NH3 mass transport dynamics, affects on other species should also be considered. The thermodynamics is a multi-component system, the various species behavior being inter-connected. For example, if NH3 time scales to reach equilibrium become large, what happens to other key species, such as H2O, HNO3, etc interacting with the organic surface. See discussion below on diffusivities of various species through an organic film affecting reactive uptake. The conclusion from below is that water will also have a similar time scale to reach equilibrium as ammonia, by the mechanism proposed here, and nitric acid will take about 2 times as long to reach equilibrium. How this will be handled in the CTM and how this is reconciled with existing data and publications on water uptake of particles, etc, should be specifically discussed, along with a detailed analysis of exactly how an organic film will affect reactive uptake. That is, exactly what is the mechanism that slows NH3, but not other species? Maybe it is differences in accommodation coefficients. If so, is this reasonable given measured accommodation coefficients? It should be explicitly stated what the possible physical explanation is for this proposed resistance to NH3 uptake.

See response to discussion of NH_3 uptake below.

4) pH matters, not molar ratios, when concerned about acidity effects. The goal of all this work, as noted by the authors in the abstract, is to predict the effects of aerosol pH on other aerosol properties or processes. Eg, from the abstract, where it states that … uptake of ammonia has important implications for aerosol mass, hygroscopicity, and acidity. It also states that … decrease sulfate aerosol will not have the co-benefit of suppressing acid-catalyzed secondary organic aerosol (SOA) formation. The key is aerosol pH, not molar ratios. As already noted, a reported analyses [Guo et al., 2016; Guo et al., 2015], suggests that in terms of partitioning of semi-volatile species, ISORROPIA works fairly well. That is, the models provide accurate

predictions of properties of interest related to pH, something that molar ratios cannot do, as far as I can tell.

We now clarify in the text (page 4 lines 23-25) that we do not use molar ratios as a proxy for pH and instead in this work we explore only the measureable quantities aerosol ammonium and sulfate.

5) One aspect the film achieves, according to this work, is that in the CTM model NH3 is predicted better (in addition to molar ratios, which is discussed above). Given the large uncertainties in NH3 emissions, could this simply be fortuitous? How robust a test of the model is the use of measured versus predicted NH3? Accurate prediction of gas particle partitioning of semi-volatile species would seem a better approach. For example, can the CTM accurately predict NH4+/NH3, HNO3/NO3- partitioning, as has been done with ISORROPIA (see various references)?

Paulot et al. (2014) showed there is good confidence in US ammonia emissions, which agree within 20% for independent bottom-up and top down estimates (page 4 lines 31-32). We have also added a comparison of modeled and observed ammonium wet deposition (page 9 lines 22-25) in order to show that uncertainties in emissions are not enough to explain the large model underestimate in gas-phase ammonia, so instead the problem is due to thermodynamic partitioning. As stated in Guo et al. (2016), the even distribution of ammonia between the gas and aerosol phase in summertime makes it the instructive quantity to test model partitioning while most nitrate is present in the gas phase in the Southeast US summer.

6) An explanation for the issue of decreasing trends of sulfate and molar ratios discussed in this manuscript is given elsewhere [Weber et al., 2016]. It can simply be explained by ammonia volatility, which should be pointed out in this paper.

We state in the text (page 7 lines 18-20, 27-29) the consistency of observed trends in sulfate and molar ratios shown in Weber et al. (2016) and we have added the explanation presented by Weber et al. (2016) (page 2 line 32).

Mass Transport Limitations in Aqueous-Phase Chemistry (the following is based on Seinfeld and Pandis, 2nd Edition, 2006, Chapter 12, Section 12.2).

In trying to understand the physical details associated with the proposed interaction between NH3 and an organic film, the following analysis of characteristic times for equilibrium was undertaken, following the argument put forward in the paper. A comparison is made between NH3 and H2O since they have nearly identical molecular weights.

If the rate-limiting step for mass transfer of a gas, say NH3 in this case, from the gas to the particle surface and then through the organic film to the bulk water of the particle interior, (ultimately leading to conversion of NH3 to NH4+), is gas transport through an organic film on the perimeter of the particle, the characteristic time (τ) for the system to reach equilibrium will be in proportion to:

τNH3 α Rp2/(γ DNH3-aerosol), (from S & P equation 12.61)

where Rp could be thought of as the thickness of the film, γ the accommodation coefficient and DNH3-aerosol the diffusivity of NH3 in the organic layer. If we assume that the gases of interest will all have fairly similar accommodation coefficients, all being fairly sticky, and effective Henry's law constants (similar solubility in the OA phase) the time scales comes down to diffusivity (S&P Eq 12.62), or roughly the ratio depends on sqrt(molecular weight) of the solute (Eq 12.61).

Water (18 g/mole) has a very similar molecular weight as NH3 (17 g/mole) so time scales to reach equilibrium for these two species should be roughly equal. The ratio of equilibration time scales of NH3 and H2O due to the organic film is very roughly then = sqrt(18/17) = 1.03, or approximately 1. Thus, with similar accommodation coefficients and solubility in the OA, if NH3 is not in equilibrium due to the film, water is also not, and will behave very similar to NH3. This would contradict many studies demonstrating that in the ambient atmosphere water is in equilibrium, thus NH3 should also be, by this analyses, or the assumptions are wrong.

Consider a different semi-volatile species, say HNO3 (molecular weight=63 g/mole). In this case the time scales for equilibrium for HNO3 relative to NH3 will be sqrt(63/17) = 1.9. Thus nitric acid takes about 2 times as long to reach equilibrium. How can this be reconciled based on ambient data showing good agreement with measured partitioning of nitric acid and nitrate under most conditions (eg, [Guo et al., 2016])? How would this be included in the overall CTM?

Note that all other semi-volatile species of importance when assessing aerosol pH (e.g, HCl MW=36 g/mole, organic acids…) will have larger molecular weights than NH3, so it will take even longer for them to reach equilibrium. Maybe this all can be explained by differences in mass accommodation coefficients? In fact, it seems the only plausible way.

If possible, the authors should attempt to explicitly state in the text by what mechanism the NH3 is selectively impeded, as these could be measured to test the hypothesis of the paper. Overall, the situation is getting very complicated relative to a straight thermodynamic analysis (assumes equilibrium) that appears to agree with observations of liquid water content and partitioning of semi-volatile species sensitive to pH.

Liggio et al. (2011) shows that the predicted characteristic timescale (for uptake controlled by accommodation and diffusion) for equilibrium using an accommodation coefficient of 1.0 is only appropriate for the organic-free experiments while the measured timescale for equilibrium for experiments with ambient particles are on the order of hours rather than seconds. We note this point and as we now cite Daumer et al. (1992) that also showed a retardation of the ammonium-sulfate equilibrium when sulfuric acid particles are coated with organic films (page 8 lines 5-8).

Laboratory measurements of organic aerosol (Wong et al., 2014) and observations of ambient particles (Raatikainen et al., 2013) have shown the accommodation coefficient for water is > 0.1 meaning it is above the threshold where a kinetic limitation is expected to have an effect on particle growth. Additionally, while we do not explore the effect in this work, Liu et al. (2015) has shown that reactions between ammonia and organics can occur and even compete with the uptake of ammonia by acidic sulfate aerosol. As the most abundant source of gas-phase reduced nitrogen, we would expect the formation of nitrogen-containing organic fragments to be important for ammonia but not for nitrate. We have added these points to the Conclusions (page 10 line 32-page 11 line 1, page 11 lines 4-6).

We also now discuss in the Conclusions the work of Guo et al. (2016) on the partitioning of wintertime nitrate and underscore the need for more work to assess the impact of organics on the partitioning of water and semi-volatile species (page 11 lines 3-8).

Guo, H., A. P. Sullivan, P. Campuzano-Jost, J. C. Schroder, F. D. Lopez-Hilfiker, J. E. Dibb, J. L. Jimenez, J. A. Thornton, S. S. Brown, A. Nenes, and R. J. Weber (2016), Fine particle pH and the partitioning of nitric acid during winter in the northeastern United States, J. Geophys. Res. Atmos., 121(17), 10,355-310,376.

Guo, H., L. Xu, A. Bougiatioti, K. M. Cerully, S. L. Capps, J. R. Hite, A. G. Carlton, S.-H. Lee, M. H. Bergin, N. L. Ng, A. Nenes, and R. J. Weber (2015), Predicting particle water and pH in the southeastern United States, Atmos. Chem. Phys., 15, 5211–5228.

Weber, R. J., H. Guo, A. G. Russell, and A. Nenes (2016), High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years, Nature Geoscience, 9(10.1038/ngeo2665), 282-285.

References

Daumer, B., Niessner, R., and Klockow, D.: Laboratory studies of the influence of thin organic films on the neutralization reaction of H_2SO_4 aerosol with ammonia, Journal of Aerosol Science, 23, 315-325, 10.1016/0021-8502(92)90001-c, 1992.

Liu, Y., Liggio, J., Staebler, R., and Li, S. M.: Reactive uptake of ammonia to secondary organic aerosols: kinetics of organonitrogen formation, Atmospheric Chemistry and Physics, 15, 13569-13584, 10.5194/acp-15-13569-2015, 2015.

Marais, E.A., D.J. Jacob, J.R. Turner, and L.J. Mickley, Evidence of long-term decrease of biogenic secondary organic aerosol in response to SO_2 emission controls, submitted to Environ. Res. Lett., 2016.

Martin, S. T., Hung, H. M., Park, R. J., Jacob, D. J., Spurr, R. J. D., Chance, K. V., and Chin, M.: Effects of the physical state of tropospheric ammonium-sulfate-nitrate particles on global aerosol direct radiative forcing, Atmospheric Chemistry and Physics, 4, 183-214, 2004.

Paulot, F., Jacob, D. J., Pinder, R. W., Bash, J. O., Travis, K., and Henze, D. K.: Ammonia emissions in the United States, European Union, and China derived by high-resolution inversion of ammonium wet deposition data: Interpretation with a new agricultural emissions inventory (MASAGE_NH3), Journal of Geophysical Research-Atmospheres, 119, 4343-4364, 10.1002/2013jd021130, 2014.

Raatikainen, T., Nenes, A., Seinfeld, J. H., Morales, R., Moore, R. H., Lathem, T. L., Lance, S., Padró, L. T., Lin, J. J., Cerully, K. M., Bougiatioti, A., Cozic, J., Ruehl, C. R., Chuang, P. Y., Anderson, B. E., Flagan, R. C., Jonsson, H., Mihalopoulos, N., and Smith, J. N.: Worldwide data sets constrain the water vapor uptake coefficient in cloud formation, Proceedings of the National Academy of Sciences, 110, 3760-3764, 10.1073/pnas.1219591110, 2013.

Wong, J. P. S., Liggio, J., Li, S. M., Nenes, A., and Abbatt, J. P. D.: Suppression in droplet growth kinetics by the addition of organics to sulfate particles, Journal of Geophysical Research-Atmospheres, 119, 12222-12232, 10.1002/2014jd021689, 2014.

Yu, S. C., Dennis, R., Roselle, S., Nenes, A., Walker, J., Eder, B., Schere, K., Swall, J., and Robarge, W.: An assessment of the ability of three-dimensional air quality models with current thermodynamic equilibrium models to predict aerosol NO3, Journal of Geophysical Research-Atmospheres, 110, 25, 10.1029/2004jd004718, 2005.

Zhang, J., Chameides, W. L., Weber, R., Cass, G., Orsini, D., Edgerton, E., Jongejan, P., and Slanina, J.: An evaluation of the thermodynamic equilibrium assumption for fine particulate composition: Nitrate and ammonium during the 1999 Atlanta Supersite Experiment, Journal of Geophysical Research-Atmospheres, 108, 11, 10.1029/2001jd001592, 2002.

Inconsistency of ammonium-sulfate aerosol ratios with thermodynamic models in the eastern US: a possible role of organic aerosol

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Abstract. Thermodynamic models predict that sulfate aerosol ($S(VI) \equiv H_2SO_4(aq) + HSO_4^- + SO_4^{2-}$) should take up available ammonia (NH_3) quantitatively as ammonium (NH_4^+) until the ammonium sulfate stoichiometry $(NH_4)_2SO_4$ is close to being reached. This uptake of ammonia has important implications for aerosol mass, hygroscopicity, and acidity. When ammonia is in excess, the ammonium-sulfate aerosol ratio $R = [NH_4^+]/[S(VI)]$ should approach 2 with excess ammonia remaining in the gas phase. When ammonia is in deficit, it should be fully taken up by the aerosol as ammonium and no significant ammonia should remain in the gas phase. Here we report that sulfate aerosol in the eastern US in summer has a low ammonium-sulfate ratio despite excess ammonia, and we show that this is at odds with thermodynamic models. The ammonium-sulfate ratio averages only 1.04 ± 0.21 mol mol^{-1} in the Southeast, even though ammonia is in large excess as shown by the ammonium-sulfate ratio in wet deposition and by the presence of gas-phase ammonia. It further appears that the ammonium-sulfate aerosol ratio is insensitive to the supply of ammonia, remaining low even as the wet deposition ratio exceeds 6 mol mol^{-1}. While the ammonium-sulfate ratio in wet deposition has increased by 5.8% a^{-1} from 2003 to 2013 in the Southeast US, consistent with SO_2 emission controls, the ammonium-sulfate aerosol ratio has decreased by 1.4-3.0% a^{-1}. Thus the aerosol is becoming more acidic even as SO_2 emissions decrease and while ammonia emissions are staying constant; this is incompatible with simple sulfate-ammonium thermodynamics. A tentative explanation is that sulfate particles are increasingly coated by organic material, retarding the uptake of ammonia. Indeed, the ratio of organic aerosol (OA) to sulfate in the Southeast increased from 1.1 to 2.4 g g^{-1} over the 2003-2013 period as sulfate decreased. We implement a simple kinetic mass transfer limitation for ammonia uptake to sulfate aerosols in the GEOS-Chem chemical transport model and find that we can reproduce both the observed ammonium-sulfate aerosol ratios and the concurrent presence of gas-phase ammonia. If sulfate aerosol becomes more acidic as OA/sulfate ratios increase, then controlling SO_2 emissions to decrease sulfate aerosol will not have the co-benefit of suppressing acid-catalyzed secondary organic aerosol (SOA) formation.

1. Introduction

Sulfuric acid (H_2SO_4) produced in the atmosphere by oxidation of sulfur dioxide (SO_2) has very low vapor pressure in the presence of water vapor and immediately forms aqueous sulfate aerosol, S(VI) ≡ $H_2SO_4(aq) + HSO_4^- + SO_4^{2-}$. This sulfate aerosol is a major component of fine particulate matter ($PM_{2.5}$, less than 2.5 µm diameter). The acid dissociation of sulfate is mostly driven by ammonia (NH_3) emitted from agriculture and natural sources and partitioning between the gas and aerosol phases ($NH_x \equiv NH_3(g) + NH_3(aq) + NH_4^+$). Depending on the supply of ammonia, sulfate aerosol may be speciated as sulfuric acid ($H_2SO_4(aq)$), ammonium bisulfate (NH_4^+, HSO_4^-), ammonium sulfate ($2NH_4^+$, SO_4^{2-}), and combinations in between. This speciation has important implications for aerosol mass, hygroscopicity, and acidity (Martin, 2000). When ammonia is in excess, standard thermodynamic models predict that sulfate aerosol should be mainly present as ammonium sulfate with an ammonium-sulfate ratio $R = [NH_4^+]/[S(VI)]$ approaching 2 on a molar basis (Seinfeld and Pandis, 2006). This thermodynamic behavior is indeed observed in a wide range of environments (Zhang et al., 2002; Martin et al., 2004; Yu et al., 2005). However, surface and aircraft observations in the Southeast US in summer find R to be in the range 1.0-1.6 mol mol^{-1} even with excess ammonia in the gas phase (Attwood et al., 2014; Guo et al., 2015; Kim et al., 2015). Here we examine the prevalence of this departure from expected thermodynamic behavior by analyzing aerosol and wet deposition data across the eastern US with focus on the Southeast, and we suggest a tentative explanation.

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SO_2 emissions in the Southeast US declined by 63% from 2003 to 2013 due to regulatory controls on coal combustion (Hidy et al., 2014; US EPA, 2015). One would expect from standard sulfate-ammonium thermodynamics that this would result in an increase in the ammonium-sulfate ratio R. However, observations show that the sulfate and ammonium components of the aerosol decreased at similar rates over the period so that R did not increase (Hand et al., 2012; Blanchard et al., 2013; Kim et al., 2015; Saylor et al., 2015; Weber et al., 2016), adding to the thermodynamic puzzle.

Weber et al. (2016) presented a detailed thermodynamic analysis of 1998-2013 observations of sulfate and ammonium aerosol and gas-phase ammonia at a rural site in the Southeast (Centreville, Alabama). They find a decrease in R from 1.8 to 1.5 mol mol^{-1} over the period even as the sulfate concentrations decrease, with significant ammonia (0.1-1 µg m^{-3}, ~ 0.1-1 ppb) remaining in the gas phase throughout the period. They show with the commonly used ISORROPIA II thermodynamic model (Fountoukis and Nenes, 2007) that the presence of this gas-phase ammonia is compatible with high aerosol acidity (pH 0-1.5) due to the semi-volatility of ammonia. However, their model calculations predict values for R in excess of 1.9 mol mol^{-1}, significantly higher than observed. As pointed out below, sulfate aerosol with R below 1.8 mol mol^{-1} should have very low ammonia vapor pressure (<< 0.1 µg m^{-3}) according to

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ISORROPIA. There thus remains a difficulty in reconciling their simultaneous observations of significant gas-phase ammonia (indicating ammonia in excess) and low values of R (indicating ammonia in deficit). A low value of R could be explained if alkaline cations other than ammonium contributed to sulfate neutralization, or if part of S(VI) was in the form of organosulfates; however, observations in the Southeast US show that neither of these effects is significant (Budisulistiorini et al., 2015; Hettiyadura et al., 2015; Kim et al., 2015; Liao et al., 2015; Rattanavaraha et al., 2016). The chemical composition of individual sulfate particles may deviate from the bulk, but it is not clear how such inhomogeneity could explain the observed departure from simple thermodynamics.

Liggio et al. (2011) found in laboratory experiments that uptake of ammonia by sulfuric acid aerosol is hindered by the presence of organic gases, and proposed that competition for uptake between ammonia and organic gases slows down considerably the approach to thermodynamic equilibrium. Kim et al. (2015) hypothesized that this could explain the observations of low ammonium-sulfate ratios. Organic aerosol (OA) often dominates over sulfate (Zhang et al., 2007), and in particular in the Southeast US in summer where there is a large OA source from biogenic hydrocarbons (Kim et al., 2015; Marais et al., 2016a). Mixing of organic and sulfate aerosol may slow down mass transfer due to phase separation, in which the organic aerosol fraction coats the predominantly aqueous inorganic core, as has been observed in many laboratory studies of organic-ammonium-sulfate particles (Anttila et al., 2007; Ciobanu et al., 2009; Bertram et al., 2011; Koop et al., 2011; You et al., 2013) as well as in the field in the Southeast US (You et al., 2012).

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2. Thermodynamics of the H_2SO_4-NH_3 system

H_2SO_4-HNO_3-NH_3 mixtures in the atmosphere form sulfate-nitrate-ammonium (SNA) aerosol following well-established thermodynamic rules (Martin, 2000). Nitrate partitions into the aerosol only when ammonia is in excess of sulfate and temperatures are low (Ansari and Pandis, 1998; Park et al., 2004). Nitrate is a negligibly small component of the aerosol in the Southeast US in summer (Ford and Heald, 2013; Kim et al., 2015). Here we focus on the H_2SO_4-NH_3 system, ignoring HNO_3 which is unimportant for our argument.

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The thermodynamics of the H_2SO_4-NH_3 system is determined by the supply of total sulfate (S(VI)) and ammonia (NH_x), relative humidity (RH), and temperature (T). Here we consider an aqueous aerosol (which may be metastable) in equilibrium with the gas phase. S(VI) is exclusively in the aerosol phase as the sum of H_2SO_4(aq) and its acid dissociation products. NH_x partitions between the gas and the aerosol phase as $NH_x \equiv NH_3(g) + NH_3(aq) + NH_4^+$. NH_3(aq) is a negligibly small component of NH_x under all atmospheric conditions.

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Figure 1 (left panel) shows the ammonium-sulfate ratio R = $[NH_4^+]/[S(VI)]$ and the aerosol pH at thermodynamic equilibrium in the H_2SO_4-NH_3 system, calculated by ISORROPIA II as a function of the input ratio $[NH_x]/[S(VI)]$. The calculations are for an aqueous aerosol with RH = 70% and T = 298 K, typical of conditions in the Southeast US in summer. Curves are shown for [S(VI)] = 1 and 5 μg m^{-3}, representing a range of moderately polluted conditions. The ammonium-sulfate ratio R closely follows the total $[NH_x]/[S(VI)]$ molar ratio up to a value of 1.8 (depending on the S(VI) concentration), and from there asymptotically approaches 2 as ammonia becomes in excess of sulfuric acid. Gas-phase ammonia is less than 0.01 μg m^{-3} for $[NH_x]/[S(VI)]$ below 2, at odds with the Weber et al. (2016) observations of $R < 1.8$ mol mol^{-1} with $[NH_3(g)] > 0.1$ μg m^{-3}. The aerosol pH calculated by ISORROPIA remains low (0.5-1.75) even with ammonia in large excess. This was previously pointed out by Guo et al. (2015) and Xu et al. (2015), and reflects the small aerosol liquid water content combined with the limited solubility of ammonia. It explains why gaseous ammonia is observed in the Southeast US at levels consistent with thermodynamic models even when the aerosol is acidic according to the pH metric (Nowak et al., 2006; Guo et al., 2015; Weber et al., 2016).

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The right panel of Figure 1 shows the same thermodynamic analysis using the Extended Aerosol Inorganic Model (E-AIM; Wexler and Clegg, 2002), which makes fewer assumptions than ISORROPIA II. We use E-AIM IV (Friese and Ebel, 2010), available interactively from http://www.aim.env.uea.ac.uk/aim/aim.php. E-AIM and ISORROPIA predict similar pH values, as pointed out by Hennigan et al. (2015), but E-AIM is much slower than ISORROPIA in approaching the R = 2 asymptote. Thus the Weber et al. (2016) observations could be accommodated by the E-AIM thermodynamic model in the $[NH_x]/[S(VI)] > 2$ regime. However, E-AIM still cannot reproduce the much lower values of R observed at other sites in the Southeast nor can it explain the trend of decreasing R as SO_2 emissions decrease. It has been shown that ammonium-sulfate aerosol ratios are not a simple proxy for aerosol pH (Hennigan et al., 2015). Here, we focus only on the the measureable quantity, R, and we describe these observations further in what follows.

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3. Ammonium-sulfate ratios in aerosol and precipitation

Figure 2 (top left panel) shows the NH_3/SO_2 molar emission ratio for the eastern US in summer 2013. Here and throughout this paper, mean ratios are presented as the ratios of the mean quantities. The emissions are from the 2011 National Emission Inventory (NEI) of the US Environmental Protection Agency (EPA), scaled to 2013 as described by Kim et al. (2015). There is good confidence in US ammonia emissions, which agree within 20% in independent bottom-up and top-down estimates (Paulot et al., 2014). Most of the domain has an emission ratio higher than 2, indicating excess ammonia. Total emission in the eastern US (domain of Figure 2, east of 95°W) is 45 Gmol NH_3 and 15 Gmol SO_2 for the three summer

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months, corresponding to a NH_3/SO_2 emission ratio of 3.0 mol mol^{-1}. About a third of emitted SO_2 may be removed by dry deposition rather than produce sulfate (Chin and Jacob, 1996), so that ammonia would be even more in excess, although 20-30% of ammonia may also be removed by dry deposition in the eastern US (Li et al., 2016).

The excess of ammonia is apparent in the $[NH_4^+]/[S(VI)]$ wet deposition flux data from the National Atmospheric Deposition Program (NADP) National Trends Network (NTN; http://nadp.sws.uiuc.edu/data/ntn/), shown in the top right panel of Figure 2. Both aerosol NH_4^+ and $NH_3(g)$ are efficiently scavenged by precipitation, so that the ammonium wet deposition flux relates to total ammonia emission. Similarly, both sulfate and SO_2 are efficiently scavenged so that the sulfate wet deposition flux relates to total SO_2 emission. The mean ammonium-sulfate ratio in the wet deposition flux data over the eastern US domain of Figure 2 is 3.0 mol mol^{-1}, again indicating ammonia in excess. Values less than 2 are mainly confined to the industrial Midwest (where the NH_3/SO_2 emission ratio is low) and to the Gulf Coast where precipitation may have a strong maritime influence. This excess of ammonia in the emission and wet deposition data is consistent with general observations of significant gas-phase ammonia concentrations at Southeast US sites (You et al., 2014; Guo et al., 2015; Saylor et al., 2015; Weber et al., 2016).

The bottom panels of Figure 2 show the ammonium-sulfate ratio in aerosol data from EPA's Chemical Speciation Network (CSN; Solomon et al., 2014), the Southeastern Aerosol Research and Characterization Study (SEARCH; Edgerton et al., 2005), and the Southern Oxidant and Aerosol Study (SOAS; Hu et al., 2015). The bottom right panel shows an alternate estimate of the ratio as $R_N = ([NH_4^+]-[NO_3^-])/[S(VI)]$ in order to remove the component of ammonium associated with ammonium nitrate (Weber et al, 2016). We expect R_N and R to bracket the effective ammonium-sulfate ratio, depending on whether aerosol nitrate is associated with ammonium or with other cations. The difference between the two is small in the Southeast US where the contribution of nitrate in summer is very small (Ford and Heald, 2013; Kim et al., 2015). Nitrate at the ensemble of Southeast US sites averages 0.25 ± 0.08 μg m^{-3} in summer 2013, representing less than 4% of $PM_{2.5}$ mass. Aerosol amines are present in low concentrations in the Southeast US (You et al., 2014) and concentrations of alkaline cations other than ammonium (e.g., Ca^{2+}, Mg^{2+}) are also too low to affect significantly the charge balance, as previously shown by Kim et al. (2015). Concentrations of these other alkaline cations are reported at the CSN sites, and we find for the ensemble of CSN sites in Figure 2 that they would modify R on average by 0.11 mol mol^{-1}.

Results in Figure 2 show that the ammonium-sulfate aerosol ratio is consistently well below 2, which is thermodynamically inconsistent with the presence of excess ammonia. The mean (± standard deviation) aerosol ratios for CSN sites in the domain of Figure 2 are $R_N = 1.08 \pm 0.26$ mol mol^{-1} and $R = 1.44 \pm 0.34$ mol mol^{-1}. Mean values for the five SEARCH sites in the Southeast are $R_N = 1.52 \pm 0.18$ mol

mol^{-1} and R = 1.62 ± 0.17 mol mol^{-1}. Aerosol mass spectrometer (AMS) measurements for the SOAS ground site in Centreville, Alabama in June-July 2013 give R_N = 0.85 ± 0.31 mol mol^{-1} and R = 0.93 ± 0.29 mol mol^{-1}, consistent with Particle into Liquid Sampler (PILS) measurements at the same site (Guo et al., 2015). AMS measurements onboard the NASA SEAC^{4}RS aircraft (Wagner et al., 2015) in the Southeast US boundary layer (below 2 km altitude) in August 2013 averaged R_N = 1.29 ± 0.44 mol mol^{-1} and R = 1.39 ± 0.52 mol mol^{-1}. Low values of R are consistent with the lack of nitrate in the aerosol (Guo et al., 2015; Weber et al., 2016).

One sigma (1σ) precision estimates for CSN network sulfate and ammonium aerosol concentrations are 6% and 8% respectively (Flanagan et al., 2006). For the SEARCH network the precision statistics are reported as median absolute differences (Edgerton et al., 2005). Assuming the measurement error is normally distributed these precision statistics can be converted to 1σ values (Rousseeuw and Croux, 1993) of 3% for sulfate and 5% for ammonium, respectively. The corresponding propagated uncertainties for R are 0.1 mol mol^{-1} (CSN) and 0.06 mol mol^{-1} (SEARCH).

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Differences in ammonium filter measurement methods between the CSN and SEARCH networks likely account for the higher values of R at the SEARCH sites. CSN samples for ion analysis are collected using a nylon filter downstream of a magnesium oxide denuder (Solomon et al., 2014). The use of a single nylon filter is prone to a negative bias because of volatilization losses of ammonia from ammonium nitrate (Yu et al., 2006). SEARCH samples for ion analysis are collected using a Teflon/nylon filter pack downstream of sodium bicarbonate and citric acid denuders. Best-estimate ammonium concentrations are calculated using the nonvolatile ammonium from the Teflon filter plus the stoichiometric ammonium associated with the nitrate measured on the nylon backup filter; this approach assumes that the particles volatilizing from the Teflon front filter are solely ammonium nitrate (Edgerton et al., 2005). Comparing these methods, CSN could be prone to a positive artifact because an acid-coated denuder is not used to remove gaseous ammonia but this bias is likely outweighed by the negative artifact when ammonium nitrate volatilizes and the resulting ammonia is not quantitatively retained by the nylon filter. However, Yu et al. (2006) showed in summertime observations at Great Smoky Mountains National Park (Tennessee) that ammonium losses could not be explained by particulate nitrate and suggested that organic ammonium salts could contribute to measured ammonium. If organic ammonium salts were retained on the filters at CSN or SEARCH sites, this would mean a lower effective ammonium-sulfate ratio.

Figure 2 shows more acidic conditions (lower ammonium-sulfate ratios) in the Southeast than in the Northeast. The Southeast CSN sites (south of 37°N) have R_N = 0.81 ± 0.21 mol mol^{-1} and R = 1.04 ± 0.21 mol mol^{-1}, while the Northeast sites have R_N = 1.17 ± 0.22 mol mol^{-1} and R = 1.57 ± 0.27 mol mol^{-1}. The difference between R_N and R is less in the Southeast because the contribution of nitrate to aerosol composition is very small. The same regional mean pattern is seen in the ammonium-sulfate wet deposition flux ratios (2.23 ± 0.80 mol mol^{-1} in Southeast, 2.99 ± 1.33 mol mol^{-1} in Northeast). The emission ratio NH_3/SO_2 is 3.28 mol mol^{-1} in the Southeast and 2.69 mol mol^{-1} in the Northeast, but SO_2 may be oxidized to sulfate more efficiently in the Southeast because of higher oxidant concentrations and longer residence times.

Figure 3 shows the relationship in the Southeast between aerosol and wet deposition ammonium-sulfate ratios for collocated sites, compared to thermodynamic predictions from E-AIM IV and ISORROPIA II. Here we take the observed wet deposition ammonium-sulfate ratio to be a measure of the $[NH_x]/[S(VI)]$ ratio input to thermodynamic models, which should be qualitatively correct. We see that the observed ammonium-sulfate aerosol ratio does not follow thermodynamic predictions and shows no correlation with the wet deposition ammonium-sulfate ratio. The aerosol ratio remains between 0.92 (R_N) and 1.15 mol mol^{-1} (R) even as the wet deposition ratio exceeds 6 mol mol^{-1}.

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The departure of the ammonium-sulfate aerosol ratio from thermodynamic predictions is also apparent in observed long-term trends. Figure 4 shows 2003-2013 trends in the Southeast US in summer at CSN and NADP sites. Sulfate wet deposition fluxes and aerosol concentrations both decrease by 6-8% a^{-1}, consistent with the trend in SO_2 emissions (Hand et al., 2012). There is no significant change in NH_4^+ wet deposition fluxes, as expected from constant NH_3 emissions during this period (Xing et al., 2013; Saylor et al., 2015). However, aerosol ammonium decreases at a rate similar to sulfate (-8.5% a^{-1}). Figure 5 shows trends at SEARCH sites, which also show aerosol sulfate and ammonium declining at a similar rate (-9.2% a^{-1} and -9.1% a^{-1} respectively), consistent with results previously shown by Weber et al. (2016). Such a parallel decrease of sulfate and ammonium would be expected only if the ammonium-sulfate aerosol ratio was very close to the asymptotic value of 2, in which case aerosol ammonium would be limited by the supply of sulfate; however, the observed ammonium-sulfate aerosol ratios are much lower. Thermodynamic predictions in Figures 1 and 3 show that as the supply of sulfate decreases relative to NH_x, the ammonium-sulfate aerosol ratio should increase. Marais et al. (2016b) shows that standard thermodynamics predict a significant decrease in aerosol acidity in response to the decrease in sulfate. However, the opposite is observed. The ammonium-sulfate aerosol ratio decreases by 3.0% a^{-1} at CSN sites and 1.4% a^{-1} at SEARCH sites, consistent with Weber et al. (2016) who showed a decline in the ratio by 1.4% a^{-1} for 1998-2013 aerosol observations at the Centreville, AL SEARCH site. Thus the aerosol is becoming more acidic even as SO_2 emission decreases.

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4. Possible mass transfer limitation by organic aerosol?

One possible explanation for the low and decreasing ammonium-sulfate aerosol ratios observed in the Southeast US is that organic aerosol (OA) may affect SNA thermodynamics or slow down the achievement of SNA thermodynamic equilibrium. We propose a tentative explanation of the observations based on the latter. As shown in Figure 5, the OA/S(VI) ratio in the Southeast increases rapidly over the 2003-2013 period in response to decreasing SO_2 emissions. Liggio et al. (2011) found in laboratory experiments using ambient air that uptake of ammonia by acidic sulfate aerosol is slowed by the uptake of organic gases. Measured timescales to reach equilibrium for experiments where organics were present were on the order of hours, significantly longer than the timescale of seconds measured for organic-free experiments. Daumer et al. (1992) previously noted a retardation in ammonia uptake for sulfuric acid particles coated with organic films. Liggio et al. (2011) reported reactive uptake coefficients (γ) for ammonia as a function of the mass ratio of OA to sulfate in their experiments. γ is defined as the probability that an ammonia molecule impacting the acidic sulfate aerosol will be taken up as NH_4^+. For OA to sulfate mass ratios of 0.14, 0.25, and 0.55, Liggio et al. (2011) reported γ values of 4×10^{-3}, 2×10^{-4}, and 5×10^{-4} respectively, in contrast to γ ≈ 1 for organic-free experiments.

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The results of Liggio et al. (2011) suggest a possible mass transfer limitation to ammonia uptake by the aerosol phase dependent on the local OA concentration. This might be explained by an OA surfactant effect or other phase separation. Laboratory studies have shown liquid-liquid phase separation of organic-ammonium-sulfate particles for oxygen to carbon elemental ratios (O:C) ≤ 0.8 (You and Bertram, 2015). Boundary layer observations from the SEAC^{4}RS aircraft campaign over the Southeast US in summer 2013 indicate a mean O:C ratio of 0.75 ± 0.22, suggesting that phase separation may occur.

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The values of γ reported by Liggio et al. (2011) can be used to describe a kinetic limitation to ammonia uptake where the net uptake of $NH_3(g)$ by the SNA aerosol is given by

$$-\frac{d[NH_3(g)]}{dt} = k\left([NH_3(g)] - [NH_3(g)]_{eq}\right) \qquad (1)$$

The mass transfer rate constant k [s^{-1}] is applied in equation (1) to the difference between the local concentration of $NH_3(g)$ and that computed from SNA thermodynamic equilibrium. k is related to γ (Jacob, 2000) by:

$$k = \int_0^\infty 4\pi a^2 \left(\frac{a}{D_g} + \frac{4}{\gamma v}\right)^{-1} n(a)\,da \qquad (2)$$

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where a is the wet aerosol radius, D_g is the gas phase diffusion coefficient, v is the mean molecular speed, and $n(a)$ is the number size distribution of sulfate aerosol.

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We implemented this crude kinetic limitation to ammonia uptake by SNA aerosol into the GEOS-Chem chemical transport model (CTM) version 9-02, previously applied by Kim et al. (2015) to simulation of aerosol observations from the NASA SEAC^{4}RS aircraft campaign over the Southeast US in summer-fall 2013 (Toon et al., 2016). The simulation includes detailed oxidant-aerosol chemistry as described by Kim et al. (2015) and Travis et al. (2016). Ammonia and SO_2 emissions are from the EPA National Emission Inventory for 2011 modified for 2013, with the emission ratios of Figure 2. SNA aerosol thermodynamics follows ISORROPIA II. ISORROPIA II in GEOS-Chem uses the metastable phase state in which the aerosol phase is always aqueous. The standard GEOS-Chem model assumes that SNA aerosol is in thermodynamic equilibrium at all times. Here we introduce the kinetic limitation to ammonia uptake described above.

Kim et al. (2015) presented detailed comparisons of results from the standard GEOS-Chem model assuming SNA thermodynamic equilibrium to aerosol observations collected from aircraft, surface sites, and satellites during SEAC^{4}RS. They showed that GEOS-Chem simulates successfully and without bias the observed sulfate and OA concentrations from the CSN network and the SEAC^{4}RS aircraft. However, their simulated ammonium concentrations were too high. Figure 6 shows that the ammonium-sulfate aerosol ratio in the standard model over most of the eastern US is close to 2 mol mol^{-1}, as expected from SNA thermodynamics with ammonia in excess; but the observed ratios are much lower. A reduced major axis (RMA) regression for the SEAC^{4}RS flight tracks gives a standard model ratio of 2.08 ± 0.02 mol mol^{-1}, whereas the observations give a ratio of 1.21 ± 0.08 mol mol^{-1}. The standard model ratio is slightly in excess of 2 because of the contribution of nitrate aerosol.

Figure 7 compares the gas-phase ammonia concentrations in the standard model to observations at the SEARCH sites. The model simulates concentrations of 0.05-1.2 μg m^{-3}, biased low by 44%. The standard model reproduces the mean observed wet deposition fluxes of ammonium over the Southeast US in summer (0.15 ± 0.10 kg N ha^{-1} month^{-1} modeled, 0.19 ± 0.12 kg N ha^{-1} month^{-1} observed) showing that uncertainty in ammonia emissions is not sufficient to explain the underestimate in gas-phase ammonia. The presence of gas-phase ammonia in the standard model is contingent on excess ammonia and an ammonium-sulfate aerosol ratio close to 2 (Figure 1). The problem is thus to explain the joint presence of gas-phase ammonia and low ammonium-sulfate aerosol ratios in the observations. Kinetic mass transfer limitation of ammonia uptake by SNA aerosols following equations (1) and (2) can solve that problem, as shown in Figures 6 and 7. Observed OA to sulfate mass ratios in the eastern US in summer 2013 average 1.89 ± 0.83 g g-1 at CSN sites and 2.44 ± 1.11 g g^{-1} at SEARCH sites (Figure 5), exceeding the maximum ratio of 0.55 reported by Liggio et al. (2011). Similarly, OA to sulfate ratios in the model are much greater than 0.55 throughout the eastern US boundary layer. We assume in GEOS-Chem that γ = 5×10^{-4} wherever the OA to

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sulfate ratio exceeds 0.55, following Liggio et al. (2011). This implies a timescale of over one day for ammonia to reach equilibrium.

GEOS-Chem with this kinetic limitation captures the low ammonium-sulfate ratio in the CSN observations in the Southeast (R = 1.14 ± 0.21 observed, 1.02 ± 0.10 modeled) and overcorrects in the Northeast (R = 1.51 ± 0.21 observed, 1.06 ± 0.21 modeled). OA/S(VI) concentration ratios are lower in the Northeast and so the kinetic limitation could be less. The ammonium-sulfate ratio in the SEAC^{4}RS aircraft observations is also better simulated as indicated by RMA regressions for the flight tracks in Figure 6 (1.39 ± 0.03 modeled, 1.21 ± 0.08 observed). The model is further successful at reproducing the gas-phase ammonia concentrations at the SEARCH sites, with no significant bias. In the absence of kinetic limitation, such low ammonium-sulfate ratios would be incompatible with the presence of significant gas-phase ammonia concentrations (Figure 1).

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5. Conclusions

Observation networks in the eastern US show low ammonium-sulfate aerosol ratios even when total ammonia is in large excess. This departs from expected H_2SO_4-NH_3 thermodynamic equilibrium and has important implications for aerosol mass, hygroscopicity, and acidity. The ammonium-sulfate ratio $R = [NH_4^+]/[S(VI)]$ averages 1.04 mol mol^{-1} in the Southeast and 1.57 mol mol^{-1} in the Northeast in summer, even though ammonia is in excess as indicated by the wet deposition flux ratios and by the observations of gas-phase ammonia. Observed long-term trends for 2003-2013 show that aerosol sulfate and ammonium decreased together in response to SO_2 emission controls, whereas one would thermodynamically expect the ammonium-sulfate ratio to increase. In fact, the ammonium-sulfate ratio decreased by 1-3% a^{-1} during the 2003-2013 period while SO_2 emissions decreased.

There appears to be a fundamental problem in reconciling from a thermodynamic perspective the joint observations of gas-phase ammonia and low ammonium-sulfate ratios. We suggest that this apparent departure from thermodynamic behavior may be caused by an elevated and increasing organic aerosol (OA) mass fraction, modifying or retarding the achievement of H_2SO_4-NH_3 thermodynamic equilibrium. Laboratory experiments by Liggio et al. (2011) indicate that the reactive uptake coefficient (γ) for uptake of ammonia by sulfate aerosol decreases greatly in the presence of OA. Implementation of a crude representation of this kinetic limitation in the GEOS-Chem chemical transport model greatly improves the agreement of the model with surface and aircraft observations of the ammonium-sulfate ratio in the eastern US, and also simulates successfully the observed gas-phase ammonia concentrations. Better understanding of OA effects on sulfate aerosol thermodynamics is needed. In addition to the phase separation hypothesis explored here, it has also been shown experimentally that reactions between ammonia and organics can occur (Liu et al., 2015) with similar uptake coefficients to those measured by Liggio et al. (2011). A mass transfer retardation of thermodynamic equilibrium may also have broader implications for the partitioning of semi-volatile species and for hygroscopicity. Previous work has shown good agreement between observed and modeled nitrate partitioning during winter in the eastern US (Guo et al., 2016) and organics have not been shown to affect the uptake of water to the degree that it would be a limiting factor for particle growth (Wong et al., 2014). More work is needed to measure the sensitivity of semi-volatile species to the presence of organic aerosol versus other factors controlling partitioning such as temperature and relative humidity, and the implications for aerosol pH.

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Deleted: An increasing organic coating of the aerosol as sulfate decreases could possibly explain the decrease in the ammonium-sulfate ratio in the Southeast US with time and hence the decrease in aerosol pH noted by Weber et al. (2016). Recent work has suggested that controlling SO_2 emissions in the US to decrease sulfate aerosol and improve $PM_{2.5}$ air quality could have a major co-benefit from suppressing acid-catalyzed biogenic secondary organic aerosol (SOA) formation (Pye et al., 2013; Marais et al., 2016). However, this co-benefit would not occur if the increasing OA/sulfate ratio causes the aerosol acidity to actually decrease.

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References

Alexander, B., Park, R. J., Jacob, D. J., Li, Q. B., Yantosca, R. M., Savarino, J., Lee, C. C. W., and Thiemens, M. H.: Sulfate formation in sea-salt aerosols: Constraints from oxygen isotopes, Journal of Geophysical Research-Atmospheres, 110, 12, 10.1029/2004jd005659, 2005.

Ansari, A. S., and Pandis, S. N.: Response of inorganic PM to precursor concentrations, Environmental Science & Technology, 32, 2706-2714, 10.1021/es971130j, 1998.

Anttila, T., Kiendler-Scharr, A., Mentel, T. F., and Tillmann, R.: Size dependent partitioning of organic material: evidence for the formation of organic coatings on aqueous aerosols, Journal of Atmospheric Chemistry, 57, 215-237, 10.1007/s10874-007-9067-9, 2007.

Attwood, A. R., Washenfelder, R. A., Brock, C. A., Hu, W., Baumann, K., Campuzano-Jost, P., Day, D. A., Edgerton, E. S., Murphy, D. M., Palm, B. B., McComiskey, A., Wagner, N. L., de Sa, S. S., Ortega, A., Martin, S. T., Jimenez, J. L., and Brown, S. S.: Trends in sulfate and organic aerosol mass in the Southeast U.S.: Impact on aerosol optical depth and radiative forcing, Geophysical Research Letters, 41, 7701-7709, 10.1002/2014gl061669, 2014.

Bertram, A. K., Martin, S. T., Hanna, S. J., Smith, M. L., Bodsworth, A., Chen, Q., Kuwata, M., Liu, A., You, Y., and Zorn, S. R.: Predicting the relative humidities of liquid-liquid phase separation, efflorescence, and deliquescence of mixed particles of ammonium sulfate, organic material, and water using the organic-to-sulfate mass ratio of the particle and the oxygen-to-carbon elemental ratio of the organic component, Atmospheric Chemistry and Physics, 11, 10995-11006, 10.5194/acp-11-10995-2011, 2011.

Blanchard, C. L., Hidy, G. M., Tanenbaum, S., Edgerton, E. S., and Hartsell, B. E.: The Southeastern Aerosol Research and Characterization (SEARCH) study: Temporal trends in gas and PM concentrations and composition, 1999-2010, Journal of the Air & Waste Management Association, 63, 247-259, 10.1080/10962247.2012.748523, 2013.

Budisulistiorini, S. H., Li, X., Bairai, S. T., Renfro, J., Liu, Y., Liu, Y. J., McKinney, K. A., Martin, S. T., McNeill, V. F., Pye, H. O. T., Nenes, A., Neff, M. E., Stone, E. A., Mueller, S., Knote, C., Shaw, S. L., Zhang, Z., Gold, A., and Surratt, J. D.: Examining the effects of anthropogenic emissions on isoprene-derived secondary organic aerosol formation during the 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee ground site, Atmospheric Chemistry and Physics, 15, 8871-8888, 10.5194/acp-15-8871-2015, 2015.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Ruiz, L. H., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.:

Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmospheric Chemistry and Physics, 15, 253-272, 10.5194/acp-15-253-2015, 2015.

Chin, M., and Jacob, D. J.: Anthropogenic and natural contributions to tropospheric sulfate: A global model analysis, Journal of Geophysical Research: Atmospheres, 101, 18691-18699, 10.1029/96JD01222, 1996.

Ciobanu, V. G., Marcolli, C., Krieger, U. K., Weers, U., and Peter, T.: Liquid-Liquid Phase Separation in Mixed Organic/Inorganic Aerosol Particles, Journal of Physical Chemistry A, 113, 10966-10978, 10.1021/jp905054d, 2009.

Daumer, B., Niessner, R., and Klockow, D.: Laboratory studies of the influence of thin organic films on the neutralization reaction of H_2SO_4 aerosol with ammonia, Journal of Aerosol Science, 23, 315-325, 10.1016/0021-8502(92)90001-c, 1992.

Edgerton, E. S., Hartsell, B. E., Saylor, R. D., Jansen, J. J., Hansen, D. A., and Hidy, G. M.: The southeastern aerosol research and characterization study: Part II. Filter-based measurements of fine and coarse particulate matter mass and composition, Journal of the Air & Waste Management Association, 55, 1527-1542, 2005.

Flanagan, J. B., Jayanty, R. K. M., Rickman, E. E., and Peterson, M. R.: PM2.5 speciation trends network: Evaluation of whole-system uncertainties using data from sites with collocated samplers, Journal of the Air & Waste Management Association, 56, 492-499, 2006.

Ford, B., and Heald, C. L.: Aerosol loading in the Southeastern United States: reconciling surface and satellite observations, Atmospheric Chemistry and Physics, 13, 9269-9283, 10.5194/acp-13-9269-2013, 2013.

Fountoukis, C., and Nenes, A.: ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K+-Ca2+-Mg2+-Nh(4)(+)-Na+-SO42--NO3--Cl--H2O aerosols, Atmospheric Chemistry and Physics, 7, 4639-4659, 2007.

Friese, E., and Ebel, A.: Temperature Dependent Thermodynamic Model of the System H+-NH4+-Na+-SO42-NO3--Cl--H2O, Journal of Physical Chemistry A, 114, 11595-11631, 10.1021/jp101041j, 2010.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite, J. R., Carlton, A. G., Lee, S. H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, Atmospheric Chemistry and Physics, 15, 5211-5228, 10.5194/acp-15-5211-2015, 2015.

Guo, H., Sullivan, A. P., Campuzano-Jost, P., Schroder, J. C., Lopez-Hilfiker, F. D., Dibb, J. E., Jimenez, J. L., Thornton, J. A., Brown, S. S., Nenes, A., and Weber, R. J.: Fine particle pH and the partitioning of nitric acid during winter in the northeastern United States, Journal of Geophysical Research-Atmospheres, 121, 10355-10376, 10.1002/2016jd025311, 2016.

Hand, J. L., Schichtel, B. A., Malm, W. C., and Pitchford, M. L.: Particulate sulfate ion concentration and SO2 emission trends in the United States from the early 1990s through 2010, Atmospheric Chemistry and Physics, 12, 10353-10365, 10.5194/acp-12-10353-2012, 2012.

Hansen, D. A., Edgerton, E. S., Hartsell, B. E., Jansen, J. J., Kandasamy, N., Hidy, G. M., and Blanchard, C. L.: The southeastern aerosol research and characterization study: Part 1-overview, Journal of the Air & Waste Management Association, 53, 1460-1471, 2003.

Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., and Nenes, A.: A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles, Atmospheric Chemistry and Physics, 15, 2775-2790, 10.5194/acp-15-2775-2015, 2015.

Hettiyadura, A. P. S., Stone, E. A., Kundu, S., Baker, Z., Geddes, E., Richards, K., and Humphry, T.: Determination of atmospheric organosulfates using HILIC chromatography with MS detection, Atmospheric Measurement Techniques, 8, 2347-2358, 10.5194/amt-8-2347-2015, 2015.

Hidy, G. M., Blanchard, C. L., Baumann, K., Edgerton, E., Tanenbaum, S., Shaw, S., Knipping, E., Tombach, I., Jansen, J., and Walters, J.: Chemical climatology of the southeastern United States, 1999-2013, Atmospheric Chemistry and Physics, 14, 11893-11914, 10.5194/acp-14-11893-2014, 2014.

Hu, W. W., Campuzano-Jost, P., Palm, B. B., Day, D. A., Ortega, A. M., Hayes, P. L., Krechmer, J. E., Chen, Q., Kuwata, M., Liu, Y. J., de Sa, S. S., McKinney, K., Martin, S. T., Hu, M., Budisulistiorini, S. H., Riva, M., Surratt, J. D., St Clair, J. M., Isaacman-Van Wertz, G., Yee, L. D., Goldstein, A. H., Carbone, S., Brito, J., Artaxo, P., de Gouw, J. A., Koss, A., Wisthaler, A., Mikoviny, T., Karl, T., Kaser, L., Jud, W., Hansel, A., Docherty, K. S., Alexander, M. L., Robinson, N. H., Coe, H., Allan, J. D., Canagaratna, M. R., Paulot, F., and Jimenez, J. L.: Characterization of a real-time tracer for isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements, Atmospheric Chemistry and Physics, 15, 11807-11833, 10.5194/acp-15-11807-2015, 2015.

Jacob, D. J.: Heterogeneous chemistry and tropospheric ozone, Atmospheric Environment, 34, 2131-2159, 10.1016/s1352-2310(99)00462-8, 2000.

Kim, P. S., Jacob, D. J., Fisher, J. A., Travis, K., Yu, K., Zhu, L., Yantosca, R. M., Sulprizio, M. P., Jimenez, J. L., Campuzano-Jost, P., Froyd, K. D., Liao, J., Hair, J. W., Fenn, M. A., Butler, C. F., Wagner, N. L., Gordon, T. D., Welti, A., Wennberg, P. O., Crounse, J. D., St Clair, J. M., Teng, A. P., Millet, D. B., Schwarz, J. P., Markovic, M. Z., and Perring, A. E.: Sources, seasonality, and trends of southeast US aerosol: an integrated analysis of surface, aircraft, and satellite observations with the GEOS-Chem chemical transport model, Atmospheric Chemistry and Physics, 15, 10411-10433, 10.5194/acp-15-10411-2015, 2015.

Koop, T., Bookhold, J., Shiraiwa, M., and Poschl, U.: Glass transition and phase state of organic compounds: dependency on molecular properties and implications for secondary organic aerosols in the atmosphere, Physical Chemistry Chemical Physics, 13, 19238-19255, 10.1039/c1cp22617g, 2011.

Li, Y., Schichtel, B. A., Walker, J. T., Schwede, D. B., Chen, X., Lehmann, C. M. B., Puchalski, M. A., Gay, D. A., and Collett, J. L.: Increasing importance of deposition of reduced nitrogen in the United States, Proceedings of the National Academy of Sciences of the United States of America, 113, 5874-5879, 10.1073/pnas.1525736113, 2016.

Liao, J., Froyd, K. D., Murphy, D. M., Keutsch, F. N., Yu, G., Wennberg, P. O., St Clair, J. M., Crounse, J. D., Wisthaler, A., Mikoviny, T., Jimenez, J. L., Campuzano-Jost, P., Day, D. A., Hu, W. W., Ryerson, T. B., Pollack, I. B., Peischl, J., Anderson, B. E., Ziemba, L. D., Blake, D. R., Meinardi, S., and Diskin, G.: Airborne measurements of organosulfates over the continental US, Journal of Geophysical Research-Atmospheres, 120, 2990-3005, 10.1002/2014jd022378, 2015.

Liggio, J., Li, S. M., Vlasenko, A., Stroud, C., and Makar, P.: Depression of Ammonia Uptake to Sulfuric Acid Aerosols by Competing Uptake of Ambient Organic Gases, Environmental Science & Technology, 45, 2790-2796, 10.1021/es103801g, 2011.

Liu, Y., Liggio, J., Staebler, R., and Li, S. M.: Reactive uptake of ammonia to secondary organic aerosols: kinetics of organonitrogen formation, Atmospheric Chemistry and Physics, 15, 13569-13584, 10.5194/acp-15-13569-2015, 2015.

Marais, E. A., Jacob, D. J., Jimenez, J. L., Campuzano-Jost, P., Day, D. A., Hu, W., Krechmer, J., Zhu, L., Kim, P. S., Miller, C. C., Fisher, J. A., Travis, K., Yu, K., Hanisco, T. F., Wolfe, G. M., Arkinson, H. L., Pye, H. O. T., Froyd, K. D., Liao, J., and McNeill, V. F.: Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application to the southeast United States and co-benefit of SO2 emission controls, Atmospheric Chemistry and Physics, 16, 1603-1618, 10.5194/acp-16-1603-2016, 2016a.

Marais, E.A., D.J. Jacob, J.R. Turner, and L.J. Mickley, Evidence of long-term decrease of biogenic secondary organic aerosol in response to SO_2 emission controls, submitted to Environmental Research Letters, 2016b.

Martin, S. T.: Phase transitions of aqueous atmospheric particles, Chemical Reviews, 100, 3403- 3453, 10.1021/cr990034t, 2000.

Rachel Silvern 2/16/2017 3:17 PM
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Martin, S. T., Hung, H. M., Park, R. J., Jacob, D. J., Spurr, R. J. D., Chance, K. V., and Chin, M.: Effects of the physical state of tropospheric ammonium-sulfate-nitrate particles on global aerosol direct radiative forcing, Atmospheric Chemistry and Physics, 4, 183-214, 2004.

Nowak, J. B., Huey, L. G., Russell, A. G., Tian, D., Neuman, J. A., Orsini, D., Sjostedt, S. J., Sullivan, A. P., Tanner, D. J., Weber, R. J., Nenes, A., Edgerton, E., and Fehsenfeld, F. C.: Analysis of urban gas phase ammonia measurements from the 2002 Atlanta Aerosol Nucleation and Real-Time Characterization Experiment (ANARChE), Journal of Geophysical Research-Atmospheres, 111, 14, 10.1029/2006jd007113, 2006.

Park, R. J., Jacob, D. J., Field, B. D., Yantosca, R. M., and Chin, M.: Natural and transboundary pollution influences on sulfate-nitrate-ammonium aerosols in the United States: Implications for policy, Journal of Geophysical Research-Atmospheres, 109, 10.1029/2003jd004473, 2004.

Paulot, F., Jacob, D. J., Pinder, R. W., Bash, J. O., Travis, K., and Henze, D. K.: Ammonia emissions in the United States, European Union, and China derived by high-resolution inversion of ammonium wet deposition data: Interpretation with a new agricultural emissions inventory (MASAGE_NH3), Journal of Geophysical Research-Atmospheres, 119, 4343-4364, 10.1002/2013jd021130, 2014.

Rattanavaraha, W., Chu, K., Budisulistiorini, H., Riva, M., Lin, Y. H., Edgerton, E. S., Baumann, K., Shaw, S. L., Guo, H. Y., King, L., Weber, R. J., Neff, M. E., Stone, E. A., Offenberg, J. H., Zhang, Z. F., Gold, A., and Surratt, J. D.: Assessing the impact of anthropogenic pollution on isoprene-derived secondary organic aerosol formation in PM2.5 collected from the Birmingham, Alabama, ground site during the 2013 Southern Oxidant and Aerosol Study, Atmospheric Chemistry and Physics, 16, 4897-4914, 10.5194/acp-16-4897-2016, 2016.

Rousseeuw, P. J., and Croux, C.: Alternatives to the Median Absolute Deviation, Journal of the American Statistical Association 88, 1273-1283, 10.2307/2291267, 1993.

Saylor, R., Myles, L., Sibble, D., Caldwell, J., and Xing, J.: Recent trends in gas-phase ammonia and PM2.5 ammonium in the Southeast United States, Journal of the Air & Waste Management Association, 65, 347-357, 10.1080/10962247.2014.992554, 2015.

Seinfeld, J. H., and Pandis, S. N.: Atmospheric Chemistry and Physics: From Air Pollution to Climate Change, 2nd Edition ed., John Wiley & Sons, Inc., New York, 2006.

Solomon, P. A., Crumpler, D., Flanagan, J. B., Jayanty, R. K. M., Rickman, E. E., and McDade, C. E.: US National PM2.5 Chemical Speciation Monitoring Networks-CSN and IMPROVE: Description of networks, Journal of the Air & Waste Management Association, 64, 1410-1438, 10.1080/10962247.2014.956904, 2014.

Toon, O. B., Maring, H., Dibb, J., Ferrare, R., Jacob, D. J., Jensen, E. J., Luo, Z. J., Mace, G. G., Pan, L. L., Pfister, L., Rosenlof, K. H., Redemann, J., Reid, J. S., Singh, H. B., Thompson, A. M., Yokelson,

Rachel Silvern 2/16/2017 3:17 PM

Deleted: Pye, H. O. T., Liao, H., Wu, S., Mickley, L. J., Jacob, D. J., Henze, D. K., and Seinfeld, J. H.: Effect of ... [2]

R., Minnis, P., Chen, G., Jucks, K. W., and Pszenny, A.: Planning, implementation, and scientific goals of the Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC(4)RS) field mission, Journal of Geophysical Research-Atmospheres, 121, 4967-5009, 2016.

Travis, K., Jacob, D. J., Fisher, J. A., Kim, P. S., Marais, E. A., Zhu, L., Yu, K., Miller, C., Yantosca, R. M., Sulprizio, M. P., Thompson, A., Wennberg, P. O., Crounse, J. D., St. Clair, J. M., Cohen, R. C., Laughner, J. L., Dibb, J. E., Hall, R. S., Ullmann, K., Wolfe, G. M., Pollack, I. B., Peischl, J., Neuman, J. A., and Zhao, X.: Why do models overestimate surface ozone in the Southeast United States?, Atmospheric Chemistry and Physics, 16, 13561-13577, 10.5194/acp-16-13561-2016, 2016.

US Environmental Protection Agency (EPA): Air Trends: Sulfur Dioxide, http://www3.epa.gov/airtrends/sulfur.html (last access 22 January 2016), 2015.

Wagner, N. L., Brock, C. A., Angevine, W. M., Beyersdorf, A., Campuzano-Jost, P., Day, D., de Gouw, J. A., Diskin, G. S., Gordon, T. D., Graus, M. G., Holloway, J. S., Huey, G., Jimenez, J. L., Lack, D. A., Liao, J., Liu, X., Markovic, M. Z., Middlebrook, A. M., Mikoviny, T., Peischl, J., Perring, A. E., Richardson, M. S., Ryerson, T. B., Schwarz, J. P., Warneke, C., Welti, A., Wisthaler, A., Ziemba, L. D., and Murphy, D. M.: In situ vertical profiles of aerosol extinction, mass, and composition over the southeast United States during SENEX and SEAC(4)RS: observations of a modest aerosol enhancement aloft, Atmospheric Chemistry and Physics, 15, 7085-7102, 10.5194/acp-15-7085-2015, 2015.

Weber, R. J., Guo, H., Russell, A. G., and Nenes, A.: High aerosol acidity despite declining atmospheric sulfate concentrations over the past 15 years, Nature Geoscience, 9, 282-285, 2016.

Wexler, A. S., and Clegg, S. L.: Atmospheric aerosol models for systems including the ions H+, NH4+, Na+, SO42-, NO3-,Cl-, Br-, and H2O, Journal of Geophysical Research-Atmospheres, 107, 10.1029/2001jd000451, 2002.

Wong, J. P. S., Liggio, J., Li, S. M., Nenes, A., and Abbatt, J. P. D.: Suppression in droplet growth kinetics by the addition of organics to sulfate particles, Journal of Geophysical Research-Atmospheres, 119, 12222-12232, 10.1002/2014jd021689, 2014.

Xing, J., Pleim, J., Mathur, R., Pouliot, G., Hogrefe, C., Gan, C. M., and Wei, C.: Historical gaseous and primary aerosol emissions in the United States from 1990 to 2010, Atmospheric Chemistry and Physics, 13, 7531-7549, 10.5194/acp-13-7531-2013, 2013.

Xu, L., Guo, H. Y., 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

Rachel Silvern 2/16/2017 3:17 PM

Deleted: M., Sulprizio, M. P., Thompson, A., Wennberg, P. O., Crounse, J. D., St. Clair, J. M., Cohen, R. C., Laughner, J. L., Dibb, J. E., Hall, R. S., Ullmann, K., Wolfe, G. M., Pollack, I. B., Peischl, J., ... [3]

United States, Proceedings of the National Academy of Sciences of the United States of America, 112, 37-42, 10.1073/pnas.1417609112, 2015.

You, Y., Renbaum-Wolff, L., Carreras-Sospedra, M., Hanna, S. J., Hiranuma, N., Kamal, S., Smith, M. L., Zhang, X. L., Weber, R. J., Shilling, J. E., Dabdub, D., Martin, S. T., and Bertram, A. K.: Images reveal that atmospheric particles can undergo liquid-liquid phase separations, Proceedings of the National Academy of Sciences of the United States of America, 109, 13188-13193, 10.1073/pnas.1206414109, 2012.

You, Y., Renbaum-Wolff, L., and Bertram, A. K.: Liquid-liquid phase separation in particles containing organics mixed with ammonium sulfate, ammonium bisulfate, ammonium nitrate or sodium chloride, Atmospheric Chemistry and Physics, 13, 11723-11734, 10.5194/acp-13-11723-2013, 2013.

You, Y., Kanawade, V. P., de Gouw, J. A., Guenther, A. B., Madronich, S., Sierra-Hernandez, M. R., Lawler, M., Smith, J. N., Takahama, S., Ruggeri, G., Koss, A., Olson, K., Baumann, K., Weber, R. J., Nenes, A., Guo, H., Edgerton, E. S., Porcelli, L., Brune, W. H., Goldstein, A. H., and Lee, S. H.: Atmospheric amines and ammonia measured with a chemical ionization mass spectrometer (CIMS), Atmospheric Chemistry and Physics, 14, 12181-12194, 10.5194/acp-14-12181-2014, 2014.

You, Y., and Bertram, A. K.: Effects of molecular weight and temperature on liquid-liquid phase separation in particles containing organic species and inorganic salts, Atmospheric Chemistry and Physics, 15, 1351-1365, 10.5194/acp-15-1351-2015, 2015.

Yu, S. C., Dennis, R., Roselle, S., Nenes, A., Walker, J., Eder, B., Schere, K., Swall, J., and Robarge, W.: An assessment of the ability of three-dimensional air quality models with current thermodynamic equilibrium models to predict aerosol NO_3, Journal of Geophysical Research-Atmospheres, 110, 25, 10.1029/2004jd004718, 2005.

Yu, X. Y., Lee, T., Ayres, B., Kreidenweis, S. M., Malm, W., and Collett, J. L.: Loss of fine particle ammonium from denuded nylon filters, Atmospheric Environment, 40, 4797-4807, 10.1016/j.atmosenv.2006.03.061, 2006.

Zhang, J., Chameides, W. L., Weber, R., Cass, G., Orsini, D., Edgerton, E., Jongejan, P., and Slanina, J.: An evaluation of the thermodynamic equilibrium assumption for fine particulate composition: Nitrate and ammonium during the 1999 Atlanta Supersite Experiment, Journal of Geophysical Research-Atmospheres, 108, 11, 10.1029/2001jd001592, 2002.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., DeCarlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimono, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, Geophysical Research Letters, 34, 10.1029/2007gl029979, 2007.

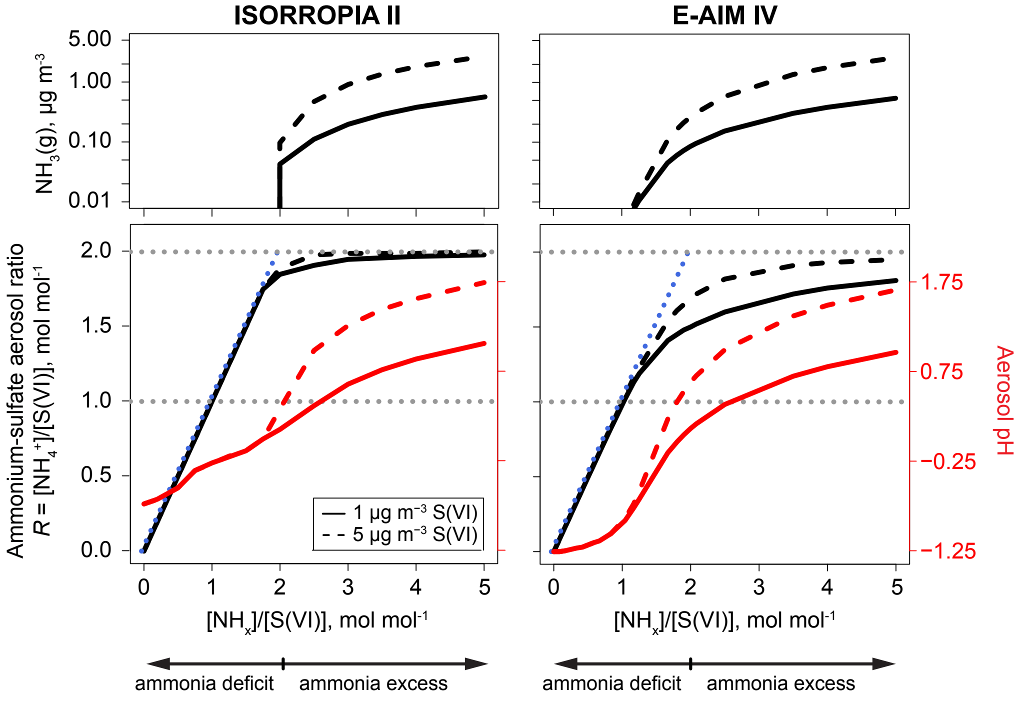

Figure 1. Thermodynamic properties of the sulfate-ammonium aerosol system as a function of the ratio of total ammonia ($NH_x \equiv NH_3(g) + NH_3(aq) + NH_4^+$) to total sulfate (S(VI)). A ratio lower than 2 indicates ammonia in deficit, a ratio higher than 2 indicates ammonia in excess. The figure plots the equilibrium gas-phase ammonia concentration (top panels), the ammonium-sulfate aerosol ratio (R = [NH_4^+]/[S(VI)]), and the aerosol pH. Values are computed with the thermodynamic models ISORROPIA II (left) and E-AIM IV (right) as a function of input [NH_x] with either 1 or 5 μg m^{-3} S(VI). Both models are applied in the forward mode (total [S(VI)] and [NH_x] used as input) for a metastable aqueous aerosol with 70% relative humidity and 298 K. The 1:1 line for the relationship of R to [NH_x]/[S(VI)] is shown in blue. The gray dotted lines show the ammonium-sulfate ratio R = 1 corresponding to NH_4HSO_4 and R = 2 corresponding to $(NH_4)_2SO_4$.

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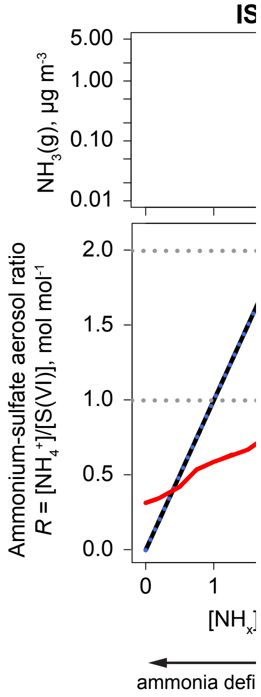

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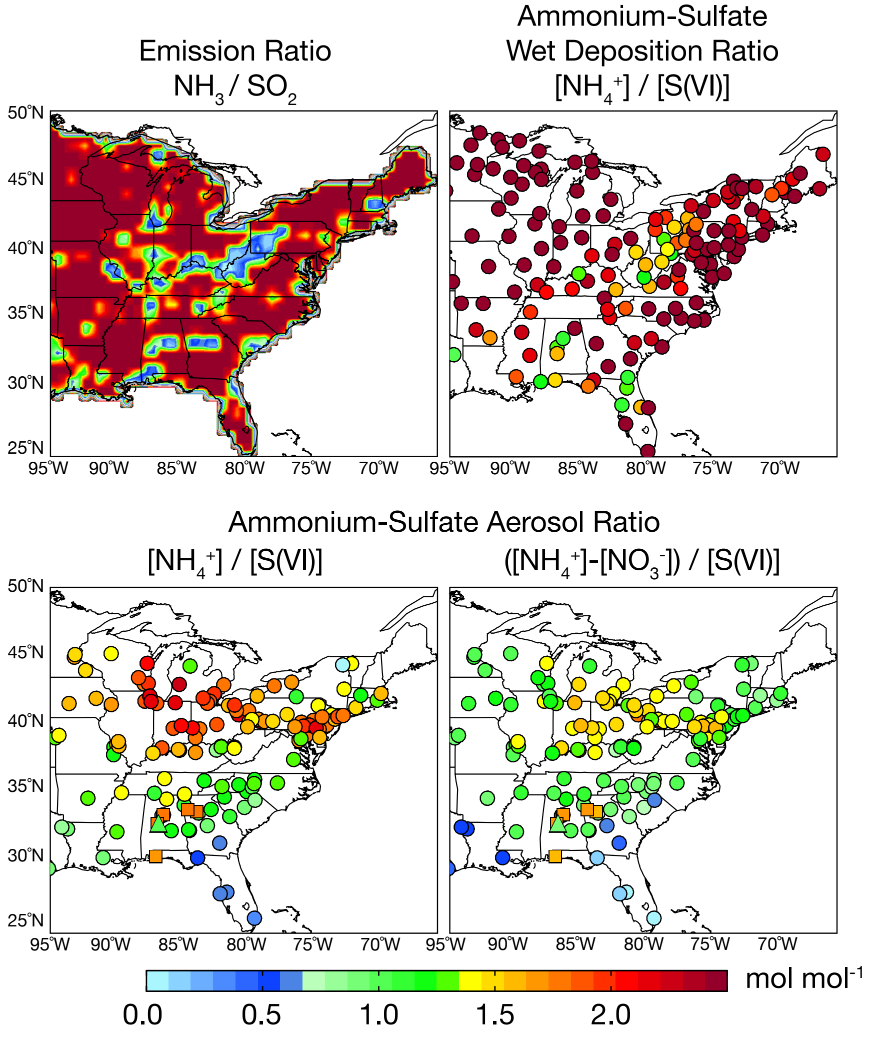

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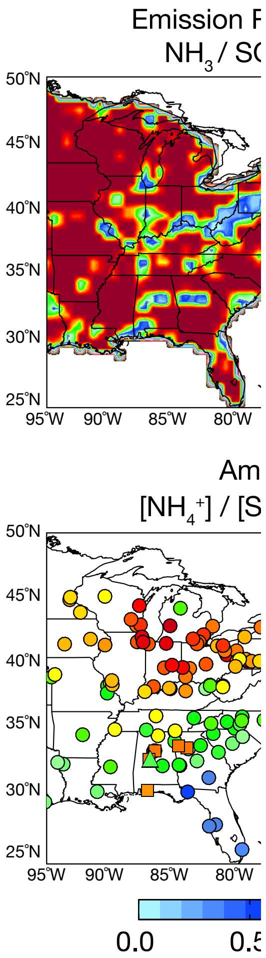

Figure 2. Ammonium-sulfate ratios in seasonally averaged data for the eastern US in summer 2013 (JJA). The top left panel shows the NH_3/SO_2 molar emission ratio from the EPA National Emission Inventory (NEI) on a 0.5°×0.5° grid. The top right panel shows the $[NH_4^+]/[S(VI)]$ molar wet deposition flux ratio from the National Acid Deposition Network (NADP). The bottom panels show the molar aerosol ratios from the EPA Chemical Speciation Network (CSN; circles), the Southeastern Aerosol Research and Characterization Study (SEARCH; squares), and the Southern Oxidant and Aerosol Study (SOAS; triangles). Measurements from CSN and SEARCH are $PM_{2.5}$ and measurements from SOAS are PM_1. The bottom left panel shows $R = [NH_4^+]/[S(VI)]$ and the bottom right panel shows $R_N = ([NH_4^+]-[NO_3^-])/[S(VI)]$ where the subtraction of $[NO_3^-]$ is to remove the contribution of NH_4^+ to NH_4NO_3 aerosol. In both the wet deposition and aerosol data, we removed primary sea-salt sulfate on the basis of measured Na^+

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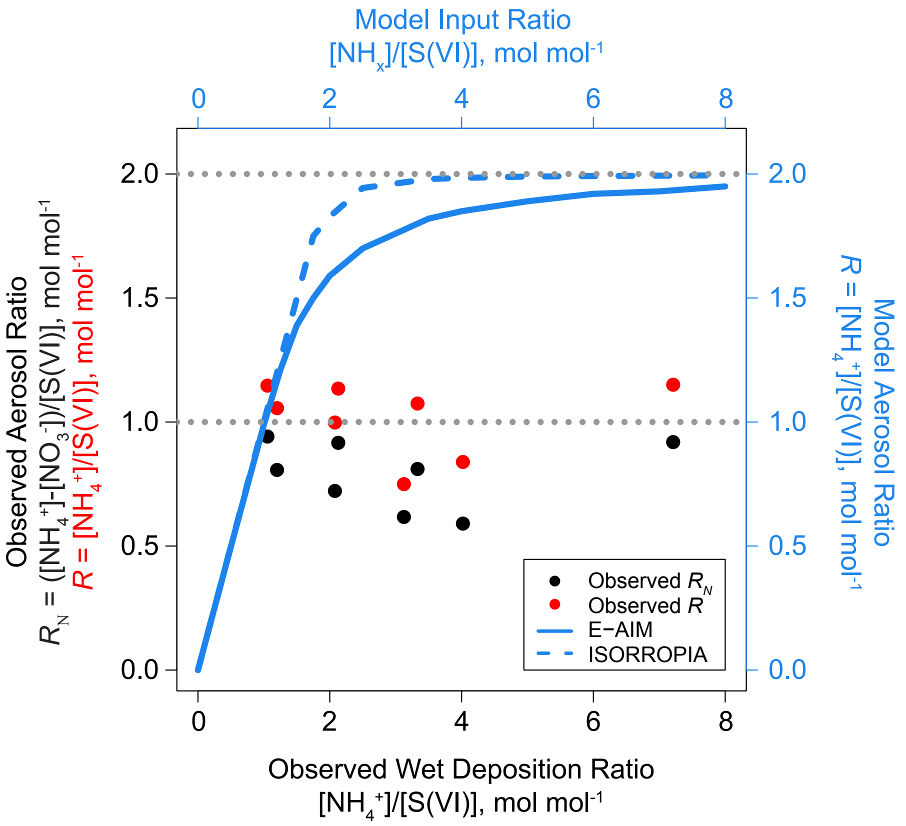
as in Alexander et al. (2005); this represents a significant correction for coastal sites. Here and elsewhere, mean ratios are calculated as the ratios of the mean quantities.



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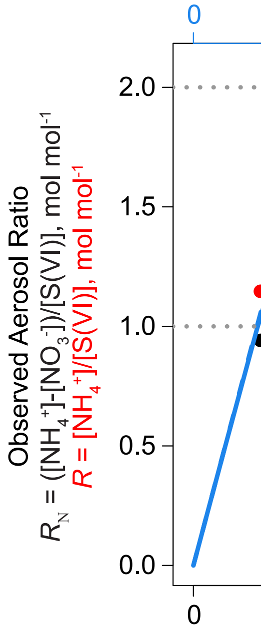

Figure 3. Relationship between the ammonium-sulfate ratio in aerosol and in precipitation. The points show the mean observed aerosol ratios from CSN sites vs. the wet deposition flux ratios from NADP sites for summer 2013 at collocated sites in the Southeast US (95-81.5° W, 30.5-37° N) on a 0.5°×0.5° grid. The black points remove ammonium associated with NH_4NO_3 and the red points do not. The gray dotted lines show the ratio $R = 1$ corresponding to NH_4HSO_4 and $R = 2$ corresponding to $(NH_4)_2SO_4$. The blue curves show the thermodynamic model curves as in Figure 1 but for both E-AIM IV and ISORROPIA II. Both models are applied in the forward mode with total input of NH_x and S(VI) as constraint and for 2 µg m^{-3} S(VI) at 298 K and 70% relative humidity.

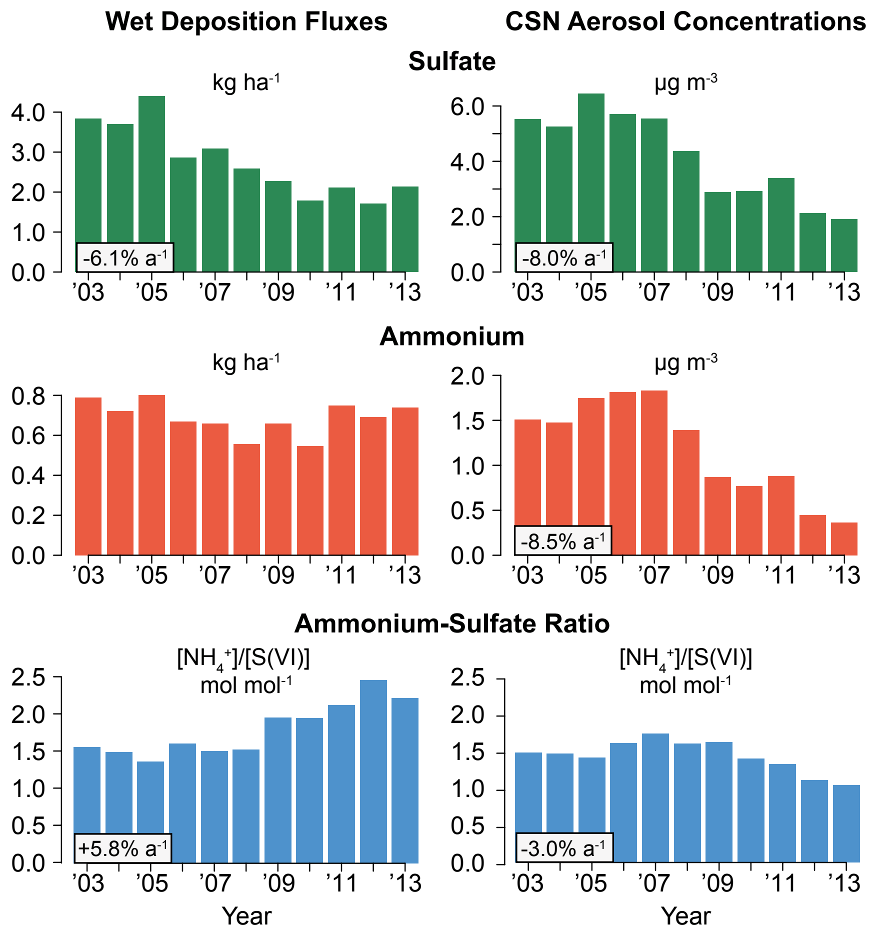

Figure 4. 2003-2013 summertime (JJA) trends of sulfate, ammonium, and ammonium-sulfate ratios in wet deposition and aerosol for the Southeast US (95-81.5° W, 30.5-37° N). Values are averages for the NADP and CSN sites in Figure 2. Trends are calculated using the Theil-Sen estimator and are shown when significant at a 95% confidence level.

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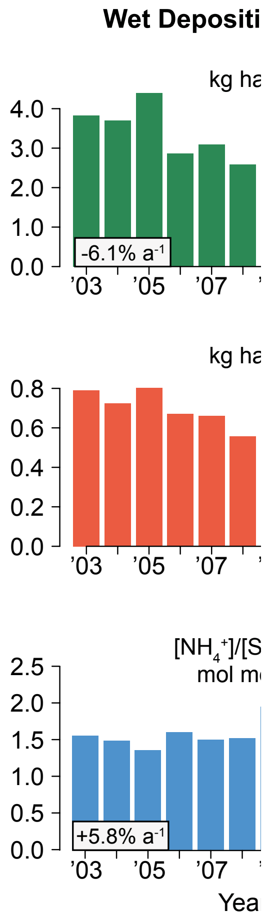

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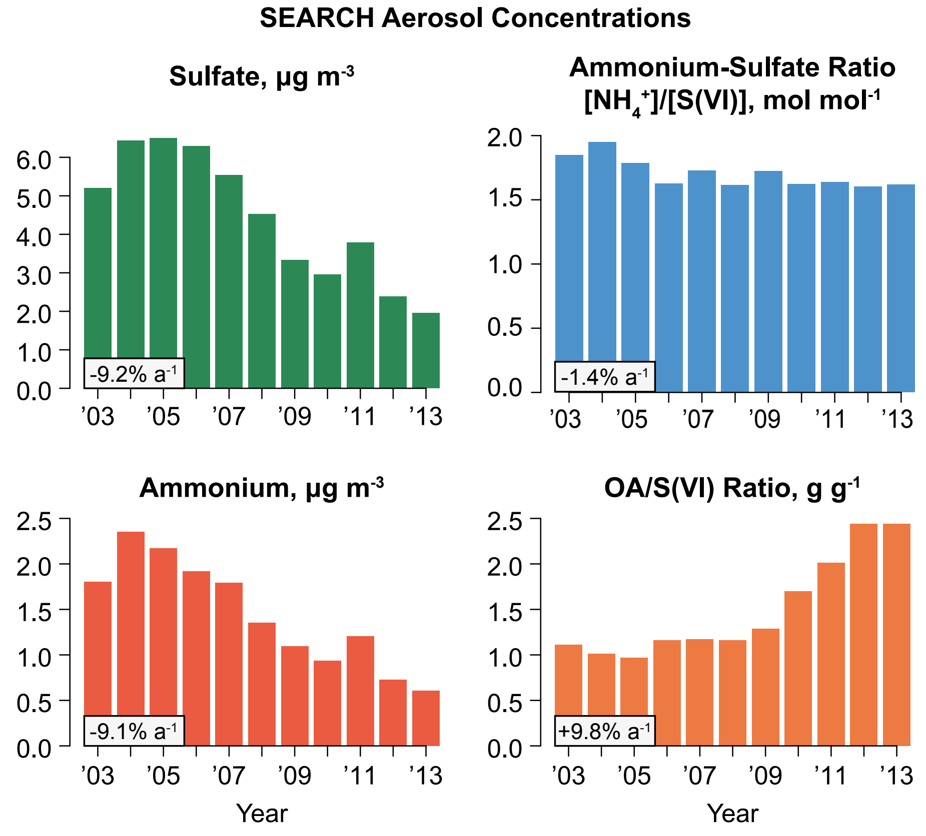

Figure 5. 2003-2013 summertime (JJA) trends in aerosol concentrations and ratios at the five SEARCH sites (BHM, CTR, JST, OLF, YRK) with locations shown in Figure 2. The organic aerosol (OA) concentration is inferred from measured organic carbon (OC) and an OA/OC mass ratio of 2.24 (Canagaratna et al., 2015; Kim et al., 2015). Trends are calculated using the Theil-Sen estimator and are shown when significant at a 95% confidence level.

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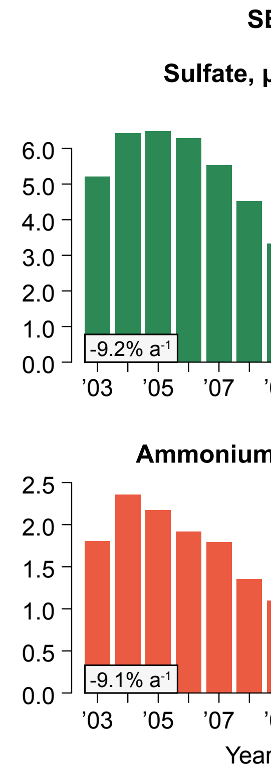

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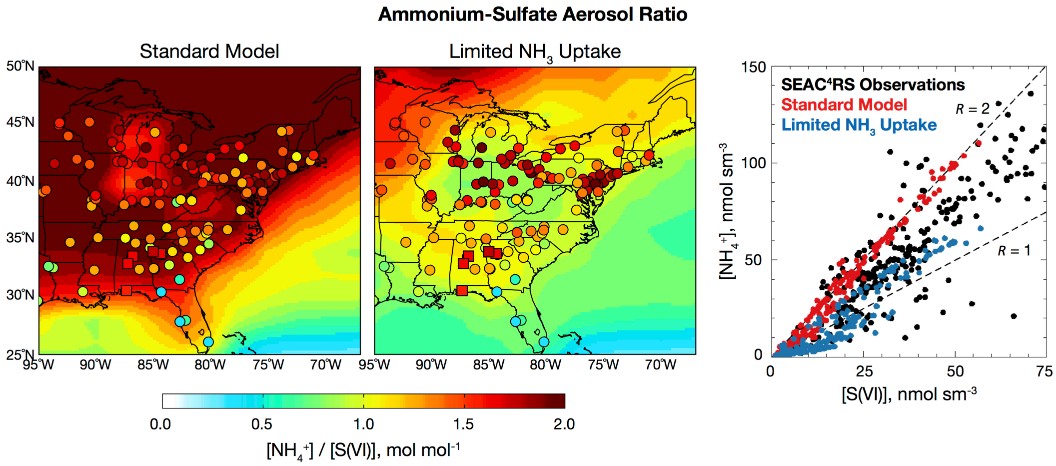

Figure 6. Ammonium-sulfate aerosol ratio $R = [NH_4^+]/[S(VI)]$ in the GEOS-Chem chemical transport model and comparison to observations in August 2013. The left and central panels show mean surface air values in the model (background contours) and in the observations at the CSN and SEARCH sites (circles and squares, respectively). The left panel shows results from the standard model assuming sulfate-nitrate-ammonium (SNA) aerosol thermodynamics, while the central panel shows results from the model including kinetic mass transfer limitation to ammonia uptake by SNA aerosol. The right panel compares the two model simulations to aircraft observations over the Southeast US below 2 km altitude from the SEAC^{4}RS aircraft campaign. The model is sampled along the flight tracks (Kim et al., 2015). "sm^{-3}" refers to standard cubic meter of air at standard conditions of temperature and pressure (273 K, 1 atm), so that nmol sm^{-3} is a mixing ratio unit. Dashed lines indicate the ratios $R = 1$ corresponding to NH_4HSO_4 and $R = 2$ corresponding to $(NH_4)_2SO_4$.

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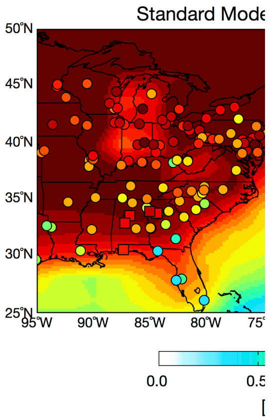

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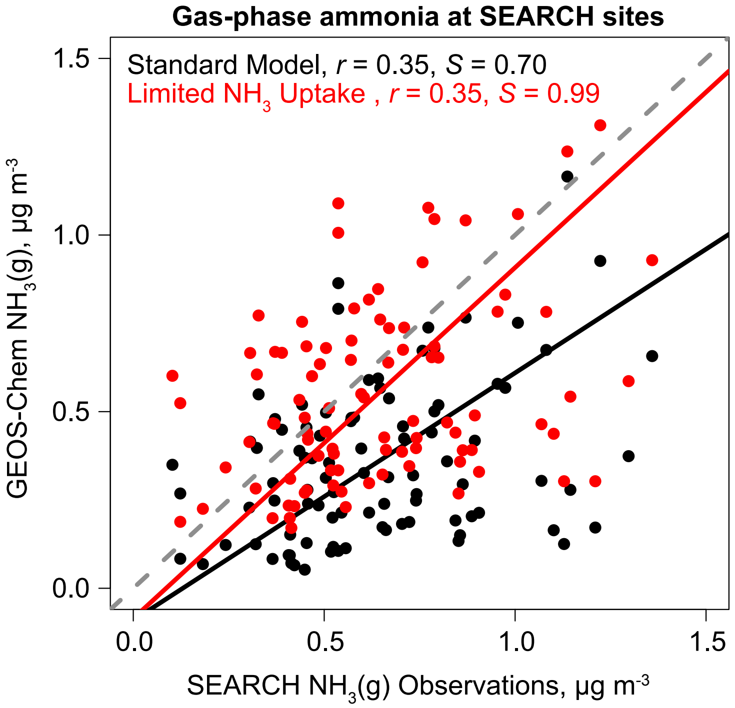

Figure 7. Gas-phase concentrations of ammonia at the Southeast US SEARCH sites in summer (JJA) 2013 (Hansen et al., 2003). Values are midday averages (10-16 local time) for the individual SEARCH sites shown in Figures 2 and 6 and for individual days. GEOS-Chem results are shown for the standard model assuming sulfate-nitrate-ammonium (SNA) aerosol thermodynamics and the model including kinetic mass transfer limitation to ammonia uptake by SNA aerosols. Solid lines show reduced major axis regressions and the 1:1 line is dashed. Correlation coefficients (*r*) and regression slopes (*S*) are given inset.