Response to Reviewer #1

We are grateful to the reviewer for the helpful comments and guidance that have led to important improvements of the original manuscript. Our point-by-point responses are listed below. Reviewer's comments are in black font, and authors' responses are in dark blue. Page and line numbers refer to the discussion paper acp-2020-575. The revised figures and Supplementary Information are attached in the end.

This work looks at the modeled vs. observed trends in sulfate and organic aerosol in the southeast US and finds that the model OA is overly dependent on sulfate, due to the impact of sulfate on acid-catalyzed reactive uptake of epoxydiols. The authors use the month-to-month variability in OA during summers to provide a new constraint on SOA formation mechanisms. Overall, this paper is well-written and within the scope of ACP and should be published after minor revisions.

Major comments.

1. Page 8, line 151 – The statement "The 2x2.5 simulations are adequate when modeling continental boundary layer chemistry (Yu et al., 2016)" is true for ozone and NOx, but not for isoprene oxidation pathways. Yu et al. showed a large shift from high-NO_x to low-NO_x oxidation (Fig. 3), which would impact IEPOX production and SOA from isoprene. Please address this limitation of your work, and how an overestimate in the high NO_x pathway would impact your results. Possibly a small sensitivity study is warranted to address this issue. Could it be that the model actually would have even more IEPOX SOA at high resolution and the problem would be worse?

Figure 3 in Yu et al. actually showed a shift from low-NO_x to high-NO_x regime when switching from a coarse grid to a fine grid, which may help alleviate the issue of IEPOX-SOA overestimation in this paper (because IEPOX is a product from the low-NO_x pathway of isoprene oxidation). Due to the memory limitation of our local supercomputer system, we were unable to conduct a nested simulation at fine resolution using the complexSOA scheme.

We remove the sentence citing Yu et al. (2016) in the model description in Section 2.2.1 and add the following discussion in Section 4 Line 460: "The CT_H01 scheme … may serve as a simplified representation for climate models. **Simulations in this study are conducted at a horizontal resolution of 2°×2.5°, which is comparable to most global climate models. However, as shown by Yu et al. (2016), from coarse to fine horizontal resolution, there will be a shift from low-NO_x to high-NO_x pathway for isoprene oxidation. Therefore, using a fine resolution may reduce the production of IEPOX and IEPOX-SOA, which needs further investigation.** For all kinds of models, long-term filter-based measurements, especially intraseasonal MMV, are important observational constraints that should be considered in model development."

2. Is there a reason you didn't use observations past 2013?

We use the 2000-2013 observations to compare with our model results because we use the NEI2011 emission inventory in our model simulations, which does not provide annual emission scaling factors after year 2013. We may update to NEI2014 which includes information for emissions after 2013 in future studies. As the main goal of this study is to show and explain the discrepancies between model and observations in early 2000s, we think using the current NEI2011 emission inventory is sufficient for this study.

3. Could you comment on how the lack of nonvolatile cations in ISORROPIA might impact your calculated aerosol acidity and generally effect your results? (https://pdfs.semanticscholar.org/f642/9d2c07179b7624c795aed5bf37b20aa0e2a8.pdf)

Theoretically, the lack of nonvolatile cations (NVCs) in ISORRPIA may lead to a higher aerosol ammonium-to-sulfate ratio and a lower aerosol pH (i.e. more acidic), based on Guo et al., 2018. In that paper, Guo et al. did a sensitivity study by applying observation-inferred Na^+ in ISORROPIA in the southeast US, which improved the trend of ion ratios but did not change the trends in ISORROPIA-predicted pH using fixed Na^+ concentration (Figure 6b in Guo et al., 2018).

The GEOS-Chem v12.1.1 does include NVCs (e.g. Na^+, Ca^{2+}, Mg^{2+} from anthropogenic and sea salt aerosol) in ISORROPIA (Pye et al., 2009, Pye et al., 2020), but they are not validated against measurements. In our study, the high H^+ concentration (low aerosol pH) in August 2000-2008 is mainly caused by low NH_3 emissions and high sulfate. The uncertainties associated with nonvolatile cations may lead to perturbations in aerosol pH and H^+ concentration, which matters for the formation of IEPOX-SOA. However, as stated in Guo et al., the contribution of NVCs is relatively small (and may introduce more uncertainties), and aerosol pH is not very sensitive to NVCs, the extent to which the modeled OA would be impacted by considering NVCs might be small.

In the methods Section 2.2.1 at Line 144, we modify the sentence to: "GEOS-Chem v12.1.1 considers sulfate, nitrate, and ammonium from all sectors, and fine-mode Na^+, Ca^{2+}, Mg^{2+}, Cl^- from anthropogenic and sea salt sources, and employs the ISORROPIA II thermodynamic model (Fountoukis and Nenes, 2007; Pye et al., 2009; Song et al., 2018) to calculate aerosol water content and aerosol acidity (Pye et al., 2020)."

We mentioned the uncertainties associated with NVCs and acidity calculation in the results Section 3.3.2 at Line 373: "Due to the high uncertainty associated with the derived NH_3 emission product and acidity calculation (Guo et al., 2015, 2018; Silvern et al., 2017; Song et al., 2018; Tao and Murphy, 2019), we conducted another simulation 'CT_H01' that fix a_{H+} level at 0.1 mol/L when calculating IEPOX uptake rate …"

In the discussion Section 4 at Line 496: "The NH_3 emissions (which are critical for the calculation of aerosol acidity) are highly uncertain (Dammers et al., 2019), and the acidity calculation is further complicated by non-volatile cations (Guo et al., 2018) and meteorological conditions (Guo et al., 2015; Tao and Murphy, 2019)."

Minor comments.

4. Page 1, line 34 – The statement "Biogenic SOA may account for 60-100% of OA" is confusing, if you are going to call it biogenic SOA, but then discuss anthropogenic influence,

maybe call it something else, like biogenic-derived SOA or similar. Also, Kim et al., 2015 say that biogenic isoprene and monoterpenes account for 60% of OA, where do you get the 100% value?

Biogenic SOA is a term that usually refers to SOA formed from oxidation of biogenic volatile organic compounds. Over forest-covered regions biogenic SOA may account for up to 100% (e.g. Figure 2 in Xu et al., 2015).

To avoid confusion, we change the sentence to "Biogenic SOA **(formed from atmospheric oxidation of BVOCs)** may account for 60-100%..."

5. Page 5, line 70 – What about the role of NOx (and nitrate) in regulating aerosol water?

Nitrate contributes to a very small fraction of fine particles in the southeast US in summer. To be more comprehensive we add "NO_x plays a complex role in regulating oxidation capacity, different oxidation pathways **and aerosol water content through aerosol nitrate.**"

6. Figure S1 – it is implied that the CSN sites are in Figure S1, which only shows SEARCH and IMPROVE.

Figure S1 has been revised. CSN sites are included as black dots. Due to the discontinuity of measurement protocol and techniques, 2000-2013 averaged OA concentrations are not shown for CSN sites.

7. Page 7, line 126 – Where does the baseline model agricultural NH3 come from?

In the US region, the baseline model NH_3 emission (from all sectors including agriculture) come from the EPA's National Emission Inventory NEI11v1. In other regions NH_3 emission come from the Community Emissions Data System (CEDS) inventory.

This information is included in Section 2.2.1 Line 124-128: "The global anthropogenic (including agricultural) emissions are from the Community Emissions Data System (CEDS) inventory, with the US region replaced by the EPA's National Emission Inventory for 2011 (NEI11v1). The monthly mean anthropogenic emissions of CO, SO_2, NO_x, NH_3, VOCs, OC and black carbon are scaled to the year 2011 using the ratio of EPA's national annual emission totals from 2000 to 2013 (Travis et al., 2016)."

8. Page 7 line 126 – Do you mean you scale the emissions from 2011 backwards to 2000 and forwards to 2013 using the annual emission totals from EPA? What do you mean by "mapped over 0.1x0.1"

Yes. The other years' emissions are scaled using ratios of EPA's annual emission total in each year relative to the emission in 2011. The emissions have a horizontal resolution of 0.1°x0.1°. We removed the words "mapped over 0.1x0.1" to avoid confusion as this information is not necessary.

We change the sentence to: “The monthly mean anthropogenic emissions of CO, SO_2, NO_x, NH_3, VOCs, OC and black carbon are scaled to the year 2011 using the ratio of EPA’s national annual emission totals from 2000 to 2013 (Travis et al., 2016).”

9. Page 8, line 134 – The GEOS-Chem complex scheme is also described in great detail by Pai et al., 2020. “An evaluation of global organic aerosol schemes using airborne observations”

The Pai et al. 2020 has been added here as a reference.

10. Page 8, line 148. It is confusing to dive in and describe sensitivity studies without showing us the problem in Figure 1. I don’t think it would be out of place to say that the default model, shown in Figure 1, overestimates the trend in organic aerosol largely due to ... and we run 4 sensitivity studies to address this discrepancy...

We add: “The default modeled OA shows a stronger decreasing trend from 2000 to 2013, and a large month-to-month variability in early 2000s, different from the observations (more details in Figure 1, 2 and Section 3.1). To address this model-observation discrepancy, we do four sets of 2°×2.5° simulations: …”

11. Page 9, line 154 – It would be helpful to tell the reader that these sensitivity simulations will be described in Sections 2.2.2 etc..

We add: “The sensitivity simulations are further explained in Section 2.2.2-2.2.3 and Section 3.3.”

12. Page 9, line 163 – do you mean at “the” or “from the” SOAS2013 campaign (citation?)

We change the sentence to: “The default IEPOX-SOA mechanism in GEOS-Chem uses aerosol-phase reaction rates from laboratory chamber studies with pure acidic inorganic particles (Gaston et al., 2014; Riedel et al., 2015), and a representative effective Henry’s law constant obtained by matching the model to the observations **from the** SOAS2013 campaign **(Marais et al., 2016)**, to estimate the reactive uptake coefficient γ_{IEPOX}.”

13. Do the authors expect that not including non-volatile cations in ISOROPPIA could impact their findings?

See response to comment #3.

14. Page 10, line 178 – Can you provide some evidence/citations for us that there might be such a coating effect? Or is the ethylene glycol supposed to be representative enough of real organic aerosol coating ammonium bisulfate? Please just clarify a little more here.

Here we add a sentence: “In the real atmosphere, inorganic aerosol is generally internally mixed with other organics. The presence of an organic coating may alter the aerosol properties and suppress the uptake of IEPOX onto acidified sulfate aerosol (Anttila et al., 2006; Gaston et al., 2014).”

The reasoning is of adding a coating effect is also explained at the beginning of Section 3.3.1 (L330-337): “The modeled IEPOX-SOA shows a much stronger sensitivity to aerosol acidity than suggested by field observations, which found weak or no correlation between observed IEPOX-SOA and derived aerosol acidity (Budisulistiorini et al., 2015; Lin et al., 2013; Worton et al., 2013; Xu et al., 2015b). Lack of consideration of organic coating effect may provide one possible explanation. In the real atmosphere, inorganic aerosol is generally internally mixed with other organics (Anttila et al., 2006; Murphy et al., 2006). The presence of an organic coating may alter the solubility and diffusion properties at the surface of inorganic particles and diminish further uptake of IEPOX.”

We also add at Line 180 about the limitation of ethylene glycol and the uncertainties with the linear fitted function: “In the real atmosphere when inorganic cores are coated with more viscous SOA (Zhang et al., 2018b), coating effect may be stronger because ethylene glycol is a low viscosity material. However, this simplified linear function does not consider the decreased viscosity and reduced coating effect at higher RH conditions (which is common in summertime southeast US) (Gaston et al., 2014; Zhang et al., 2018b), and prevents further IEPOX uptake when the mass fraction of OA (χ_{org}) is larger than 0.7, therefore this linear function may mimic a strong coating effect even though ethylene glycol is less viscous than real atmospheric SOA. The uncertainties need to be addressed in further studies with a more realistic coating parameterization (Li et al., 2020; Schmedding et al., 2019; Zhang et al., 2019b).”

15. Page 10, line 189 - Please elaborate a little more on the findings of Jo et al., 2019 since this seems important.

Jo et al. is also a modeling study. Here this effect is because the standard GEOS-Chem assumes no organic coating, and the aerosol surface and radius only consider inorganics (sulfate-ammonium-nitrate). By considering organic coating, the total aerosol surface and radius both increase which tends to increase the IEPOX uptake rate constant. Jo et al. found in some conditions (high aerosol pH and high IEPOX diffusion coefficient) the IEPOX uptake rate may even increase. The coating parameterizations in Jo et al. and in our study are different.

We remove the statement “consistent with another study (Jo et al., 2019)” to avoid confusion. We modify the sentence as: “The default GEOS-Chem with no organic coating calculates surface area of inorganic aerosol (Jo et al., 2019). By adding the coating effect, the increased particle radius R_p and surface area S_a of the mixed particle will partially offset (but does not outweigh) the impact of reduced reaction probability $\gamma_{IEPOX\_modified}$.”

16. In Section 2.2.3 – How do your emissions results compare to the NH3 emissions derived from wet deposition in Paulot et al., 2014? Paulot F., Jacob, D.J., Pinder R.W., Bash J.O., Travis, K., Henze D.K., Ammonia emissions in the United States, Europe, and China derived by high-resolution inversion of ammonium wet deposition data: Interpretation with a new agricultural emissions inventory (MASAGE_NH3), J. Geophys. Res., 119, 4,343-4,364, 2014.

This CrIS-derived product has higher NH_3 emissions than the estimates from Paulot et al. (2014) (see Table 1 and more details in Cao et al., 2020).

17. Page 13, line 241 – Do the sulfate trends refer to Figure 2? If so, please reference it here.

We change to: “Compared to the slow decrease in OA, a faster declining trend is found for sulfate from IMPROVE (-6.9%/year) and SEARCH (-6.7%/year) for the same period **(Figure 2)**.”

18. Page 11, line 199 – Is this due to improved farming practices as output increases? Or some other explanation? I am surprised NH3 is not increasing and would assume other readers might appreciate a little more detail.

NH_3 emissions have no significant trend in 2000-2013. The NH_3 gas concentration is increasing based on other observations, but it is not what we discussed here.

To avoid confusion, we add “There is no significant trend **of NH_3 emissions** from 2000 to 2013 (Figure S4), consistent with other studies suggesting nearly constant NH_3 emissions from 2001 to 2014 (Butler et al., 2016).”

19. Section2.2.3 – It would help the reader if there was a plot of the bottom-up and top-down NH3 emissions.

We add a Figure S3 to show the map of the default NEI11 (bottom-up) and the CrIS-derived (top-down) NH_3 emissions in June, July and August (averaged over 2000-2013).

20. Page11, line 208 – What surface observations? Please clarify what you mean, are there separate independent NH3 surface observations you compare against? Again, a plot would be useful here. Same for the seasonal cycle. These can be in the supplement according to the author’s preference.

The top-down NH_3 emissions are derived and validated in another paper Cao et al., 2020. Here we use the new NH_3 emissions as a sensitivity test to show how sensitive IEPOX-SOA is to aerosol acidity and NH_3 emissions. We do not include any validation plots because they might deviate from the main focus of this paper. Instead we add the citation and add the text:

“The CrIS-derived NH_3 emissions have been validated against surface observations of NH_3 concentration from the Ammonia Monitoring Network (AMoN) and NH_4^+ wet deposition measurements from the National Atmospheric Deposition Program (NADP). More details can be found in Cao et al. (2020).”

21. Page11, line217 – For clarity, please specific that these are “model” IEPOX-SOA, sulfate aerosol etc.

We change to: “In this study we did a multivariate regression analysis of **modeled** monthly IEPOX-SOA (μg/m^3) against **modeled** sulfate aerosol (μg/m^3), aerosol acidity a_{H+} (mol/L) and isoprene emission ($ISOP_{emis}$ mg/m^2/hr).”

22. Page 13, line 244 – Why not sample the model at the locations of the sites? Would that make a difference to your trend?

The modeled summertime OA, if sampled at the locations of sites, has an average of 6.9 µg/m^3 and a trend of 5.0%/year. These results are similar to the model results averaged over the whole southeast US domain (an average of 6.7 µg/m^3 and a trend of 4.9%/year). For simplicity and to be consistent with other analysis in this study, we only show the model results averaged over the whole domain here.

Here we add the text: "Modeling results are averaged over the domain [29°~37°N, 74°~96°W] excluding ocean grid cells (Figure S1). The 2000-2013 JJA-averaged OA from the default model is 6.7 µg/m^3, higher than OA from IMPROVE and SEARCH. Modeled total OA mass decreases at a rate of 4.9%/year, about 1.9 (1.6) times faster than IMPROVE (SEARCH) OA (student's t-test $p<0.001$). **By sampling the model results at the locations of the IMPROVE and SEARCH sites, the modeled summertime OA has an average of 6.9 µg/m^3 and a trend of 5.0%/year, similar to the model results averaged over the whole southeast US domain. For simplicity, we show only the domain-averaged model results in all figures and analysis.**"

23. Figure 1 – can you explain the periods of enhanced OA around 2006 and 2011?

The enhanced OA in 2006 and 2011 is due to high isoprene emissions (Figure 3). In Section 3.2 Line 326 we change to: "Isoprene emission contributes to the overall interannual variability, for example leading to the relatively low IEPOX-SOA in 2003-2004 and the peaks in 2000, 2006 and 2011 (Figure 3)."

24. Figure 2 – It could be helpful to include the trends on this figure similar to Figure 1.

Figure 2 has been modified to include trends of OA and sulfate.

25. Page 15, line 302 – Figure 3 is difficult to interpret, please provide a little more description of what is shown here, particularly what is mean by "divided by 1 standard deviations."

We add the following descriptions: "Figure 3 shows the standardized monthly surface IEPOX-SOA concentration, sulfate concentration, aerosol H^+ activity and isoprene emission from the default model. For each variable, the monthly gridded data has been first averaged over the southeast US. Then, we calculate the one standard deviation of all monthly data (June, July and August data from 2000 to 2013). Finally, the domain-averaged monthly data has been divided by its standard deviation, so the variables are standardized to be unitless and their variability can be compared directly."

26. Page 16 , line 325 – Is isoprene interannual variability explained by temperature? Temperature is an important driver of aerosol partitioning, should it not be included in Table S1 and Figure 3? Does temperature explain any of the interannual variation in Figure 1?

Yes, temperature is an important factor controlling the variability of isoprene emissions and therefore SOA. In GEOS-Chem, SOA formed by aqueous-phase uptake of isoprene products (which dominates the total OA in the southeast US as shown in Figure 1) is assumed to be non-volatile, and temperature plays a minor role in these processes. The monoterpene-derived SOA is considered to be semi-volatile and formed by reversible gas-aerosol partitioning, which is influenced by temperature. But monoterpene-SOA contributes to a smaller fraction of OA (Figure 1). Here we focus on the variability of IEPOX-SOA (which is non-volatile), and we already consider isoprene emission as a main driver. Therefore, we do not consider temperature as an additional independent driver of IEPOX-SOA in Table S1 and Figure 3.

Earlier at Line 295 we add: "We use the GEOS-Chem model here to examine the simulated IEPOX-SOA dependence on sulfate, aerosol acidity, and emissions of isoprene which produce IEPOX at high yields under low-NO_x conditions (Paulot et al., 2009). **Temperature impacts the formation of IEPOX-SOA mainly through regulating isoprene emissions but does not influence partitioning as IEPOX-SOA is treated as non-volatile in GEOS-Chem. Therefore, temperature is not examined as another driver in addition to isoprene emissions.**"

27. Page 18, line 376 – I assume that the H+ value during 2013SOAS was calculated with a thermodynamic model, although constrained by observations. Please clarify.

Yes. We change the wording here to: "we conducted another simulation 'CT_H01' that fix a_{H+} level at 0.1 mol/L when calculating IEPOX uptake rate, corresponding to the **predicted** a_{H+} value **(constrained by observations)** during the 2013 SOAS campaign (Weber et al., 2016)."

28. Page 19, line 378 – Can you comment on why the model agrees much better with SOAS2013 observations and 2013 OA in Figure 1, and what the limitations are of testing your revised IEPOX uptake at the low end of the SO2 emissions trend?

Figure 1 is not about SOAS2013 campaign data. Figure 1 shows the comparison between the default model results and the long-term filter measurements of OA from surface networks IMPROVE and SEARCH. Our revised IEPOX uptake agrees well with the long-term surface measurement in 2000-2013 (Figure 4C and 4D), which is the main focus of our paper. The 2000-2013 period covers a broad range of SO_2 emissions. The revised IEPOX-SOA also compares well with the SOAS2013 data (Figure S6).

In Line 378, we add: "The two simulations, CT_newNH$_3$ and CT_H01, yield similar long-term trends of IEPOX-SOA in the southeast US (Figure S5), **and they agree better with the long-term surface OA measurements from IMPROVE and SEARCH than the default model (Figure 4C and 4D).** For the SOAS2013 campaign, the CT_H01 scheme simulates an average IEPOX-SOA concentration of 0.74 $\mu g/m^3$, similar to 0.81 $\mu g/m^3$ in the default model, and agrees well with the two independent Aerosol Mass Spectrometer measurements (0.97 $\mu g/m^3$ from obs_GT and 0.68 $\mu g/m^3$ from obs_CU, see daily time series in Figure S6)."

29. General comment – why not consider trends in ammonium? Particularly to help support your improved NH3 emissions scenario?

The long-term observation network IMPROVE does not have measurements of ammonium aerosol. SEARCH shows a downward trend of ammonium aerosol, similar to the trend of sulfate

(Silvern et al., 2017). In the model ammonium (aerosol NH_4^+) is highly correlated with sulfate and has a very similar trend as sulfate, so we do not show the trends in ammonium here. The month-to-month variability of NH_3 emissions is what matters that leads to high aerosol H^+ in August in early 2000s (and therefore IEPOX-SOA). The NH_3 emissions do not have significant long-term trends based on EPA's annual emission totals.

We add the trends of aerosol NH_4^+/SO_4^{2-} ratio to Figure S4, and change the text in Section 3.2 around L308: "The default NH_3 emissions from NEI11v1 suggest no significant long-term trend from 2000 to 2013. In general, ammonium aerosol is strongly correlated with sulfate and has a similar declining trend as sulfate (Silvern et al., 2017). However, the NH_3 emissions in August are about 25% lower than in June and July (Figure S4). As a result, in August before 2008, the aerosol NH_4^+/SO_4^{2-} ratio is smaller (Figure S4) and the a_{H+} is up to 3 times higher than June, leading to high production of IEPOX-SOA in August."

30. Page 22, line 467 – By gas-aerosol partitioning, do you mean reversible uptake of isoprene oxidation products? Could you be more specific on this?

a. Generally, the final paragraph that goes through potential reasons for the remaining model discrepancies is very useful but needs additional explanation. The sentence starting "Despite a large MMV in IEPOX-SOA is confusing, please rephrase to more clearly state your meaning.

For the above questions, we change the text as follows: "Such discrepancies may suggest a more important role of SOA pathways that are less dependent on inorganic aerosol, such as **terpene-SOA formed by reversible** gas-aerosol partitioning. **Terpene-SOA is included in GEOS-Chem (yellow color in Figure 1), and contributes to 8~24% of total OA, which might be underestimated compared to recent field studies. Xu et al. (2015a) finds a large MMV in IEPOX-SOA, but** the less-oxidized oxygenated OA (LO-OOA, an indicator for freshly-formed monoterpene SOA) and the more-oxidized oxygenated OA (MO-OOA, also likely from biogenic sources) **have little MMV in summer months, and** they contribute to more than 50% of total OA mass in the southeast US (Xu et al., 2018). The important role of monoterpenes SOA is also confirmed by molecular level characterization of organic aerosols (Zhang et al., 2018a)."

b. Is monoterpene SOA included in the GEOS-Chem simulations? If so, is the lack of MMV captured by the model? I am generally just confused by the discussion here. Are you trying to say that other SOA pathways, not in the model, might have less MMV and therefore improve model performance of the long-term trend?

Yes, monoterpene SOA is included in GEOS-Chem (see changes above). In Figure 1 yellow color represents terpene SOA (mostly monoterpene and also some sesquiterpene, see Section 2.2.1 Line 137). Terpene SOA and anthropogenic SOA are referred to as dry SOA (Line 53). They have small MMV (Figure 2B) but they only contribute to a small fraction of total OA especially when comparing to IEPOX-SOA in early 2000s (Figure 1). We would like to strengthen that monoterpene SOA may be underestimated in GEOS-Chem, compared to the field measurements (Xu et al., 2018; Zhang et al., 2018), see Line 508-515. Other pathways that are less dependent on sulfate and aerosol acidity (and probably less MMV), not in the model now, may improve the model performance and need further examination (Line 515-525).

Reference:

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Response to Reviewer #2

We are grateful to the reviewer for the helpful comments and guidance that have led to important improvements of the original manuscript. Our point-by-point responses are listed below. Reviewer's comments are in black font, and authors' responses are in dark blue. Page and line numbers refer to the discussion paper acp-2020-575. The revised figures and Supplementary Information are attached in the end.

Summary: The author compared the long-term trend of organic aerosol and sulfate mass loading from field measurement with GEOS-Chem simulations in this manuscript, with the model showing a steeper decrease in the OA mass loading and larger monthto-month variability than the field data. The long-term trend of sulfate, on the other hand, was well captured by the model when comparing with the field data. By applying coating effect, constant aerosol acidity, and a different NH3 emission product, the modeling results match the field data better, suggesting further study is needed to address the weak dependence of OA formation and sulfate. The manuscript is overall clearly written, but may need to address the following aspects before publishing.

First, the author did a good job explaining the modeling results in Section 3, but it was not very clear at certain sections which modeling results agree with the field measurement and which do not. The author may need to improve clarity about the modeling-field data comparisons when describing the modeling results, especially in line 251 when the author discusses that the contribution of IEPOX-SOA to total OA mass decreases from 61% to 28% from the early 2000s to 2013. Does this modeling result agree with previous field measurements (such as the results from Xu. et al. 2015 and Budisulistiorini,et al. 2016)? Maybe the author can include a sentence or two to compare the modeling data with the field data.

Section 3.1 mainly compares modeling results with long-term surface filter measurements from IMPRAOVE and SEARCH networks, focusing on the long-term trend and month-to-month variability of OA (Figure 1 and 2). We also compare the modeling results with the SOAS2013 field campaign data later in Section 3.3.2 Line 379-385 and Figure S6.

Here we add a sentence about the contribution of IEPOX-SOA: "The contribution of IEPOX-SOA to total OA mass decreases from 61% in the early 2000s to 28% in 2013. **The simulated IEPOX-SOA in 2013 compares well with previous field studies which suggested that IEPOX-SOA contributed to 18~40% in southeast US sites in summer 2013 (Budisulistiorini et al., 2016; Xu et al., 2015).**"

The manuscript also concluded that coating can improve the modeling result because thinner coating may enhance the formation of IEPOX-SOA. There are a few papers that also measured/modelled the effects of SOA coating on the formation of IEPOX-SOA. For instance, Zhang et al. 2018, Jo et al., 2019, and the subsequent study by Schmedding et al. 2019 discussed the effects of pre-existing coating on the formation of IEPOX-SOA. Does the result in this manuscript using ethylene glycol agree with previous studies using authentic SOA? In addition, Jo et al. 2019 shows that the uptake of IEPOX would increase with increasing coating for most of the situations using GEOS-Chem due to increasing surface tension, contrary to a decreasing uptake with coating effect in this manuscript. Could the author explain why the trends are different in these two studies?

Compared to the default GEOS-Chem with no coating effect at all, adding a coating effect reduces (not enhances) the production of IEPOX-SOA in the summertime southeast US (Figure 4C, orange line as compared to magenta line). Jo et al. applied the parameterizations from Zhang et al., 2018 (using monoterpene-SOA as a coating material) and is different from what we used here. In Gaston et al. (2014) which we applied in this study, ethylene glycol is a relatively low viscosity material, but the simplified linear function fitted using RH=50% conditions may mimic a strong coating effect, because it does not consider the reduced viscosity and weaker coating effect at higher RH conditions, and it assumes no IEPOX uptake when the fraction of organics is higher than 70%. As a result, the added aerosol surface and particle radius does not overweigh the impact of reduced uptake coefficient when considering coating.

In Section 2.2.2 Line 180 we add: "In the real atmosphere when inorganic cores are coated with more viscous SOA (Zhang et al., 2018b), coating effect may be stronger because ethylene glycol is a low viscosity material. However, this simplified linear function does not consider the decreased viscosity and reduced coating effect at higher RH conditions (which is common in summertime southeast US) (Gaston et al., 2014; Zhang et al., 2018b), and prevents further IEPOX uptake when the mass fraction of OA (χ_{org}) is larger than 0.7, therefore this linear function may mimic a strong coating effect even though ethylene glycol is less viscous than real atmospheric SOA. The uncertainties need to be addressed in further studies with a more realistic coating parameterization (Li et al., 2020; Schmedding et al., 2019; Zhang et al., 2019b). We assume all OA is coated outside the inorganic aerosol core when calculating the IEPOX reactive uptake. The default GEOS-Chem with no organic coating calculates surface area of inorganic aerosol. By adding the coating effect, the increased particle radius R_p and surface area S_a of the mixed particle will partially offset (but does not overweigh) the impact of reduced reaction probability $\gamma_{IEPOX\_modified}$."

The manuscript used a fixed acidity to reduce the modelled month-to-month variation of IEPOX-SOA so that the results match better with the field data. It seems this large month-to-month variation in modeling only appeared before 2008, while the month-to-month variation decreased significantly after 2008 even with the default modeling scenario. Can the author explain why there is such a large difference in the month-to-month variation before and after 2008 in the default modeling scenario? Was it due to difference in NH3 emission inventory before and after 2008 or other reasons?

We explained the large MMV before 2008 in Section 3.2. The main idea is that when sulfate is high before 2008, the relatively low NH_3 emission in August is insufficient relative to sulfate and leads to a much higher aerosol H^+ (than in June and July), which then leads to high IEPOX-SOA. After 2008 when sulfate becomes small, aerosol H^+ becomes less sensitive to the supply of NH_3, so even there are still monthly differences in NH_3 emissions, the MMV of IEPOX-SOA is smaller.

In Section 2.2.2 At Line 301-303 we have the explanation: "Prior to 2008, IEPOX-SOA production is largely enhanced by abundant sulfate. Due to this high level of sulfate (about >4 μg/m^3), the modeled aerosol acidity becomes particularly sensitive to variations in NH_3 emissions. … The NH_3 emissions in August are about 25% lower than in June and July (Figure S4). As a result, in August before 2008, the aerosol NH_4^+/SO_4^{2-} ratio is smaller (Figure S4) and a_{H+} is up to 3 times higher than June (Figure 4B), leading to high production of IEPOX-SOA in August. Both sulfate and aerosol acidity appear to be the dominant contributors to MMV of OA during this period. After 2008, IEPOX-SOA formation is substantially suppressed, due to small SO_2 emissions and low modeled aerosol acidity a_{H+} with small monthly variability."

In addition, after updating the NH3 inventory with the new emission inventory from CrIS satellite observation, the author stated in line 384-385 that this scenario (CT_newNH3) performed a bit worse than the fixed acidity scenario (CT_H01). I wonder whether that was due to coating effects not correctly represented by using ethylene glycol rather than the results from authentic coatings. Besides the paper mentioned above, Li et al. 2020 and Zhang et al. also used simplified equations that can estimate the phase state of a few IEPOX-SOA species that might be helpful in performing future modeling.

Thank you for the suggestions. The CT_newNH_3 simulation may be influenced by both the simplified coating scheme as well as uncertainties associated with NH_3 emissions. In the text we have:

"The CT_newNH_3 scheme simulates an average IEPOX-SOA concentration of 0.34 μg/m^3, lower than the observation and the other models by a factor of >2, due to both the simplified coating effect and small aerosol a_{H+} values (a_{H+}<0.1mol/L, Figure 4B)." The Li et al. and Zhang et al. papers have been added to the model description Section 2.2.2 (see response to the second comment).

Minor comments: Why would there be a large increase of the default IEPOX-SOA during 2005-2008? The manuscript mentioned about higher correlation of IEPOX-SOA with acidity during this period of time. Was this abrupt increase of IEPOX-SOA caused by lower NH3 emissions between 2005-2008?

The high IEPOX-SOA in 2005-2007 is a result of both high sulfate, high aerosol acidity in August and high isoprene emissions.

In Section 3.2 at Line 314, we add: "The high IEPOX-SOA in 2000-2001 and 2005-2007 is a result of high sulfate aerosol, high aerosol acidity due to low NH_3 supply relative to high sulfate, and high isoprene emissions during these periods (Figure 3, Figure 4B)."

Line 171: There are multiple papers discussing about different Henry's law constants for IEPOX. The author did discuss in line 439 but probably should include other relevant papers, such as Woo et al., 2015, Budisulistiorini et al., 2016, Pye et al., 2017, and Zhang et al., 2018.

Thank you for the suggestions. We add at Line 439:

"the Henry's law constant for IEPOX uptake was tuned using measurements from the SOAS2013 campaign and was found to be 1.7×10^7 M/atm, 10 times smaller than suggested by

Gaston et al. (2014) based on laboratory experiments **and about half of the suggested value (3×10^7 M/atm) in some other studies (Budisulistiorini et al., 2017; Nguyen et al., 2014; Pye et al., 2017; Woo and McNeill, 2015; Zhang et al., 2018b)**."

Line 477-478: One other potential mechanism I can think of is the non-linear feedback between sulfate and IEPOX-SOA production discussed in recent studies. For instance, Riva et al. 2019 and Zhang et al. both show that IEPOX-SOA fraction could and sulfate are nonlinear due to chemical reactions, acidity, and the coating effects of IEPOX-SOA are intertwined and nonlinear due to the formation of organosulfates.

Thank you for the suggestions. We mentioned the non-linearity at Line 408-410, and the Zhang et al. paper has been added as a reference now:

"Recent studies (Riva et al., 2019) suggested that the IEPOX-SOA production per unit mass of sulfate likely increases with decreasing sulfate due to changes in aerosol properties, such as acidity, morphology, phase state and viscosity, as well as formation of organosulfates, suggesting non-linearity between IEPOX-SOA and sulfate (Riva et al., 2019; Zhang et al., 2019)."

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List of major changes in the manuscript

In this list, only major changes in the figures and main text are included. Other minor changes or rephrase of wording are included in the Responses to reviewers #1 and #2, and are shown in the attached manuscript with tracking changes. The page and line numbers refer to the revised version of the manuscript.

1. Another affiliation has been added to the author Eloise A. Marais.

2. Line 145, added the description of non-volatile cations and the thermodynamic model: "GEOS-Chem v12.1.1 considers sulfate, nitrate, and ammonium from all sectors, and fine-mode Na^+, Ca^{2+}, Mg^{2+}, Cl^- from anthropogenic and sea salt sources, and employs the ISORROPIA II thermodynamic model (Fountoukis and Nenes, 2007; Pye et al., 2009; Song et al., 2018) to calculate aerosol water content and aerosol acidity (Pye et al., 2020)."

3. Line 159, added the description: "The default modeled OA shows a stronger decreasing trend from 2000 to 2013, and a large month-to-month variability in early 2000s, different from the observations (more details in Figure 1, 2A and Section 3.1). To address this model-observation discrepancy, we do four sets of 2°×2.5° simulations: … The sensitivity simulations are further explained in Section 2.2.2-2.2.3 and Section 3.3."

4. Line 187, added the description: "In the real atmosphere, inorganic aerosol is generally internally mixed with other organics. The presence of an organic coating may alter the aerosol properties and suppress the uptake of IEPOX onto acidified sulfate aerosol (Anttila et al., 2006; Gaston et al., 2014)."

5. Line 197, added the discussion of the uncertainties associated with coating parameterization: "In the real atmosphere when inorganic cores are coated with more viscous SOA (Zhang et al., 2018b), coating effect may be stronger because ethylene glycol is a low viscosity material. However, this simplified linear function does not consider the decreased viscosity and reduced coating effect at higher RH conditions (which is common in summertime southeast US) (Gaston et al., 2014; Zhang et al., 2018b), and prevents further IEPOX uptake when the mass fraction of OA (χ_{org}) is larger than 0.7, therefore this linear function may mimic a strong coating effect even though ethylene glycol is less viscous than real atmospheric SOA. The uncertainties need to be addressed in further studies with a more realistic coating parameterization (Li et al., 2020; Schmedding et al., 2019; Zhang et al., 2019b). We assume all OA is coated outside the inorganic aerosol core when calculating the IEPOX reactive uptake. The default GEOS-Chem with no organic coating calculates surface area of inorganic aerosol (Jo et al., 2019). By adding the coating effect, the increased particle radius R_p and surface area S_a of the mixed particle will partially offset (but does not outweigh) the impact of reduced reaction probability $\gamma_{IEPOX\_modified}$."

6. Line 220, added: "The default NEI11 and CrIS-derived NH_3 emissions averaged over 2000-2013 are compared in Figure S3." Line 225, added: "The CrIS-derived NH_3 emissions have been validated against surface observations of NH_3 concentration from the Ammonia Monitoring

Network (AMoN) and wet deposition measurements from the National Atmospheric Deposition Program (NADP). More details can be found in Cao et al. (2020)."

7. Line 281, added: "By sampling the model results at the locations of the IMPROVE and SEARCH sites, the modeled summertime OA has an average of 6.9 $\mu g/m^3$ and a trend of 5.0%/year, similar to the model results averaged over the whole southeast US domain. For simplicity, we show only the domain-averaged model results in all figures and analysis."

8. Line 288, added: "The simulated IEPOX-SOA in 2013 compares well with previous field studies which suggested that IEPOX-SOA contributed to 18~40% in southeast US sites in summer 2013 (Budisulistiorini et al., 2016; Xu et al., 2015b)."

9. Line 333, added the temperature effect: "Temperature impacts the formation of IEPOX-SOA mainly through regulating isoprene emissions but does not influence partitioning as IEPOX-SOA is treated as non-volatile in GEOS-Chem. Therefore, temperature is not examined as another driver in addition to isoprene emissions."

10. Line 343, added the description of Figure 3: "Figure 3 shows the standardized monthly surface IEPOX-SOA concentration, sulfate concentration, aerosol H^+ activity and isoprene emission from the default model. For each variable, the monthly gridded data has been first averaged over the southeast US. Then, we calculate the one standard deviation of all monthly data (June, July and August data from 2000 to 2013). Finally, the domain-averaged monthly data has been divided by its standard deviation, so the variables are standardized to be unitless and their variability can be compared directly."

11. Line 351, modified to: "The default NH_3 emissions from NEI11v1 suggest no significant long-term trend from 2000 to 2013. In general, ammonium aerosol is strongly correlated with sulfate and has a similar declining trend as sulfate (Silvern et al., 2017). However, the NH_3 emissions in August are about 25% lower than in June and July (Figure S4). As a result, in August before 2008, the aerosol NH_4^+/SO_4^{2-} ratio is smaller (Figure S4) and a_{H+} is up to 3 times higher than June (Figure 4B), leading to high production of IEPOX-SOA in August."

12. Line 371, modified to: "Isoprene emission contributes to the overall interannual variability, for example leading to the relatively low IEPOX-SOA in 2003-2004 and the peaks in 2000, 2006 and 2011 (Figure 3). The high IEPOX-SOA in 2000-2001 and 2005-2007 is a result of high sulfate aerosol, high aerosol acidity due to low NH_3 supply relative to high sulfate, and high isoprene emissions during these periods (Figure 3, Figure 4B)."

13. Line 460, added: "Recent studies (Riva et al., 2019) suggested that the IEPOX-SOA production per unit mass of sulfate likely increases with decreasing sulfate due to changes in aerosol properties, such as acidity, morphology, phase state and viscosity, **as well as formation of organosulfates, suggesting non-linearity between IEPOX-SOA and sulfate (Riva et al., 2019; Zhang et al., 2019a).**"

14. Line 490, added: "In the default scheme, the Henry's law constant for IEPOX uptake was tuned using measurements from the SOAS2013 campaign and was found to be 1.7×10^7 M/atm,

10 times smaller than suggested by Gaston et al. (2014) based on laboratory experiments **and about half of the suggested value (3×10^7 M/atm) in some other studies (Budisulistiorini et al., 2017; Nguyen et al., 2014; Pye et al., 2017; Woo and McNeill, 2015; Zhang et al., 2018b).**"

15. Line 513, added discussion on the limitation of using a coarse horizontal resolution: "Simulations in this study are conducted at a horizontal resolution of 2°×2.5°, which is comparable to most global climate models. However, as shown by Yu et al. (2016), from coarse to fine horizontal resolution, there will be a shift from low-NO_x to high-NO_x pathway for isoprene oxidation. Therefore, using a fine resolution may reduce the production of IEPOX and IEPOX-SOA, which needs further investigation."

16. Line 524, added: "Such discrepancies may suggest a more important role of SOA pathways that are less dependent on inorganic aerosol, such as terpene-SOA formed by reversible gas-aerosol partitioning. Terpene-SOA is included in GEOS-Chem (yellow color in Figure 1), and contributes to 8~24% of total OA, which might be underestimated compared to recent field studies."

17. Figure 2 has been revised to add the trend lines of organic aerosol and sulfate.

18. Figure S1 has been revised to add the location of CSN sites.

19. Added Figure S3 to compare the two NH_3 emission inventories.

20. Figure S4 (previous Figure S3) has been revised to add the trend of aerosol ammonium-to-sulfate ratio.

Long-term observational constraints of organic aerosol dependence on inorganic species in the southeast US

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Keywords: Secondary organic aerosol; IEPOX; isoprene; coating; aerosol acidity.

Abstract

Organic aerosol (OA), with a large biogenic fraction in summertime southeast US, adversely impacts on air quality and human health. Stringent air quality controls have recently reduced anthropogenic pollutants including sulfate, whose impact on OA remains unclear. Three filter measurement networks provide long-term constraints on the sensitivity of OA to changes in inorganic species, including sulfate and ammonia. The 2000-2013 summertime OA decreases by 1.7~1.9%/year with little month-to-month variability, while sulfate declines rapidly with significant monthly difference in early 2000s. In contrast, modeled OA from a chemical-transport model (GEOS-Chem) decreases by 4.9%/year with much larger monthly variability, largely due to the predominant role of acid-catalyzed reactive uptake of epoxydiols (IEPOX) onto sulfate. The overestimated modeled OA dependence on sulfate can be improved by implementing a coating effect and assuming constant aerosol acidity, suggesting the needs to revisit IEPOX reactive uptake in current models. Our work highlights the importance of secondary OA formation pathways that are weakly dependent on inorganic aerosol in a region that is heavily influenced by both biogenic and anthropogenic emissions.

1. Introduction

Organic aerosol (OA) accounts for a large fraction of ambient fine particulate matter mass, which strongly affects air quality, regional climate, and human welfare (Jimenez et al., 2009). Since the implementation of the Clean Air Act Amendments of 1990, there has been a significant decline in ambient aerosol in the United States, mostly due to reductions in inorganic aerosol mass following changes in emissions of sulfur dioxide (SO_2), nitrogen oxides (NO_x =NO+ NO_2), as well as reductions in black carbon (EPA, 2011), leaving OA as the major component of fine particulate matter (50~70%) over the southeast US, especially in summer (Attwood et al., 2014; Kim et al., 2015). OA can be directly emitted by combustion processes (primary organic aerosol, POA) or secondarily formed (SOA) from the atmospheric oxidation of biogenic volatile organic compounds (BVOCs), mainly isoprene and monoterpenes, and also precursors from anthropogenic sources and biomass burning (Hayes et al., 2015; Hodshire et al., 2019). OA has also been declining across much of the US over the past few decades, primarily due to decreased anthropogenic emissions from vehicle and residential fuel-burning, except for the southeast US (Ridley et al., 2018). The southeast US is one of the largest BVOC emission hotspots in the world (Guenther et al., 2006), and at the same time is heavily populated with large anthropogenic emissions of pollutants. Biogenic SOA (formed from atmospheric oxidation of BVOCs) may account for 60-100% of OA in summertime southeast US (Kim et al., 2015; Xu et al., 2015b). To what extent biogenic SOA could be mediated through emission control strategies remains an open question (Carlton et al., 2010; Mao et al., 2018).

The oxidation of BVOCs produces hundreds of intermediate products. Some products have low volatility that can partition onto the condensed phase, while some gas-phase products can react in the aqueous phase to form SOA. SOA formed from uptake of isoprene epoxydiols (IEPOX-SOA) (Paulot et al., 2009) appears to be the major confirmed aqueous SOA product globally, being important in all high isoprene and lower NO regions (Hu et al., 2015), along with glyoxal formed from isoprene and aromatics (Fu et al., 2008). Formation of SOA in clouds was investigated in the southeast US and found to be not statistically significant (Wagner et al., 2015). These pathways have been implemented into 3-dimensional global atmospheric chemistry and climate models using two different approaches. First, to simulate the partitioning of organic vapors, the BVOC oxidation products can be grouped based on their volatility (Volatility Basis Set, VBS), and the product yields and vapor pressures are parameterized for each surrogate precursor (Donahue et al., 2006; Pankow, 1994). Such empirical VBS schemes are usually derived using dry laboratory chamber experiments (with relative humidity RH<10%) and do not explicitly depend on aerosol water, RH, or inorganic aerosol mass or composition. Therefore, here we refer to the SOA formed through partitioning calculated by VBS as dry SOA. Second, a more explicit representation of aqueous SOA formation from isoprene products has been used recently, which incorporates dependence on inorganic aerosol volume and aerosol acidity (Budisulistiorini et al., 2017; Ervens et al., 2011; Fu et al., 2008; Marais et al., 2016; Pye et al., 2013). The relative contribution of dry versus aqueous SOA to total OA mass in the atmosphere is uncertain and has limited observational constraints.

Long-term field measurements show a decreasing trend of OA in the southeast US (Attwood et al., 2014; Hidy et al., 2014; Kim et al., 2015), which is likely linked to reductions in anthropogenic POA and SOA (Blanchard et al., 2016; Ridley et al., 2018), sulfate (Blanchard et al., 2016; Malm et al., 2017; Marais et al., 2017; Xu et al., 2015b, 2016) and NO_x (Carlton et al., 2010; Pye et al., 2010, 2019; Xu et al., 2015b). The influence of sulfate on OA is thought to be mainly due to its influence on the uptake of isoprene gas-phase oxidation products, which are often small molecules that cannot directly condense due to high vapor pressure, but may undergo aqueous-phase reactive uptake onto wet sulfate particles to form aqueous SOA, as suggested by extensive laboratory and field studies (Budisulistiorini et al., 2015; Hu et al., 2015; Li et al., 2016; Liggio et al., 2005; McNeill et al., 2012; Riedel et al., 2016; Shrivastava et al., 2017; Surratt et al., 2010; Tan et al., 2012; Xu et al., 2016, 2015b). NO_x plays a complex role in regulating oxidation capacity, different oxidation pathways and aerosol water content through aerosol nitrate (Kiendler-Scharr et al., 2016; Kroll et al., 2005, 2006; Li et al., 2018; Ng et al., 2017; Presto et al., 2005; Shrivastava et al., 2019; Zheng et al., 2015; Ziemann and Atkinson, 2012). Prior 3-D modeling studies with different SOA mechanisms provide different explanations for the long-term OA trend observed in the southeast US. For example, the dry SOA calculated by VBS framework with NO_x-dependent yields implies a small decrease in OA following the reductions of NO_x (Pye et al., 2013; Zheng et al., 2015), but has little dependence on changes in inorganic aerosol mass such as sulfate. On the other hand, models using aqueous SOA formation from isoprene attributed the decreasing OA from 1991 to 2013 to reductions in sulfate (Marais et al., 2017) but showed greater interannual variability than was observed. The driving mechanism for the OA trend in the southeast US remains to be elucidated.

Here we use observations from three surface filter-based networks (IMPROVE, SEARCH, CSN), combined with a 3-dimensional chemical transport model GEOS-Chem v12.1.0, to examine the long-term trend and more importantly, the month-to-month variability of OA in the southeast US during 2000-2013. The results provide new observational constraints on the drivers of OA variability and the SOA formation mechanisms in the southeast US.

2. Methods

2.1 Observational datasets.

We use surface filter-based measurement of fine particulate matter mass and composition (including organic carbon, OC) in 2000-2013 from three networks: the Interagency Monitoring of Protected Visual Environments (IMPROVE) (Solomon et al., 2014), the SouthEastern Aerosol Research and Characterization (SEARCH) (Edgerton et al., 2005), and the Environmental Protection Agency's $PM_{2.5}$ National Chemical Speciation Network (CSN) (Solomon et al., 2014). We select 21 IMPROVE sites, 3 SEARCH rural sites and 36 CSN sites within the southeast US region [29°~37°N, 74°~96°W] (Figure S1). The SEARCH sites are organized in rural/urban pairs (Edgerton et al., 2005) and only the data from the rural sites are used here to represent background conditions. IMPROVE sites are mostly rural (Solomon et al., 2014). The OC measurement in the CSN network in 2004-2009 gradually shifted to a different protocol and analytical technique than the early 2000s, which led to the discontinuity in long-term trend (Figure S2), therefore we only use CSN data to examine the monthly variability of OA, and focus on IMPROVE and SEARCH for all analysis. The 3-day OC measurement from IMPROVE and daily OC from SEARCH and CSN are averaged to monthly values. A factor of 2.1 is used to convert measured organic carbon (OC) to organic aerosol mass, as suggested by the southeast US field measurements (Pye et al., 2017; Schroder et al., 2018).

We use OA measurements by Aerosol Mass Spectrometer (AMS) from the Southern Oxidant and Aerosol Studies campaign (SOAS) at the Centerville, AL Site in 06/01/2013-07/15/2013 (SOAS2013). The OA measurements and derived IEPOX-SOA factor calculated by Positive Matrix Factorization (PMF) analysis (Hu et al., 2015; Xu et al., 2015a, 2018) are from two independent groups: one group from Georgia Institute of Technology led by Prof. Nag Lee Ng, the other from University of Colorado Boulder led by Prof. Jose L. Jimenez, denoted as Obs_GT and Obs_CU, respectively.

2.2 Modeling framework

2.2.1 GEOS-Chem

In this study we use the 3-dimensional global chemical transport model GEOS-Chem version 12.1.1 (DOI: 10.5281/zenodo.2249246, https://github.com/geoschem/) with detailed O_3-NO_x-HO_x-CO-VOC-aerosol tropospheric chemistry (Bey et al., 2001; Mao et al., 2013). Isoprene chemistry is described in (Fisher et al., 2016; Travis et al., 2016). GEOS-Chem is driven by offline meteorology 1999-2013 from the NASA Modern-Era Retrospective analysis for Research and Applications, version 2 (MERRA-2 https://gmao.gsfc.nasa.gov/reanalysis/MERRA-2/). The global anthropogenic (including agricultural) emissions are from the Community Emissions Data System (CEDS) inventory, with the US region replaced by the EPA's National Emission Inventory for 2011 (NEI11v1). The monthly mean anthropogenic emissions of CO, SO_2, NO_x, NH_3, VOCs, OC and black carbon are scaled to the year 2011 using the ratio of EPA's national annual emission totals from 2000 to 2013 (Travis et al., 2016). Biomass burning emissions are from Global Fire Emissions Database version 4 (GFED4) (Randerson et al., 2015). Biogenic emissions of isoprene and terpenes are online calculated by the Model of Emissions of Gases and

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Aerosols from Nature (MEGAN2.1) (Guenther et al., 2012) that is also driven by MERRA-2 meteorology.

For organic aerosol, we employ the complexSOA scheme for SOA modeling for all simulations in this study (Marais et al., 2016; Pai et al., 2020; Pye et al., 2010). POA are regarded as nonvolatile. This SOA modeling includes a 4-product Volatility-Basis-Set (VBS) for SOA formation from reversible condensation of oxidation products of biogenic terpenes (including monoterpenes and sesquiterpenes), and anthropogenic VOCs, referred to as terpene-SOA and anthropogenic SOA, respectively. The SOA calculated through VBS parameterization is fitted based on dry chamber (RH<10%) results independent of inorganic aerosol, aerosol water and RH (Pye et al., 2010). The complexSOA scheme also includes aqueous SOA formed from reactive uptake of isoprene oxidation products, including IEPOX, glyoxal, C_4 epoxides, methylglyoxal, non-IEPOX product of the ISOPOOH oxidation and hydroxynitrates from NO_3-initiated oxidation (Marais et al., 2016). GEOS-Chem v12.1.1 considers sulfate, nitrate, and ammonium from all sectors, and fine-mode Na^+, Ca^{2+}, Mg^{2+}, Cl^- from anthropogenic and sea salt sources, and employs the ISORROPIA II thermodynamic model (Fountoukis and Nenes, 2007; Pye et al., 2009; Song et al., 2018) to calculate aerosol water content and aerosol acidity (Pye et al., 2020).

We run the default GEOS-Chem model at 4°×5° latitude by longitude continuously from 10/01/1999 to 12/31/2013. For each year, the restart file at 05/01 from the continuous 4°×5° simulation has been regridded to 2°×2.5° and is used to initiate 2°×2.5° simulations from 05/01 to 08/31 each year. The May results are discarded as spin-up and the results of June, July and August are used for analysis.

Deleted: The 2°×2.5° simulations are adequate when modeling continental boundary layer chemistry (Yu et al., 2016).

The default modeled OA shows a stronger decreasing trend from 2000 to 2013, and a large month-to-month variability in early 2000s, different from the observations (more details in Figure 1, 2A and Section 3.1). To address this model-observation discrepancy, we do four sets of 2°×2.5° simulations: Default (using default complexSOA scheme); CT (with coating effect for IEPOX reactive uptake); CT_newNH$_3$ (with coating effect and US NH$_3$ emissions replaced by satellite-derived NH$_3$ inventory); CT_H01 (with coating effect and fixing aerosol acidity a_{H+} at 0.1 mol/L when calculating IEPOX reactive uptake). The sensitivity simulations are further explained in Section 2.2.2-2.2.3 and Section 3.3.

2.2.2 Coating

The default IEPOX-SOA mechanism in GEOS-Chem uses aerosol-phase reaction rates from laboratory chamber studies with pure acidic inorganic particles (Gaston et al., 2014; Riedel et al., 2015), and a representative effective Henry's law constant obtained by matching the model to the observations from the SOAS2013 campaign (Marais et al., 2016), to estimate the reactive uptake coefficient γ_{IEPOX}. In the default scheme, γ_{IEPOX} is calculated as follows:

$$\frac{1}{\gamma_{IEPOX}} = \frac{R_p\omega}{4D_g} + \frac{1}{\alpha} + \frac{1}{\Gamma_{aq}}$$

$$\Gamma_{aq} = \frac{4VRTH_{aq}k_{aq}}{S_a\omega}$$

Where R_p is the particle radius of the inorganic sulfate-nitrate-ammonium particle (cm), ω is the mean molecular speed (cm/s), D_g is the gas-phase diffusion coefficient (0.1 cm^2/s), α is the mass accommodation coefficient (α=0.1), S_a is the total (wet) particle surface area (cm^2/cm^3), V is the total (wet) particle volume (cm^3/cm^3), R is the ideal gas constant (L atm/mol/K), T is temperature

(K), H_{aq} is the Henry's law coefficient (1.7×10^{7} M/atm), and k_{aq} is the first-order reaction rate constant (s^{-1}):

$$k_{aq} = k_{H^+}[H^+] + k_{nuc}[nuc]a_{H^+} + k_{ga}[ga]$$

where k_{H^+} (=0.036 $M^{-1}s^{-1}$), k_{nuc} (=2×10^{-4} $M^{-1}s^{-1}$) and k_{ga} (=7.3×10^{-4} $M^{-1}s^{-1}$) are the reaction rates due to acid-catalyzed ring-opening, presence of nucleophiles (including nitrate and sulfate) and presence of bisulfate acids, respectively (Gaston et al., 2014; Marais et al., 2016).

In the real atmosphere, inorganic aerosol is generally internally mixed with other organics. The presence of an organic coating may alter the aerosol properties and suppress the uptake of IEPOX onto acidified sulfate aerosol (Anttila et al., 2006; Gaston et al., 2014). We implement a linear coating effect for the IEPOX-SOA formation. The coating effect is fitted using laboratory-derived values of γ_{IEPOX} on particles containing both ammonium bisulfate and ethylene glycol under RH=50% conditions (Gaston et al., 2014). In the coating scheme, γ'_{IEPOX} is calculated as above with R_p, V and S_a updated considering OA coated outside the inorganic core. Then, the fitted function is applied to modify γ'_{IEPOX}:

$$\gamma_{IEPOX\_modified} = \gamma'_{IEPOX} \times (1 - 1.3 \times \chi_{org})$$

where χ_{org} is the mass fraction of OA in the mixed particle including both the inorganic aerosol and OA. When χ_{org}>0.7, the IEPOX uptake will be terminated, i.e. $\gamma_{IEPOX\_modified} = 0$. In the real atmosphere when inorganic cores are coated with more viscous SOA (Zhang et al., 2018b), coating effect may be stronger because ethylene glycol is a low viscosity material. However, this simplified linear function does not consider the decreased viscosity and reduced coating effect at higher RH conditions (which is common in summertime southeast US) (Gaston et al., 2014; Zhang et al., 2018b), and prevents further IEPOX uptake when the mass fraction of OA (χ_{org}) is larger than 0.7, therefore this linear function may mimic a strong coating effect even though ethylene glycol is less viscous than real atmospheric SOA. The uncertainties need to be addressed in further studies with a more realistic coating parameterization (Li et al., 2020; Schmedding et al., 2019; Zhang et al., 2019b). We assume all OA is coated outside the inorganic aerosol core when calculating the IEPOX reactive uptake. The default GEOS-Chem with no organic coating calculates surface area of inorganic aerosol (Jo et al., 2019). By adding the coating effect, the increased particle radius R_p and surface area S_a of the mixed particle will partially offset (but does not outweigh) the impact of reduced reaction probability $\gamma_{IEPOX\_modified}$.

2.2.3 Satellite-derived NH_3 emissions

We use the Cross-track Infrared Sounder (CrIS) satellite-derived NH_3 emissions (Cao et al., 2020) in a sensitivity test in this study. The top-down monthly NH_3 emissions over the contiguous US at 0.25° × 0.3125° latitude by longitude are derived from CrIS v1.5 measurements of NH_3 profiles (Shephard and Cady-Pereira, 2015) for the year 2014 through a 4D-Var approach using GEOS-Chem and its adjoint model (Henze et al., 2007). The CrIS-derived emissions are then regridded to 0.1°×0.1° to replace the default NEI11 emissions for the year 2011 and applied the same annual scaling factors for 2000-2013. The default NEI11 and CrIS-derived NH_3 emissions averaged over 2000-2013 are compared in Figure S3. There is no significant trend of NH_3 emissions from 2000 to 2013 (Figure S4), consistent with other studies suggesting nearly constant NH_3 emissions from 2001 to 2014 (Butler et al., 2016). The CrIS-derived emissions used the HTAPv2 emissions inventory as the prior emissions, which is based on the 2008 NEI emissions over the US (Janssens-Maenhout et al., 2015). The CrIS-derived NH_3

emissions have been validated against surface observations of NH_3 concentration from the Ammonia Monitoring Network (AMoN) and wet deposition measurements from the National Atmospheric Deposition Program (NADP). More details can be found in Cao et al. (2020). Using the top-down emissions in GEOS-Chem increases the correlation coefficient (*r*) between modeled monthly mean NH_3 concentration and surface observations from 0.74 to 0.93 and reduces the normalized mean bias of domain-averaged annual mean simulated NH_3 by a factor of 1.9. The seasonal cycle of simulated wet NH_4^+ deposition is also improved (*r* increased from 0.70 to 0.86), but the normalized mean bias of domain-averaged annual simulated wet NH_4^+ increases from 0.34 to 0.96 due to overly strong wet scavenging in the model. The latter issue was ultimately resolved in Cao et al. (2020) and the final top-down emissions reported therein differ from those reported here; nevertheless, the emissions estimates used here provide a valuable basis for conducting a sensitivity experiment.

Deleted: The top-down annual mean emissions are ~52% higher than the prior emissions, likely because the prior emissions underestimate agricultural emissions, in particular springtime fertilizer and livestock sources over the Central US. Meanwhile, some smaller values then the prior emissions were found in the Central Valley, southern Minnesota, northern Iowa and southeast North Carolina during warm months.

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2.3 Multivariate linear regression analysis

In this study we did a multivariate regression analysis of modeled monthly IEPOX-SOA (μg/m^3) against modeled sulfate aerosol (μg/m^3), aerosol acidity a_{H+} (mol/L) and isoprene emission ($ISOP_{emis}$ mg/m^2/hr):

$$IEPOX\text{-}SOA = \beta_1 \times sulfate + \beta_2 \times a_{H^+} + \beta_3 \times ISOP_{emis} + b$$

Mean values have been subtracted from all variables, which are then divided by standard deviations. β_1, β_2 and β_3 are standardized partial regression coefficients associated with sulfate aerosol, a_{H+} and isoprene emission, and can be directly compared to evaluate the relative importance of the three variables. We apply the regression analysis using monthly data within different time frames (2000-2013, 2000-2004, 2005-2008 and 2009-2013 as in Table S1) to determine the evolving importance of variables.

3. Results

3.1 Long-term trend and month-to-month variability (MMV) of OA

In the southeast US, observations from the IMPROVE and SEARCH network both show a reduction in summertime surface OA concentration from 2000 to 2013 (Figure 1). Observational results are averaged using 21 IMPROVE sites and 3 SEARCH sites within the southeast US. OA concentration averaged over June-July-August (JJA) 2000-2013 is 4.2 μg/m^3 from the IMPROVE sites, and 5.7 μg/m^3 from SEARCH sites. A similar ~30% summertime low bias on the IMPROVE sites was documented by Kim et al. (2015) compared to the SEARCH sites, which is thought to be due to evaporation of OA from the filters after collection, as the IMPROVE filters stay several days on site after sampling and are shipped without refrigeration, while the SEARCH filters are analyzed in-situ. Despite different magnitudes, OA from the two networks demonstrate similar trends and interannual variability. The 2000-2013 trend of JJA OA mass is -1.7%/year for IMPROVE and -1.9%/year for SEARCH. Compared to the slow decrease in OA, a faster declining trend is found for sulfate from IMPROVE (-6.9%/year) and SEARCH (-6.7%/year) for the same period (Figure 2).

Compared to the observations, the default GEOS-Chem model predicts a steeper decreasing trend of OA mass during 2000-2013 (Figure 1). Modeling results are averaged over the domain [29°~37°N, 74°~96°W] excluding ocean grid cells (Figure S1). The 2000-2013 JJA-averaged

OA from the default model is 6.7 μg/m^3, higher than OA from IMPROVE and SEARCH. Modeled total OA mass decreases at a rate of 4.9%/year, about 1.9 (1.6) times faster than IMPROVE (SEARCH) OA (student's t-test $p<0.001$). By sampling the model results at the locations of the IMPROVE and SEARCH sites, the modeled summertime OA has an average of 6.9 μg/m^3 and a trend of 5.0%/year, similar to the model results averaged over the whole southeast US domain. For simplicity, we show only the domain-averaged model results in all figures and analysis. The strong reduction in total OA mass is dominated by aqueous SOA, especially through reactive uptake of IEPOX, with no decreasing trend in other components (Figure 1). The contribution of IEPOX-SOA to total OA mass decreases from 61% in the early 2000s to 28% in 2013. The simulated IEPOX-SOA in 2013 compares well with previous field studies which suggested that IEPOX-SOA contributed to 18~40% in southeast US sites in summer 2013 (Budisulistiorini et al., 2016; Xu et al., 2015b).

A main constraint comes from the MMV of OA in the southeast US. IMPROVE and SEARCH OA observations show little variability among June, July and August, despite large MMV of sulfate in early 2000s (Figure 2A). We find similar behavior from another observation network, CSN. The discontinuity in OA trend in the CSN network is due to different protocols applied (Figure S2). Within sites using the same protocol, there are no systematic monthly differences, which agrees with IMPROVE and SEARCH. In contrast, modeled OA displays large MMV between June, July and August from 2000 to 2008, where OA in July and August is 1~3 times of June values (Figure 2A). Such large MMV is dominated by aqueous SOA, especially from the reactive uptake of IEPOX. Prior to 2008, the simulated IEPOX-SOA alone can be up to a factor 2 higher than the observed total OA (Figure 2). The other components including POA and dry

SOA (including terpene-SOA and Anthropogenic SOA) formed through partitioning together have low concentrations and small MMV. The default model well captures the variability of observed sulfate (Figure 2A), with an average of 3.8 μg/m^3 and a trend of -6.9%/year, as compared to -6.9%/year (average concentration 4.2 μg/m^3) from IMPROVE and -6.7%/year (average concentration 4.3 μg/m^3) from SEARCH.

The large MMV in the model suggests a much stronger modeled OA dependence on sulfate than observations. In 2000-2004, changes in modeled sulfate from June to July and/or August correspond to large MMV of modeled OA mass. In contrast, little MMV is found in observed OA mass during the same months despite large MMV in observed sulfate (Figure 2A). From a linear regression analysis using all monthly data in 2000-2013, the OA-to-sulfate regression slope is m=0.29 (r^2=0.25) from IMPROVE, m=0.51 (r^2=0.43) from SEARCH, and m=1.87 (r^2=0.57) from the default model, even though the default model well captures the magnitude, trend, and monthly variability of observed sulfate. In summary, simulated total OA mass in the standard GEOS-Chem model, dominated by IEPOX-SOA, has a steeper decreasing trend from 2000 to 2013 than the observations, and has a large MMV indicating strong dependence on sulfate.

3.2 What controls the modeled IEPOX-SOA variability?

The strong dependence of IEPOX-SOA on sulfate is well-established by laboratory and field work: wet sulfate particles provide the surface and volume of liquid media for IEPOX reactive uptake (Budisulistiorini et al., 2017; Eddingsaas et al., 2010; Riva et al., 2016; Xu et al., 2015b, 2016), and serve as nucleophiles for nucleophilic addition to form organosulfates (Nguyen et al., 2014; Surratt et al., 2007b). Sulfate (SO_4^{2-}), together with ammonium (NH_4^+), nitrate (NO_3^-) and other ions, regulates proton (H^+) activity (a_{H+}) that can catalyze the ring-opening of epoxide group leading to the formation of IEPOX-SOA (Gaston et al., 2014; Pye et al., 2013; Surratt et al., 2007a). However, some recent studies suggest that IEPOX-SOA is not well correlated with aerosol acidity estimated from thermodynamic models (Budisulistiorini et al., 2015; Lin et al., 2013; Xu et al., 2015b), although the lack of direct measurements of aerosol acidity may be a limitation. We use the GEOS-Chem model here to examine the simulated IEPOX-SOA dependence on sulfate, aerosol acidity, and emissions of isoprene which produce IEPOX at high yields under low-NO_x conditions (Paulot et al., 2009). Temperature impacts the formation of IEPOX-SOA mainly through regulating isoprene emissions but does not influence partitioning as IEPOX-SOA is treated as non-volatile in GEOS-Chem. Therefore, temperature is not examined as another driver in addition to isoprene emissions. We do not treat aerosol water as an independent driver because the dilution effect of aerosol water is implicitly considered in the inorganic sulfate-ammonium-nitrate aerosol volume and acidity calculation, and studies have shown that particle water is not a limiting factor unless the particle is purely dry (Nguyen et al., 2014; Riva et al., 2016; Xu et al., 2015b) which is rare in summertime in the southeast US.

We find that the large MMV of OA in the model is mainly driven by sulfate concentrations and aerosol acidity. Figure 3 shows the standardized monthly surface IEPOX-SOA concentration, sulfate concentration, aerosol H^+ activity and isoprene emission from the default model. For each variable, the monthly gridded data has been first averaged over the southeast US. Then, we calculate the one standard deviation of all monthly data (June, July and August data from 2000 to 2013). Finally, the domain-averaged monthly data has been divided by its standard deviation, so the variables are standardized to be unitless and their variability can be compared directly. Prior to 2008, IEPOX-SOA production is largely enhanced by abundant sulfate (Gaston et al., 2014). Due to this high level of sulfate (about >4 μg/m^3), the modeled aerosol acidity becomes particularly sensitive to variations in NH_3 emissions. The default NH_3 emissions from NEI11v1 suggest no significant long-term trend from 2000 to 2013. In general, ammonium aerosol is strongly correlated with sulfate and has a similar declining trend as sulfate (Silvern et al., 2017). However, the NH_3 emissions in August are about 25% lower than in June and July (Figure S4). As a result, in August before 2008, the aerosol NH_4^+/SO_4^{2-} ratio is smaller (Figure S4) and a_{H+} is up to 3 times higher than June (Figure 4B), leading to high production of IEPOX-SOA in August. Both sulfate and aerosol acidity appear to be the dominant contributors to MMV of OA during this period. After 2008, IEPOX-SOA formation is substantially suppressed, due to small SO_2 emissions and low modeled aerosol acidity a_{H+} with small monthly variability. Isoprene emissions also contribute to the month-to-month and interannual OA variability in the model.

The multivariate linear regression analysis of IEPOX-SOA quantitatively determines the relative importance of its three drivers in the model. Using all monthly data in 2000-2013, the standardized regression coefficients (β) associated with a_{H+}, sulfate aerosol concentration and isoprene emission are β=0.50 (r^2=0.71), β=0.39 (r^2=0.64) and β=0.34 (r^2=0.18), respectively, suggesting that aerosol acidity is the dominant controlling factor. The three variables together explain 88% of the variability of IEPOX-SOA. Their relative importance changes over time (Table S1). Aerosol acidity strongly correlates with IEPOX-SOA in 2005-2008 (β=0.57, r^2=0.82) but its role becomes much weaker after 2008 (β=0.27, r^2=0.56). Sulfate aerosol is always the first or second most important driver, especially in 2000-2004 (β=0.46, r^2=0.76).

Isoprene emission contributes to the overall interannual variability, for example leading to the relatively low IEPOX-SOA in 2003-2004 and the peaks in 2000, 2006 and 2011 (Figure 3). The high IEPOX-SOA in 2000-2001 and 2005-2007 is a result of high sulfate aerosol, high aerosol acidity due to low NH_3 supply relative to high sulfate, and high isoprene emissions during these periods (Figure 3, Figure 4B).

3.3 Narrowing the gap between model and observation

3.3.1 Coating

Several reasons may lead to the large monthly variations of the modeled OA. The modeled IEPOX-SOA shows a much stronger sensitivity to aerosol acidity than suggested by field observations, which found weak or no correlation between observed IEPOX-SOA and derived aerosol acidity (Budisulistiorini et al., 2015; Lin et al., 2013; Worton et al., 2013; Xu et al., 2015b). Lack of consideration of organic coating effect may provide one possible explanation. In the real atmosphere, inorganic aerosol is generally internally mixed with other organics (Anttila et al., 2006; Murphy et al., 2006). The presence of an organic coating may alter the solubility and diffusion properties at the surface of inorganic particles and diminish further uptake of IEPOX. We implemented a linear coating effect for the IEPOX uptake in a sensitivity simulation 'CT', in which both the magnitude of γ_{IEPOX} and its sensitivity to acidity have been reduced. Figure 4A shows a schematic illustrating the dependence of the γ_{IEPOX} coating effect on acidity a_{H+} and organic mass fraction (χ_{org}). The original γ_{IEPOX} without coating is represented at χ_{org}=0. The orange line in Figure 4A shows the approximate position of JJA-averaged acidity and organic mass fraction in the 'CT' simulation. Adding a coating reduces γ_{IEPOX} by almost half, but the impact on the total reactive uptake rate of IEPOX is partially compensated by the corresponding increase in particle surface area. The sensitivity of γ_{IEPOX} to acidity has also been reduced especially during the early 2000s (Figure 4A). The CT simulation reduces the southeast US JJA-averaged IEPOX-SOA concentrations by 0.3~1.8 μg/m^3 (Figure 4C).

3.3.2 NH_3 emissions and aerosol acidity

Second, recent studies present contradictory results and explanations on the long-term trend of aerosol acidity in the southeast US (Pye et al., 2020; Silvern et al., 2017; Weber et al., 2016). In this study, we show that the decreasing trend of aerosol acidity from the standard GEOS-Chem model is mainly caused by high acidity in August before 2008, which corresponds to insufficient NH_3 emissions in high sulfate environments. The NEI11v1 inventory is used in the default configuration, in which NH_3 emissions in June and July are 30% higher than in August (Figure S4), but not all NH_3 emission inventories agree with such pattern (Paulot et al., 2014). We did a sensitivity test ('CT_newNH$_3$') replacing the default US NH_3 emissions from NEI11v1 by a new NH_3 emission product derived from CrIS satellite observations, which has higher emissions and smaller MMV among June, July and August (Figure S4). In the 'CT_newNH$_3$' simulation, the resulting simulated aerosol acidity is substantially changed in 2000-2008 (Figure 4B). The high acidity (a_{H+}=0.55~0.9 mol/L) in August has been reduced to around 0.2 mol/L and is much closer to June and July values (Figure 3). The results suggest that the fine particles in the southeast US are within a regime where the acidity (a_{H+} in units of mol/L) is sensitive to NH_3 emissions relative to sulfate concentration, though corresponding pH changes are small (pH within 0.5~1.5, Figure S4). Small changes in NH_3 may lead to large changes in a_{H+} especially when sulfate concentrations are high, resulting in high month-to-month variability of the IEPOX uptake. After updating the NH_3 emissions using the satellite-based estimates, the model simulates a much more stable trend in aerosol acidity from 2000 to 2013 (Figure 4B), consistent with recent thermodynamic modeling studies that suggested steady aerosol acidity despite large reductions in observed sulfate (Pye et al., 2020; Weber et al., 2016).

Due to the high uncertainty associated with the derived NH_3 emission product and acidity calculation (Guo et al., 2015, 2018; Silvern et al., 2017; Song et al., 2018; Tao and Murphy, 2019), we conducted another simulation 'CT_H01' that fix a_{H+} level at 0.1 mol/L when calculating IEPOX uptake rate, corresponding to the predicted a_{H+} value (constrained by observations) during the 2013 SOAS campaign (Weber et al., 2016). The two simulations, CT_newNH$_3$ and CT_H01, yield similar long-term trends of IEPOX-SOA in the southeast US (Figure S5), and they agree better with the long-term surface OA measurements from IMPROVE and SEARCH than the default model (Figure 4C and 4D). For the SOAS2013 campaign, the CT_H01 scheme simulates an average IEPOX-SOA concentration of 0.74 μg/m^3, similar to 0.81 μg/m^3 in the default model, and agrees well with the two independent Aerosol Mass Spectrometer measurements (0.97 μg/m^3 from obs_GT and 0.68 μg/m^3 from obs_CU, see daily time series in Figure S6). The CT_newNH$_3$ scheme simulates an average IEPOX-SOA concentration of 0.34 μg/m^3, lower than the observation and the other models by a factor of >2, due to both the simplified coating effect and small aerosol a_{H+} values (a_{H+}<0.1mol/L, Figure 4B). In general, the fixed acidity in the CT_H01 simulation well captures the measured IEPOX-SOA from the SOAS2013 campaign (Figure S6), and improves the modeled total OA mass relative to the observations: The modeled long-term decreasing rate of JJA-average OA from 2000 to 2013 has been reduced from 4.9%/year to 3.2%/year, better compared to the IMPROVE

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(1.7%/year) and SEARCH (1.9%/year) observations, but is still higher (Figure 4C). The modeled MMV of OA have also been greatly reduced (Figure 4D).

3.3.3 Relationships between OA and sulfate

The formation of aqueous SOA explicitly depends on sulfate aerosol and aerosol acidity which is also impacted by sulfate. The default model, in which a large fraction of simulated total OA mass is from aqueous SOA (mostly IEPOX-SOA), shows a stronger dependence of total OA on sulfate than the observations (Figure 5). The OA-to-sulfate regression slope calculated using monthly OA and sulfate (averaged from all sites beforehand for each network) is m=1.87 for the default simulation, much higher than m=0.29 from IMPROVE and m=0.51 from SEARCH. Such strong dependence is clearly demonstrated by the MMV of IEPOX-SOA (Figure 2). Adding the coating effect and fixing a_{H+}=0.1 mol/L substantially reduces the MMV of IEPOX-SOA and the simulated monthly OA-to-sulfate slope (m=1.02).

Despite the model improvement against the observations in terms of OA and IEPOX-SOA magnitude and long-term relationship with sulfate, the CT_H01 scheme needs to be further improved. The rate of OA decreases per year in CT_H01 is about 0.8 times higher than the long-term observations, with modeled MMV still larger than observations in early 2000s (Figure 4D). Recent studies (Riva et al., 2019) suggested that the IEPOX-SOA production per unit mass of sulfate likely increases with decreasing sulfate due to changes in aerosol properties, such as acidity, morphology, phase state and viscosity, as well as formation of organosulfates, suggesting non-linearity between IEPOX-SOA and sulfate (Riva et al., 2019; Zhang et al., 2019a). Further modeling studies with separated IEPOX-SOA species and detailed aerosol properties are needed to achieve a better mechanistic understanding of the dependence of OA on inorganic aerosol.

4. Summary and Discussion

Significant reduction of SO_2 emissions, combined with monthly variations of sulfate and NH_3 emissions, provide a unique dataset to test the sensitivity of biogenic SOA formation to inorganic species. Observations from two networks (IMPROVE and SEARCH) show a slowly decreasing trend in total OA mass from 2000 to 2013 in the southeast US (-1.7%/year from IMPROVE and -1.9%/year from SEARCH), in contrast to a much faster rate of sulfate reduction (-6.9%/year from IMPROVE and -6.7%/year from SEARCH). The standard version of GEOS-Chem model was able to reproduce the long-term trend of sulfate (-6.7%/year), but with a faster decrease of OA (-4.9%/year) and larger interannual variability.

The MMV of total OA mass during summers provides a novel observational constraint on SOA formation mechanism. Remarkably, we find little MMV of OA from all three surface networks (IMPROVE, SEARCH and CSN) during summer months in 2000-2013, despite larger MMV in sulfate and NH_3 emissions. This is in contrast to the standard version of the GEOS-Chem model, which shows a much larger MMV of OA during 2000-2008. Large MMV of OA in the standard model is mainly due to the high sensitivity of modeled IEPOX-SOA to sulfate and aerosol acidity (and NH_3 emissions) when sulfate aerosol is abundant. The resulting strong correlation between OA and sulfate also appears to be at odds with long-term observations (Figure 5). Incorporating a coating effect for IEPOX uptake and fixing aerosol acidity, have together improved the model performance in terms of OA trend, variability and the relationship between OA and sulfate, though further improvement is needed.

There are many uncertainties associated with the calculation of IEPOX-SOA formation. In the default scheme, the Henry's law constant for IEPOX uptake was tuned using measurements from the SOAS2013 campaign and was found to be 1.7×10^7 M/atm, 10 times smaller than suggested by Gaston et al. (2014) based on laboratory experiments and about half of the suggested value (3×10^7 M/atm) in some other studies (Budisulistiorini et al., 2017; Nguyen et al., 2014; Pye et al., 2017; Woo and McNeill, 2015; Zhang et al., 2018b). The default simulation agrees well with surface IEPOX-SOA data from SOAS2013 and SEAC4RS 2013 aircraft campaigns (Marais et al., 2016) but overestimates OA magnitude and MMV against long-term observations from IMPROVE and SEARCH. The CT_newNH$_3$ simulation reproduces the long-term OA trend but underestimates IEPOX-SOA by a factor of 2 against SOAS 2013. The coating effect may be stronger than used here, as Gaston et al. (2014) used a low viscosity organic material in the experiments. The NH$_3$ emissions (which are critical for the calculation of aerosol acidity) are highly uncertain (Dammers et al., 2019), and the acidity calculation is further complicated by non-volatile cations (Guo et al., 2018) and meteorological conditions (Guo et al., 2015; Tao and Murphy, 2019). Uncertainties are also associated with the volatility of IEPOX-SOA. Some studies suggested a large fraction of IEPOX-SOA compounds (e.g. 2-methyltetrol) are semi-volatile and can re-evaporate back into gas-phase (Ambro et al., 2019; Isaacman-VanWertz et al., 2016), while other studies suggest IEPOX-SOA products are mostly nonvolatile or low volatility (Hu et al., 2016; Lopez-Hilfiker et al., 2016). As multiple parameters may be tuned in the model to fit observations, further laboratory, field and modeling studies are needed to integrate Henry's law constant, IEPOX-SOA yields, volatility, coating effect and acidity dependence for a better mechanistic understanding. The CT_H01 scheme lacks mechanical representation of detailed aerosol properties like phase state, acidity, viscosity and morphology, but reasonably captures both the OA and IEPOX-SOA magnitude (compared to both the three filter measurement networks and the SOAS2013 campaign), long-term variability and relationship with sulfate (Figure 4, 5, S6), therefore may serve as a simplified representation for climate models. Simulations in this study are conducted at a horizontal resolution of 2°×2.5°, which is comparable to most global climate models. However, as shown by Yu et al. (2016), from coarse to fine horizontal resolution, there will be a shift from low-NO_x to high-NO_x pathway for isoprene oxidation. Therefore, using a fine resolution may reduce the production of IEPOX and IEPOX-SOA, which needs further investigation. For all kinds of models, long-term filter-based measurements, especially intraseasonal MMV, are important observational constraints that should be considered in model development.

Even with our improved model, the rate of OA decrease per year is still 0.8 times higher the long-term observations, and still shows a higher MMV than observations particularly in early 2000s (Figure 4D). Such discrepancies may suggest a more important role of SOA pathways that are less dependent on inorganic aerosol, such as terpene-SOA formed by reversible gas-aerosol partitioning. Terpene-SOA is included in GEOS-Chem (yellow color in Figure 1), and contributes to 8~24% of total OA, which might be underestimated compared to recent field studies. Xu et al. (2015a) finds a large MMV in IEPOX-SOA, but the less-oxidized oxygenated OA (LO-OOA, an indicator for freshly-formed monoterpene SOA) and the more-oxidized oxygenated OA (MO-OOA, also likely from biogenic sources) have little MMV in summer

Deleted: Despite a large MMV in IEPOX-SOA, months, and they contribute to more than 50% of total OA mass in the southeast US (Xu et al., 2018). The important role of monoterpenes SOA is also confirmed by molecular level characterization of organic aerosols (Zhang et al., 2018a). Other pathways may contribute to SOA to some extent and may add to the predicted SOA formed by partitioning, including biogenic SOA from auto-oxidation (Bianchi et al., 2019; Pye et al., 2019), in-cloud SOA formation that may be less dependent on acidity than aqueous SOA (Tsui et al., 2019), a small but underestimated contribution of anthropogenic SOA (Schroder et al., 2018; Shah et al., 2019), and other possible mechanisms (Schwantes et al., 2019). Further quantifying the relative importance of the different pathways will allow a more accurate quantification of the anthropogenic influence on biogenic SOA and the associated radiative forcing.

Data availability

The observational datasets from long-term filter measurement networks IMPROVE and CSN are available at http://views.cira.colostate.edu/fed/QueryWizard/Default.aspx. The SEARCH observational datasets are available by contacting E. Edgerton. The model code and modeling results are available by contacting Y. Zheng and J. Mao.

Acknowledgement

YZ and JM acknowledge funding from NOAA NA18OAR4310114. HC and DKJ recognize support from NASA 80NSSC18K0689. WH and JLJ acknowledge funding from NSF AGS-1822664. EAM acknowledges funding from NERC/EPSRC (award number EP/R513465/1). The authors acknowledge the Electric Power Research Institute (EPRI) and Southern Company for support of the SEARCH network and Atmospheric Research & Analysis. IMPROVE and CSN data are accessed from the Federal Land Manger Environmental Database. YZ thanks helpful discussions with Arlene M. Fiore, Róisín Commane and V. Faye McNeill.

Author Contributions:

Y.Z. and J.M. designed the research, performed the simulations and conducted the analysis. J.A.T. and E.M.M. provided guidance on aerosol coating parameterization. H.C. and D.K.H. provided the CrIS-derived NH_3 emission. N.L.N, W.H. and J.L.J. provided data from the SOAS2013 field campaign. E.E. provided data from the SEARCH network. Y.Z. wrote the paper with all coauthors providing input.

Competing interests

The authors declare no competing interests.

Additional information

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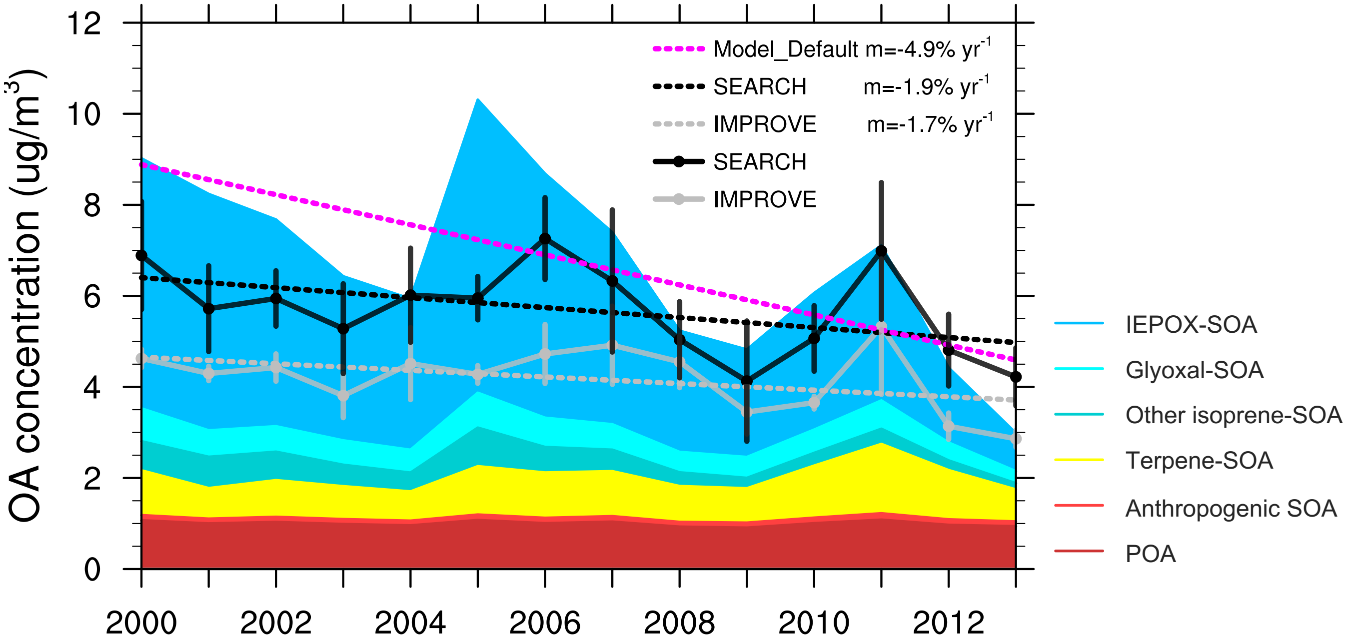

Figure 1. Comparison of June-July-August averaged surface OA concentration (μg/m^3) over the southeast US between the default model and the observation from IMPROVE and SEARCH network. Colored shades represent different components of modeled OA. IEPOX-, glyoxal-, and other isoprene-SOA are from aqueous uptake of isoprene oxidation products. Terpene- and anthropogenic SOA are dry SOA calculated using volatility-basis-set.

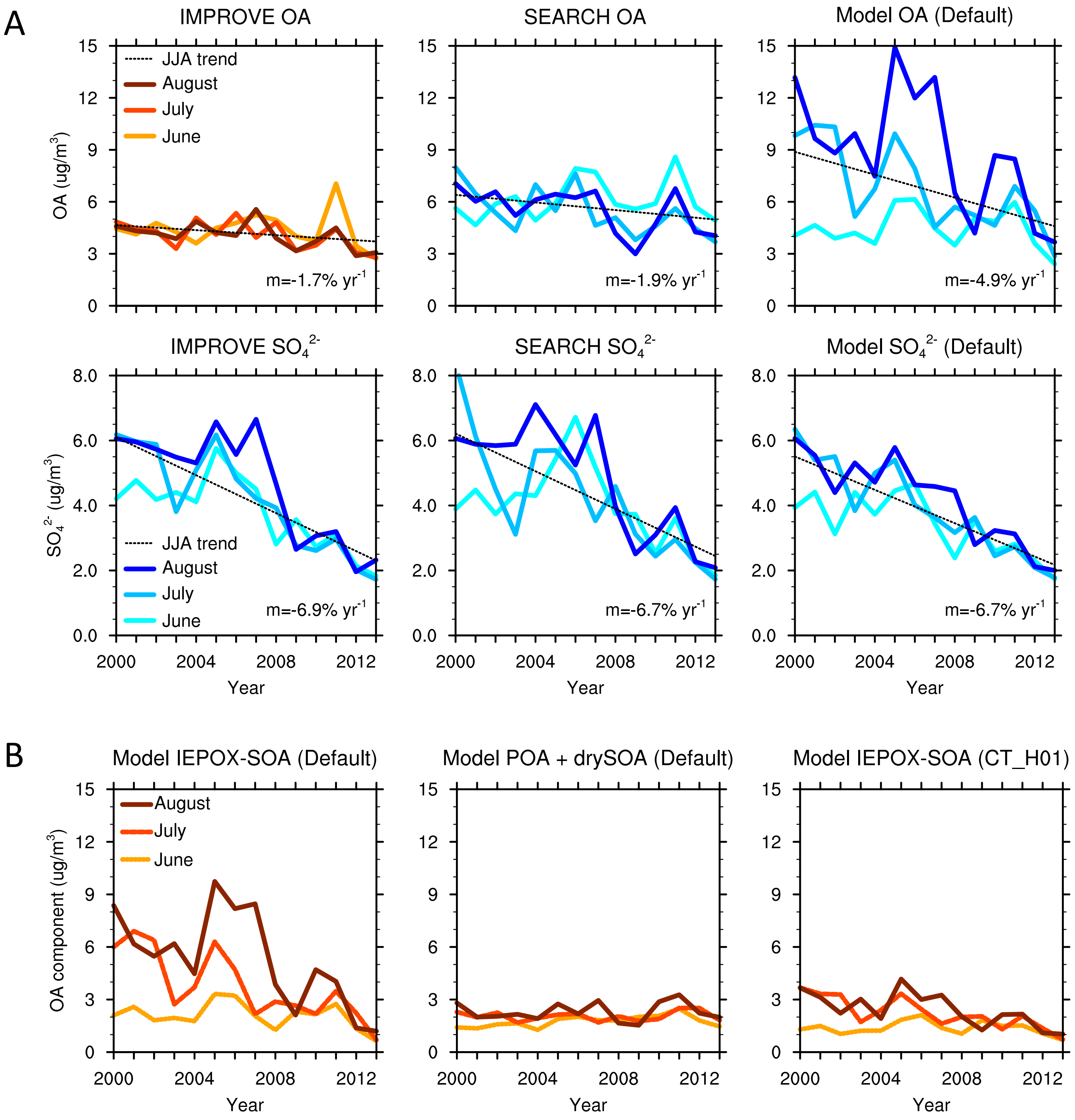

Figure 2. (A) Monthly surface OA and sulfate (SO_4^{2-}) concentration (μg/m^3) averaged over the southeast US from IMPROVE, SEARCH and the default model. **(B)** Monthly surface concentrations of IEPOX-SOA and the sum of POA and dry SOA from the default model, and IEPOX-SOA from the CT_H01 simulation.

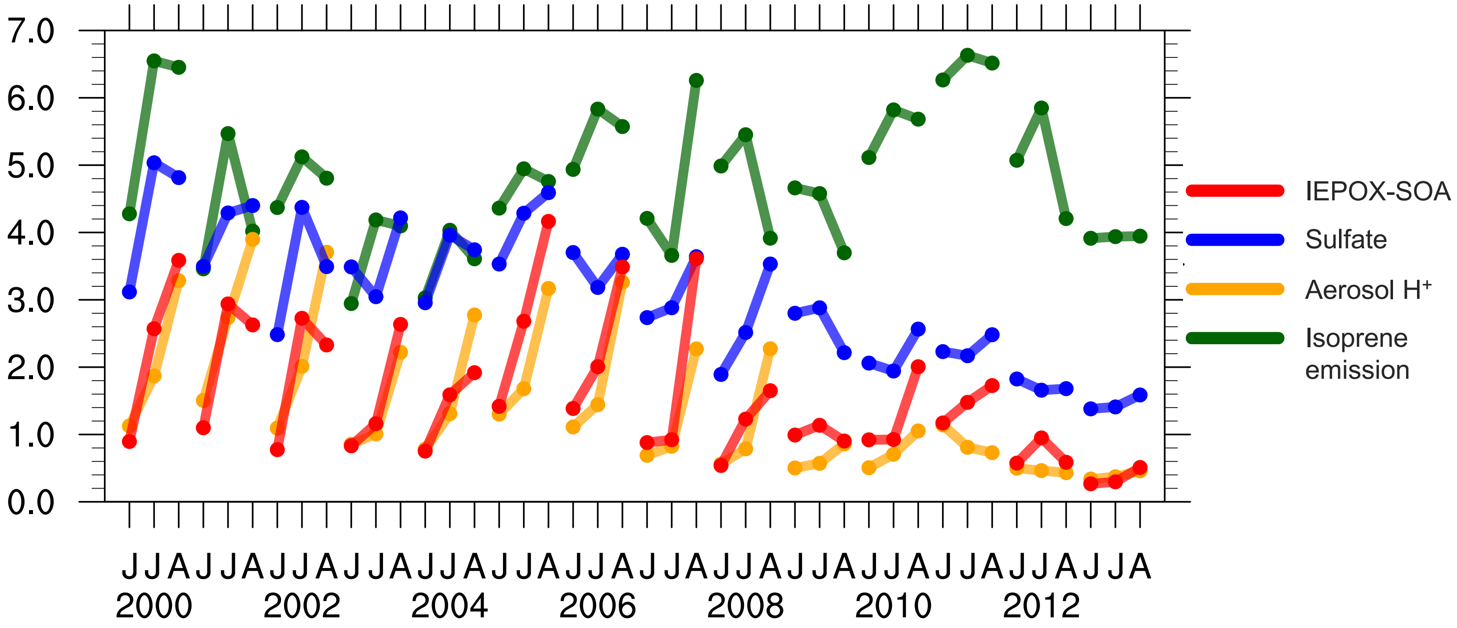

Figure 3. Standardized monthly surface IEPOX-SOA concentration, sulfate concentration, aerosol H^+ activity and isoprene emission from the default model. All variables are averaged over the southeast US, and have been divided by 1 standard deviations, therefore are unitless.

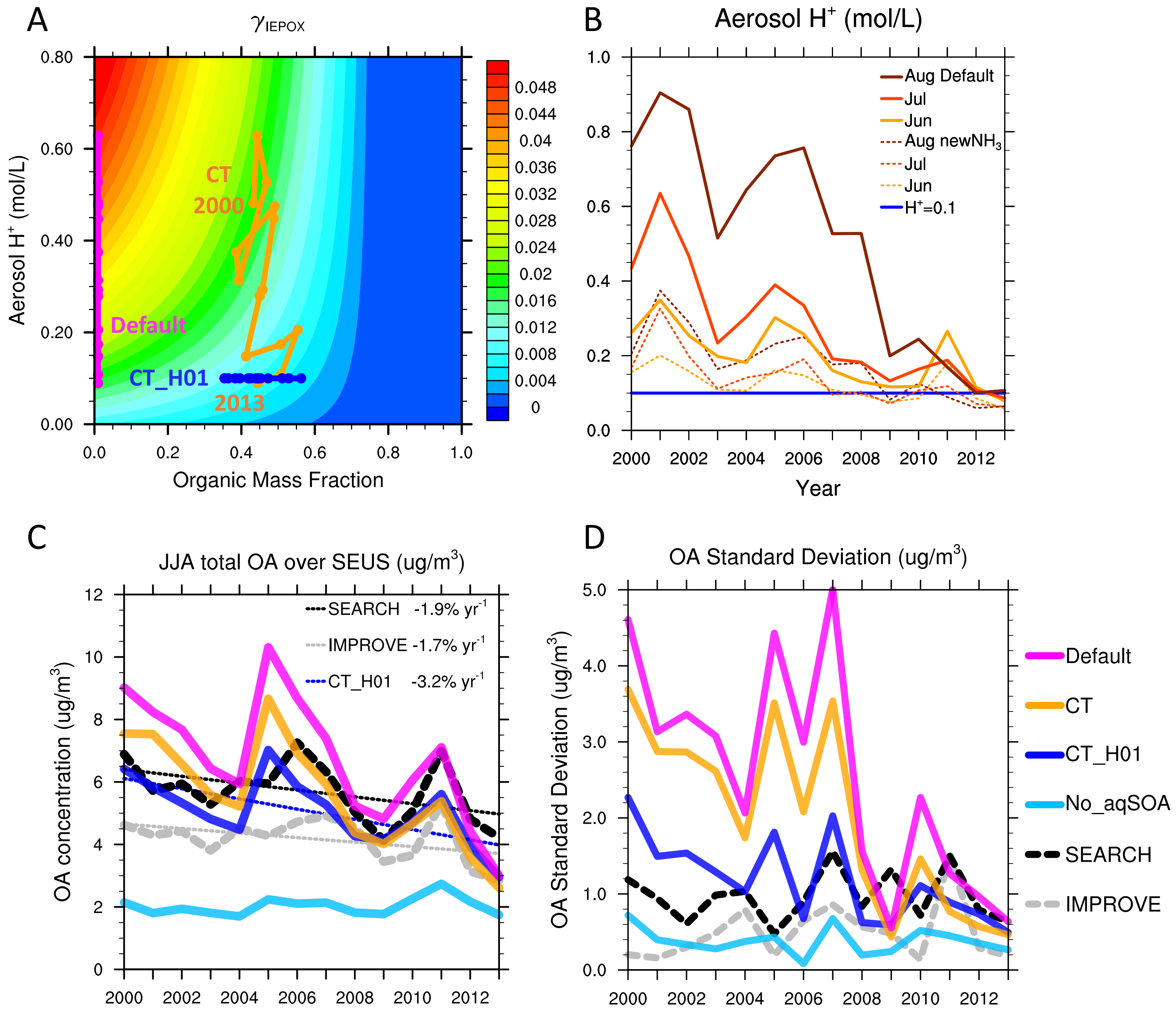

Figure 4. **(A)** Schematic diagram of IEPOX reactive uptake coefficient (γ_{IEPOX}). Colored lines indicate the position of JJA-averaged organic mass fraction and aerosol H^+ activity in 2000-2013 from the 'Default', 'CT' and 'CT_H01' simulations. **(B)** Simulated aerosol acidity (mol/L) from the default, 'CT_newNH$_3$' and 'CT_H01' simulations. **(C)** JJA-averaged surface OA (μg/m^3) from IMPROVE, SEARCH and all model simulations. **(D)** Standard deviation of OA (μg/m^3) between June, July and August from IMPROVE, SEARCH and all model simulations. All results are averaged over the southeast US.

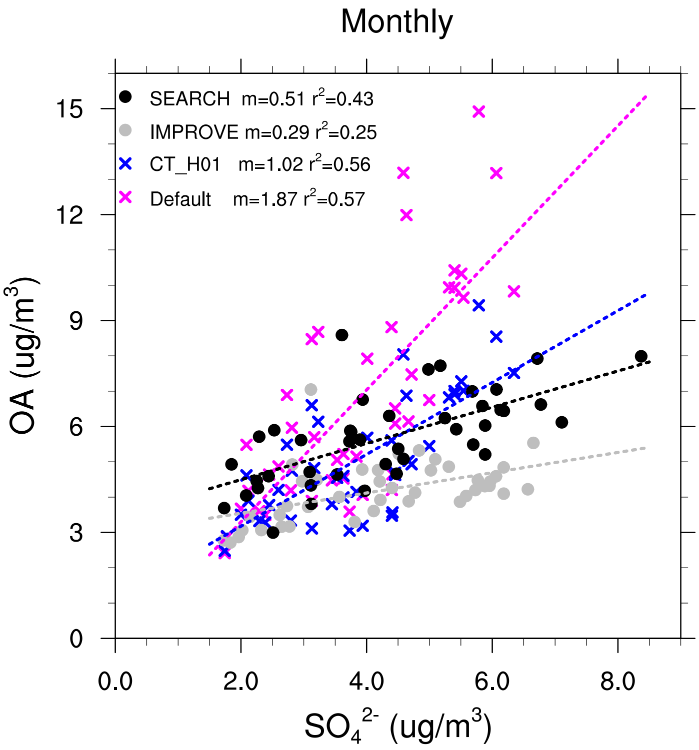

Figure 5. Relationships between monthly OA and sulfate concentrations (μg/m^3). Each dot represents monthly data averaged from all sites from each network within the southeast US.

Supplementary Information

Table S1. Multivariate linear regression analysis of modeled IEPOX-SOA. $\boldsymbol{\beta}_{1,}$ $\boldsymbol{\beta}_2$ and $\boldsymbol{\beta}_3$ are standardized partial regression coefficients associated with sulfate, aerosol H^+ activity and isoprene emission. R^2 represent the square of correlation between IEPOX-SOA and the linear-fitted function. The r_1^2, r_2^2 and r_3^2 within parentheses are square of direct correlation between IEPOX-SOA and each variable.

	Sulfate $\boldsymbol{\beta}_1$ **(r_1^2)**	**H^+ activity** $\boldsymbol{\beta}_2$ **(r_2^2)**	**ISOP emission** $\boldsymbol{\beta}_3$ **(r_3^2)**	**R^2**
2000-2013	0.39 (0.64)	0.50 (0.71)	0.34 (0.18)	0.88
2000-2004	0.46 (0.76)	0.43 (0.64)	0.25 (0.55)	0.93
2005-2008	0.34 (0.62)	0.57 (0.82)	0.31 (0.24)	0.94
2009-2013	0.45 (0.55)	0.27 (0.56)	0.42 (0.53)	0.84

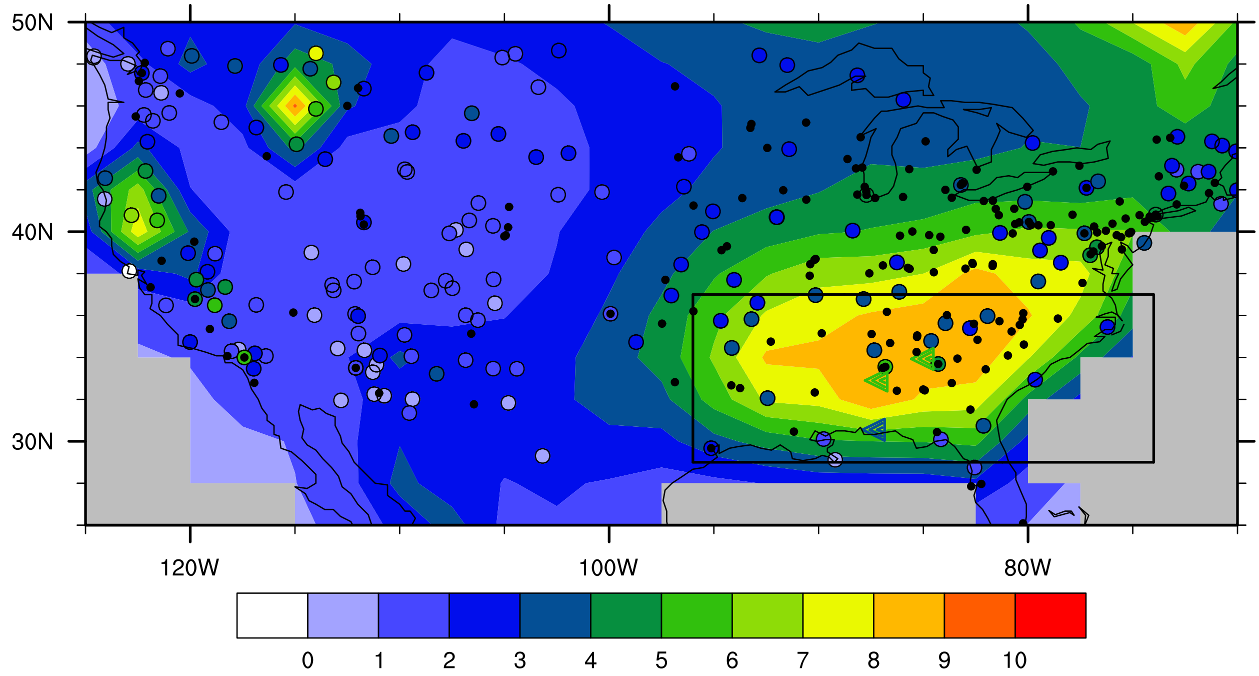

Figure S1. OA concentration (μg/m^3) averaged in JJA 2000-2013 from the default model and the IMPROVE and SEARCH networks. Rectangle defines the SEUS region. Circles and triangles represent sites from IMPROVE and SEARCH, respectively. Black dots represent the location of CSN sites, but due to the discontinuity of CSN organic carbon measurements, the 2000-2013 OA concentrations are not shown for CSN sites.

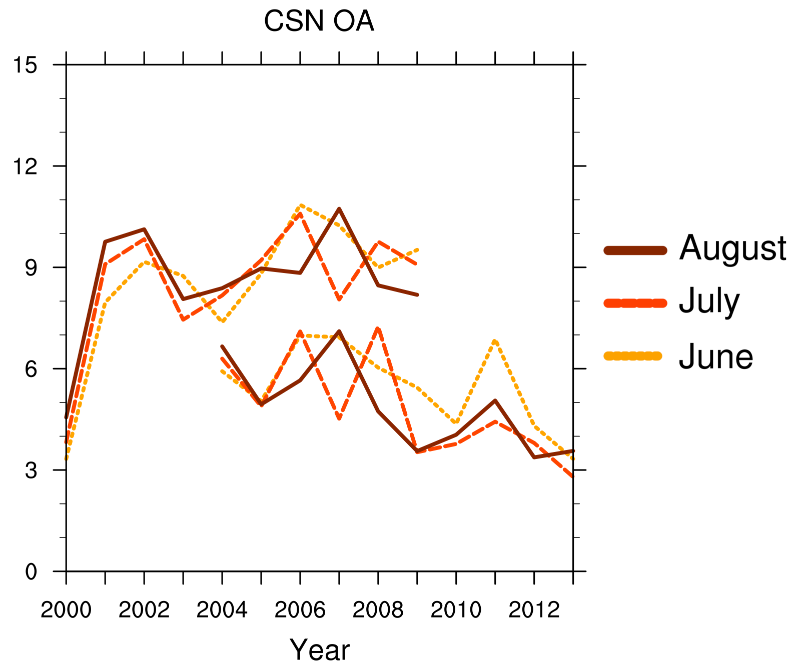

Figure S2. Monthly observed OA from the CSN networks. Units are μg/m^3.

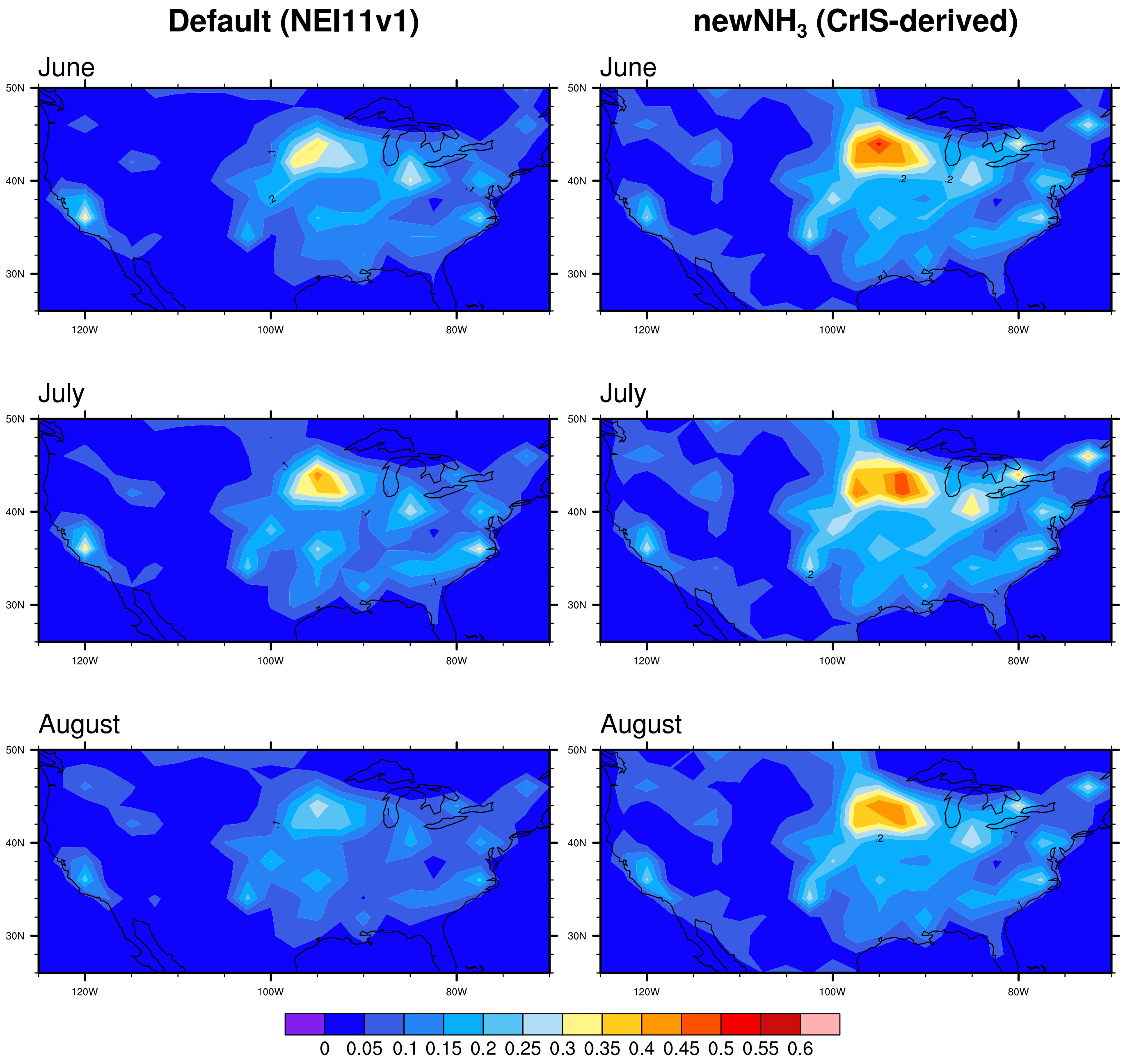

Figure S3. Monthly NH_3 emissions from the default NEI11v1 emission inventory and the CrIS-derived emission inventory used in the 'CT_NH_3' sensitivity simulation. Emissions are averaged in 2000-2013.

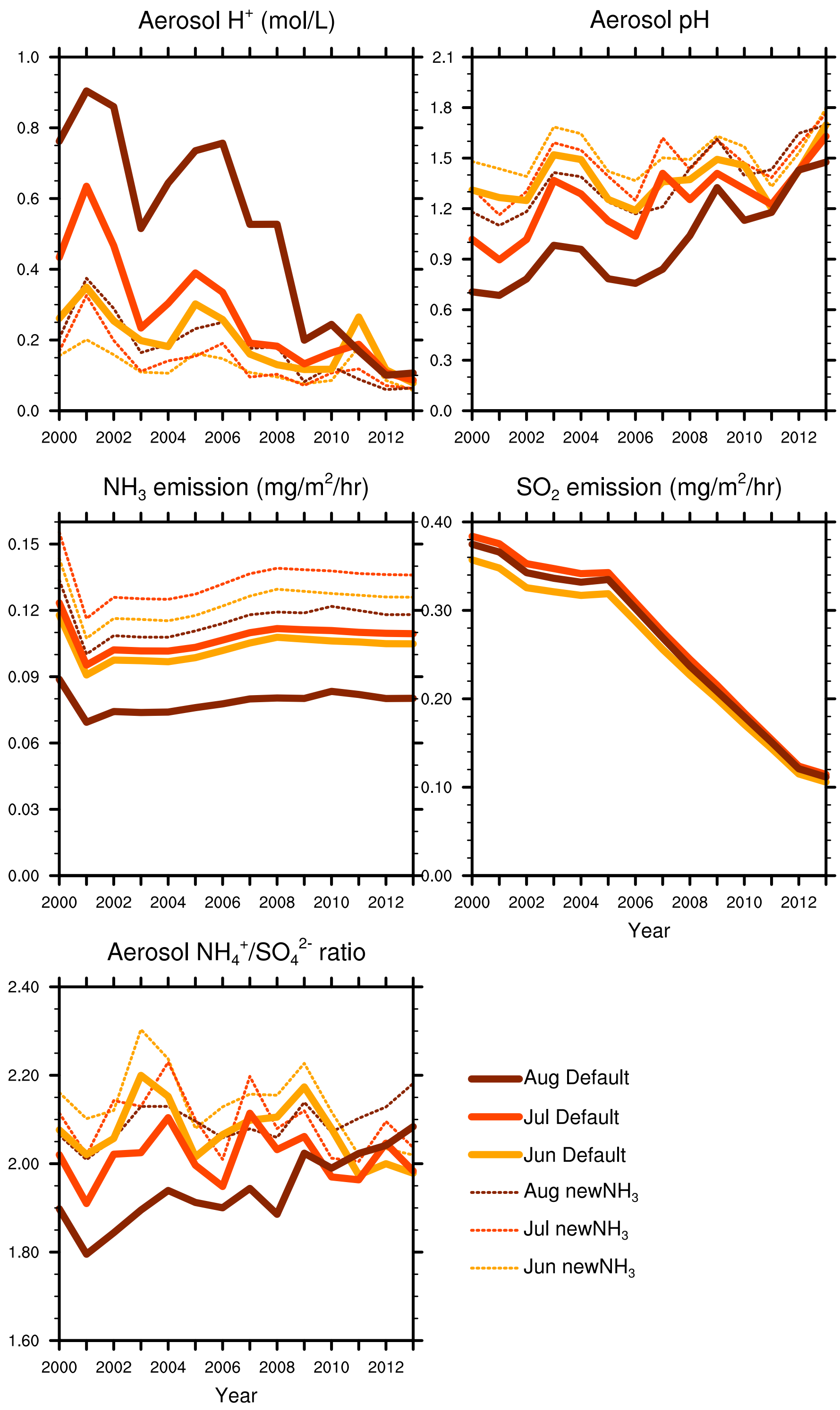

Figure S4. Monthly surface aerosol H^+ activity (mol/L), NH_3 emission, SO_2 emission (mg/m^2/hr) and aerosol NH_4^+/SO_4^{2-} ratio from the default and 'CT_newNH$_3$' simulations.

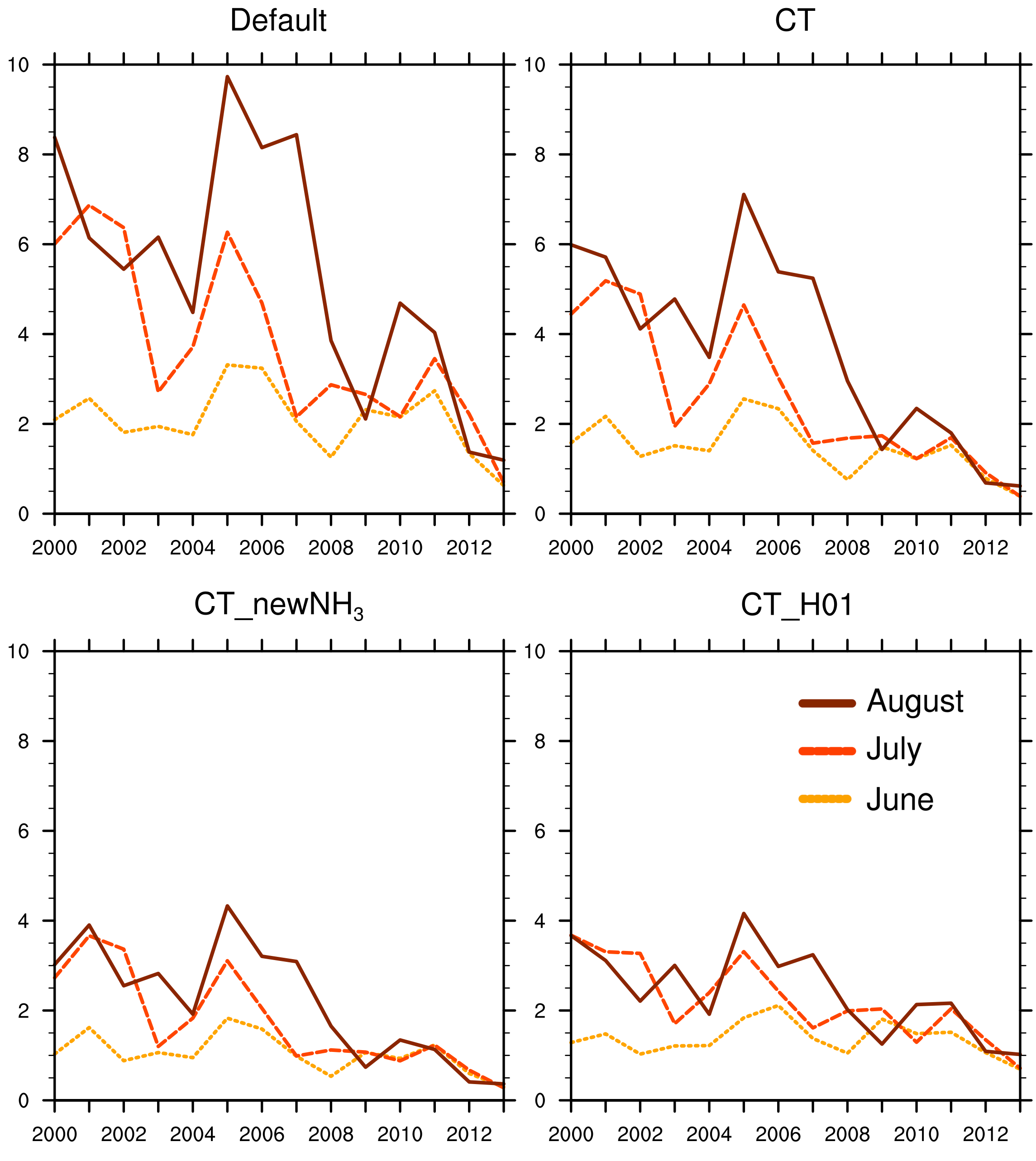

Figure S5. The monthly surface IEPOX-SOA concentration (μg/m^3) over the SEUS from all simulations.

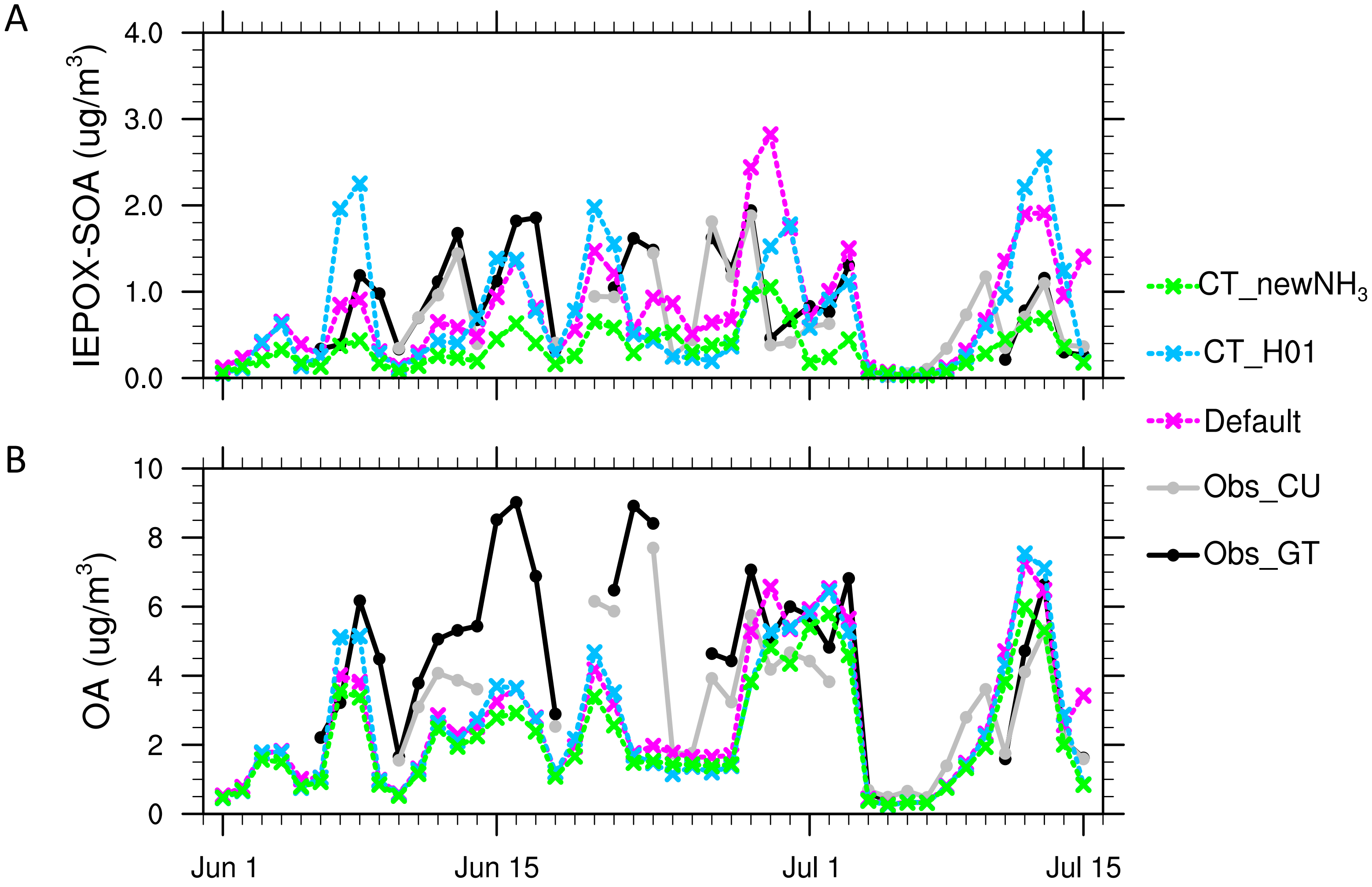

Figure S6. Comparison of **(A)** IEPOX-SOA, **(B)** OA between AMS measurement and the default and CT_H01 simulations in the SOAS campaign from June 01 to July 15, 2013. In (A), IEPOX-SOA is obtained by a Positive Matrix Factorization (PMF) analysis of the AMS-measured OA. Units are µg/m^3.