We thank the two anonymous reviewers 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 (Silvern2016_Manuscript_Reviews.pdf) and the difference version between the original and revised manuscript begins on page 11.

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Response to Reviewer #1

The crux of the puzzle being addressed in this paper is stated on page 2, lines 15 and 16, which states:

10   [There appears to be a mechanism that maintains the neutralization ratio at a low value even as the SO_2/NH_3 emission ratio decreases.] Ignoring for the moment the ambiguity of the term neutralization ratio (discussed below), this very issue was identified in a recent paper [Weber et al., 2016] where it was shown that a thermodynamic model predicts this precise drop in neutralization ratio (ie, molar ratio) with decreasing $SO_4=$ and steady NH_3 levels. The cause was identified to be due to the semi-volatile nature of

15   ammonia and the insensitivity of the system to gas phase NH_3 concentrations. Equilibrium partitioning of ammonia predicts lower ammonium-sulfate molar ratios as sulfate concentrations drop. The model was verified by comparison to observations [Guo et al., 2016; Guo et al., 2015]; the thermodynamic model predictions of the partitioning (gas- particle concentration ratios) of semi-volatile species, such as ammonia and nitric acid, are consistent with observations. Furthermore, the paper explained why little nitrate aerosol

20   has been observed despite large reductions in sulfate.

We have amended the text (page 2 line 24-page 3 line 1) to address the findings of Weber et al. (2016) and to put our work in context of that paper. This is very useful. Our work goes beyond the Weber paper by pointing out the thermodynamic inconsistency in the simultaneous observations of low ammonium-sulfate

25   ratios (R) and significant gas-phase ammonia. The Weber paper claims consistency but the values of R from their model calculations (Figure 2, "past") are higher than observed. We now point out that low values of nitrate are consistent with low values of R, citing Guo et al. (2015) and Weber et al. (2016) (page 6 lines 2-3).

30   In this paper, the authors propose a different cause for acidity (actually a $NH_4+/2SO_4=$ molar ratios less than 1) despite the presence of gas phase ammonia. They suggest that impedance of gas phase ammonia uptake by fine aqueous particles due to an outer organic film is the cause. Simply put, since sulfate is nonvolatile, this increases the time to equilibrium, results in an average (I guess) predicted lower particle ammonium concentration, which lowers the molar ratio. There is no discussion on what happens when

35   equilibrium is reached; presumably this model cannot explain the molar ratios at that point. A question is, why the different conclusions. One explanation may be due to the different analysis approach taken. One group has focused on pH predictions, and then using the predicted pH to assess it's affects on verifiable processes (comparing predicted and measured partitioning of various species), whereas in this work, the question is framed around observed vs predicted ammonium/sulfate molar ratios and using them to

40   interpret ambient data (referred to here as MR). No other verification is provided (ie, comparison of some pH dependent process or species concentration to observations, such as nitrate aerosol).

Our main focus in this paper is to point out the thermodynamic inconsistency between observed low ammonium-sulfate ratios and gas-phase ammonia, clarified now in the text (page 2 line 32-page 3 line 1).

45   We would be remiss if we didn't come up with a tentative explanation, but we now use the word "tentative" in the abstract and text, because it is certainly not our intention to claim that this crude parameterization of kinetic limitation to uptake is the final word. We point out in the conclusions that this explanation would have a number of other implications but to our knowledge there are no available observations that would rule it out. As requested by the reviewer we have added an evaluation of gas-phase

50   ammonia (page 9 lines 18-22, 29-32 with a new Figure 7, page 24).

First off, do the authors have a possible explanation why simply ammonia volatility is insufficient to explain these observations? It would seem prudent to least include a brief discussion stating that an alternative explanation to what they are proposing has been offered, briefly describe it and state why an alterative explanation is necessary. The logic used here seems odd. The authors use E-AIM or ISORROPIA in the analysis (and seem to accept that they largely agree with each other), but adjust the NH3 uptake to get these model predicted MR to agree with observations. But it has been shown that the same model (ISORROPIA) explains these observations. I conclude the issue is that MRs are not a robust nor reliable way to assess model predicted aerosol pH nor it's effects, and this is the fundamental cause for the different views.

The Weber et al. (2016) paper does not show agreement between model and observed R. We now devote a new paragraph of the introduction to point this out – this is indeed important to show how our paper goes beyond Weber et al. so we are very thankful to the reviewer for raising the issue and we believe that we have addressed it in the revision.

Why do the authors use MRs when investigating particle pH? Although commonly used in many different forms (e.g., ion balances, gas ratios, etc) it has been shown that MR do not provide quantitative insight on pH [Guo et al., 2016; Guo et al., 2015; Hennigan et al., 2015; Weber et al., 2016], but instead can lead to confusion and imprecise conclusions (see a list of them in specific comments below). Given this, it is not clear what their utility is. The author's show that the particle MR is not related to pH in any straightforward way (see fig 1) and that pH remains very low despite MR near or approaching 1. Given that pH is what controls aerosol processes related to acidity, such as partitioning of semi-volatile acids, acid catalyzed reactions, etc, and not MR, the use of MR to infer acidity is problematic.

Our focus is not on investigating particle pH. Our focus is on reconciling the joint occurrence of low R and high gas-phase ammonia. We have clarified this in revision, and also completely purged the word "neutralization" from the text at the reviewer's suggestion and to make this clearer.

As an example, what do the authors mean by their commonly used term, sulfate neutralization? Or sometimes, the term is just, aerosol neutralization, such as in the figures and in the text (pg 5 line 32). It is also in the title of the paper. Strictly, is one to interpret this to mean that the MR is 1 or greater? However, it also seems to be used to imply (or at least it gives the impression) that the authors are referring to overall particle acidity (i.e., pH), such that a MR of 1 implies a neutral aerosol. Example, page 8 line 7 and 8 states: quote [The aerosol in the standard model is fully neutralized throughout the eastern US (mean f = 1.00), at odds with observations.], end quote. But than Fig 1 shows that the pH is nowhere near neutral as f approaches 1; a contradiction. Including with their Fig 1, a plot of specifically f vs pH, would be very insightful, I believe. There are many instances in this paper of similar ambiguous statements (discussed more below).

In order to address the reviewer's concern we have (1) eliminated the "neutralization" terminology throughout the text, and (2) replaced f by R = [NH$_4^+$]/[S(VI)] to facilitate comparison with Weber et al. (1) should help to avoid the impression that we are focusing on aerosol pH, which we are not. See response above regarding distinction between pH and MR. Figure 1 (page 18) shows a plot of R and pH.

In any case, molar ratios are used in this work. The author's point is that the molar ratio predicted by the thermodynamic model is higher than what is observed, and so there is either an issue with the thermodynamic model or with the assumptions the model is based on. This paper proposes the latter, that NH3 mass transport limitations due to organic films are the cause and that it takes over a day for equilibrium to be established, thus the strict use of thermodynamic models, which assume equilibrium, give

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incorrect results. However, maybe other causes for the discrepancy are possible, eg, relating to oversimplification when using the model, such as lack of size dependent composition and the mixing state of the aerosol. What if one simply adds a small amount of other non-volatile cations, such as mineral dust, to the model; a reasonable thing to do since the data are PM2.5. This should lower the predicted MRs. Considering the likely small amount of other cations needed to significantly alter the MR, and measurement uncertainties (discussed more below), it is not clear how the authors can outright concluded that other cations play no role (ie, reference to Kim 2015 and Liao 2015). More details, provided in this paper, such as including sensitivity tests with various amounts of other cations could be very insightful.

We now address the lack of size dependent composition in the text (page 4 lines 6-7). We cannot conjure a scenario where size-dependent composition would explain the low value of R so it really shouldn't matter to the argument, and indeed Weber et al. didn't bother with it. At the reviewer's suggestion we now specifically quantify the small effect of soil dust cations in the data that we analyze and point out that the effect is small (page 5 lines 25-26).

Another issue that is not clear is the extensive comparisons of parameters, such as aerosol composition and MRs, between measurements of wet deposition versus fine particles. In the abstract it is used to infer that gas phase ammonia is in excess (meaning, presumably, not equal to zero). Fig 3 compares wet deposition neutralization ratios to those of fine particles. Generally the authors find that the wet deposition trends for sulfate and ammonium follow SO2 and NH3 emission trends and that the neutralization ratios (ie, MRs) are close to 1, as expected for excess NH3, whereas neither is true for fine particles. Are the authors inferring this provides evidence for some additional process affecting the fine particles? It is actually thermodynamically consistent and is due to the vastly different concentrations of liquid water (many orders of magnitude) associated with these systems. It is not clear how differences in MRs between fine haze particles and fog/cloud particles support the hypothesis of this manuscript and needs to be clarified? Maybe that was not the intent, but the use of wet deposition is confusing and should be clarified.

We have clarified our use of wet deposition data as it relates to emissions of ammonia and SO_2 on page 5 lines 3-6. We have also now included explicit discussion of gas-phase ammonia (page 4 lines 4-6; page 9 lines 18-22, 29-32; page 18, Figure 1; page 24, Figure 7).

Overall, this paper proposes an explanation for the persistent particle acidity despite reductions in SO2 emissions in the eastern US. Understanding the cause is clearly of great importance. In my view, the proposed explanation is speculative and largely unsupported because the use of MRs in their analysis is highly suspect. Furthermore, a much simpler explanation exists. I do believe the authors could test their hypothesis further; say by predicting concentrations of semi-volatile aerosol components that depend on pH, in different settings. I am not against publishing this paper, but believe that significant clarifications are needed throughout prior to publication. More specific detailed questions are provided below
Specific comments (in the following [. . .] indicates a quote from the manuscript)

How was the pH in Fig 1 calculated? Is it the equilibrium predicted pH, (ie, no kinetic limitation due to organic layer), or avg pH in the overall system that includes predicted pH before equilibrium is reached?

We added a clarification to the text that the pH in Figure 1 is for thermodynamic equilibrium (page 3, lines 31-32).

It is often not clear exactly what data were used for gas phase ammonia in the thermodynamic models. Was the wet deposition data used under the assumption that it represents the total sulfur and ammonia, and thus as model input? This is likely reasonable, but leads to much higher uncertainty than using direct measurements of the species involved (sulfate, ammonium, ammonia). Granted the wet deposition data is

more widely available then NH3, but still analysis for studies where all the data exists would greatly support the hypothesis of this work.

Yes indeed, and we thank the reviewer for the suggestion. We have added an evaluation of gas-phase ammonia measurements compared to model predictions (page 9 lines 18-22, 29-32; Figure 7 page 24) as well as additional discussion of ammonia predicted by thermodynamic models (page 4 lines 4-6; page 18, Figure 1). The wet deposition data shown on page 20, Figure 3 is compared to thermodynamic models under the assumption that it represents total $S(VI)$ and NH_x and is now stated in the text (page 7 lines 5-6).

If this organic film inhibits uptake of NH3, how it is likely to influence other semi-volatile species (nitric acid, HCl) and how will this impact the partitioning of these compounds. Will the model be able to accurately predict partitioning of these other species? Why not use this as a means of testing the hypothesis?

We now stress in the text that the hypothesis is tentative and that our representation of the OA effect is crude. Our focus here is mostly to offer a direction for future work.

One might expect this proposed process to be highly important in biomass burning plumes where the organic aerosol fraction is very high. Thermodynamic models appear to also work well in these cases [Bougiatioti et al., 2016]. Based on the arguments in this work one may expect them not to. The authors could investigate if there is other published work on thermodynamic predictions in smoke plumes that support their hypothesis.

Bougiatioti et al. (2016) focused on predicting aerosol pH and on average conditions in that study were more sulfate-rich than is typical of the Southeast US summer (33.8% organic aerosol by mass in Bougiatioti et al., 2016 in contrast to 55% organic aerosol in August-September 2013 in the Southeast US shown in Kim et al., 2015).

In the Abstract it states: [. . .sulfate aerosol is not fully neutralized even in the presence of excess ammonia, at odds with thermodynamic equilibrium models]. Is it ever shown in this paper that this statement is true? There is only a general reference to Seinfeld and Pandis. A thermodynamic calculation that supports this statement is needed. Also from the Abstract, last line states: [If sulfate aerosol becomes more acidic as OA/sulfate ratios increase, then controlling SO2 emissions to decrease sulfate aerosol will not have the co-benefit of suppressing acid-catalyzed secondary organic aerosol (SOA) formation.] This requires knowing how this proposed process specifically affects pH, which I don't believe is ever discussed. That is, what is the effect of this organic coating on aerosol pH?

Figure 1 (page 18) shows that ISORROPIA predicts R approaching 2 in the presence of excess ammonia and is stated in the text (page 4 lines 2-4).

We now state in the Conclusions (page 10 lines 23-25) the implication of the organic coating on the aerosol pH trend and how it could explain the observations of Weber et al. (2016).

Page 3, line 2-6 states: [Nitrate partitions into the aerosol only when ammonia is in excess of sulfate neutralization, limited by the supply of excess ammonia and dependent on temperature.] Can one provide a thermodynamic analysis proving this is true? Fig A above, suggests otherwise.

Figure 1 does not include nitrate, stated in the text (page 3 lines 23-24). Citations of the relevant literature supporting the statement in the text have been added (page 3 lines 21-22; Ansari and Pandis, 1998; Park et al., 2004).

Page 3 last sentence states: [In any case, sufficient ammonia is emitted in the eastern US to fully neutralize the sulfate contributed by SO2 emissions.] Again, can this statement be shown to be true based on a thermodynamic calculation?

This is a statement based on the relative emissions of NH_3 to SO_2 shown in Figure 2 (page 19) and has been clarified in the text (page 4 lines 28-29).

Page 4 it states: [alkaline cations other than ammonium do not contribute significantly to the neutralization (Kim et al., 2015),...] A few lines explicitly stating how this is shown in Kim would be very useful (as noted above).

We have added discussion of the influence of alkaline cations in the text (page 5 lines 22-26).

Page 4 gives f(N) from various studies, including AMS data from SOAS and SEAC4RS. Is the reported +/- the standard deviation of the data or the uncertainty in f(N). If not uncertainty, what is the uncertainty? (As an example, AMS uncertainty of 35% is often reported, which would lead to an uncertainty of about 50% for f(N). Also, in side by side comparisons, such as in SOAS and WINTER studies, systematic differences in AMS and PILS measurements of sulfate, nitrate and ammonium can easily by 20%. I suspect similar levels apply to network data. It seems that measurement uncertainty alone, both random and systematic (the latter more important here), makes asserting that there is a difference between measured and model predicted f(N) tenuous.

The mean values of R stated in this manuscript are provided with a propagated uncertainty and we now clarify this in the text (page 5 lines 28-29). SEARCH $PM_{2.5}$ measurements have a 1σ precision of 3% for sulfate and 5% for ammonium (as derived from the precision statistics reported by Edgerton et al., 2005) and CSN measurements have a 1σ precision of 6% for sulfate and 8% for ammonium (Flanagan et al. 2006). We have added to the text the corresponding propagated uncertainties for R (page 6 lines 8-9). We also note that while AMS absolute uncertainties of 35% for inorganic species are reported, the uncertainties on ratios of AMS species are lower, since the dominant source of uncertainty (collection efficiency) cancels out in the species ratio.

Page 5 Lines 29 to 31 it states: [We see that the observed aerosol neutralization does not follow thermodynamic predictions. . .] A similar statement is made in the last line on page 5. Specifically, what thermodynamic predictions are being referred to? Was a full thermodynamic model run to verify this? Please provide specific evidence to support this statement.

These statements refer to Figure 3 (page 20) as described in the text (page 7 lines 3-8) in which two thermodynamic models (E-AIM and ISORROPIA) are run and compared to observations. We have eliminated the term "neutralization" throughout the paper at the reviewer's suggestion and to clarify our intent.

Page 6 it states: [. . .the sulfate aerosol is far from neutralized, and one would expect under these conditions that the aerosol neutralization ratio should increase as the supply of sulfate decreases. But this is not observed.] What does, [one would expect], mean? Again, can these statements be proven with a thermodynamic calculation?

The statement refers to the thermodynamic predictions in Figures 1 and 3 that show the ammonium-sulfate ratio should increase as the $NH_x/S(VI)$ ratio increases and the text has been clarified on page 7 lines 17-22. Again, getting rid of "neutralization" should also help.

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The proposed mechanism to bring model predictions closer to observed MRs is to lower the NH3 uptake. This results in the equilibrium time scales increasing to roughly a day or more. Presumably this will also affect fine particle nitric acid equilibrium time scales. Even ignoring any effect this film may have on nitric acid uptake. This could have a large impact on predicted fine particle nitrate concentrations, given that in many locations there is a significant mass of cations in the coarse mode (Na+, Ca2+, . . .) that can form non-volatile forms of nitrate, if given sufficient time. Thus, it would seem the viability of this proposed mechanism could be tested by predicting nitrate aerosol levels and comparing to observations, for example during cooler periods when more nitrate partitions to fine particles. It has been noted in a number of publications that ISORROPIA can accurately predict nitrate (without this proposed mechanism). How do the authors explain this if by their mechanism the aerosol is not in equilibrium?

Nitrate concentrations are very low in the Southeast US summer, now stated in the text (page 5 lines 19-22). We have added an evaluation of gas-phase ammonia in GEOS-Chem compared to observations from the SEARCH network (page 9 lines 18-22, 29-32; Figure 7, page 24) as further supporting evidence of a kinetic limitation.

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Response to Reviewer #2

The authors present data suggesting that the sulfate in the Eastern US is not fully neutralized by ammonia despite the availability of the latter in the gas phase and argue that this could be due to mass transfer delays between the gas and particulate phase caused by organics. This is clearly an important issue that has received a lot of attention in the literature during the last few years. The paper is well written, however, the evidence provided to support its major conclusion is rather weak and it neglects other simpler explanations. It also neglects important work that has been published recently explaining similar observations with existing aerosol thermodynamics models. These problems are discussed below.

(1) Evidence that the aerosol is in equilibrium in the Southeast US The authors conclude from their data analysis that the aerosol in the eastern US is not in equilibrium probably due to limitations of the mass transfer of ammonia due to the organics. However, they neglect at least two studies that have used high quality gas-phase ammonia measurements in the same area and season to investigate this issue and reached the opposite conclusion. Weber et al. (2016) showed that the measured gas-phase ammonia was in equilibrium with the particulate phase during SOAS (see for example Figure 1 in that paper). They used 1-hr as averaging time therefore the equilibration timescale should be much less than this. If there was a significant delay in the mass transfer of ammonia between the two phases there should be significant observed discrepancies. Similar conclusions were reached by Nowak et al. (2006) for the 2002 ANARChE study in Atlanta. They concluded that the agreement between the measured and predicted ammonia within the uncertainties suggests that the assumption of thermodynamic equilibrium on the 7.5 min timescale is appropriate for most of the ANARChE data examined here.

We have amended the text to discuss the findings of Weber et al. (2016) (page 2 line 24-page 3 line 1) and identify the remaining need to reconcile simultaneous observations of low ammonium-sulfate ratios (R) and significant gas-phase ammonia. We have added a discussion of gas-phase ammonia predicted by thermodynamic models (page 4 lines 4-6; Figure 1, page 18) as well as model comparisons to ammonia observations (Figure 7, page 24). We address the findings of Nowak et al. (2006) on page 4 lines 9-11.

(2) Alternative explanations Weber et al. (2016) have argued that the incomplete neutralization of sulfate in the southeast US and the corresponding changes during the last 15 years are in general consistent with our current understanding of inorganic aerosol thermodynamics. They did not need to invoke delays in mass transfer and lack of equilibrium between the two phases. The authors appear to try something similar in Figure 3 but in a rather convoluted way using wet deposition data (please see comment 6 below).

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See response to comment 1 above. Weber et al. (2016) cannot explain the low observed values of R and we have now clarified this in the text. See our responses to reviewer 1.

(3) Model evaluation The use of GEOS-Chem to test the hypothesis of delays in the mass transfer of ammonia is the most original aspect of the current work. However, the evaluation of the corresponding GEOS-Chem predictions is rather superficial given the availability of the SOAS measurements during the same summer. The ability of GEOS-Chem to reproduce observed gas-phase ammonia concentrations is critical for the authors' argument. For example, the problems of the base case simulation could be due to the overprediction of ammonia availability (e.g., due to errors in ammonia emissions) and the assumed delay in mass transfer could be correcting one error by introducing another.

In response to the reviewer, we have added an evaluation of gas-phase ammonia in GEOS-Chem in the standard model and model with limited NH_3 uptake compared to observations from the SEARCH network (page 9 lines 18-22, 29-32; Figure 7, page 24). We point out that different ammonia emission inventories for the US agree to within 20% in summer (page 4 lines 27-28; Paulot et al., 2014). We now emphasize the thermodynamic inconsistency between low R and high $NH_3(g)$ as a key original component of this work.

(4) Terminology and details about calculated quantities I found the terminology used in the paper quite confusing. For example, the terms "sulfate neutralization" and "aerosol neutralization" are used throughout the paper instead of the ammonium to sulfate molar or equivalent ratio. Sometimes the nitrate is also used sometimes it is not. In all cases the other cations that could, in principle at least, be neutralizing sulfate are not included in this neutralization ratio.

At the reviewer's suggestion we have eliminated the "neutralization" terminology throughout the text and have replaced it with "ammonium-sulfate ratios" defined as $R = [NH_4^+]/[S(VI)]$. When nitrate is included in this ratio, it is defined as $R_N = ([NH_4^+]-[NO_3^-])/[S(VI)]$ and stated explicitly. Discussion of the influence of other cations has been amended in the text (page 5 lines 22-26).

It is not clear if the different ratios shown throughout the paper correspond to PM1, PM2.5, PM10 or something else. This detail is critical given the importance of calcium, magnesium, etc., for the coarse particles.

The particle size of the measurements shown is now given on page 19 line 8 and the focus throughout the paper on fine particulate matter is now stated on page 2 lines 5-6.

It is also not clear how the authors estimate the averages of the different ratios. Do they average the concentrations and then estimate the ratios or do they estimate the ratios with some averaging time (daily?) and then average them?

Mean ratios are presented as the ratio of mean quantities, now stated in the text (page 4 line 25) and in the caption of Figure 2 (page 19 lines 12-13).

(5) Originality of hypothesis The same hypothesis regarding the organic aerosol role in mass transfer of ammonia in the southeast US has been presented Kim et al. (ACP, 2015) with a number of common authors in the two studies. This should be discussed in the introduction of the paper.

The text has been amended on page 3 lines 8-9 to address this point.

(6) Use of wet deposition data The authors use wet deposition measurements as practically a surrogate of total (gas and particulate) ammonia. This is rather tricky given that rainfall takes place during specific

meteolorogical conditions, clouds can produce sulfate, and there are of course different wet removal efficiencies for ammonia and sulfate. Despite these problems, the paper does not address the potential biases that could be introduced in the analysis because of the use of these data. This could be one of the reasons for the differences between the conclusions here and those of other studies. I realize that gas-phase ammonia measurements exist only during specific field campaigns, but there are enough of them available both in the US and Europe. Use of these measurements is clearly preferable to the wet deposition data.

We have clarified our use of wet deposition data as it relates to emissions of ammonia and SO_2 on page 5 lines 3-6. We have also added a model comparison to gas-phase ammonia measurements (Figure 7, page 24).

(7) Role of organosulfates and crustal elements Some additional information is needed regarding the potential role of organosulfates and crustal elements for the present analysis. The authors appear to assume that they are negligible for the purposes of this work. However, some quantitative arguments are needed taking for example advantage of the SOAS measurements.

As stated in the text (page 3 lines 1-5, page 5 lines 22-26) organosulfates and crustal elements are present in low concentrations in the Southeast US summer based on observations. Organosulfates were also present in low concentrations during SOAS (Budisulistiorini et al., 2015; Hettiyadura et al., 2015; Rattanavaraha et al., 2016) and these references have been added in the text (page 3 lines 4-5). We have added a calculation of the effect of crustal components specifically for the data set that we analyze (page 5, lines 25-26).

(8) Some additional minor points:

Page 2, lines 2-4. This is clearly not true when there are other cations present.

Other cations are not present in high concentrations under the conditions examined in this paper as discussed in the response to the comment above.

Figure 2a is rather misleading given that most of the sulfur dioxide is emitted by point sources. It should probably be replaced with a table with the emissions in different regions of the US (e.g., southeast, northeast, etc.).

Emissions in the eastern US are stated in the text (page 4 line 30) as well as ratios for the Southeast and Northeast (page 6 line 32).

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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.

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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, $S(VI) \equiv H_2SO_4(aq) + HSO_4^- + SO_4^{2-}$. 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). 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.

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 (Centerville, 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). 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 ISORROPIA. There thus remains a difficulty in reconciling their simultaneous observations of significant gas-phase ammonia (indicating

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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).

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) including in the Southeast US in summer where there is a large OA source from biogenic hydrocarbons (Kim et al., 2015; Marais et al., 2016). 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).

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.

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.

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.

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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}. Composition differences across the aerosol size distribution should not affect this result. 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).

We find that results are sensitive to the choice of thermodynamic model. The right panel of Figure 1 shows the same thermodynamic analysis using the Extended Aerosol Inorganic Model (E-AIM; Wexler and Clegg, 2002). 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 Hannigan 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. We describe these observations further in what follows.

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). Independent estimates of ammonia emissions for the US in summer agree within 20% (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 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 removed by dry deposition in the eastern US (Li et al., 2016).

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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 ± 0.26 mol mol^{-1} and R = 1.44 ± 0.34 mol mol^{-1}. Mean values for the five SEARCH sites in the Southeast are R_N = 1.52 ± 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

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US boundary layer (below 2 km altitude) in August 2013 averaged $R_N = 1.29 \pm 0.44$ mol mol^{-1} and $R = 1.39 \pm 0.52$ 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) or 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).

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 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 $R_N = 0.81 \pm 0.21$ mol mol^{-1} and $R = 1.04 \pm 0.21$ mol mol^{-1}, while the Northeast sites have $R_N = 1.17 \pm 0.22$ mol mol^{-1} and $R = 1.57 \pm 0.27$ 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

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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 at least 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}.

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 flux, 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, but the opposite is observed. The 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 at the Centreville, AL SEARCH site. Thus the aerosol is becoming more acidic even as SO_2 emission decreases.

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

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organic gases. They reported reactive uptake coefficients (γ) for ammonia as a function of the mass ratio of OA to sulfate. 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 $\gamma \approx 1$ for organic-free experiments.

The results of Liggio et al. (2011) suggest a mass transfer limitation to ammonia uptake by the aerosol phase dependent on the local OA concentration. A possible explanation would be 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 be present in this region.

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

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

The mass transfer rate constant k [s^{-1}] is applied 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:

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

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

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 aerosol simulations for 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 formation follows the ISORROPIA II thermodynamic model implemented in GEOS-Chem by Pye et al. (2009). ISORROPIA II in GEOS-Chem uses the metastable phase state in which the aerosol phase is always aqueous and dissolved

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salts can be supersaturated and do not precipitate. The standard GEOS-Chem model assumes thermodynamic equilibrium for SNA aerosol to be achieved at all times and we introduce here the kinetic limitation to ammonia uptake described above. Observed OA to sulfate mass ratios in the eastern US in summer 2013 average 1.89 ± 0.83 at CSN sites and 2.44 ± 1.11 at SEARCH sites (Figure 5), exceeding the maximum ratio of 0.55 reported by Liggio et al. (2011). Where OA to sulfate ratios are greater than 0.55, as is the case for the entire eastern US domain, we apply $\gamma = 5\times10^{-4}$, implying a timescale of over one day to reach equilibrium.

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, ammonium is 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 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. GEOS-Chem with 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 such high 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. A mass transfer retardation of thermodynamic equilibrium would have broader implications for the partitioning of semi-volatile species and for hygroscopicity.

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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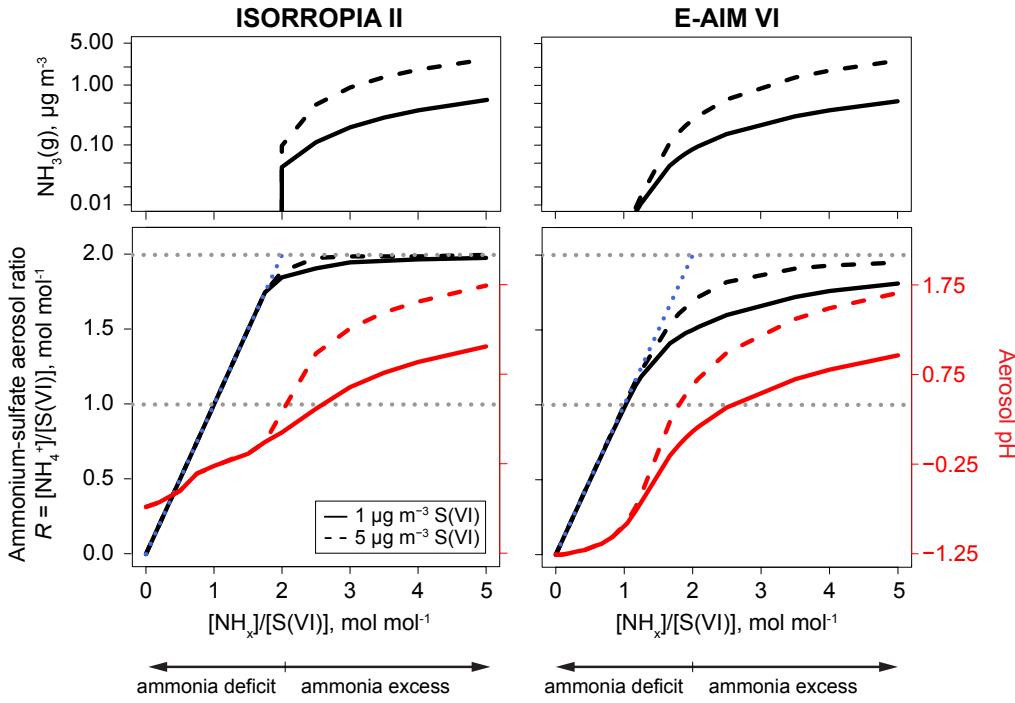
Figure 1. Thermodynamic properties of the sulfate-ammonium aerosol system as a function of the ratio of total ammonia ((NH$_x$ ≡ NH$_3$(g) + NH$_3$(aq) + NH$_4^+$) to total sulfate (S(VI)). A ratio lower than 2 indicates ammonia in deficit, a ratio higher than 2 indicates ammonia in excess. The figure 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 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$_4$HSO$_4$ and R = 2 corresponding to (NH$_4$)$_2$SO$_4$.

Emission Ratio
NH_3 / SO_2

Ammonium-sulfate Wet Deposition Ratio
$[NH_4^+] / [S(VI)]$

Ammonium-sulfate Aerosol Ratio
$[NH_4^+] / [S(VI)]$

$([NH_4^+]-[NO_3^-]) / [S(VI)]$

mol mol^{-1}

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 shown $R_N = ([NH_4^+]-[NO_3^-])/[S(VI)]$ 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^+ 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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Emission R
$NH_3 / 2SO$

$([NH_4^+]-[NO_3^-]) /$

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0.0   0.5

1.0

0.8

0.6

0.4

0.2

0.0

Observed Aerosol Neutralization Ratio
$f_N = ([NH_4^+]-[NO_3^-])/2[S(VI)])$ (mol mol^{-1})
$f = [NH_4^+]/2[S(VI)]$ (mol mol^{-1})

0.0   0.5

Observ

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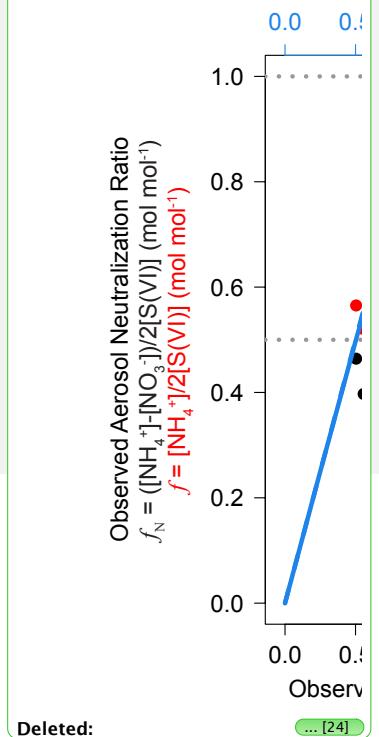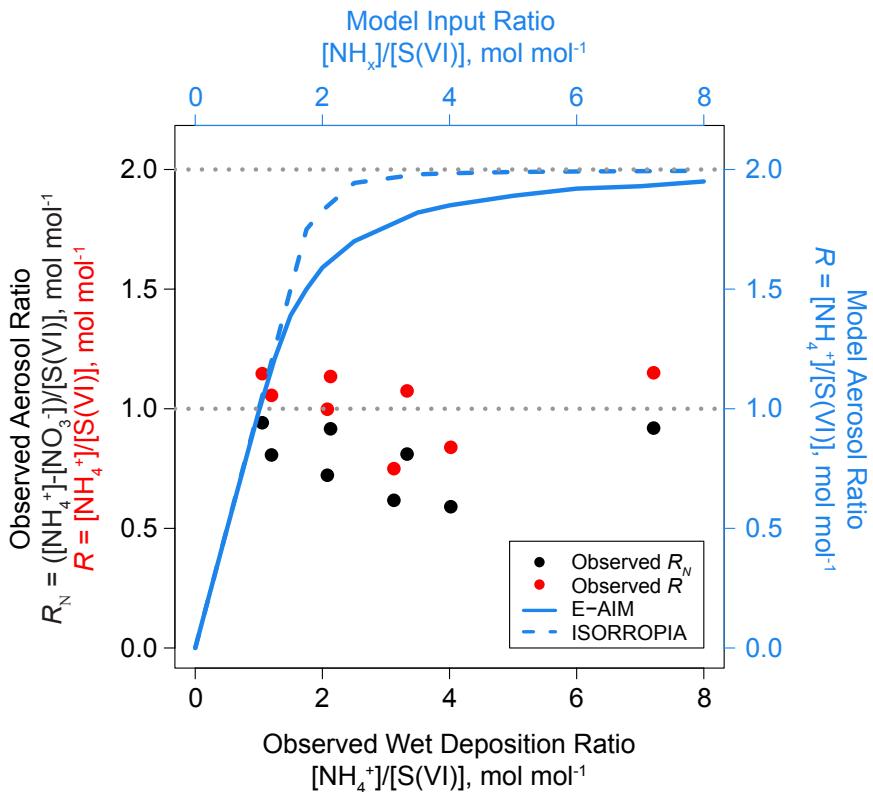
Figure 3. Relationship between the ammonium-sulfate ratio in aerosol and in precipitation. The points show the mean observed aerosol ratios from CSN sites vs. the wet deposition flux ratios from NADP sites for summer 2013 at collocated sites in the Southeast US (95-81.5° W, 30.5-37° N) on a 0.5°×0.5° 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.

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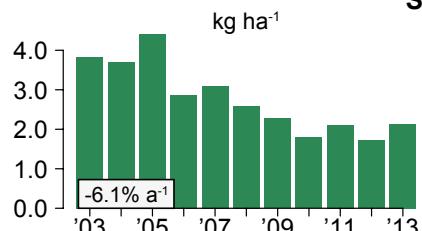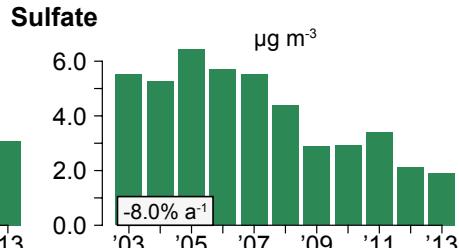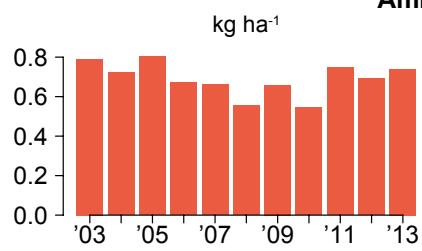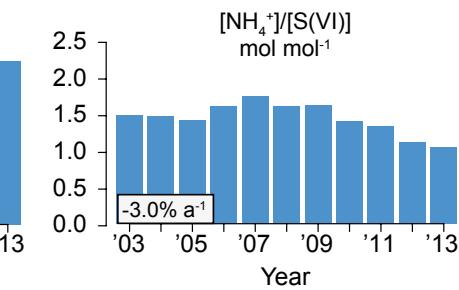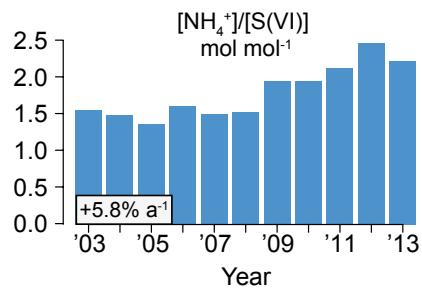
Figure 4. 2003-2013 summertime (JJA) trends of sulfate, ammonium, and ammonium-sulfate ratios in wet deposition and aerosol for the Southeast US (95-81.5° W, 30.5-37° N). Values are averages for the NADP and CSN sites in Figure 2. Trends are calculated using the Theil-Sen estimator and are shown when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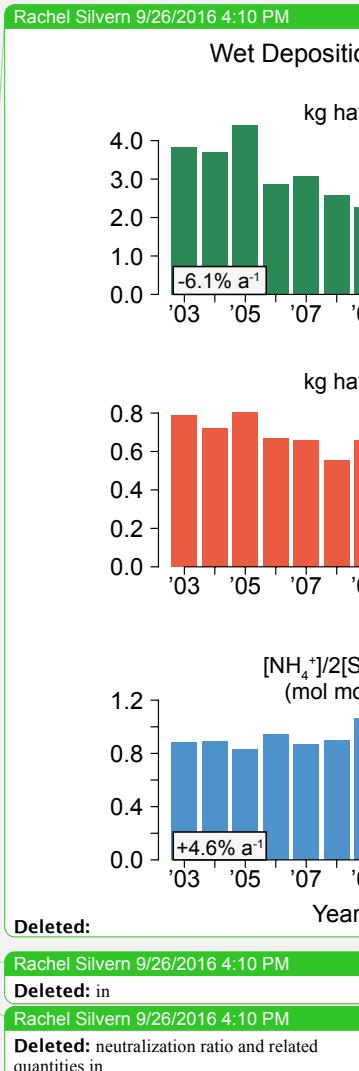
SEARCH Aerosol Concentrations

Sulfate, µg m⁻³

Ammonium-sulfate Ratio [NH₄⁺]/[S(VI)], mol mol⁻¹

Ammonium, µg m⁻³

OA/S(VI) Ratio, g g⁻¹
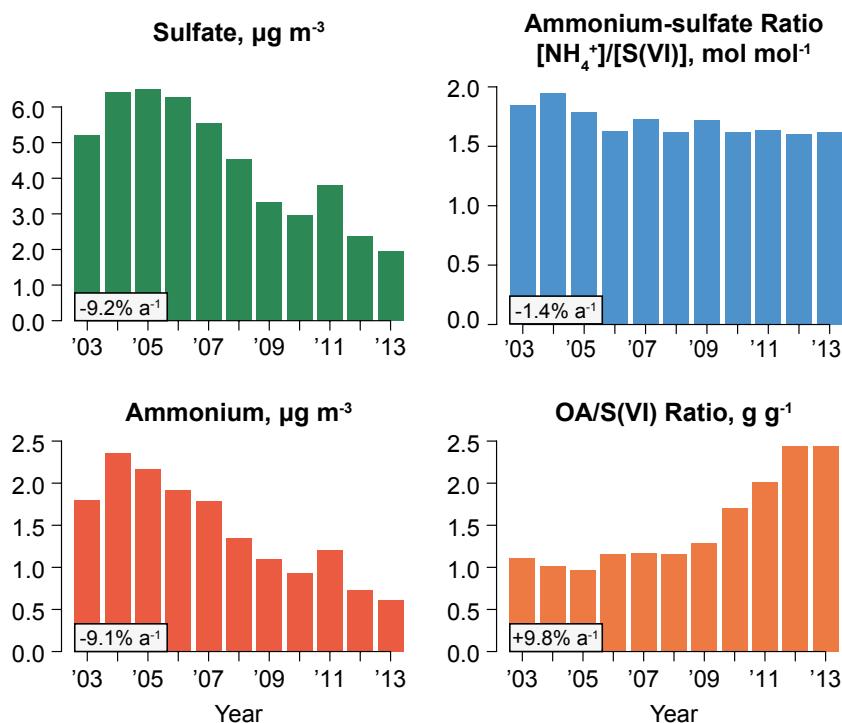
Figure 5. 2003-2013 summertime (JJA) trends in aerosol concentrations and ratios at the five SEARCH sites (BHM, CTR, JST, OLF, YRK) with continuous data shown in Figure 2. The organic aerosol (OA) concentration is inferred from measured organic carbon (OC) and an OA/OC mass ratio of 2.24 (Canagaratna 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.
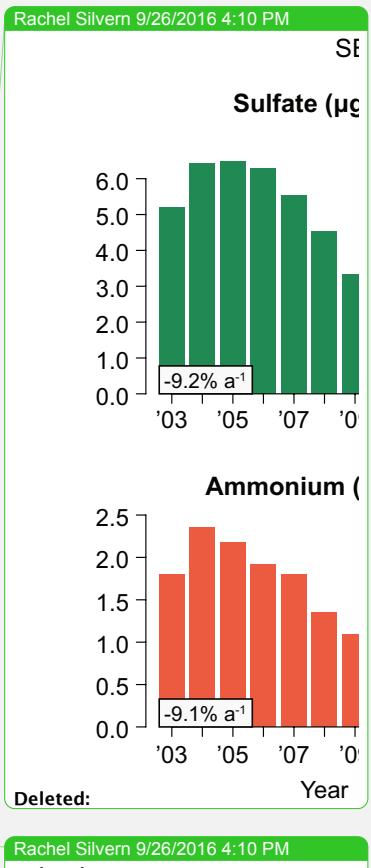
Ammonium-sulfate Aerosol Ratio
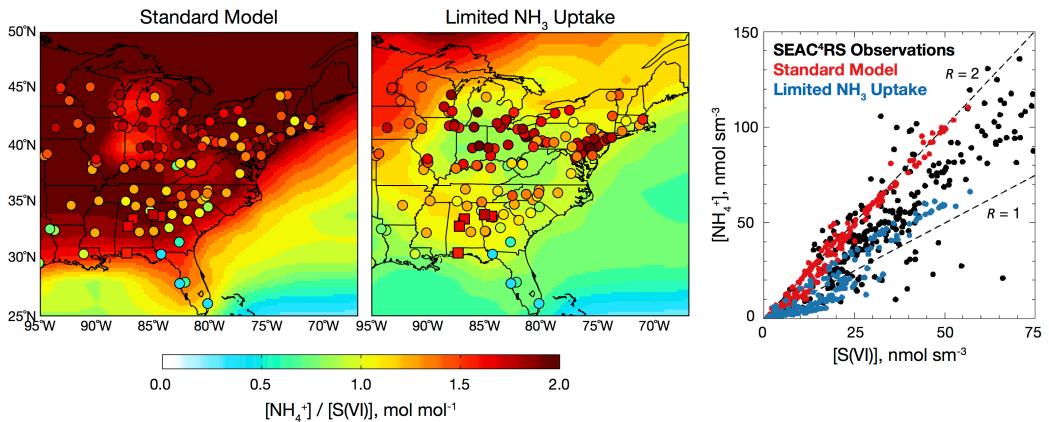
Figure 6. Ammonium-sulfate aerosol ratio $R = [NH_4^+]/[S(VI)]$ in the GEOS-Chem chemical transport model and comparison to observations in August 2013. The left and central panels show mean surface air values in the model (background contours) and in the observations at the CSN and SEARCH sites (circles 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 SEAC⁴RS 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 $(NH_4)_2SO_4$.
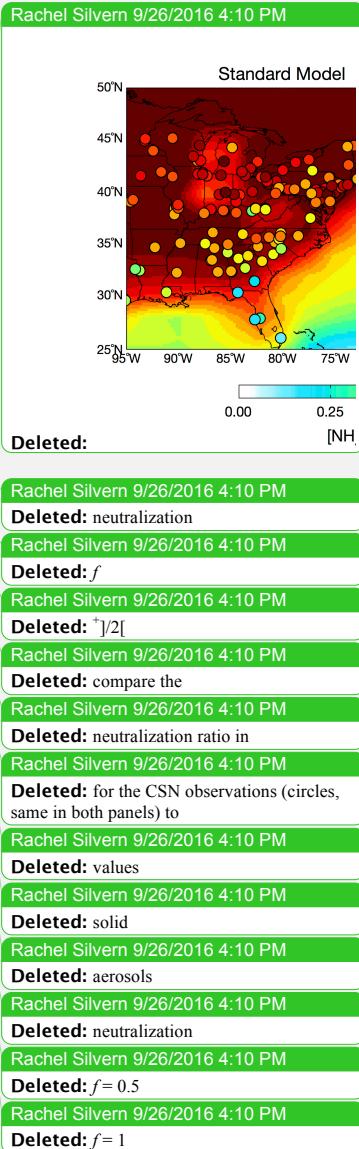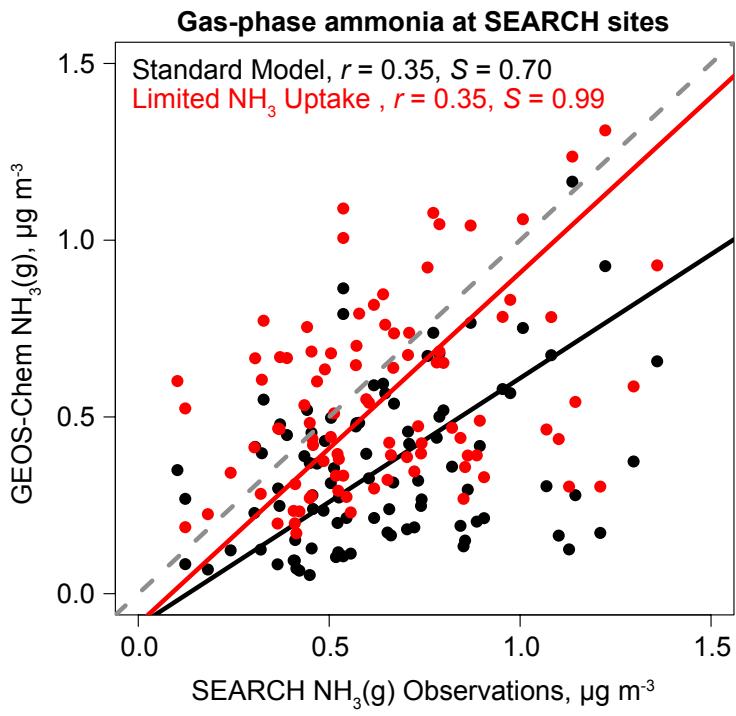
Figure 7. Gas-phase concentrations of ammonia at the Southeast US SEARCH sites in summer (JJA) 2013 (Hansen et al., 2003). Values are midday averages (10-16 local time) for the individual SEARCH sites shown in Figures 2 and 6 and for individual days. GEOS-Chem results are shown for the standard model 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.

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