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

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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.

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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 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

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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.,

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2010; Pye et al., 2010, 2019a; 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 and different oxidation pathways (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

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86 southeast US during 2000-2013. The results provide new observational constraints on the drivers
87 of OA variability and the SOA formation mechanisms in the southeast US.
88

89 2. Methods

90 2.1 Observational datasets.

91 We use surface filter-based measurement of fine particulate matter mass and composition
92 (including organic carbon, OC) in 2000-2013 from three networks: the Interagency Monitoring
93 of Protected Visual Environments (IMPROVE) (Solomon et al., 2014), the SouthEastern Aerosol
94 Research and Characterization (SEARCH) (Edgerton et al., 2005), and the Environmental
95 Protection Agency's $PM_{2.5}$ National Chemical Speciation Network (CSN) (Solomon et al.,
96 2014). We select 21 IMPROVE sites, 3 SEARCH rural sites and 36 CSN sites within the
97 southeast US region [29°~37°N, 74°~96°W] (Figure S1). The SEARCH sites are organized in
98 rural/urban pairs (Edgerton et al., 2005) and only the data from the rural sites are used here to
99 represent background conditions. IMPROVE sites are mostly rural (Solomon et al., 2014). The
100 OC measurement in the CSN network in 2004-2009 gradually shifted to a different protocol and
101 analytical technique than the early 2000s, which led to the discontinuity in long-term trend
102 (Figure S2), therefore we only use CSN data to examine the monthly variability of OA, and
103 focus on IMPROVE and SEARCH for all analysis. The 3-day OC measurement from IMPROVE
104 and daily OC from SEARCH and CSN are averaged to monthly values. A factor of 2.1 is used to
105 convert measured organic carbon (OC) to organic aerosol mass, as suggested by the southeast
106 US field measurements (Pye et al., 2017; Schroder et al., 2018).
107

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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 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 mapped over 0.1°×0.1° and scaled to the year 2011 by the ratio of national annual 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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131 Aerosols from Nature (MEGAN2.1) (Guenther et al., 2012) that is also driven by MERRA-2
132 meteorology.
133
134 For organic aerosol, we employ the complexSOA scheme for SOA modeling for all simulations
135 in this study (Marais et al., 2016; Pye et al., 2010). POA are regarded as nonvolatile. This SOA
136 modeling includes a 4-product Volatility-Basis-Set (VBS) for SOA formation from reversible
137 condensation of oxidation products of biogenic terpenes (including monoterpenes and
138 sesquiterpenes), and anthropogenic VOCs, referred to as terpene-SOA and anthropogenic SOA,
139 respectively. The SOA calculated through VBS parameterization is fitted based on dry chamber
140 (RH<10%) results independent of inorganic aerosol, aerosol water and RH (Pye et al., 2010).
141 The complexSOA scheme also includes aqueous SOA formed from reactive uptake of isoprene
142 oxidation products, including IEPOX, glyoxal, C_4 epoxides, methylglyoxal, non-IEPOX product
143 of the ISOPOOH oxidation and hydroxynitrates from NO_3-initiated oxidation (Marais et al.,
144 2016). The sulfate-nitrate-ammonium aerosol thermodynamics including aerosol acidity is
145 computed with the ISORROPIA II thermodynamic model (Fountoukis and Nenes, 2007; Pye et
146 al., 2009; Song et al., 2018).
147
148 We run the GEOS-Chem model at 4°×5° latitude by longitude continuously from 10/01/1999 to
149 12/31/2013. For each year, the restart file at 05/01 from the continuous 4°×5° simulation has
150 been regridded to 2°×2.5° and is used to initiate 2°×2.5° simulations from 05/01 to 08/31 each
151 year. The 2°×2.5° simulations are adequate when modeling continental boundary layer chemistry
152 (Yu et al., 2016). The May results are discarded as spin-up and the results of June, July and
153 August are used for analysis. We do four sets of 2°×2.5° simulations: Default (using default

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154 complexSOA scheme); CT (with coating effect for IEPOX reactive uptake); CT_newNH_3 (with
155 coating effect and US NH_3 emissions replaced by satellite-derived NH_3 inventory); CT_H01
156 (with coating effect and fixing aerosol a_{H+} at 0.1 mol/L when calculating IEPOX reactive
157 uptake).
158
159 **2.2.2 Coating**
160 The default IEPOX-SOA mechanism in GEOS-Chem uses aerosol-phase reaction rates from
161 laboratory chamber studies with pure acidic inorganic particles (Gaston et al., 2014; Riedel et al.,
162 2015), and a representative effective Henry's law constant obtained by matching the model to the
163 observations at SOAS2013 campaign, to estimate the reactive uptake coefficient γ_{IEPOX}. In the
164 default scheme, γ_{IEPOX} is calculated as follows:

165 $$\frac{1}{\gamma_{IEPOX}} = \frac{R_p \omega}{4D_g} + \frac{1}{\alpha} + \frac{1}{\Gamma_{aq}}$$

166 $$\Gamma_{aq} = \frac{4VRTH_{aq}k_{aq}}{S_a \omega}$$

167 Where R_p is the particle radius of the inorganic sulfate-nitrate-ammonium particle (cm), ω is the
168 mean molecular speed (cm/s), D_g is the gas-phase diffusion coefficient (0.1 cm^2/s), α is the mass
169 accommodation coefficient (α=0.1), S_a is the total (wet) particle surface area (cm^2/cm^3), V is the
170 total (wet) particle volume (cm^3/cm^3), R is the ideal gas constant (L atm/mol/K), T is temperature
171 (K), H_{aq} is the Henry's law coefficient (1.7×10^7 M/atm), and k_{aq} is the first-order reaction rate
172 constant (s^{-1}):

173 $$k_{aq} = k_{H^+}[H^+] + k_{nuc}[nuc]a_{H^+} + k_{ga}[ga]$$

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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).

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. $\gamma_{IEPOX\_modified} = 0$. We assume all OA is coated outside the inorganic aerosol core when calculating the IEPOX reactive uptake. The increased particle radius R_p and surface area S_a of the mixed particle will partially offset the impact of reduced reaction probability $\gamma_{IEPOX\_modified}$, consistent with another study (Jo et al., 2019).

2.2.3 Satellite-derived NH_3 emissions

We use the Cross-track Infrared Sounder (CrIS) satellite-derived NH_3 emissions 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

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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. There is no significant trend from 2000 to 2013 (Figure S3), 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 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. Using the top-down emissions in GEOS-Chem increases the correlation coefficient (r) between modeled monthly mean NH_3 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^+ 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. (submitted) 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.

2.3 Multivariate linear regression analysis

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

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

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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.

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243

244 Compared to the observations, the default GEOS-Chem model predicts a steeper decreasing
245 trend of OA mass during 2000-2013 (Figure 1). Modeling results are averaged over the domain
246 [29°~37°N, 74°~96°W] excluding ocean grid cells (Figure S1). The 2000-2013 JJA-averaged
247 OA from the default model is 6.7 $\mu g/m^3$, higher than OA from IMPROVE and SEARCH.
248 Modeled total OA mass decreases at a rate of 4.9%/year, about 1.9 (1.6) times faster than
249 IMPROVE (SEARCH) OA (student's t-test $p<0.001$). The strong reduction in total OA mass is
250 dominated by aqueous SOA, especially through reactive uptake of IEPOX, with no decreasing
251 trend in other components (Figure 1). The contribution of IEPOX-SOA to total OA mass
252 decreases from 61% in the early 2000s to 28% in 2013.

253

254 A main constraint comes from the MMV of OA in the southeast US. IMPROVE and SEARCH
255 OA observations show little variability among June, July and August, despite large MMV of
256 sulfate in early 2000s (Figure 2A). We find similar behavior from another observation network,
257 CSN. The discontinuity in OA trend in the CSN network is due to different protocols applied
258 (Figure S2). Within sites using the same protocol, there are no systematic monthly differences,
259 which agrees with IMPROVE and SEARCH. In contrast, modeled OA displays large MMV
260 between June, July and August from 2000 to 2008, where OA in July and August is 1~3 times of
261 June values (Figure 2A). Such large MMV is dominated by aqueous SOA, especially from the
262 reactive uptake of IEPOX. Prior to 2008, the simulated IEPOX-SOA alone can be up to a factor
263 2 higher than the observed total OA (Figure 2). The other components including POA and dry
264 SOA (including terpene-SOA and Anthropogenic SOA) formed through partitioning together
265 have low concentrations and small MMV. The default model well captures the variability of

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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

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289 group leading to the formation of IEPOX-SOA (Gaston et al., 2014; Pye et al., 2013; Surratt et
290 al., 2007a). However, some recent studies suggest that IEPOX-SOA is not well correlated with
291 aerosol acidity estimated from thermodynamic models (Budisulistiorini et al., 2015; Lin et al.,
292 2013; Xu et al., 2015b), although the lack of direct measurements of aerosol acidity may be a
293 limitation. We use the GEOS-Chem model here to examine the simulated IEPOX-SOA
294 dependence on sulfate, aerosol acidity, and emissions of isoprene which produce IEPOX at high
295 yields under low-NO_x conditions (Paulot et al., 2009). We do not treat aerosol water as an
296 independent driver because the dilution effect of aerosol water is implicitly considered in the
297 inorganic sulfate-ammonium-nitrate aerosol volume and acidity calculation, and studies have
298 shown that particle water is not a limiting factor unless the particle is purely dry (Nguyen et al.,
299 2014; Riva et al., 2016; Xu et al., 2015b) which is rare in summertime in the southeast US.
300
301 We find that the large MMV of OA in the model is mainly driven by sulfate concentrations and
302 aerosol acidity (Figure 3). Prior to 2008, IEPOX-SOA production is largely enhanced by
303 abundant sulfate (Gaston et al., 2014). Due to this high level of sulfate (about >4 $\mu g/m^3$), the
304 modeled aerosol acidity becomes particularly sensitive to variations in NH_3 emissions. For the
305 default model setup, we use monthly anthropogenic emissions from the EPA's National
306 Emissions Inventory 2011 (NEI11v1) in the US and adjust to each year from 2000 to 2013 using
307 national annual scaling factors (Travis et al., 2016), which suggests no significant long-term
308 trend of NH_3 emissions from 2000 to 2013 (Figure S3). The NH_3 emissions in August are about
309 25% lower than in June and July (Figure S3). As a result, the a_{H+} in August is up to 3 times
310 higher than June, leading to high production of IEPOX-SOA in August. Both sulfate and aerosol
311 acidity appear to be the dominant contributors to MMV of OA during this period. After 2008,

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312 IEPOX-SOA formation is substantially suppressed, due to small SO_2 emissions and low modeled
313 aerosol acidity a_{H+} with small monthly variability. Isoprene emissions also contribute to the
314 month-to-month and interannual OA variability in the model.
315
316 The multivariate linear regression analysis of IEPOX-SOA quantitatively determines the relative
317 importance of its three drivers in the model. Using all monthly data in 2000-2013, the
318 standardized regression coefficients (β) associated with a_{H+}, sulfate aerosol concentration and
319 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,
320 suggesting that aerosol acidity is the dominant controlling factor. The three variables together
321 explain 88% of the variability of IEPOX-SOA. Their relative importance changes over time
322 (Table S1). Aerosol acidity strongly correlates with IEPOX-SOA in 2005-2008 (β=0.57,
323 r^2=0.82) but its role becomes much weaker after 2008 (β=0.27, r^2=0.56). Sulfate aerosol is
324 always the first or second most important driver, especially in 2000-2004 (β=0.46, r^2=0.76).
325 Isoprene emission contributes to the overall interannual variability, for example leading to the
326 relatively low IEPOX-SOA in 2003-2004 and the peak in 2011 (Figure 3).
327
328 **3.3 Narrowing the gap between model and observation**
329 **3.3.1 Coating**
330 Several reasons may lead to the large monthly variations of the modeled OA. The modeled
331 IEPOX-SOA shows a much stronger sensitivity to aerosol acidity than suggested by field
332 observations, which found weak or no correlation between observed IEPOX-SOA and derived
333 aerosol acidity (Budisulistiorini et al., 2015; Lin et al., 2013; Worton et al., 2013; Xu et al.,
334 2015b). Lack of consideration of organic coating effect may provide one possible explanation. In

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335 the real atmosphere, inorganic aerosol is generally internally mixed with other organics (Anttila
336 et al., 2006; Murphy et al., 2006). The presence of an organic coating may alter the solubility and
337 diffusion properties at the surface of inorganic particles and diminish further uptake of IEPOX.
338 By implementing a linear coating effect for the IEPOX uptake, both the magnitude of γ_{IEPOX} and
339 its sensitivity to acidity have been reduced. Figure 4A shows a schematic illustrating the
340 dependence of the γ_{IEPOX} coating effect on acidity a_{H+} and organic mass fraction (χ_{org}). The
341 original γ_{IEPOX} without coating is represented at χ_{org}=0. The orange line in Figure 4A shows the
342 approximate position of JJA-averaged acidity and organic mass fraction in the model simulation
343 with coating effect (simulation name: 'CT'). Adding a coating reduces γ_{IEPOX} by almost half, but
344 the impact on the total reactive uptake rate of IEPOX is partially compensated by the
345 corresponding increase in particle surface area. The sensitivity of γ_{IEPOX} to acidity has also been
346 reduced especially during the early 2000s (Figure 4A). The CT simulation reduces the southeast
347 US JJA-averaged IEPOX-SOA concentrations by 0.3~1.8 μg/m^3 (Figure 4C).
348
349 **3.3.2 NH_3 emissions and aerosol acidity**
350 Second, recent studies present contradictory results and explanations on the long-term trend of
351 aerosol acidity in the southeast US (Pye et al., 2019b; Silvern et al., 2017; Weber et al., 2016). In
352 this study, we show that the decreasing trend of aerosol acidity from the standard GEOS-Chem
353 model is mainly caused by high acidity in August before 2008, which corresponds to insufficient
354 NH_3 emissions in high sulfate environments. The NEI11v1 inventory is used in the default
355 configuration, in which NH_3 emissions in June and July are 30% higher than in August (Figure
356 S3), but not all NH_3 emission inventories agree with such pattern (Paulot et al., 2014). We did a
357 sensitivity test replacing the default US NH_3 emissions from NEI11v1 by a new NH_3 emission

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product derived from CrIS satellite observations, which has higher emissions and smaller MMV among June, July and August (Figure S3). In the simulation with updated NH_3 emissions in the US from 2000 to 2013 ('CT_newNH_3'), 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 3B). 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 S3). 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., 2019b; 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 observed a_{H+} value 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 S4). For the SOAS2013 campaign at Centerville, AL from 06/01/2013 to 07/15/2013, 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

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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 S5). 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 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 S5), 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 (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).

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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. 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

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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. 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-

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450 volatile and can re-evaporate back into gas-phase (Ambro et al., 2019; Isaacman-VanWertz et
451 al., 2016), while other studies suggest IEPOX-SOA products are mostly nonvolatile or low
452 volatility (Hu et al., 2016; Lopez-Hilfiker et al., 2016). As multiple parameters may be tuned in
453 the model to fit observations, further laboratory, field and modeling studies are needed to
454 integrate Henry's law constant, IEPOX-SOA yields, volatility, coating effect and acidity
455 dependence for a better mechanistic understanding. The CT_H01 scheme lacks mechanical
456 representation of detailed aerosol properties like phase state, acidity, viscosity and morphology,
457 but reasonably captures both the OA and IEPOX-SOA magnitude (compared to both the three
458 filter measurement networks and the SOAS2013 campaign), long-term variability and
459 relationship with sulfate (Figure 4, 5, S5), therefore may serve as a simplified representation for
460 climate models. For all kinds of models, long-term filter-based measurements, especially
461 intraseasonal MMV, are important observational constraints that should be considered in model
462 development.
463
464 Even with our improved model, the rate of OA decrease per year is still 0.8 times higher the
465 long-term observations, and still shows a higher MMV than observations particularly in early
466 2000s (Figure 4D). Such discrepancies may suggest a more important role of SOA pathways that
467 are less dependent on inorganic aerosol, such as the gas-aerosol partitioning. Despite a large
468 MMV in IEPOX-SOA, Xu et al. (2015a) finds the less-oxidized oxygenated OA (LO-OOA, an
469 indicator for freshly-formed monoterpene SOA) and the more-oxidized oxygenated OA (MO-
470 OOA, also likely from biogenic sources) with little MMV in summer months, and they
471 contribute to more than 50% of total OA mass in the southeast US (Xu et al., 2018). The
472 important role of monoterpenes SOA is also confirmed by molecular level characterization of

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473 organic aerosols (Zhang et al., 2018). Other pathways may contribute to SOA to some extent and
474 may add to the predicted SOA formed by partitioning, including biogenic SOA from auto-
475 oxidation (Bianchi et al., 2019; Pye et al., 2019a), in-cloud SOA formation that may be less
476 dependent on acidity than aqueous SOA (Tsui et al., 2019), a small but underestimated
477 contribution of anthropogenic SOA (Schroder et al., 2018; Shah et al., 2019), and other possible
478 mechanisms (Schwantes et al., 2019). Further quantifying the relative importance of the different
479 pathways will allow a more accurate quantification of the anthropogenic influence on biogenic
480 SOA and the associated radiative forcing.
481
482

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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.

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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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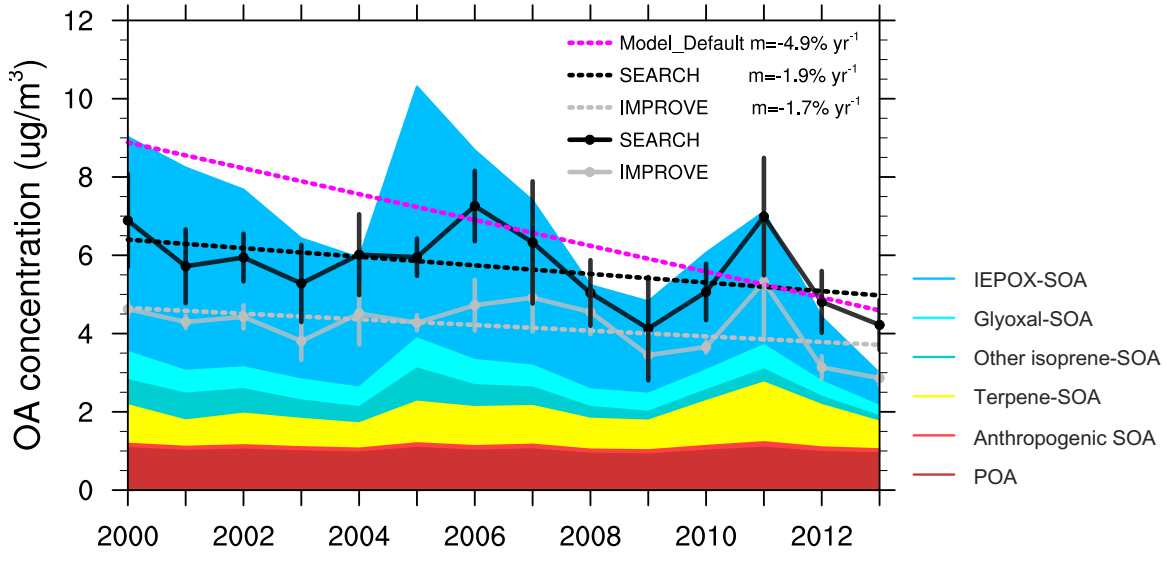

Figure 1. Comparison of June-July-August averaged surface OA concentration (μg/m^3) over the southeast US between the default model and the observation from IMPROVE and SEARCH network. Colored shades represent different components of modeled OA. IEPOX-, glyoxal-, and other isoprene-SOA are from aqueous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

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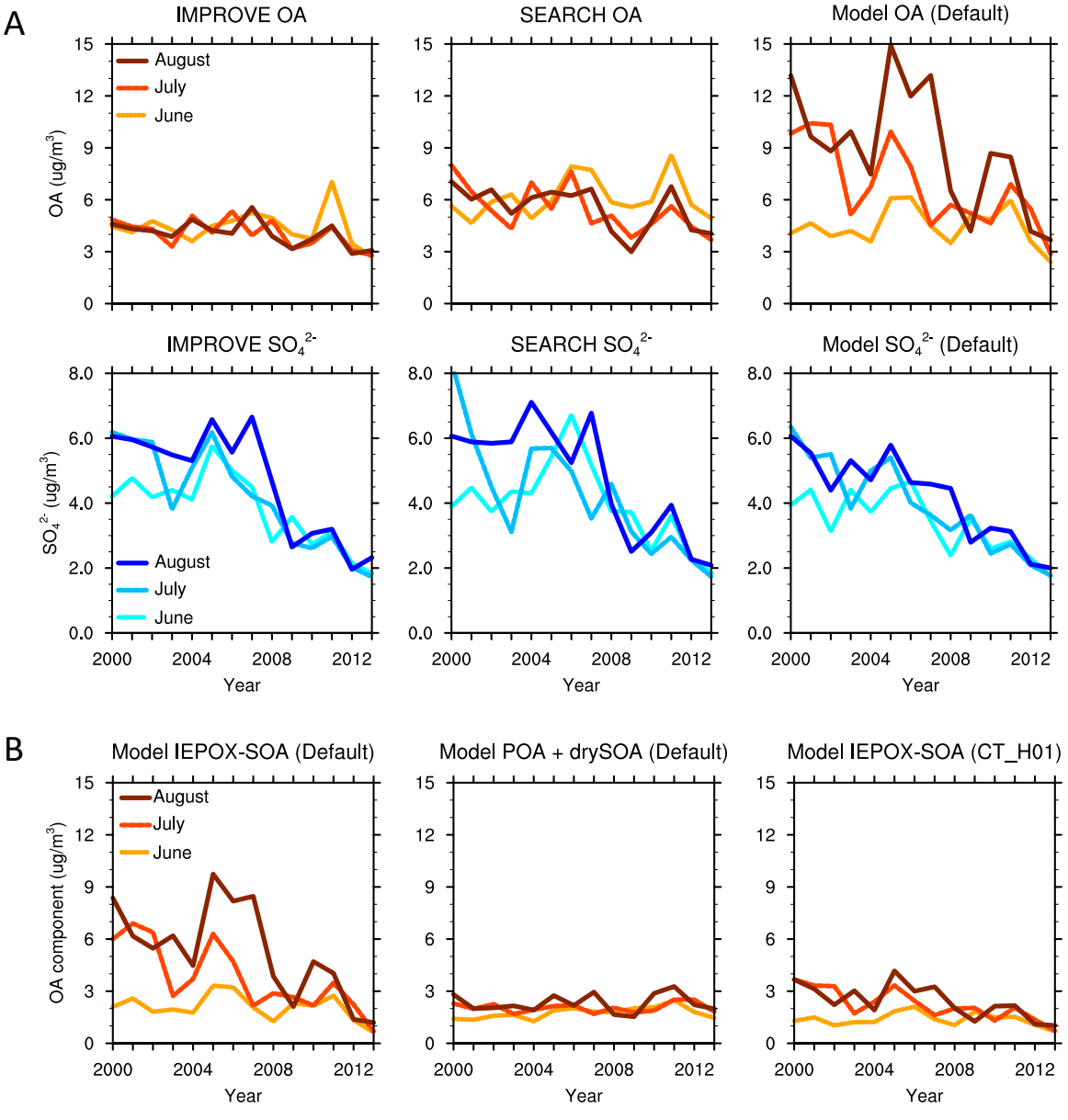

Figure 2. (A) Monthly surface OA and sulfate (SO_4^{2-}) concentration (μg/m^3) averaged over the southeast US from IMPROVE, SEARCH and the default model. **(B)** Monthly surface concentrations of IEPOX-SOA and the sum of POA and dry SOA from the default model, and IEPOX-SOA from the CT_H01 simulation.

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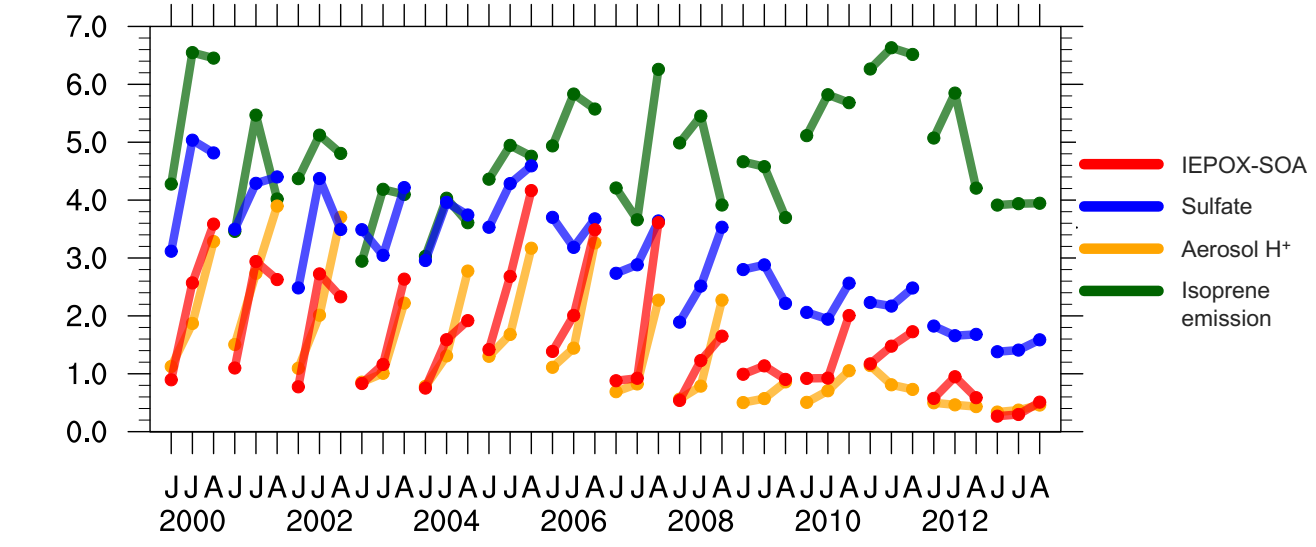

Figure 3. Standardized monthly surface IEPOX-SOA concentration, sulfate concentration, aerosol H^+ activity and isoprene emission from the default model. All variables are averaged over the southeast US, and have been divided by 1 standard deviations, therefore are unitless.

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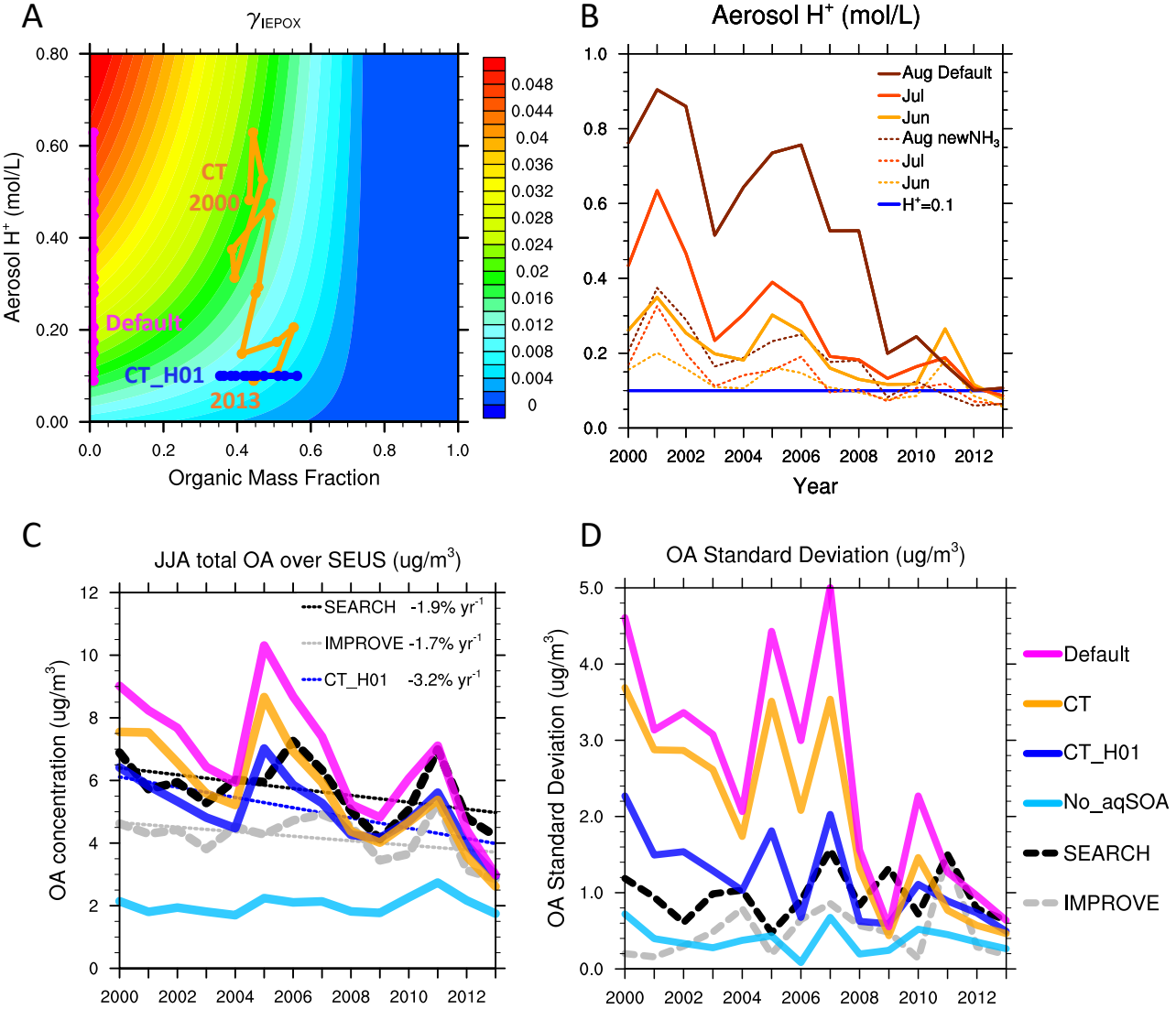

Figure 4. **(A)** Schematic diagram of IEPOX reactive uptake coefficient (γ_{IEPOX}). Colored lines indicate the position of JJA-averaged organic mass fraction and aerosol H^+ activity in 2000-2013 from the 'Default', 'CT' and 'CT_H01' simulations. **(B)** Simulated aerosol acidity (mol/L) from the default,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

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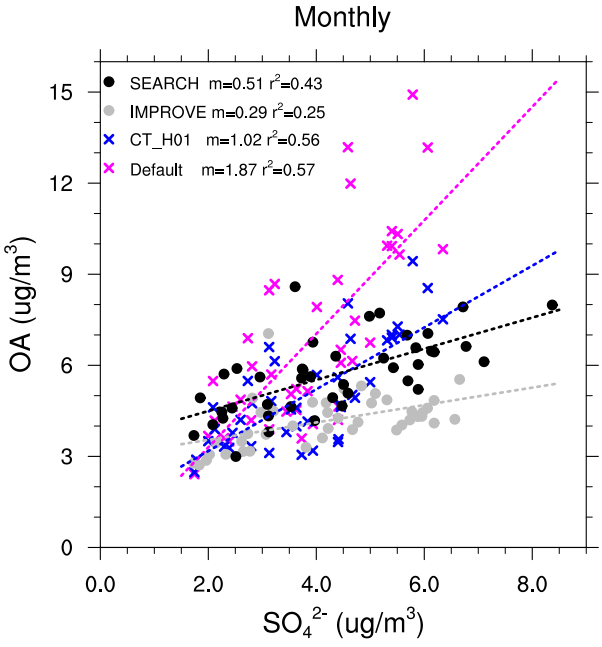

Figure 5. Relationships between monthly OA and sulfate concentrations (μg/m^3). Each dot represents monthly data averaged from all sites from each network within the southeast US.