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)."

References:

Budisulistiorini, S. H. et al. Seasonal characterization of submicron aerosol composition and organic aerosol sources in the southeastern United States: Atlanta, Georgia,and Look Rock, Tennessee. Atmos. Chem. Phys. 16, 5171-5189, doi:10.5194/acp-16-5171-2016 (2016).

Budisulistiorini, S. H. et al. Simulating Aqueous-Phase Isoprene-Epoxydiol (IEPOX) Secondary Organic Aerosol Production During the 2013 Southern Oxidant and Aerosol Study (SOAS). Environ. Sci. Technol. 51, 5026-5034, doi:10.1021/acs.est.6b05750 (2017).

Li, Y., Day, D. A., Stark, H., Jimenez, J. L. & Shiraiwa, M. Predictions of the glass transition temperature and viscosity of organic aerosols from volatility distributions. Atmos. Chem. Phys. 20, 8103-8122, doi:10.5194/acp-20-8103-2020 (2020).

Pye, H. O. T. et al. On the implications of aerosol liquid water and phase separation for organic aerosol mass. Atmos. Chem. Phys. 17, 343-369, doi:10.5194/acp17-343-2017 (2017).

Schmedding, R. et al. α-Pinene-Derived organic coatings on acidic sulfate aerosol impacts secondary organic aerosol formation from isoprene in a box model. Atmos. Environ., 456-462, doi:https://doi.org/10.1016/j.atmosenv.2019.06.005 (2019).

Jo, D. S. et al. A simplified parameterization of isoprene-epoxydiol-derived secondary organic aerosol (IEPOX-SOA) for global chemistry and climate models: a case study with GEOS-Chem v11-02-rc. Geosci. Model Dev. 12, 2983-3000, doi:10.5194/gmd12-2983-2019 (2019).

Woo, J. L. & McNeill, V. F. simpleGAMMA v1.0 – a reduced model of secondary organic aerosol formation in the aqueous aerosol phase (aaSOA). Geosci. Model Dev. 8, 1821- 1829, doi:10.5194/gmd-8-1821-2015 (2015).

Xu, L. et al. Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States. Proc. Natl. Acad. Sci. USA 112, 37-42, doi:10.1073/pnas.1417609112 (2015).

Zhang, Y. et al. Effect of Aerosol-Phase State on Secondary Organic Aerosol Formation from the Reactive Uptake of Isoprene-Derived Epoxydiols (IEPOX). Environ. Sci. Technol. Lett. 5, 167-174, doi:10.1021/acs.estlett.8b00044 (2018).

Zhang, Y. et al. Joint Impacts of Acidity and Viscosity on the Formation of Secondary Organic Aerosol from Isoprene Epoxydiols (IEPOX) in Phase Separated Particles. ACS Earth and Space Chemistry 3, 2646-2658, doi:10.1021/acsearthspacechem.9b00209 (2019).

Zhang, Y. et al. The Cooling Rate- and Volatility-Dependent Glass-Forming Properties of Organic Aerosols Measured by Broadband Dielectric Spectroscopy. Environ. Sci. Technol. 53, 12366-12378, doi:10.1021/acs.est.9b03317 (2019).

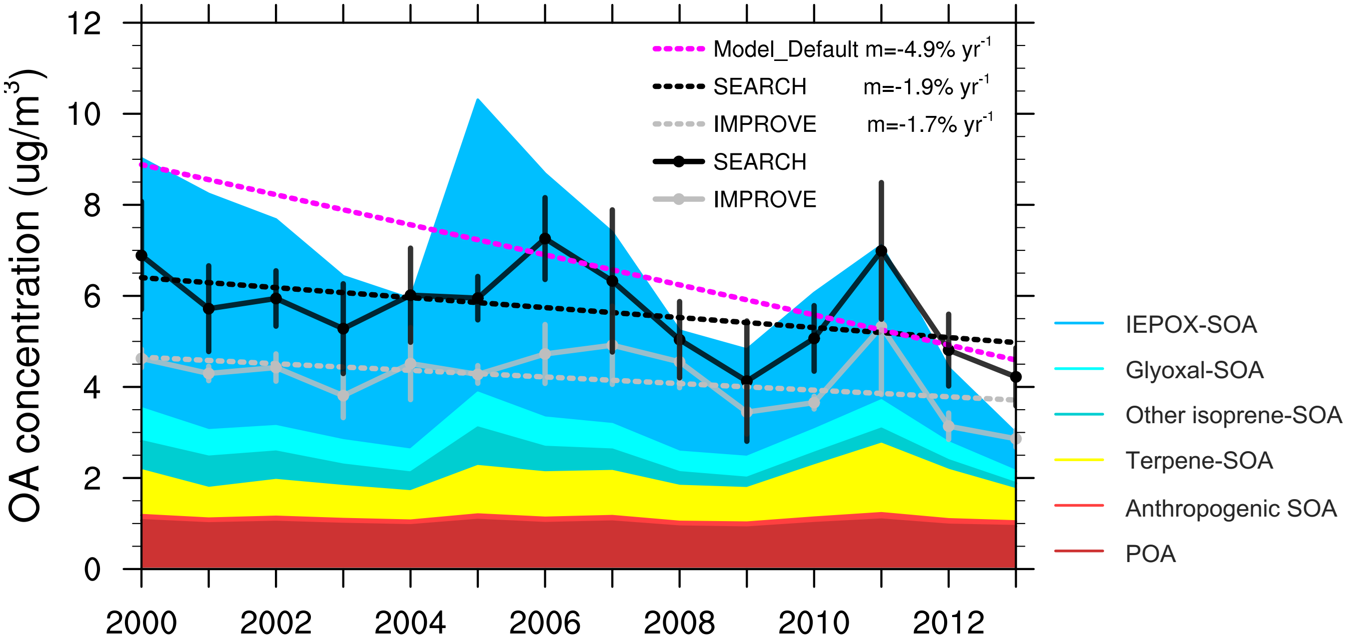

Figure 1. Comparison of June-July-August averaged surface OA concentration (μg/m^3) over the southeast US between the default model and the observation from IMPROVE and SEARCH network. Colored shades represent different components of modeled OA. IEPOX-, glyoxal-, and other isoprene-SOA are from aqueous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

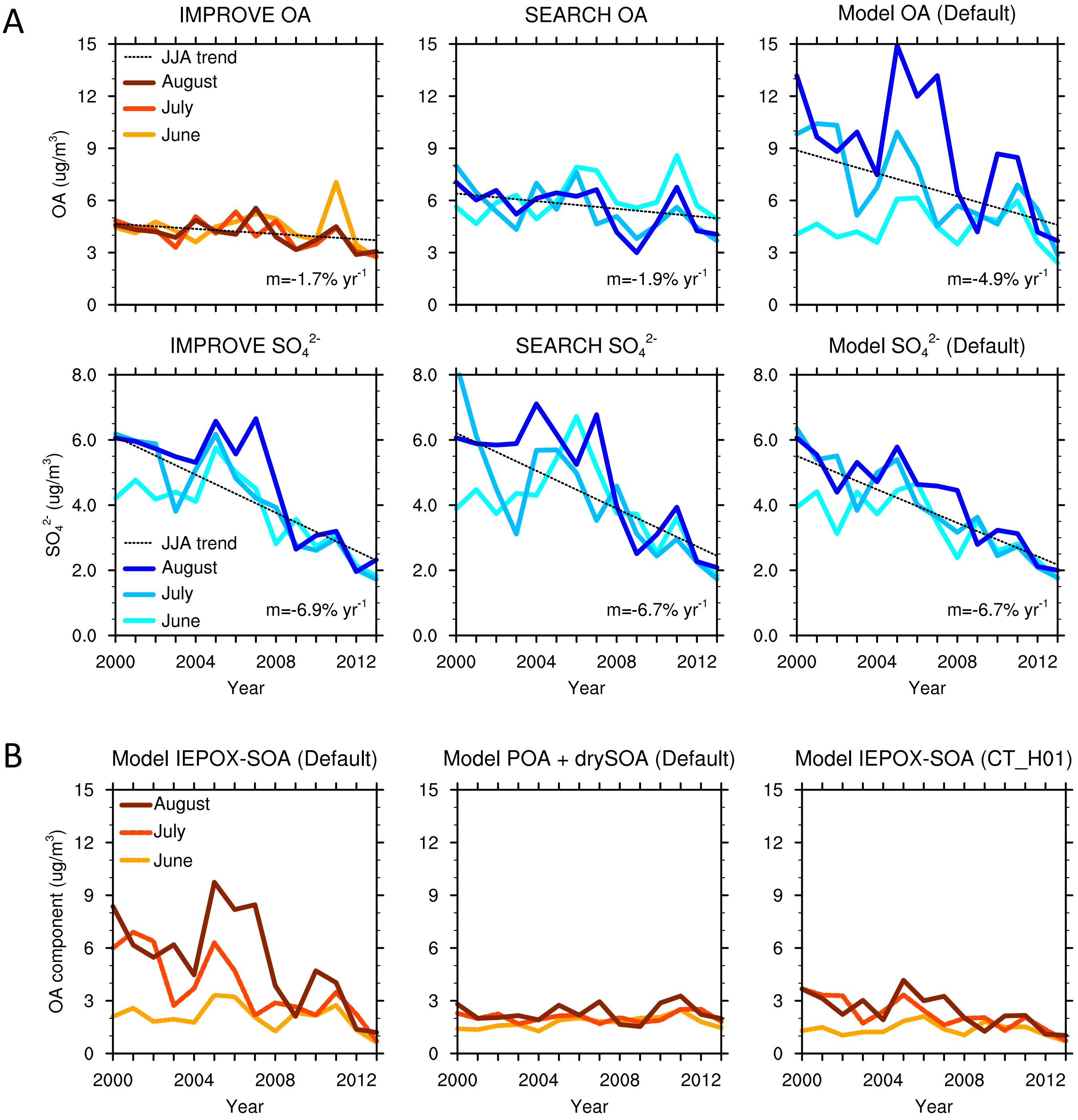

Figure 2. (A) Monthly surface OA and sulfate (SO_4^{2-}) concentration (μg/m^3) averaged over the southeast US from IMPROVE, SEARCH and the default model. **(B)** Monthly surface concentrations of IEPOX-SOA and the sum of POA and dry SOA from the default model, and IEPOX-SOA from the CT_H01 simulation.

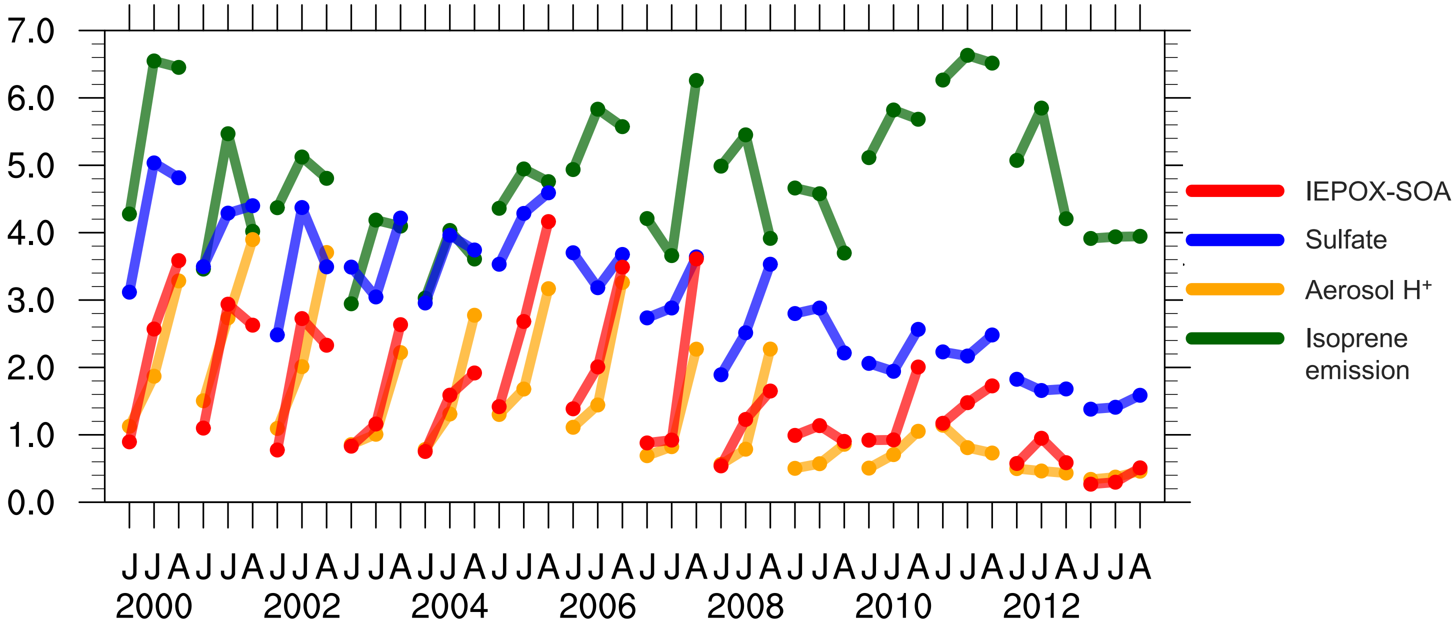

Figure 3. Standardized monthly surface IEPOX-SOA concentration, sulfate concentration, aerosol H^+ activity and isoprene emission from the default model. All variables are averaged over the southeast US, and have been divided by 1 standard deviations, therefore are unitless.

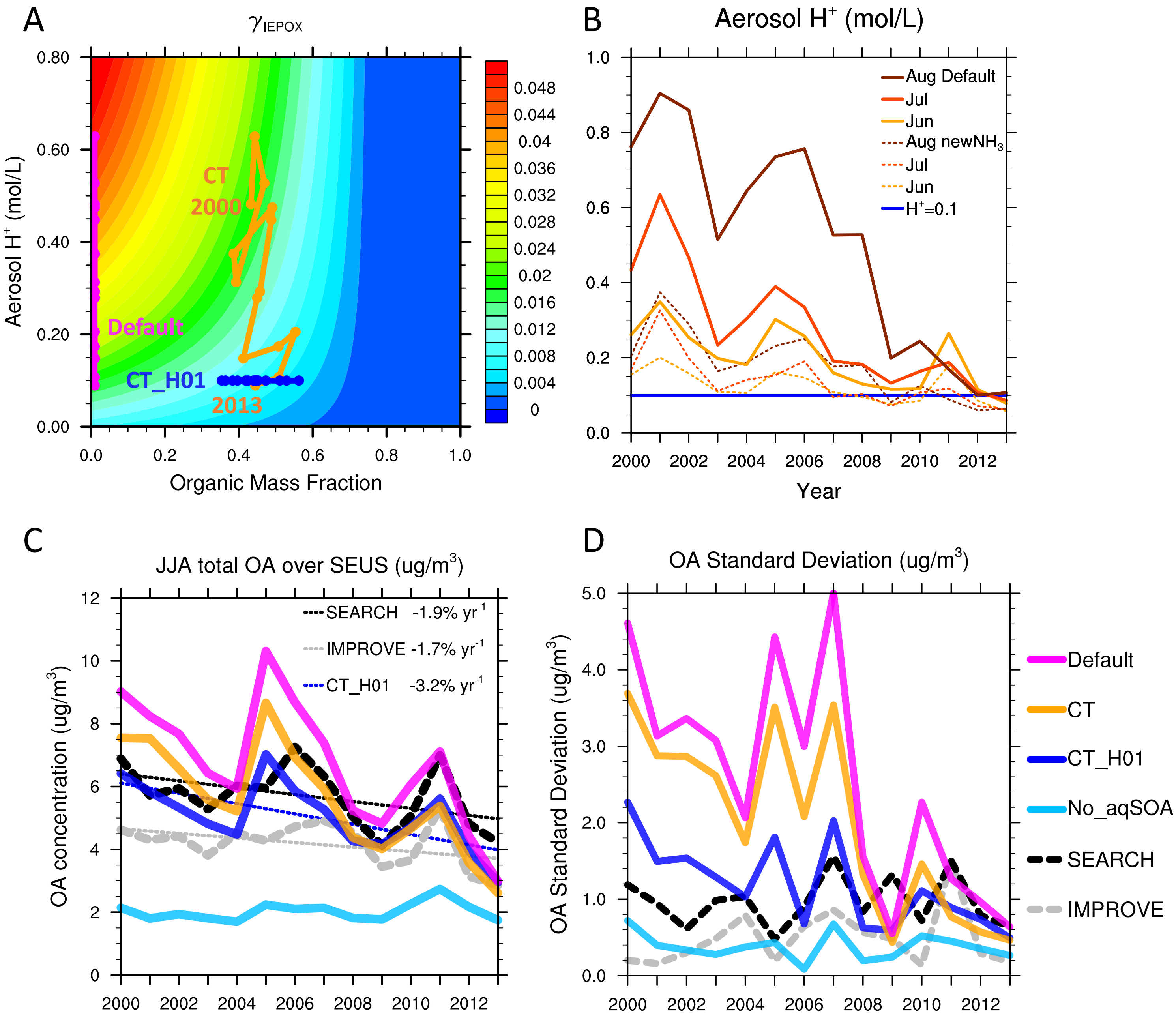

Figure 4. **(A)** Schematic diagram of IEPOX reactive uptake coefficient (γ_{IEPOX}). Colored lines indicate the position of JJA-averaged organic mass fraction and aerosol H^+ activity in 2000-2013 from the 'Default', 'CT' and 'CT_H01' simulations. **(B)** Simulated aerosol acidity (mol/L) from the default,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

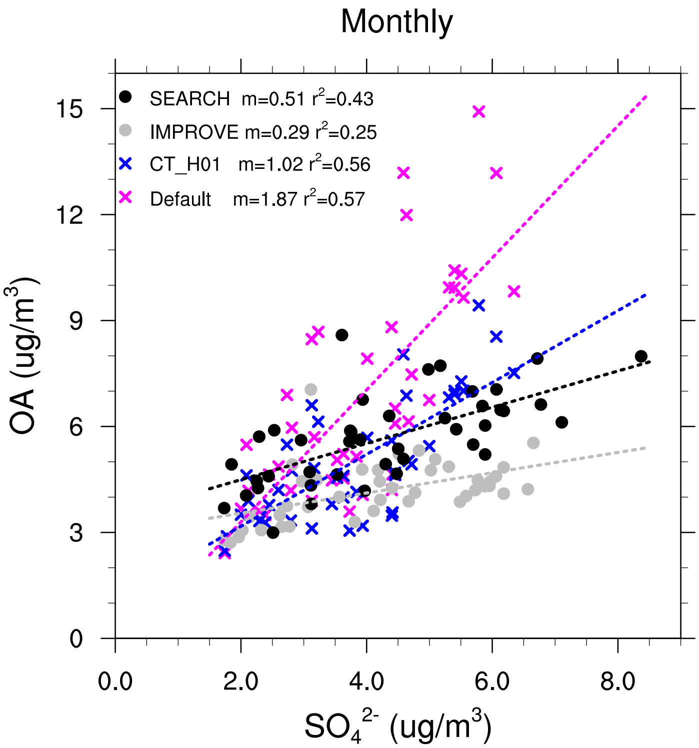

Figure 5. Relationships between monthly OA and sulfate concentrations (μg/m^3). Each dot represents monthly data averaged from all sites from each network within the southeast US.

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

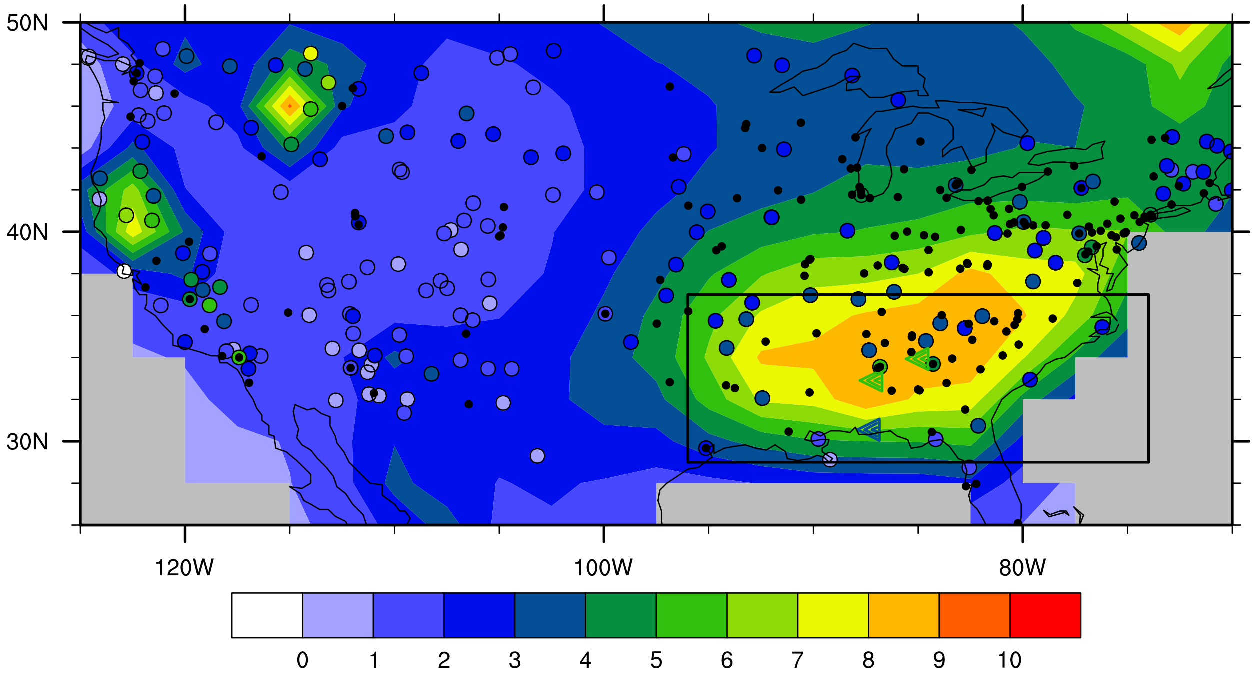

Figure S1. OA concentration ($\mu g/m^3$) averaged in JJA 2000-2013 from the default model and the IMPROVE and SEARCH networks. Rectangle defines the SEUS region. Circles and triangles represent sites from IMPROVE and SEARCH, respectively. Black dots represent the location of CSN sites, but due to the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

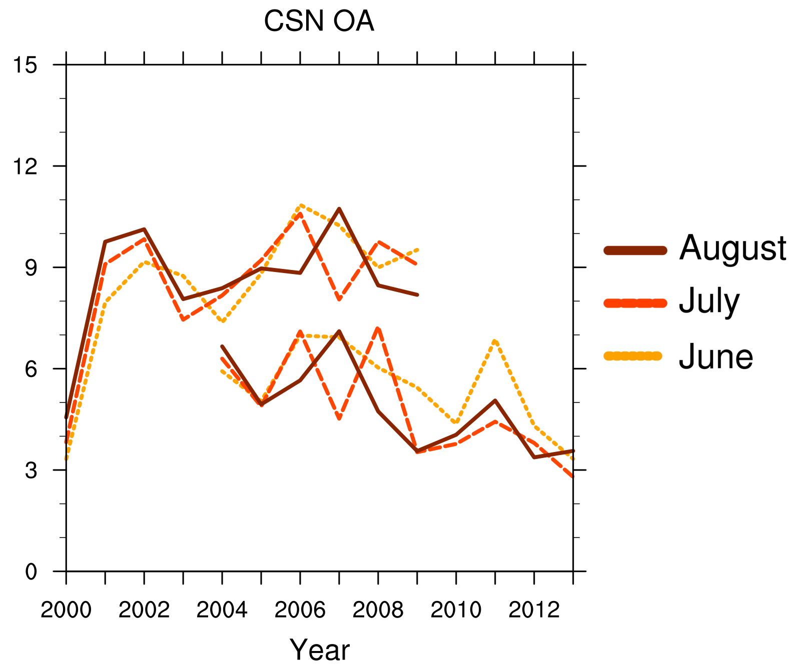

Figure S2. Monthly observed OA from the CSN networks. Units are μg/m^3.

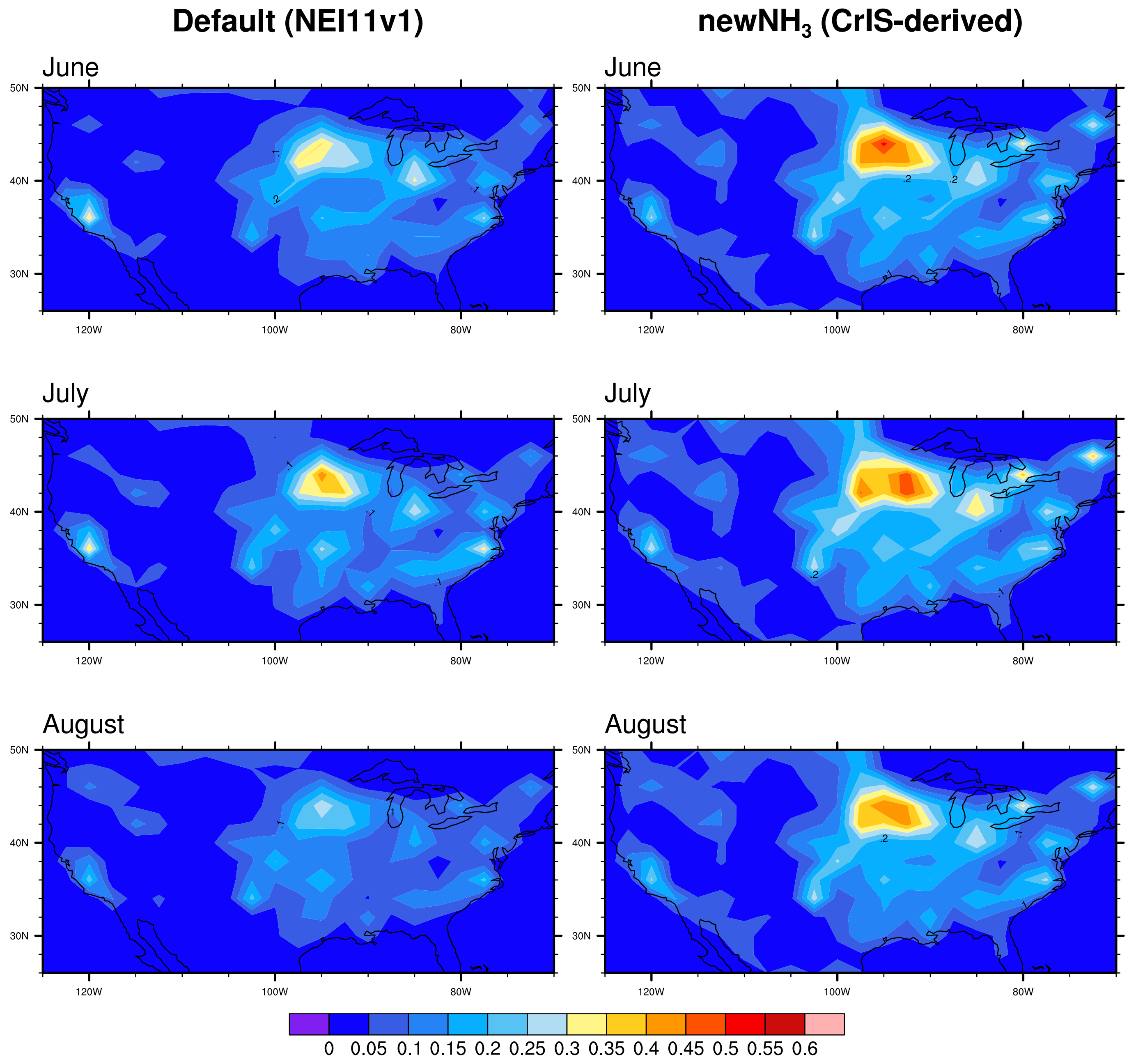

Figure S3. Monthly NH_3 emissions from the default NEI11v1 emission inventory and the CrIS-derived emission inventory used in the 'CT_NH_3' sensitivity simulation. Emissions are averaged in 2000-2013.

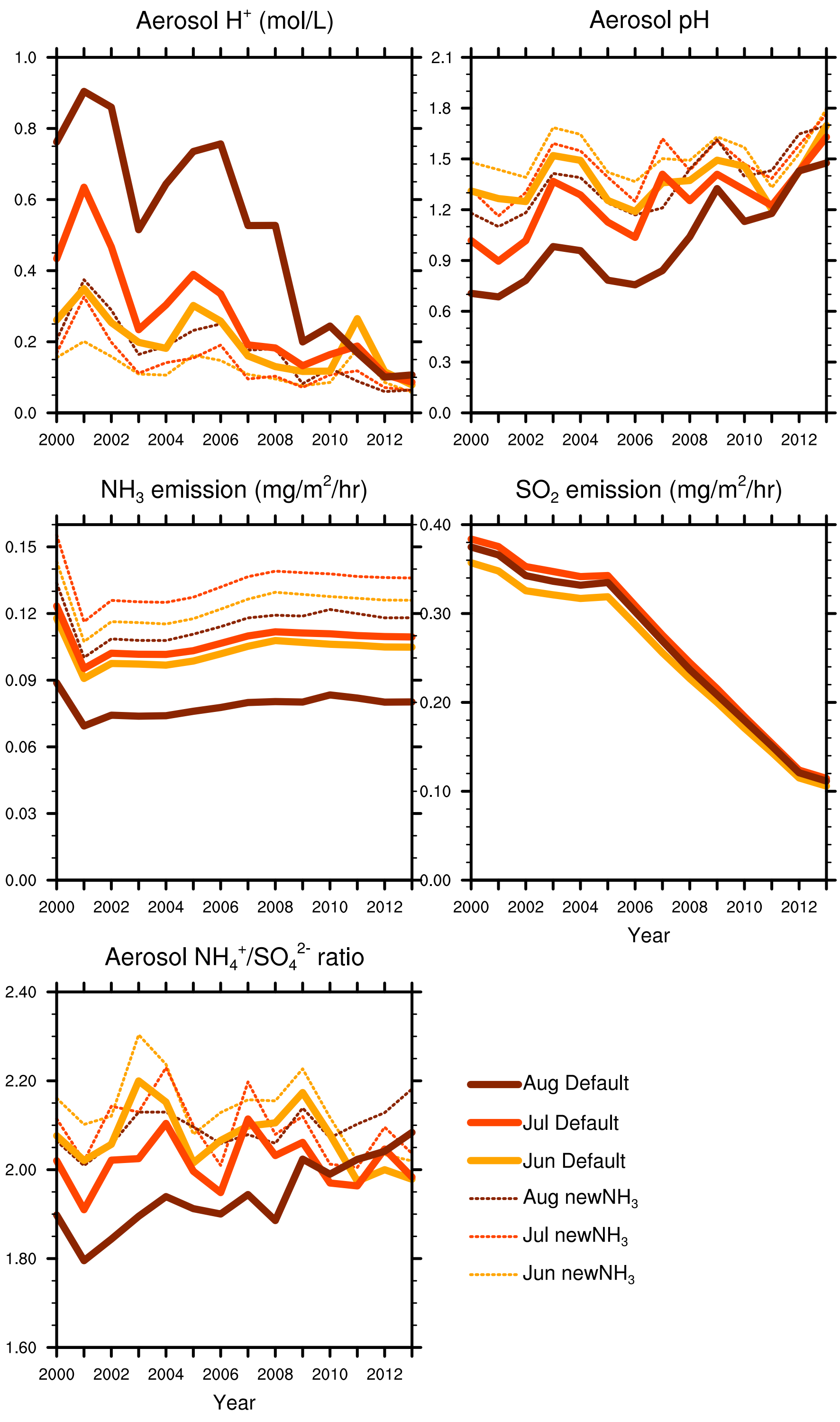

Figure S4. Monthly surface aerosol H$^+$ activity (mol/L), NH$_3$ emission, SO$_2$ emission (mg/m^2/hr) and aerosol NH$_4^+$/SO$_4^{2-}$ ratio from the default and 'CT_newNH$_3$' simulations.

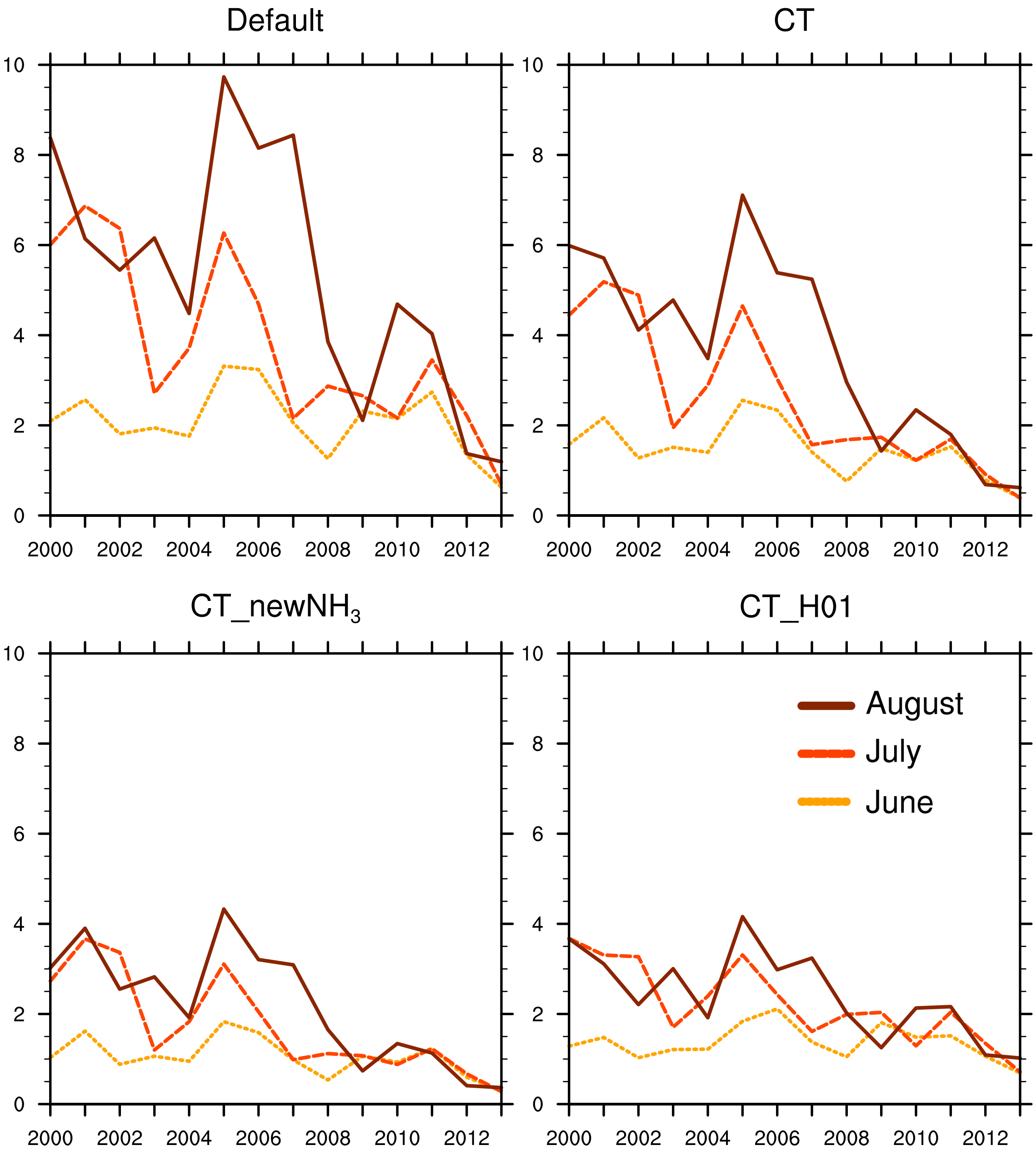

Figure S5. The monthly surface IEPOX-SOA concentration (μg/m^3) over the SEUS from all simulations.

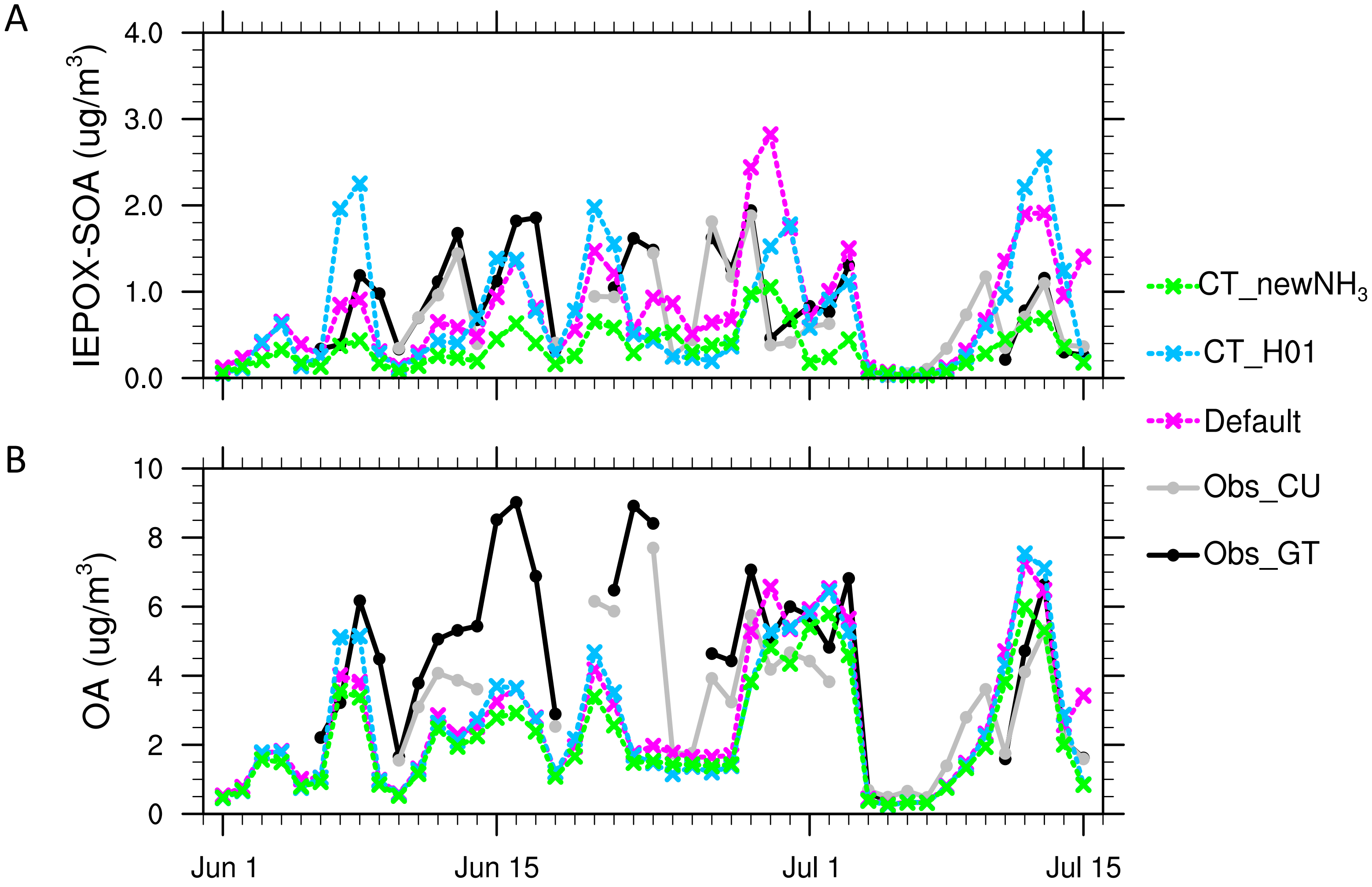

Figure S6. Comparison of **(A)** IEPOX-SOA, **(B)** OA between AMS measurement and the default and CT_H01 simulations in the SOAS campaign from June 01 to July 15, 2013. In (A), IEPOX-SOA is obtained by a Positive Matrix Factorization (PMF) analysis of the AMS-measured OA. Units are µg/m^3.