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 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)."

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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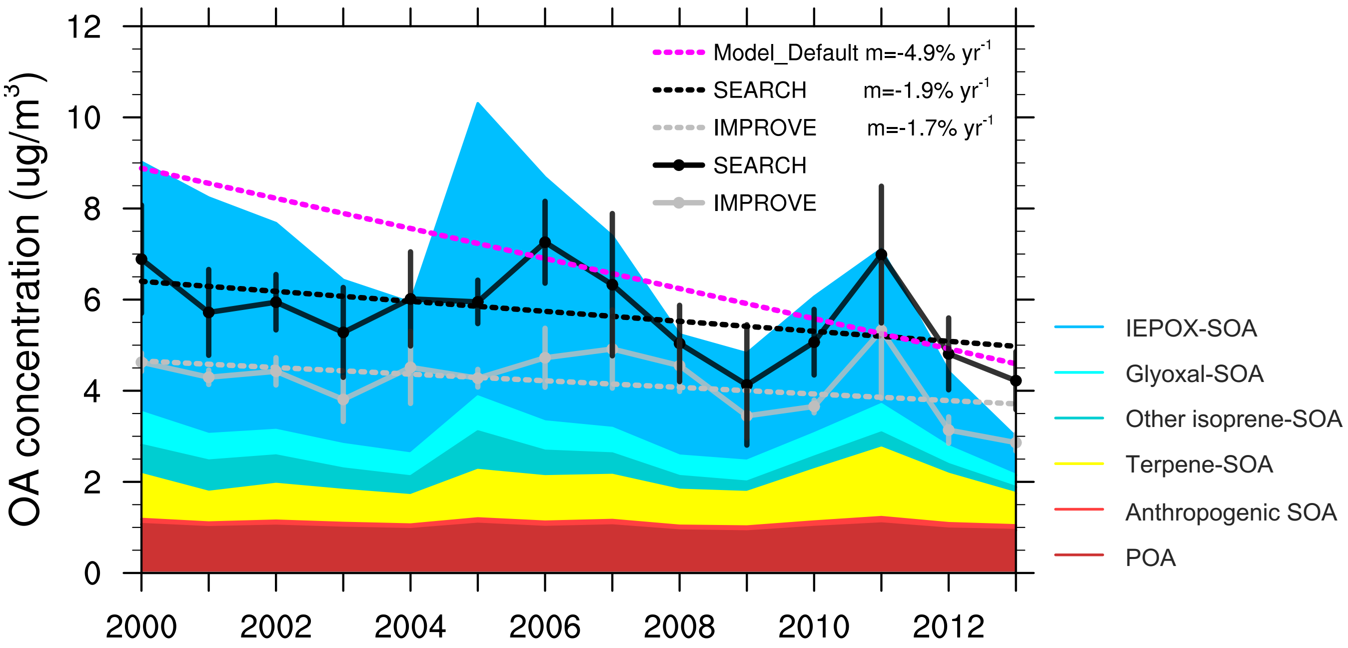

Figure 1. Comparison of June-July-August averaged surface OA concentration (μg/m^3) over the southeast US between the default model and the observation from IMPROVE and SEARCH network. Colored shades represent different components of modeled OA. IEPOX-, glyoxal-, and other isoprene-SOA are from aqueous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

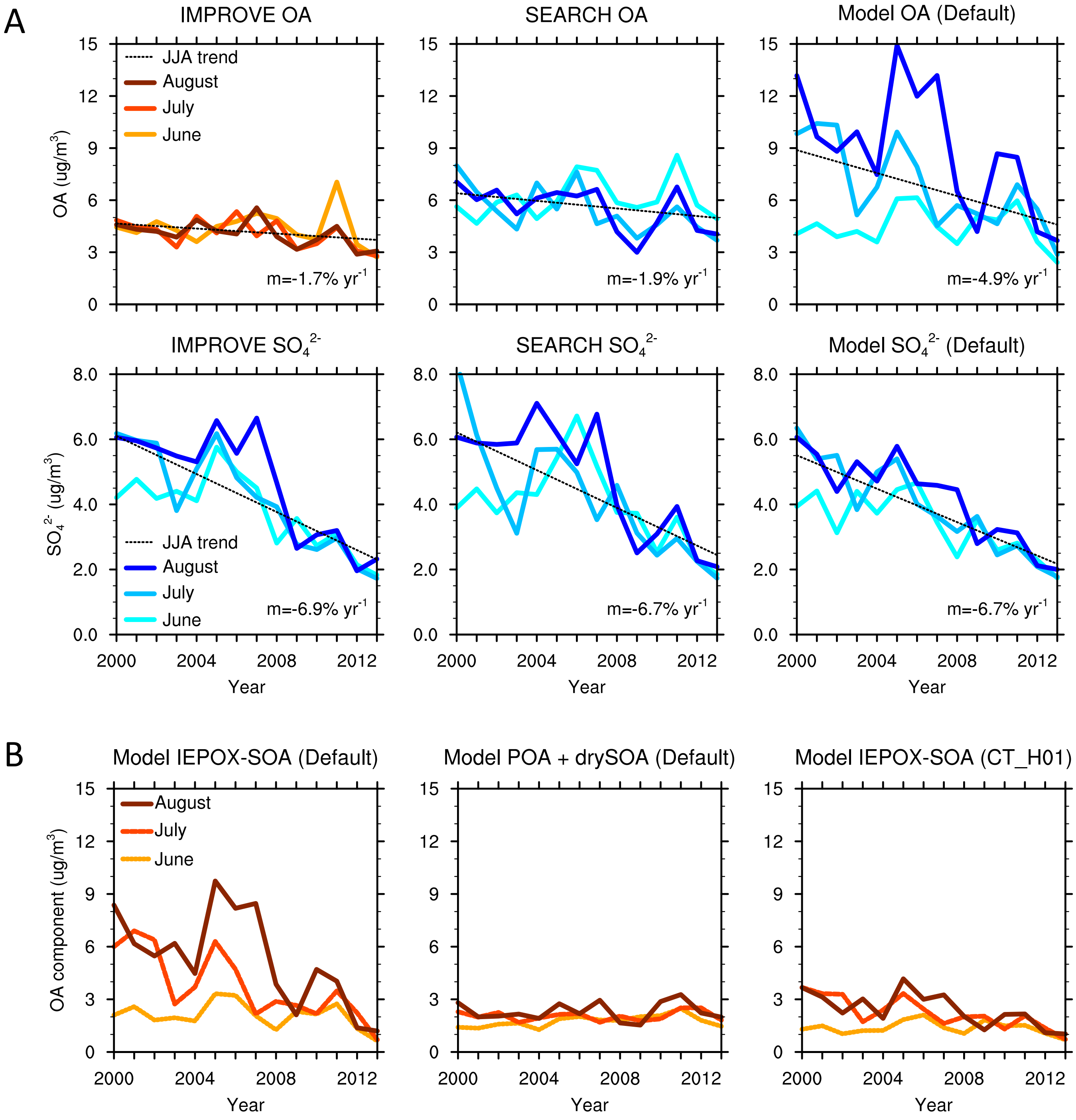

Figure 2. (A) Monthly surface OA and sulfate (SO_4^{2-}) concentration (μg/m^3) averaged over the southeast US from IMPROVE, SEARCH and the default model. **(B)** Monthly surface concentrations of IEPOX-SOA and the sum of POA and dry SOA from the default model, and IEPOX-SOA from the CT_H01 simulation.

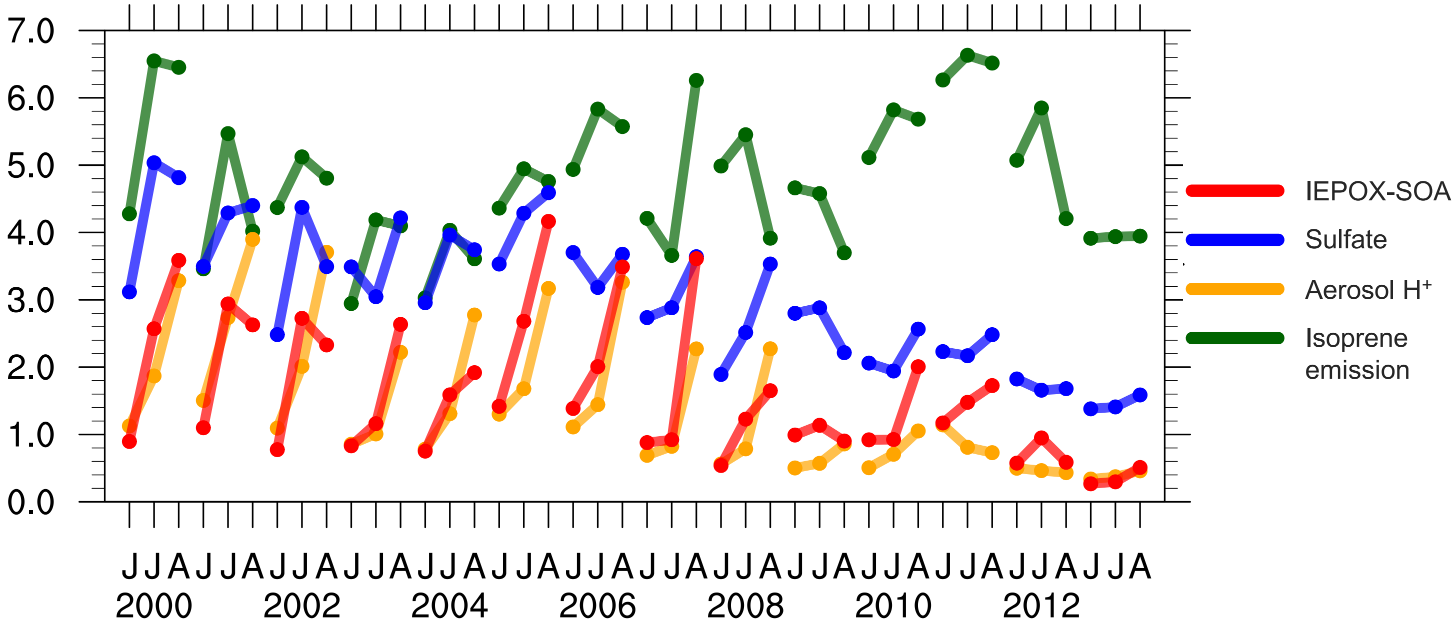

Figure 3. Standardized monthly surface IEPOX-SOA concentration, sulfate concentration, aerosol H^+ activity and isoprene emission from the default model. All variables are averaged over the southeast US, and have been divided by 1 standard deviations, therefore are unitless.

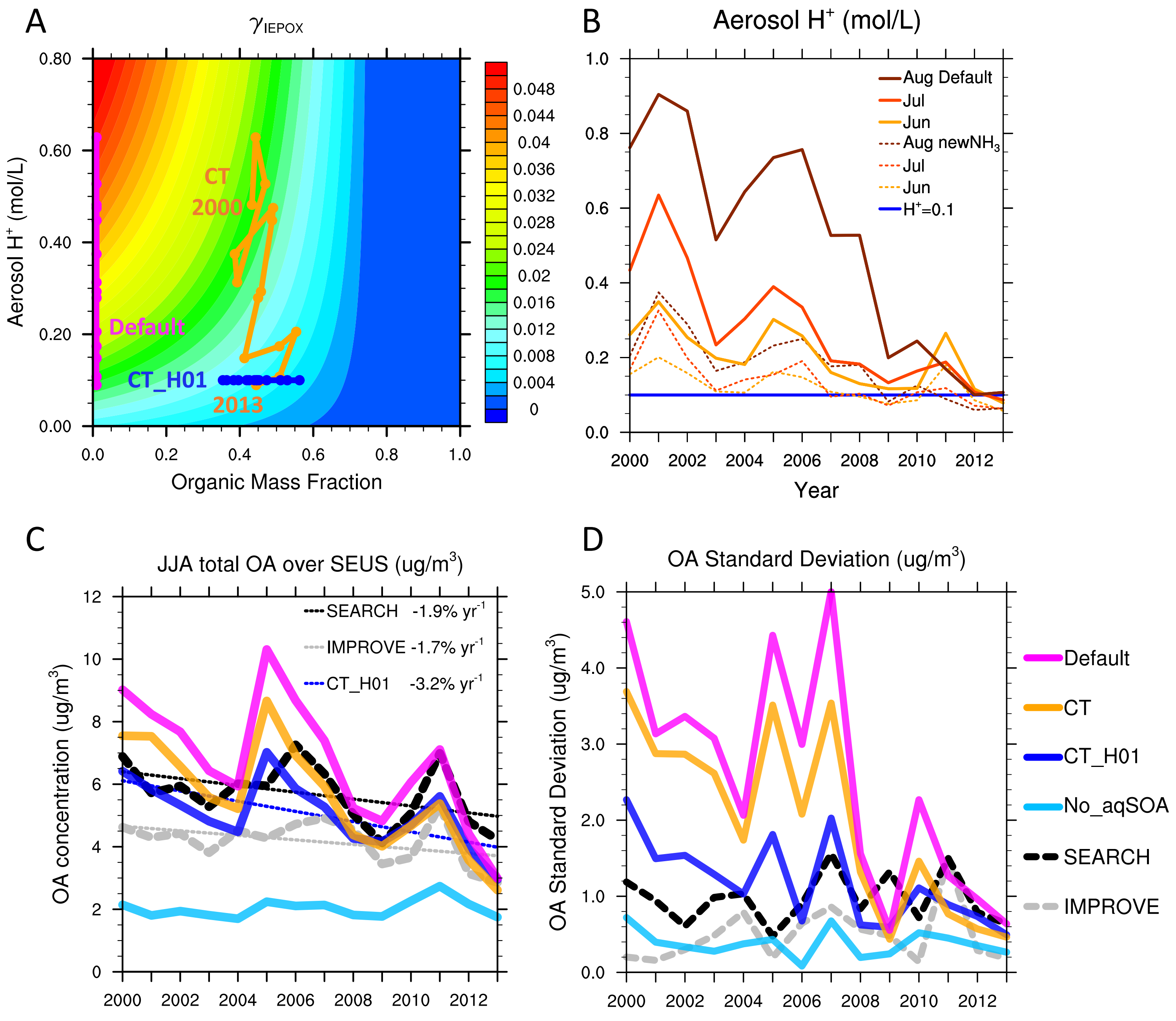

Figure 4. **(A)** Schematic diagram of IEPOX reactive uptake coefficient (γ_{IEPOX}). Colored lines indicate the position of JJA-averaged organic mass fraction and aerosol H^+ activity in 2000-2013 from the 'Default', 'CT' and 'CT_H01' simulations. **(B)** Simulated aerosol acidity (mol/L) from the default, '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.

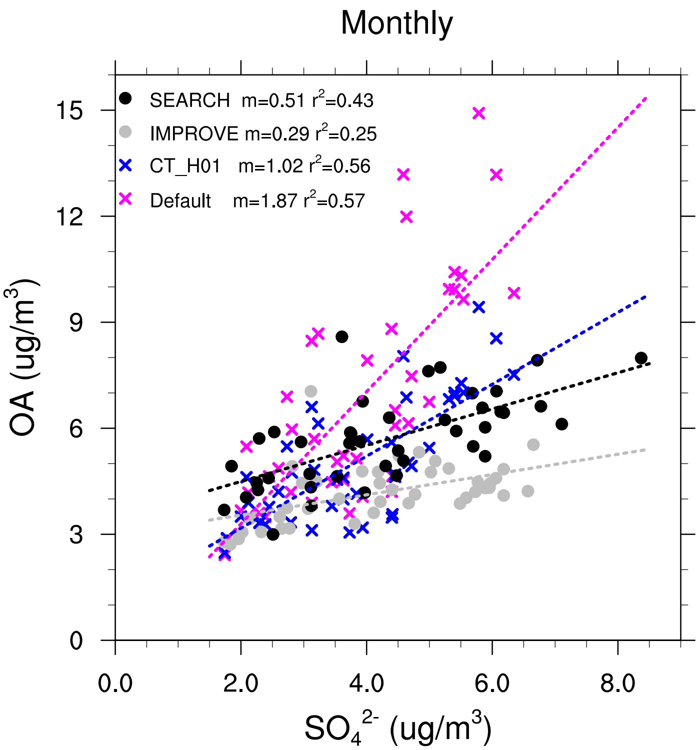

Figure 5. Relationships between monthly OA and sulfate concentrations (µg/m^3). Each dot represents monthly data averaged from all sites from each network within the southeast US.

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

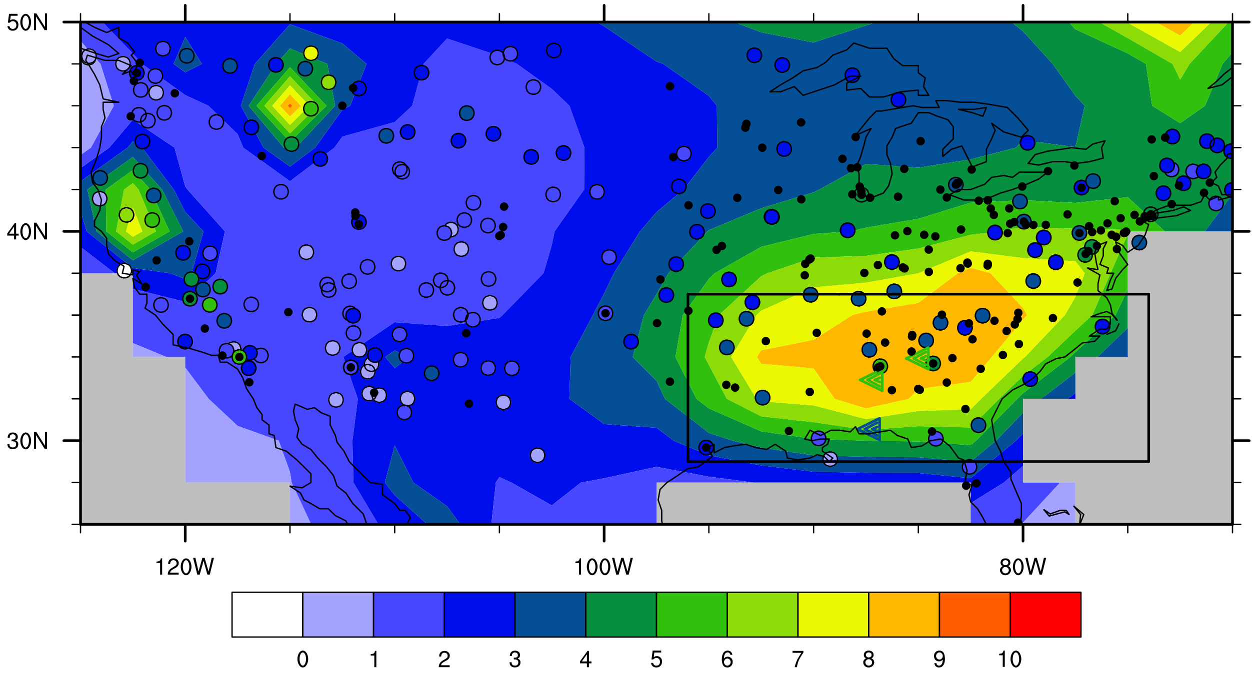

Figure S1. OA concentration (µg/m^3) averaged in JJA 2000-2013 from the default model and the IMPROVE and SEARCH networks. Rectangle defines the SEUS region. Circles and triangles represent sites from IMPROVE and SEARCH, respectively. Black dots represent the location of CSN sites, but due to the discontinuity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

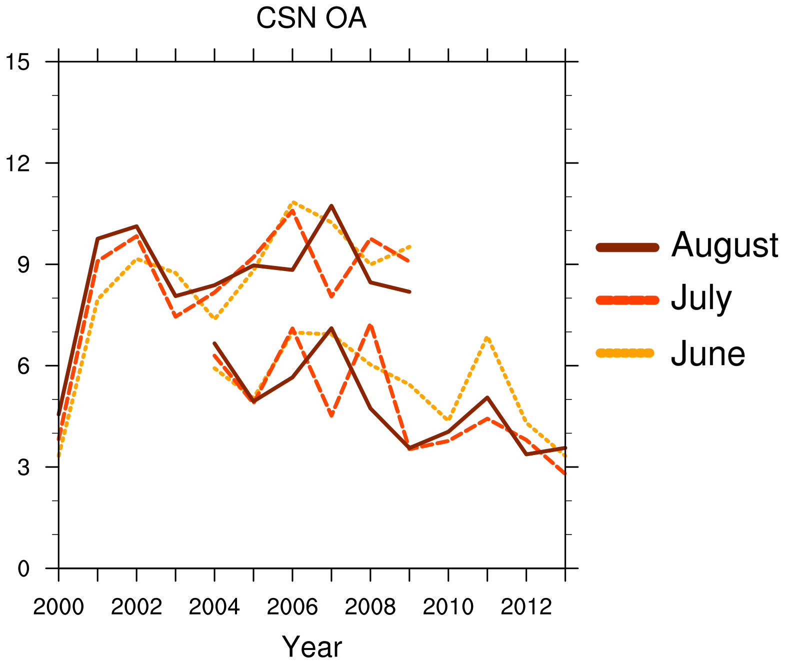

Figure S2. Monthly observed OA from the CSN networks. Units are μg/m^3.

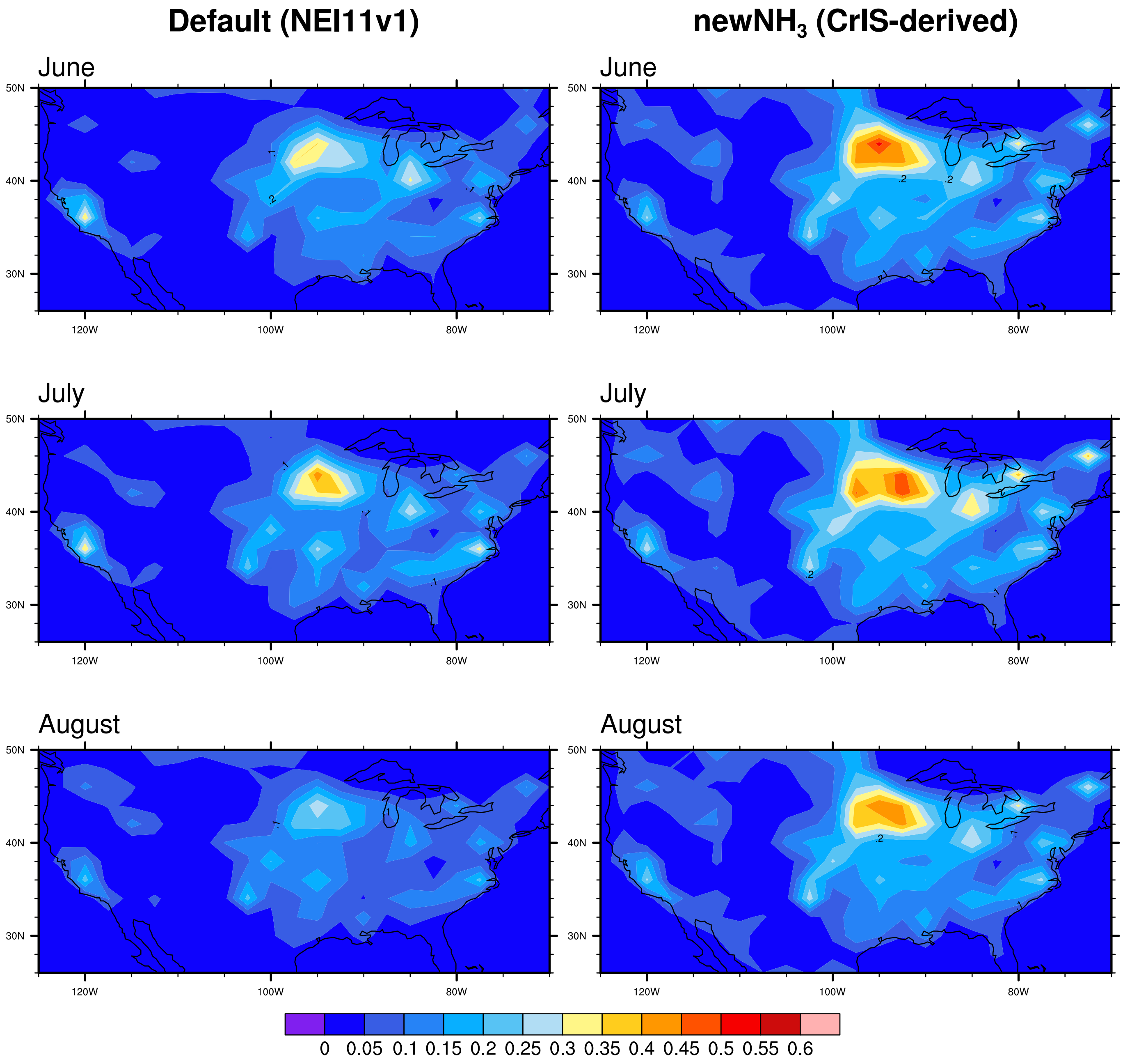

Figure S3. Monthly NH_3 emissions from the default NEI11v1 emission inventory and the CrIS-derived emission inventory used in the 'CT_NH_3' sensitivity simulation. Emissions are averaged in 2000-2013.

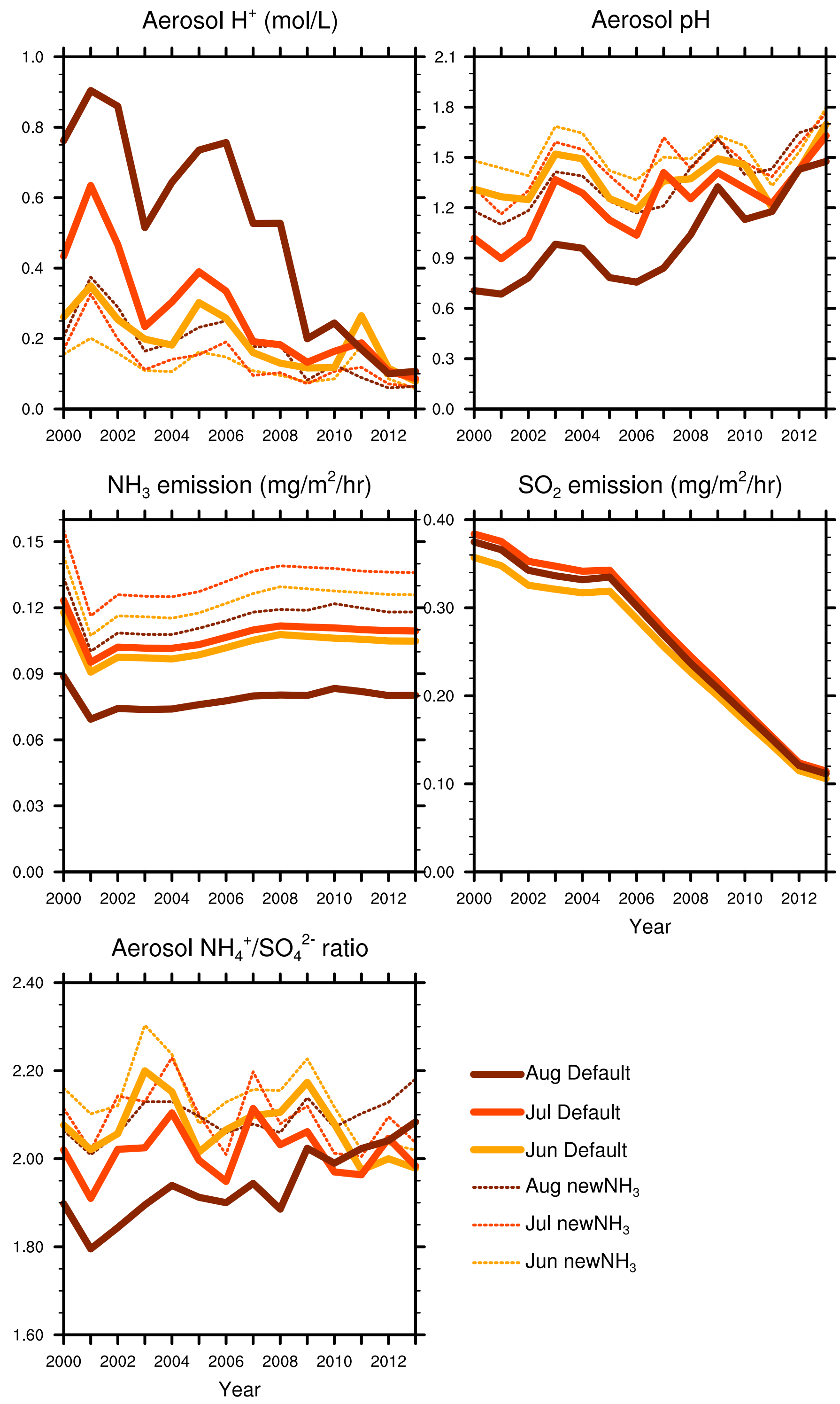

Figure S4. Monthly surface aerosol H^+ activity (mol/L), NH_3 emission, SO_2 emission (mg/m^2/hr) and aerosol NH_4^+/SO_4^{2-} ratio from the default and 'CT_newNH$_3$' simulations.

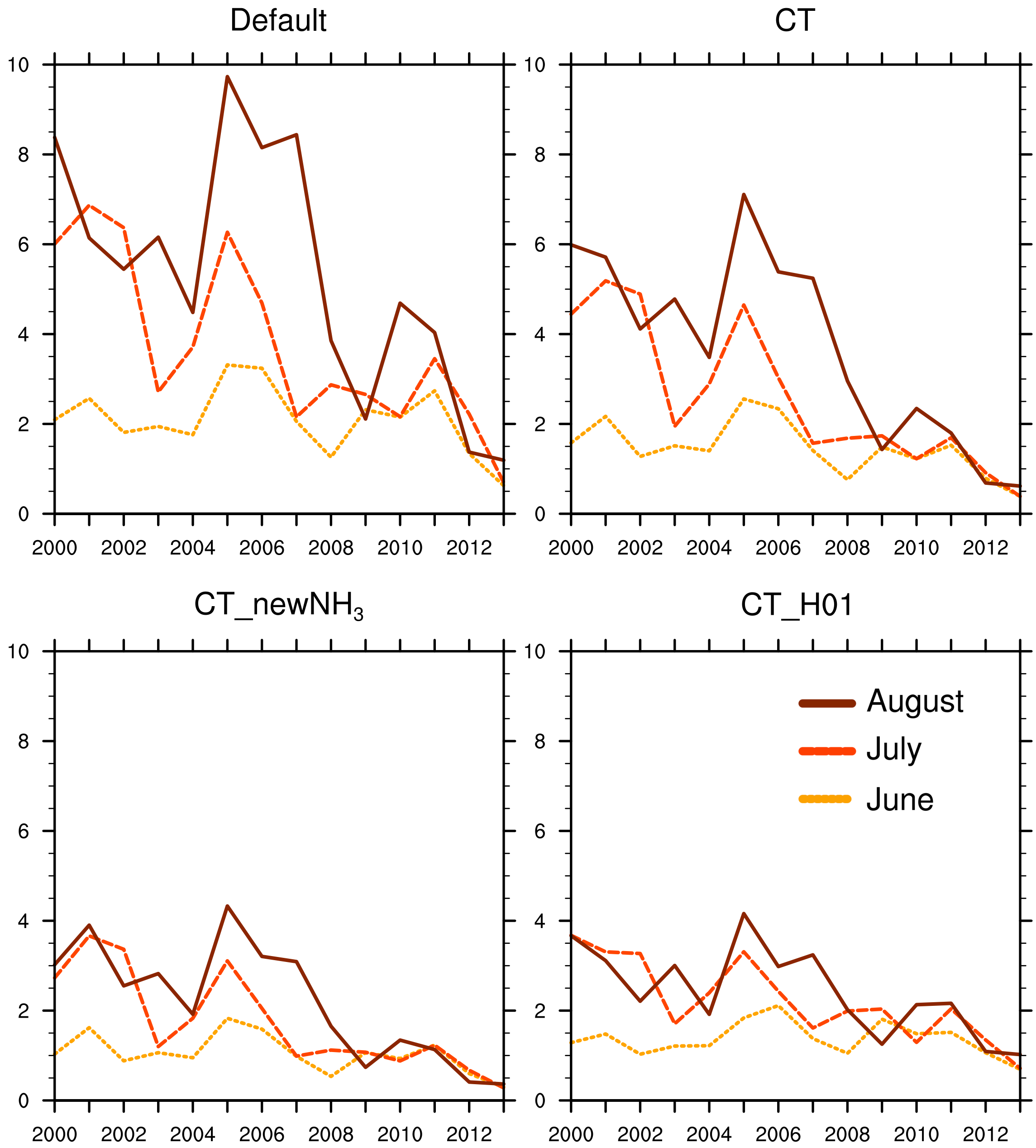

Figure S5. The monthly surface IEPOX-SOA concentration (μg/m^3) over the SEUS from all simulations.

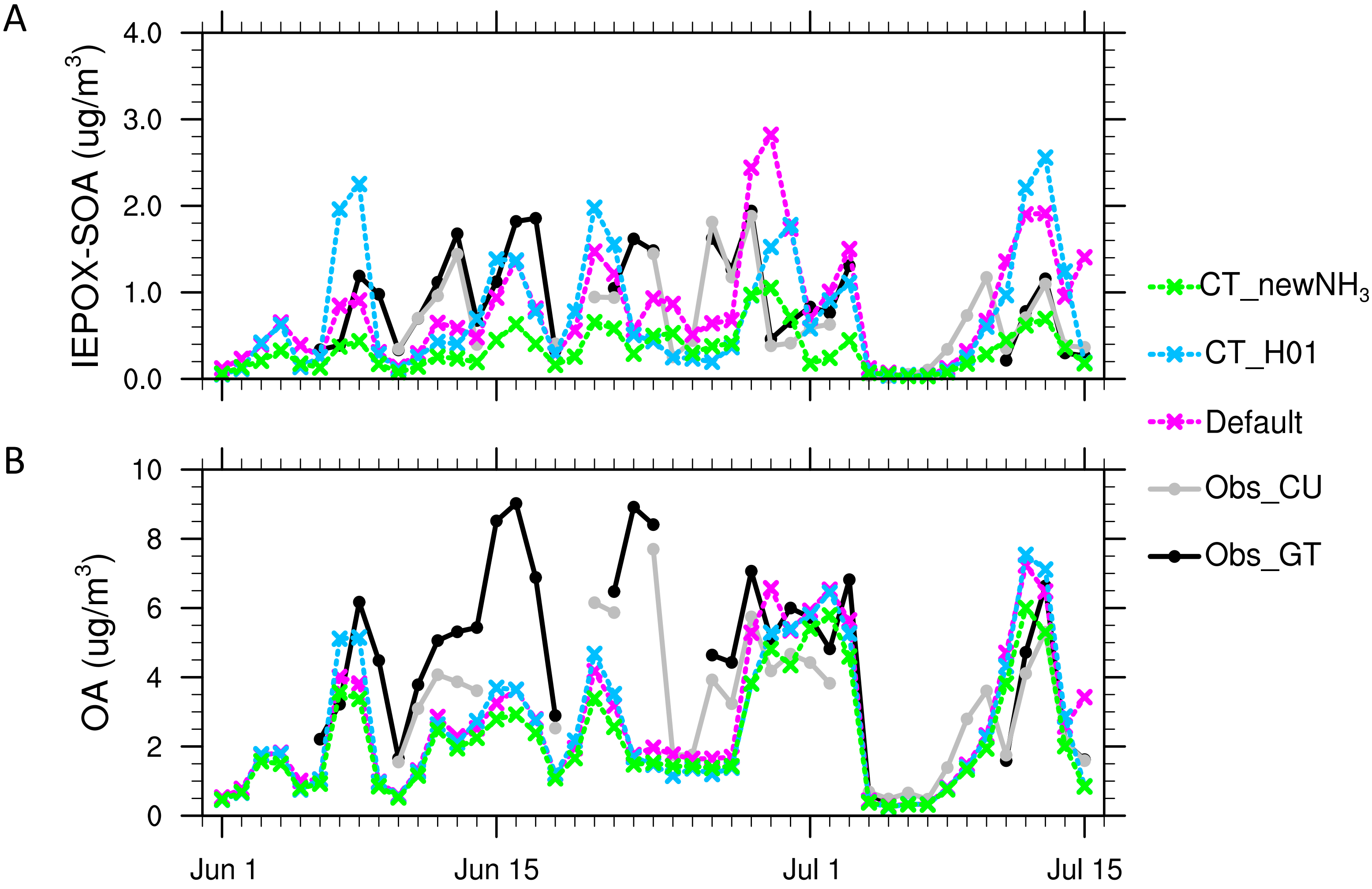

Figure S6. Comparison of **(A)** IEPOX-SOA, **(B)** OA between AMS measurement and the default and CT_H01 simulations in the SOAS campaign from June 01 to July 15, 2013. In (A), IEPOX-SOA is obtained by a Positive Matrix Factorization (PMF) analysis of the AMS-measured OA. Units are µg/m^3.