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Incomplete sulfate aerosol neutralization despite excess ammonia in the eastern US: a possible role of organic aerosol

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Abstract. Acid-base neutralization of sulfate aerosol (S(VI) $\equiv H_2SO_4(aq) + HSO_4^- + SO_4^{2-}$) by ammonia ($NH_3$) has important implications for aerosol mass, hygroscopicity, and acidity. Surface network and aircraft observations across the eastern US show that sulfate aerosol is not fully neutralized even in the presence of excess ammonia, at odds with thermodynamic equilibrium models. The sulfate aerosol neutralization ratio ($f = [NH_4^+]/2[S(VI)]$) averages only 0.51 ± 0.11 mol mol^{-1} at sites in the Southeast and 0.78 ± 0.13 mol mol^{-1} in the Northeast in summer 2013, even though ammonia is in large excess as shown by the corresponding $[NH_4^+]/2[S(VI)]$ ratio in wet deposition fluxes. There is in fact no site-to-site correlation between the two quantities; the aerosol neutralization ratio in the Southeast remains in a range 0.3-0.6 mol mol^{-1} even as the wet deposition neutralization ratio exceeds 3 mol mol^{-1}. While the wet deposition neutralization ratio has increased by 4.6% a^{-1} from 2003 to 2013 in the Southeast US, consistent with SO_2 emission controls, the aerosol neutralization ratio has decreased by 1.0-3.2% a^{-1}. Thus the aerosol is becoming more acidic even as SO_2 emissions decrease. One possible explanation is that sulfate particles are increasingly coated by organic material, retarding the uptake of ammonia. The ratio of organic aerosol (OA) to sulfate increases over the 2003-2013 period as sulfate decreases. We implement a kinetic mass transfer limitation for ammonia uptake to sulfate aerosols in the GEOS-Chem chemical transport model and find improved agreement with surface and aircraft observations of the aerosol neutralization ratio. 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) aerosol produced in the atmosphere by oxidation of sulfur dioxide (SO_2) can be partly or fully neutralized by ammonia (NH_3) emitted from agriculture and natural sources. Neutralization involves acid dissociation of H_2SO_4, conserving total sulfate S(VI) $\equiv H_2SO_4(aq) + HSO_4^- +$

SO_4^{2-}. The extent of neutralization has important implications for aerosol mass, hygroscopicity, and acidity. When ammonia is in excess, standard thermodynamic models predict that sulfuric acid should be fully neutralized with an ammonium-sulfate aerosol neutralization ratio $f = [NH_4^+]/2[S(VI)]$ approaching 1 on a molar basis (Seinfeld and Pandis, 2006). However, surface and aircraft observations in the Southeast US in summer indicate f in the range 0.5-0.8 mol mol^{-1} even in the presence of excess ammonia in the gas phase (Attwood et al., 2014; Kim et al., 2015). Here we examine the prevalence of this apparent 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 possible explanation.

SO_2 emissions in the Southeast US have 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 with $f < 1$ mol mol^{-1} that this would result in an increase in the aerosol neutralization ratio. However, observations show that sulfate and ammonium are decreasing at similar rates over the period (Hand et al., 2012; Blanchard et al., 2013; Kim et al., 2015; Saylor et al., 2015), so that the neutralization ratio has not increased. Weber et al. (2016) find a decrease in the aerosol neutralization ratio at a site in the Southeast US for 1998-2013. 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. The neutralization ratio could be kept below unity 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 (Kim et al., 2015; Liao et al., 2015).

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 considerably the approach to thermodynamic equilibrium. Organic aerosol is usually present in excess of sulfate (Zhang et al., 2007) and particularly so in the Southeast US in summer where there is a large source from biogenic hydrocarbons (Guenther et al., 2006; 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). Models to describe this thermodynamic behavior include the Extended Aerosol Inorganic Model (E-AIM; Wexler and Clegg, 2002), and

ISORROPIA (Nenes et al., 1998). E-AIM makes fewer assumptions and ISORROPIA is computationally faster but they generally give similar results (Hennigan et al., 2015). 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. Here we focus on the H_2SO_4-NH_3 system, ignoring HNO_3, which is unimportant for our argument and is negligible in the Southeast US in summer (Kim et al., 2015).

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; gas-phase H_2SO_4 is negligibly small. NH_x partitions between the gas and the aerosol phase as $NH_x \equiv NH_3(g) + NH_3(aq) +$ aerosol NH_4^+. NH_3(aq) is a negligibly small component of NH_x under all atmospheric conditions.

Figure 1 shows the neutralization ratio $f = [NH_4^+]/2[S(VI)]$ and the aerosol pH calculated by E-AIM Model IV (Friese and Ebel, 2010; http://www.aim.env.uea.ac.uk/aim/aim.php) as a function of the input ratio $[NH_x]/2[S(VI)]$ to the model. The calculations are for an aqueous aerosol with RH = 60% and T = 290 K. Curves are shown for [S(VI)] = 1 and 5 $\mu g\ m^{-3}$, representing a range of moderately polluted conditions. The neutralization ratio f closely follows the total $[NH_x]/2[S(VI)]$ molar ratio up to a value of 0.7-0.9 (depending on the S(VI) concentration), and from there asymptotically approaches 1 as ammonia becomes in excess of sulfuric acid. The aerosol pH undergoes a rapid transition from negative to positive values as ammonia becomes in excess but remains low (0.5-2.5) even with ammonia in large excess. Such a low pH in the presence of excess ammonia 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 (Nowak et al., 2006; Guo et al., 2015; Weber et al., 2016).

3. Ammonium-sulfate ratios in aerosols and precipitation

Figure 2 (top left panel) shows the $NH_3/2SO_2$ molar emission ratio for the eastern US in summer 2013 based on best estimates (Paulot et al., 2014; Kim et al., 2015). Most of the domain has a ratio in excess of 1, indicating excess ammonia. Total emission in the eastern US (domain of Figure 2, east of 95°W) is 45.2 Gmol NH_3 and 15.0 Gmol SO_2 for the three summer months, corresponding to a $NH_3/2SO_2$ emission ratio of 1.51 mol mol^{-1}. About a third of emitted SO_2 may be removed by dry deposition rather than produce sulfate (Chin and Jacob, 1996). In any case, sufficient ammonia is emitted in the eastern US to fully neutralize the sulfate contributed by SO_2 emissions.

The effect of this neutralization is apparent in the top right panel of Figure 2, which shows the neutralization ratio f = $[NH_4^+]/2[S(VI)]$ for wet deposition flux data from the National Atmospheric Deposition Program (NADP) National Trends Network (NTN; http://nadp.sws.uiuc.edu/data/ntn/). Here we have removed primary sea-salt sulfate on the basis of measured Na^+ as in Alexander et al. (2005). NH_x and sulfate are both efficiently scavenged by precipitation, and SO_2 is also efficiently scavenged as long as aqueous-phase oxidants are present in excess, which is generally the case in summer. The mean value of f in wet deposition over the eastern US domain of Figure 2 is 1.38 mol mol^{-1}. Values less than 1 are mainly confined to the industrial Midwest (where the $NH_3/2SO_2$ emission ratio is low) and to the Gulf Coast where precipitation may have a strong maritime influence.

The bottom panels of Figure 2 show the neutralization 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). We also remove primary sea-salt sulfate on the basis of measured Na^+. The bottom left panel shows aerosol neutralization defined as f_N = $([NH_4^+]-[NO_3^-])/2[S(VI)]$ in order to remove the component of ammonium associated with ammonium nitrate. The bottom right panel shows aerosol neutralization defined as f = $[NH_4^+]/2[S(VI)]$, ignoring the correction for ammonium nitrate. As stated in the Introduction, alkaline cations other than ammonium do not contribute significantly to the neutralization (Kim et al., 2015), and organosulfates do not contribute significantly to sulfate mass (Liao et al., 2015). We expect f_N and f to bracket the actual sulfate neutralization ratio, depending on whether aerosol nitrate is associated with ammonium or with another cations. The difference between the two is small in the Southeast US where the contribution of nitrate in summer is usually negligible (Ford and Heald, 2013; Kim et al., 2015).

Results in Figure 2 show that aerosol sulfate is not neutralized and that the neutralization ratio is consistently much lower than in the wet deposition data. The mean aerosol neutralization ratios for CSN sites in the domain of Figure 2 are $f_N = 0.54 \pm 0.12$ mol mol^{-1} and $f = 0.71 \pm 0.17$ mol mol^{-1}. Mean values for the five SEARCH sites in the Southeast are $f_N = 0.75 \pm 0.10$ mol mol^{-1} and $f = 0.83 \pm 0.08$ mol mol^{-1}. Aerosol mass spectrometer (AMS) measurements from the SOAS ground site in Centreville, Alabama from June-July 2013 averaged $f_N = 0.43 \pm 0.15$ mol mol^{-1} and $f = 0.46 \pm 0.14$ mol mol^{-1}. 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 $f_N = 0.64 \pm 0.22$ mol mol^{-1} and $f = 0.70 \pm 0.26$ mol mol^{-1}, as will be shown later. Values in the winter at the CSN and SEARCH sites (not shown) are comparable to summer. We focus on summer because nitrate is a much larger contributor to the aerosol in winter and complicates the interpretation.

Differences in ammonium filter measurement methods between the CSN and SEARCH networks likely account for the higher measured neutralization 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 summer at Great Smoky Mountains National Park, TN, 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 even less neutralization of sulfate than computed from the $[NH_4^+]/2[S(VI)]$ ratio.

Figure 2 shows less aerosol neutralization in the Southeast than in the Northeast. The Southeast CSN sites (south of 37°N) have $f_N = 0.41 \pm 0.09$ mol mol^{-1} and $f = 0.51 \pm 0.11$ mol mol^{-1}, while the Northeast sites have $f_N = 0.58 \pm 0.10$ mol mol^{-1} and $f = 0.78 \pm 0.13$ mol mol^{-1}. The difference between f_N and f 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 wet deposition flux data ($f = 1.01 \pm 0.38$ mol mol^{-1} in Southeast, $f = 1.43 \pm 0.64$ mol mol^{-1} in Northeast), though there is little spatial correlation between aerosol neutralization ratios and wet deposition flux ratios. The emission ratio of $NH_3/2SO_2$ is 1.64 mol mol^{-1} in the Southeast and 1.34 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 mean observed aerosol neutralization ratios from CSN and wet deposition neutralization ratios from NADP for collocated sites, compared to results from E-AIM and ISORROPIA II (Fountoukis and Nenes, 2007). We choose the Southeast because there is less correction for nitrate but the same result is found in the Northeast. The observed wet deposition neutralization ratio is a measure of the $[NH_x]/2[S(VI)]$ ratio input to the thermodynamic models. We see that the observed aerosol neutralization does not follow thermodynamic predictions and shows no dependence on the total $[NH_x]/2[S(VI)]$ input ratio as measured by the wet deposition neutralization ratio. Aerosol neutralization remains between 0.3-0.6 mol mol^{-1} even as the wet deposition neutralization ratio exceeds 1 mol mol^{-1}.

The departure of the aerosol neutralization 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, consistent with estimates that national NH_3 emissions have been steady 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). Such a parallel decrease of sulfate and ammonium would be expected if the sulfate aerosol was fully neutralized, so that aerosol ammonium is limited by the supply of sulfate. As shown above, however, 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.

Figure 4 shows trends in the sulfate neutralization ratio. The wet deposition neutralization ratio increases by 4.6% a^{-1}, exceeding unity after 2009, as would be expected from the trend in the $NH_3/2SO_2$ emission ratio. By contrast, the aerosol neutralization ratio decreases by 3.2% a^{-1} over the time period. Figure 5 also shows a significant decrease in the sulfate neutralization ratio for SEARCH sites of 1.0% a^{-1}, 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 long-term decrease in sulfate neutralization in Figures 4 and 5 is that organic aerosol (OA) may be affecting SNA thermodynamics or interfering with SNA thermodynamic equilibrium. As shown in Figure 5, the OA/S(VI) ratio in the Southeast increases rapidly over the 2003-2013 period in response to the decreasing SO_2 emissions. Liggio et al. (2011) found in laboratory experiments using ambient air that uptake of ammonia by acidic sulfate aerosol was slowed by the uptake of 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) $\leq$ 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 (Wagner et al., 2015).

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 kinetic limitation to ammonia uptake by SNA aerosol into the GEOS-Chem chemical transport model (CTM) version 9-02 applied to simulations of North America during the summer-fall 2013 period of the NASA SEAC^{4}RS aircraft campaign over the Southeast US (Toon et al., 2015). The GEOS-Chem simulation includes detailed oxidant-aerosol chemistry as described by Kim et al. (2015) and Travis et al. (2016). 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 salts can be supersaturated and do not precipitate. The standard model assumes thermodynamic equilibrium for SNA aerosol 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, exceeding the maximum ratio reported in Liggio et al. (2011). Where OA to sulfate ratios are greater than or equal to 0.55 we apply γ of 5×10^{-4}, implying a timescale of over one day to reach equilibrium.

Kim et al. (2015) used a high-resolution version of GEOS-Chem (0.25°×0.3125°) to conduct extensive comparisons of model results for SNA and OA to observations collected from aircraft, surface sites, and satellites during SEAC^{4}RS. Here we use the same model but with coarser 2°×2.5° resolution, since Yu et al. (2016) found little sensitivity of GEOS-Chem model results to resolution over that range.

Kim et al. (2015) previously showed a successful unbiased GEOS-Chem simulation of sulfate and OA concentrations from the CSN network and the SEAC^{4}RS aircraft, and we find the same result here.

Figure 6 shows the simulated sulfate aerosol neutralization ratios in GEOS-Chem from the standard model with SNA thermodynamic equilibrium and from the model including kinetic mass transfer limitation of ammonia uptake by SNA aerosols following equations (1) and (2). The model is compared to observations from the CSN network and from the SEAC^{4}RS aircraft campaign in the Southeast US below 2 km altitude. The aerosol in the standard model is fully neutralized throughout the eastern US (mean f = 1.00), at odds with observations. The model with kinetic limitation captures the extent of neutralization in the CSN observations in the Southeast (f = 0.56 ± 0.11 observed, 0.51 ± 0.05 modeled) and overcorrects in the Northeast (f = 0.75 ± 0.11 observed, 0.53 ± 0.10 modeled). Sulfate/OA concentration ratios are lower in the Northeast and so the kinetic limitation could be less. The right panel of Figure 6 shows SEAC^{4}RS aircraft observations over the Southeast and GEOS-Chem sampled along the flight tracks. The slope of the reduced major axis regression line improves from f = 1.04 ± 0.01 in the standard model to f = 0.69 ± 0.01 in the model with kinetic limitation, which agrees better with observed f = 0.60 ± 0.04.

5. Conclusions

Observation networks in the eastern US show that sulfate aerosol is only partly neutralized by ammonium 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 aerosol sulfate neutralization ratio $f = [NH_4^+]/2[S(VI)]$ averages 0.51 mol mol^{-1} in the Southeast and 0.78 mol mol^{-1} in the Northeast in summer, even though ammonia is in excess in both regions as indicated by the wet deposition flux ratios. Observed long-term trends for 2003-2013 show that aerosol sulfate and ammonium decreased together in response to SO_2 emission controls, at odds with the thermodynamic expectation of steady ammonium and increasing sulfate neutralization as the supply of SO_2 decreases. In fact, the aerosol sulfate neutralization ratio decreased by 1-3% a^{-1} during the 2003-2013 period while SO_2 decreased.

We suggest that this apparent departure of the sulfate aerosol neutralization ratio from thermodynamic behavior may be caused by an elevated and increasing organic aerosol (OA) mass fraction, modifying or retarding the achievement of NH_3-H_2SO_4 thermodynamic equilibrium. Laboratory experiments by Liggio et al. (2011) indicate that the reactive uptake coefficient (γ) for uptake of ammonia by acidic sulfate aerosol decreases greatly in the presence of OA. Implementation 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 aerosol sulfate neutralization ratio in the eastern US as compared to the standard model assuming thermodynamic equilibrium. Better understanding of OA effects on sulfate aerosol thermodynamics is needed. Recent work has suggested that controlling SO_2 emissions in the US to decrease sulfate aerosol has 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 acidity to actually increase.

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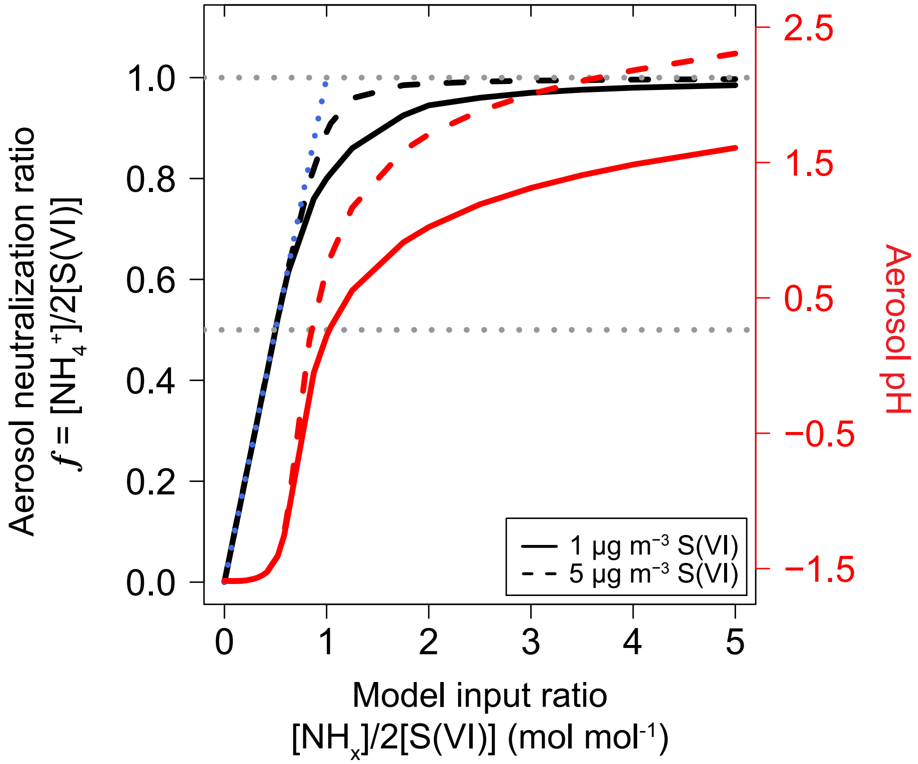

Figure 1. Aerosol neutralization ratio (f = [NH_4^+]/2[S(VI)]) and aerosol pH at thermodynamic equilibrium computed by the E-AIM model as a function of the input [NH_x]/2[S(VI)] molar ratio of total available ammonia ($NH_x \equiv NH_3(g) + NH_3(aq) + NH_4^+$) to total sulfuric acid (S(VI)) for 1 and 5 µg m^{-3} S(VI). E-AIM Model IV is applied in the forward mode (total gas + aerosol concentrations used as input) for a metastable aqueous aerosol with 60% relative humidity and 290 K. The 1:1 line for the relationship of f to [NH_x]/2[S(VI)] is shown in blue. The gray dotted lines show the neutralization ratio f = 0.5 corresponding to NH_4HSO_4 and f = 1 corresponding to $(NH_4)_2SO_4$.

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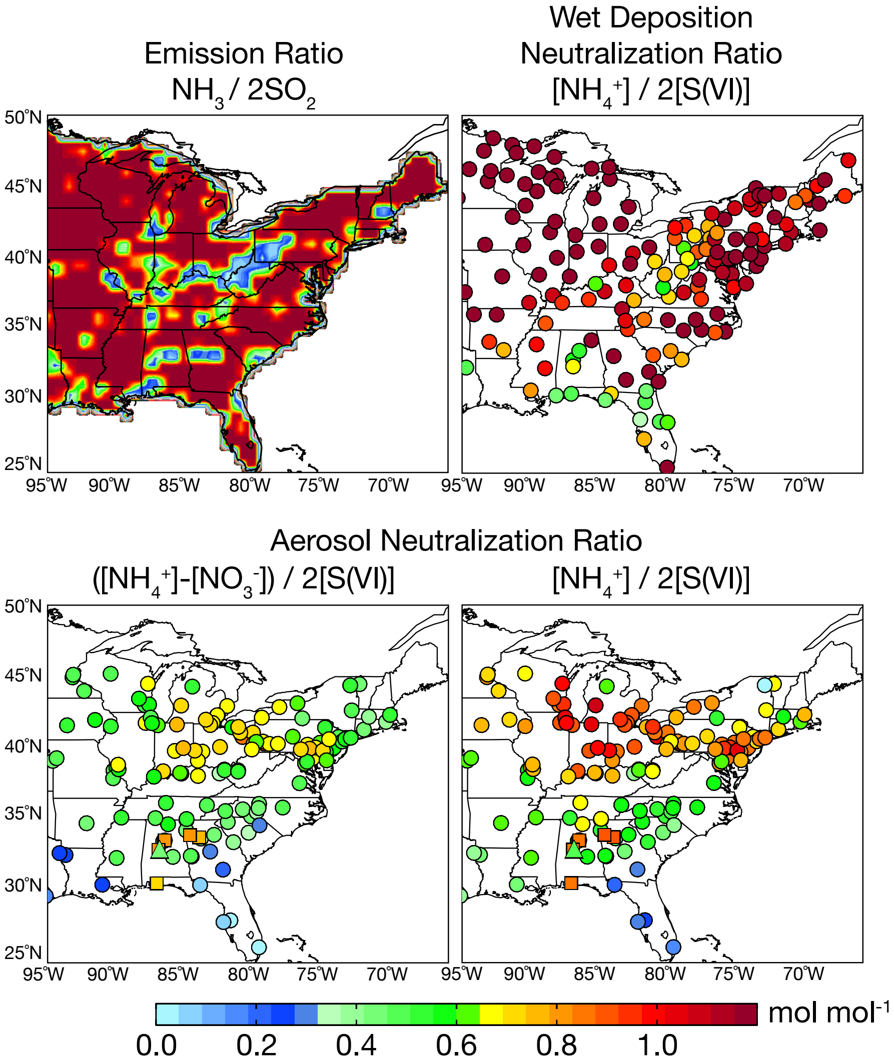

Figure 2. Sulfate neutralization by ammonia in seasonally averaged data for the eastern US in summer 2013 (JJA). The top left panel shows the $NH_3/2SO_2$ molar emission ratio averaged on a 0.5°×0.5° grid. The top right panel shows the $[NH_4^+]/2[S(VI)]$ molar wet deposition flux ratio from the National 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). The bottom left panel shows $f_N = ([NH_4^+]-[NO_3^-])/2[S(VI)]$ where the subtraction of $[NO_3^-]$ is to remove the contribution of NH_4^+ to NH_4NO_3 aerosol and the right panel shows $f = [NH_4^+]/2[S(VI)]$. 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.

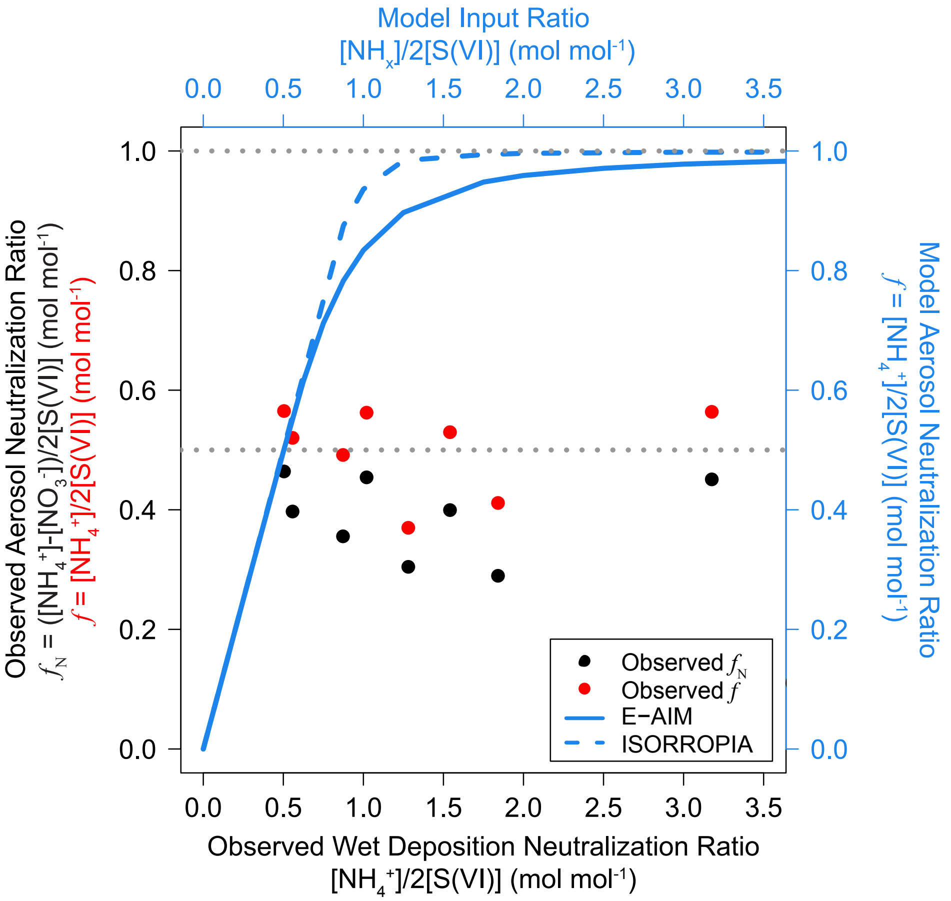

Figure 3. Relationship between the ammonium-sulfate aerosol neutralization ratio and the ratio in the total supply of ammonia and sulfate. The blue curves show the thermodynamic model curves as in Figure 1 for both E-AIM and ISORROPIA II, both run in the forward mode with total input of NH_x and S(VI) as constraint and for 2.5 μg m^{-3} S(VI) at 295 K and 70% relative humidity. The points show the mean observed aerosol neutralization ratios from CSN vs. the wet deposition flux ratios from NADP for summer 2013 for 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 neutralization ratio $f = 0.5$ corresponding to NH_4HSO_4 and $f = 1$ corresponding to $(NH_4)_2SO_4$.

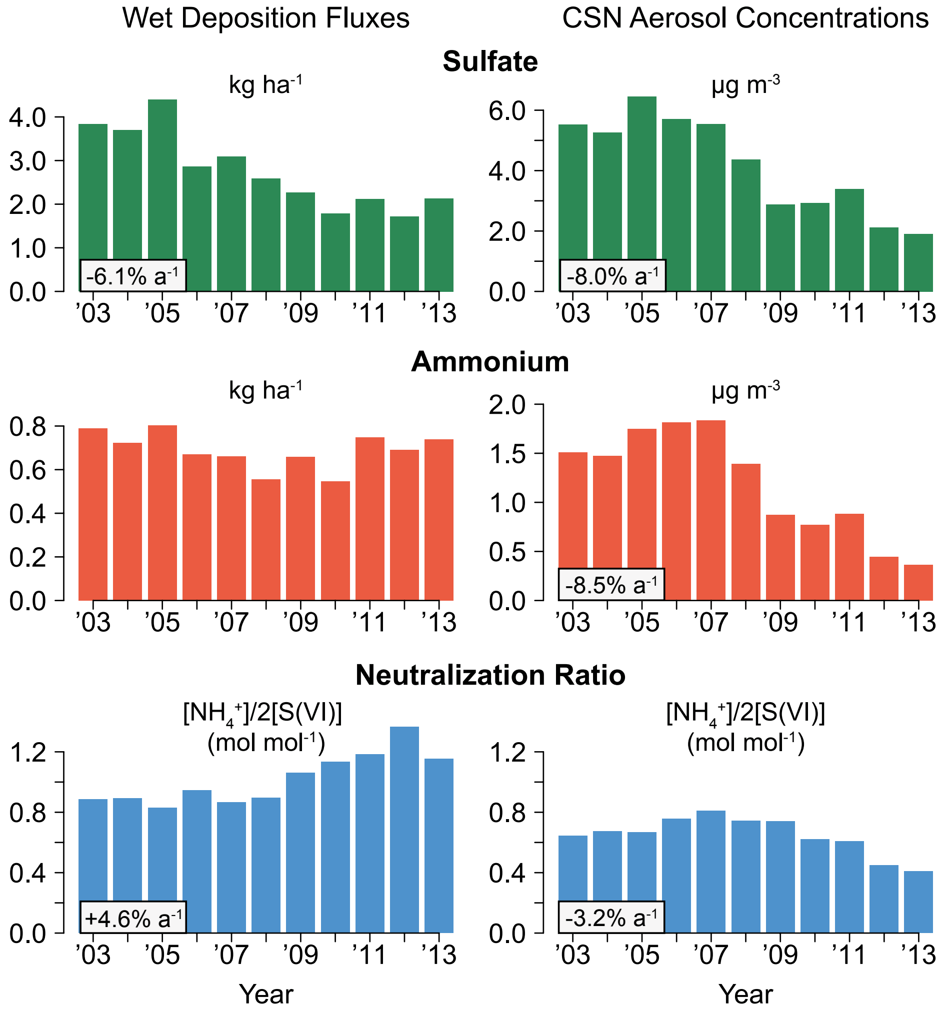

Figure 4. 2003-2013 summertime (JJA) trends in sulfate aerosol neutralization ratio and related quantities in the Southeast US (95-81.5° W, 30.5-37° N). Values are averages for the NADP and CSN sites in Figure 2. Trends are calculated using the Theil-Sen estimator and are shown when significant at a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

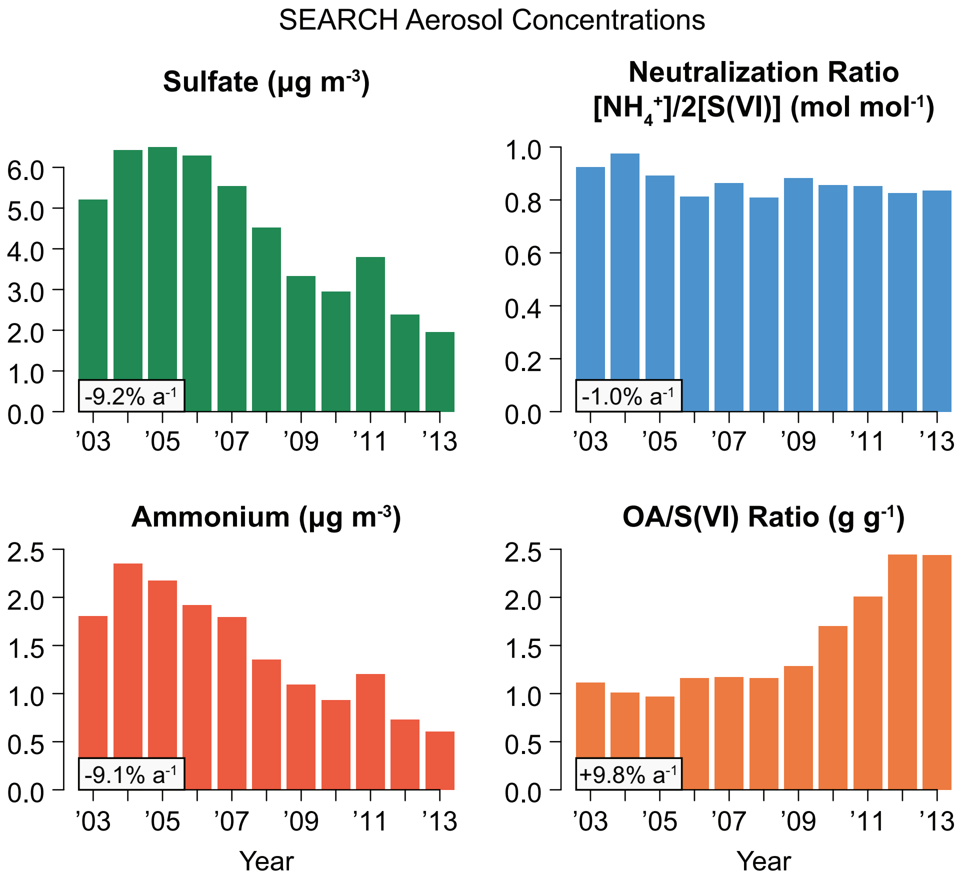

Figure 5. 2003-2013 summertime (JJA) trends in aerosol concentrations at the five SEARCH sites (BHM, CTR, JST, OLF, YRK) with continuous data, shown in Figure 2. The organic aerosol (OA) concentration is inferred from measured organic carbon (OC) and an OA/OC mass ratio of 2.24 (Canagaratna et al., 2015; 5 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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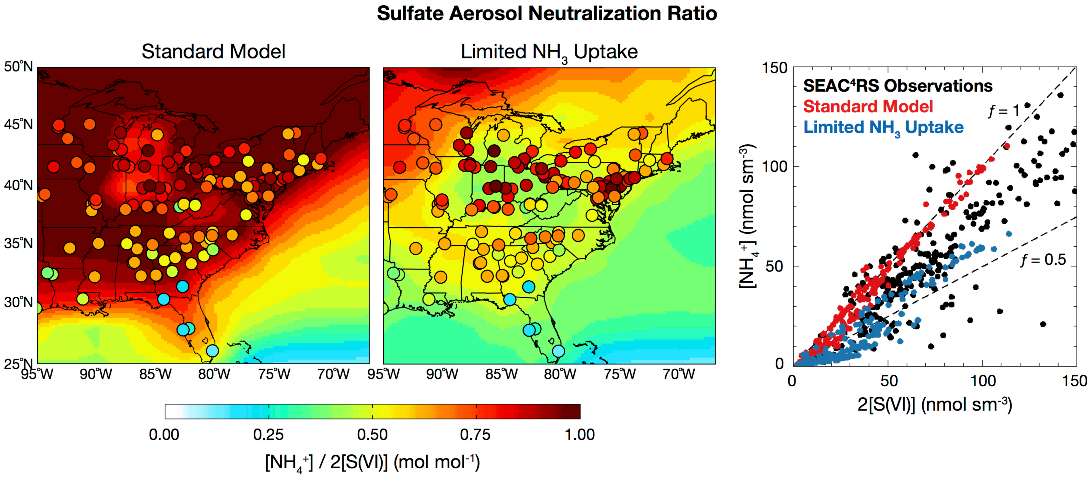

Figure 6. Sulfate aerosol neutralization ratio f = [NH$_4^+$]/2[S(VI)] in the GEOS-Chem model and comparison to observations in August 2013. The left and central panels compare the mean neutralization ratio in surface air for the CSN observations (circles, same in both panels) to the model values (background solid contours). 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 aerosols. 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 neutralization ratios $f = 0.5$ corresponding to NH_4HSO_4 and $f = 1$ corresponding to $(NH_4)_2SO_4$.