RESPONSE TO REVIEWERS

Ms. Ref. No.: Atmos. Chem. Phys. Discuss., 15, 32005-32047, 2015 (doi:10.5194/acpd-15-32005-2015).

Title: Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application to the Southeast United States and co-benefit of SO_2 emission controls.

Journal: Atmos. Chem. Phys. Discuss.

Reviewer comments are in red. Responses are in black and include page and line numbers where changes are made to the manuscript below (changes are tracked with green highlighting).

Responses to Reviewer #1:

The manuscript by Marais et al. (2015) explores the SOA formation from isoprene in the Southeast using an aqueous phase SOA mechanism coupled to detailed gas chemistry. This mechanism is shown to capture measured IEPOX SOA well. SOA comprises a large fraction of total aerosol in the atmosphere. However, current models cannot fully reproduce its total mass and spatial and temporal evolutions. One potential reason for the model-observation discrepancy is that current models tend to neglect the SOA formation from aqueous phase, although both lab studies and field measurements have shown the importance of aqueous phase SOA. The manuscript is thus very useful for SOA community.

General comment

- *My major concern is that the paper seems to exclude the SOA formed from monoterpenes, one source that is comparable to the SOA formed from isoprene in Southeast USA (Xu et al., 2015). I am wondering how the missing monoterpenes SOA would affect the modeled OA and the comparison with measured OA.*

We now clarify on page 12, lines 260-266, that monoterpene and other SOA formation in GEOS-Chem is with the SOA formation scheme of Pye et al. (2010). GEOS-Chem underestimates total OA observed during SEAC^{4}RS due to too low anthropogenic and open fire SOA in the model (page 12, lines 267-268). The HCHO-OA approach to estimate isoprene SOA yields is independent of this underestimate.

- *In addition, the authors should clarify some important processes in the model (e.g., emissions of POA and aerosol depositions) that are important for the prediction of OA concentrations.*

We now point the reader to Kim et al. (2015) for a description of model treatment of aerosol wet and dry deposition and emission of POA (page 11, lines 253-254).

Specific comments

- *Page 32009, line 12-14. The references are not appropriate. Both Virtanen et al. (2010) and Song et al. (2015) showed that under dry conditions, SOA particles are semi-solid or solid phase, rather than liquid phase, which suggests that their formation processes deviate from the reversible partitioning of SVOCs, because mixing within the solid particles is very difficult.*

The text has been corrected (page 4, lines 87-89).

- *Page 32009, line 22-26. To date several models have been developed to estimate the amount of SOA formed in the aqueous phase from the regional scale to the global scale (e.g., Carlton et al., 2008; Myriokefalitakis et al., 2011; Liu et al., 2012; Lin et al., 2012; Pye et al., 2013; Lin et al., 2014). The authors should briefly discuss previous model efforts on aqueous phase SOA.*

This omission is addressed on page 4, lines 93-96.

- *Page 32011, line 6. Can the authors explain the unit of yield "7 mol%"? Why is there "mol" in the middle?*

We now clarify its use in the text (page 6, line 136).

- *Page 32011, line 24-27. Why did the authors change the yield of C5-LVOC reported by Krechmer et al. (2015)? Any scientific justification for this? Or just an arbitrary tuning?*

The yield in Krechmer et al. (2015) led to an overestimate in simulated C_5-LVOC relative to the observations. Lowering the yield improves agreement with the observations (page 7, lines 153-155).

- *Page 32014, line 14-16. Can the authors give a references for setting up the value of gamma to be 0.1? Or it is an arbitrary large number?*

Uptake of C_5-LVOC and NT-ISOPN is limited only by mass accommodation, α, set to 0.1 in this work (page 10, lines 223-224).

- *Page 32014, line 25-27. The reasoning is not convincing. First, although the aqueous phase concentrations are low in cloud water, the total amount of SOA produced in cloud is not necessary negligible, given that the cloud water content is usually larger than aerosol water content by 3-4 orders. Second, the mechanisms for aqueous phase SOA formation are different between in cloud water and aerosol water, due to the difference in aqueous-phase concentrations between them. Consequently, the major products in cloud water are carboxylic acids (e.g., oxalic acid), while major products formed from the reactions in aerosol water are oligomers (Ervens et al., 2011).*

We have amended the text to show that omission of SOA formation in clouds is supported by observations analyzed in the Wagner et al. (2015) study (page 11, lines 240-243).

- *Page 32015, line 1-2. How about the SOA formed in stratiform cloud or fogs?*

Stratiform clouds are within the "cloud layer" analyzed by Wagner et al. (2015). We have amended the text so that the statement is general to boundary layer clouds (page 11, line 243).

- *Page 32016, line 11-19. Not clear to me what aerosols were treated as aqueous particles. Did they assume only sulfate as aqueous particles? Or also included the OA (POA and/or SOA)?*

Aqueous aerosol is treated as sulfate. We have amended page 12-13, lines 276-288 for clarity.

• Page 32013, Equation (2). How did the authors predict the concentrations of [nucl] and [HSO4-] in the model?

GEOS-Chem uses the thermodynamic equilibrium ISORROPIA model to predict [nuc] and [HSO_4^-]. This is stated in the model description Section 3 (page 12, lines 270-272); the description of k_{aq} is general to current understanding of aqueous-phase IEPOX reactions.

• Sec. 3 GEOS-Chem simulation and isoprene SOA yields. The authors should briefly describe how they treat the POA emissions and aerosol depositions in the model.

Already addressed (see response to General Comments above).

• Page 32020, line 5. "without bias" is over-stated. The model cannot capture strong IEPOX SOA peaks around June 25. The model also underestimates C5-LVOC SOA during June 18-20.

Addressed to indicate that the model reproduces SOAS mean IEPOX SOA and C_5-LVOC SOA (page 17, line 382).

• Sect. 5. Effect of anthropogenic emission reductions. Do the authors know the relative role of sulfate aerosol volume decrease vs. the aerosol acidity increase on the IEPOX SOA reduction? Which one is more important?

Aerosol acidity and volume have a similar effect on IEPOX SOA, as SO_2 emission reduction reduces aerosol volume and aerosol acidity each by ~30%, and the rate of heterogeneous uptake of IEPOX to aqueous aerosol is dependent on the product of aerosol acidity ([H^+]) and aerosol volume (page 18, lines 406-409). A similar statement is now inserted in Section 5 (page 20, line 445-449).

• Page 32023, line 9-11. This is not accurate and misleading. The traditional gas-particle partitioning model follows the Pankow (1994) absorption model, which assumes reversible partitioning to pre-existing humid OA, instead of dry OA. The problem lies in that this model was usually fit to the SOA yield data obtained from chamber studies performed under dry conditions, with very low relative humidity.

SOA formation in GEOS-Chem using the Pankow formulation is dependent on the mass of pre-existing organic aerosol and does not account for additional mass from aerosol water (see Chung and Seinfeld, 2002; Griffin et al., 1999).

• Figure 3. "OA mixing ratios" should be "OA mass concentrations.

Amended.

Responses to Reviewer #2:

In this study the isoprene aqueous SOA chemistry is considered and incorporated into the chemical transport model GEOS-Chem. The detailed formation pathways are successfully reproduced and their relative contributions to isoprene SOA are evaluated. The results of the sensitivity of isoprene SOA to the changes of SO2 emissions will help make countermeasures against air pollution. I found that the study was conducted very well and the manuscript is written clearly. I have below specific comments that the authors should consider and implement in the revised manuscript.

Specific comments

1. *Following IUPAC recommendations, I would suggest terming Gamma as "reactive uptake coefficients", rather than using "reactive uptake probabilities".*

All instances of "reactive uptake probabilities" are replaced with "reactive uptake coefficients".

2. *SOA particles are assumed as aqueous droplets in this study. Under low humidity of below ~50% RH, isoprene SOA were shown to be semi-solid or solid (Saukko et al., ACP, 12, 7517, 2012; Song et al., ACP, 2015), and in that case there will be strong kinetic limitations of gas-particle partitioning (e.g., Perraud et al., PNAS, 109, 2836, 2012; Shiraiwa & Seinfeld, GRL, 39, L24801, 2012). This study compared the simulated results with aircraft observations within the boundary layer. While as the altitude increases to the top of the boundary layer, particles might become semi-solid or solid upon decrease of temperature (e.g., Koop et al., PCCP, 13, 19238, 2011). Although investigation of particle phase is not a priority of this research, it would be very helpful to add some discussion, justification and potential bias of assumed liquid phase state for simulation uncertainties.*

The focus of this study is on isoprene SOA formation within the boundary layer (aloft OA formation is not significant; Wagner et al., 2015). Relatively humidity is sufficiently high in the boundary layer that it is reasonable to assume aerosols are liquid. We clarify this on pages 12-13, lines 276-281.

3. *Regarding eq (1): Gas-phase diffusion seems to be neglected, as gas diffusivity is not explicitly treated in eq (1). If this is true, this should be explicitly mentioned. Several studies have clearly shown that gas diffusion can play an important role in SOA growth (e.g., Tang et al., ACP, 14, 9233, 2014; Riipinen et al., ACP, 11, 3865, 2011). Please clarify and discuss.*

Gas phase diffusion is not neglected, but included in the gas uptake rate constant calculation (equation (3)). We clarify this on p. 13, lines 288-289.

4. *It would also be helpful to show the comparison of observed and simulated meteorological parameters (e.g., T and RH). They are related to particle phase determination; RH impacts the sulfate aerosol size distribution as shown in Section 3 and IEPOX sulfate formation (Liao et al., 2015); T impacts the isoprene emission as shown on Line 8, Page 32020, and meteorological parameters impact the prediction of chemical fields.*

We now compare average GEOS-Chem (GEOS-FP) and SEAC^{4}RS values of relative humidity (page 13, lines 279-280). GEOS-FP temperature is 1.6 K higher than the observations, contributing to an overestimate in MEGAN isoprene emissions. Our interpretation of isoprene SOA yields from the relationship between OA and HCHO is independent of this overestimate (page 17, lines 371-377).

5. *In the Sect. 2, I suggest including discussion on uncertainties of kaq and the potential impacts on the following simulated results.*

We now provide in Section 2 (page 10, lines 227-232) a discussion of the variability in reported values of k_{H+} and k_{nuc} used to estimate k_{aq} and point the reader to Section 4 where we show that our choice of k_{H+} and k_{nuc} is constrained with observations of total IEPOX SOA and IEPOX organosulfates.

6. *How much uncertainties are expected in column HCHO measured by OMI? (first paragraph of Section 4).*

We now provide an estimate on the error of satellite HCHO observations from the North America error analysis study by Millet et al., 2006 (page 16, lines 360-361).

7. *Line 19, Page 32020 says that the H+ -catalyzed channel is a larger contributor compared to the sulfate channels. Is this result applicable to all of the simulated areas? How about the results for higher altitudes? As shown in Fig. 2, this study seems not to consider the reactions involving SO42- leading to organosulfate formation. Will this impact the result that a direct role of sulfate in IEPOX SOA is not important? It is not clear for me whether the term of knuc[nuc][H+] in eq(2) already include organosulfate formation. Please clarify.*

We now clarify in the text that the 90% contribution applies throughout the Southeast US boundary layer (page 18, line 396).

We now state that the reactions in equation (2) lead to formation of methyltetrols in the case of H^+-catalyzed reactions and organosulfates or organonitrates for the nucleophile channels (p. 9, lines 200-203). All reactions are included in GEOS-Chem, but IEPOX and sulfate are transported separately, due to their separate treatment downstream, e.g., optical properties for estimating AOD and photolysis.

8. *Aerosol pH seems to be very critical in simulating SOA mass due to an importance of acid-catalyzed reactions. pH is modeled based on ISOROPPIA. Do you have field measurements of aerosol pH and could it be compared with modeled pH? How much uncertainty would you expect in the modeled pH?*

Aerosol pH cannot be directly measured. A publication by Guo et al. (2015) that we reference in our work (page 12, lines 274-275) validated ISORROPIA prediction of pH indirectly using observations of ammonia, as its partitioning is sensitive to model prediction of aerosol pH.

9. *Page 32021, Line 5: will nitrate take similar effects as sulfate to increase aqueous volume and acidity?*

The Southeast US summertime aerosol comprises an order of magnitude lower nitrate than sulfate mass (page 12, line 270, and Kim et al., 2015), so a change in aerosol nitrate mass concentration has little impact on aerosol volume. Our GEOS-Chem simulation of NO_x emission reductions illustrates that a 34% decrease in NO_x emissions, leading to a 32% decrease in aerosol nitrate mass concentration, has no impact on aerosol pH (Figure 7) and only a 6% reduction in aerosol volume that is in part due to the effect of NO_x on sulfate (Figure 7).

Technical Corrections

Technical corrections: - P32019, Line 4, Abad et al., 2015 is missing in the section of References.

The correct in-text citation, consistent with the reference list, is now provided (Gonzalez Abad as opposed to Abad).

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Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application to the Southeast United States and co-benefit of SO_2 emission controls

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Abstract

Isoprene emitted by vegetation is an important precursor of secondary organic aerosol (SOA), but the mechanism and yields are uncertain. Aerosol is prevailingly aqueous under the humid conditions typical of isoprene-emitting regions. Here we develop an aqueous-phase mechanism for isoprene SOA formation coupled to a detailed gas-phase isoprene oxidation scheme. The mechanism is based on aerosol reactive uptake coefficients (γ) for water-soluble isoprene oxidation products, including sensitivity to aerosol acidity and nucleophile concentrations. We apply this mechanism to simulation of aircraft (SEAC^{4}RS) and ground-based (SOAS) observations over the Southeast US in summer 2013 using the GEOS-Chem chemical transport model. Emissions of nitrogen oxides ($NO_x \equiv NO + NO_2$) over the Southeast US are such that the peroxy radicals produced from isoprene oxidation ($ISOPO_2$) react significantly with both NO (high-NO_x pathway) and HO_2 (low-NO_x pathway), leading to different suites of isoprene SOA precursors. We find a mean SOA mass yield of 3.3 % from isoprene oxidation, consistent with the observed relationship of total fine organic aerosol (OA) and formaldehyde (a product of isoprene oxidation). Isoprene SOA production is mainly contributed by two immediate gas-phase precursors, isoprene epoxydiols (IEPOX, 58% of isoprene SOA) from the low-NO_x pathway and glyoxal (28%) from both low- and high-NO_x pathways. This speciation is consistent with observations of IEPOX SOA from SOAS and SEAC^{4}RS. Observations show a strong relationship between IEPOX SOA and sulfate aerosol that we explain as due to the effect of sulfate on aerosol acidity and volume. Isoprene SOA concentrations increase as NO_x emissions decrease (favoring the low-NO_x pathway for isoprene oxidation), but decrease more strongly as SO_2 emissions decrease (due to the effect of sulfate on aerosol acidity and volume). The US EPA projects 2013-2025 decreases in anthropogenic emissions of 34% for NO_x (leading to 7% increase in isoprene SOA) and 48% for SO_2 (35% decrease in isoprene SOA). Reducing SO_2 emissions decreases sulfate and isoprene SOA by a similar magnitude, representing a factor of 2 co-benefit for $PM_{2.5}$ from SO_2 emission controls. There is some evidence for this co-benefit in observed long-term trends of OA in the Southeast US over the past decade.

Keywords: isoprene, SOA yield, IEPOX, glyoxal, SEAC^{4}RS, SOAS, formaldehyde.

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1. Introduction

Isoprene emitted by vegetation is a major source of secondary organic aerosol (SOA) (Carlton et al., 2009, and references therein) with effects on human health, visibility, and climate. There is large uncertainty in the yield and composition of isoprene SOA (Scott et al., 2014; McNeill et al., 2014), involving a cascade of species produced in the gas-phase oxidation of isoprene and their interaction with pre-existing aerosol (Hallquist et al., 2009). We develop here a new aqueous-phase mechanism for isoprene SOA formation coupled to gas-phase chemistry, implement it in the GEOS-Chem chemical transport model (CTM) to simulate observations in the Southeast US, and from there derive new constraints on isoprene SOA yields and the contributing pathways.

Organic aerosol is ubiquitous in the atmosphere, often dominating fine aerosol mass (Zhang et al., 2007), including in the Southeast US where it accounts for more than 60% in summer (Attwood et al., 2014). It may be directly emitted by combustion as primary organic aerosol (POA), or produced within the atmosphere as SOA by oxidation of volatile organic compounds (VOCs). Isoprene (C_5H_8) from vegetation is the dominant VOC emitted globally, and the Southeast US in summer is one of the largest isoprene-emitting regions in the world (Guenther et al., 2006). SOA yields from isoprene are low compared with larger VOCs (Pye et al., 2010), but isoprene emissions are much higher. Kim et al. (2015) estimated that isoprene accounts for 40% of total organic aerosol in the Southeast US in summer.

Formation of OA from oxidation of isoprene depends on local concentrations of nitrogen oxide radicals ($NO_x \equiv NO + NO_2$) and pre-existing aerosol. NO_x concentrations determine the fate of organic peroxy radicals originating from isoprene oxidation ($ISOPO_2$), leading to different cascades of oxidation products in the low-NO_x and high-NO_x pathways (Paulot et al., 2009a; 2009b). Uptake of isoprene oxidation products to the aerosol phase depends on their vapor pressure (Donahue et al., 2006), solubility in aqueous media (Saxena and Hildeman, 1996), and subsequent condensed-phase reactions (Volkamer et al., 2007). Aqueous aerosol provides a medium for reactive uptake (Eddingsaas et al., 2010; Surratt et al., 2010) with dependences on acidity (Surratt et al., 2007a), concentration of nucleophiles such as sulfate (Surratt et al., 2007b), aerosol water (Carlton and Turpin, 2013), and organic coatings (Gaston et al., 2014).

We compile in Fig. 1 the published laboratory yields of isoprene SOA as a function of initial NO concentration and relative humidity (RH). Here and elsewhere, the isoprene SOA yield is defined as the mass of SOA produced per unit mass of isoprene oxidized. Isoprene SOA yields span a wide range, from <0.1% to >10%, with no systematic difference between low-NO_x and high-NO_x pathways. Yields tend to be higher in dry chambers (RH < 10%). Under such dry conditions isoprene SOA is expected to be solid (Virtanen et al., 2010; Song et al., 2015). At humid conditions more representative of the summertime boundary layer, aerosols are likely aqueous (Bateman et al., 2014). Standard isoprene SOA mechanisms used in atmospheric models assume reversible partitioning onto pre-existing organic aerosol, fitting the dry chamber data (Odum et al., 1996). However, this may not be appropriate for actual atmospheric conditions where aqueous-phase chemistry with irreversible reactive uptake of water-soluble gases is likely the dominant mechanism (Ervens et al., 2011; Carlton and Turpin, 2013). Several regional/global models have implemented mechanisms for aqueous-phase formation of isoprene SOA (Fu et al., 2008, 2009; Carlton et al., 2008; Myriokefalitakis et al., 2011; Liu et al., 2012; Pye et al., 2013; Lin et al., 2014).

Here we present a mechanism for irreversible aqueous-phase isoprene SOA formation integrated within a detailed chemical mechanism for isoprene gas-phase oxidation, thus linking isoprene SOA formation to gas-phase chemistry and avoiding more generic volatility-based parameterizations that assume dry organic aerosol (Odum et al., 1996; Donahue et al., 2006). We use this mechanism in the GEOS-Chem CTM to simulate observations from the SOAS (surface) and SEAC^{4}RS (aircraft) field campaigns over the Southeast US in summer 2013, with focus on isoprene SOA components and on the relationship between OA and formaldehyde (HCHO). HCHO is a high-yield oxidation product of isoprene (Palmer et al., 2003) and we use the OA-HCHO relationship as a constraint on isoprene SOA yields. SOAS measurements were made at a ground site in rural Centreville, Alabama (Hu et al., 2015; http://soas2013.rutgers.edu/). SEAC^{4}RS measurements were made from the NASA DC-8 aircraft with extensive boundary layer coverage across the Southeast (Toon et al., 2016; SEAC^{4}RS Archive).

2. Chemical mechanism for isoprene SOA formation

The default treatment of isoprene SOA in GEOS-Chem at the time of this work (v9-02; http://geos-chem.org) followed a standard parameterization operating independently from the gas-phase chemistry mechanism and based on reversible partitioning onto pre-existing OA of generic semivolatile products of isoprene oxidation by OH and NO_3 radicals (Pye et al., 2010). Here we implement a new mechanism for reactive uptake by aqueous aerosols of species produced in the isoprene oxidation cascade of the GEOS-Chem gas-phase mechanism. This couples SOA formation to the gas-phase chemistry and is in accord with increased evidence for a major role of aqueous aerosols in isoprene SOA formation (Ervens et al., 2011).

The standard gas-phase isoprene oxidation mechanism in GEOS-Chem v9-02 is described in Mao et al. (2013) and is based on best knowledge at the time building on mechanisms for the oxidation of isoprene by OH (Paulot et al., 2009a; 2009b) and NO_3 (Rollins et al., 2009). Updates implemented in this work are described below and in companion papers applying GEOS-Chem to simulation of observed gas-phase isoprene oxidation products over the Southeast US in summer 2013 (Fisher et al., 2016; Travis et al., 2016). Most gas-phase products of the isoprene oxidation cascade in GEOS-Chem have high dry deposition velocity, competing in some cases with removal by oxidation and aerosol formation (Nguyen et al., 2015a; Travis et al., 2016).

Figure 2 shows the isoprene oxidation cascade in GEOS-Chem leading to SOA formation. Reaction pathways leading to isoprene SOA precursors are described below. Yields are in mass percent, unless stated otherwise. Reactive $ISOPO_2$ isomers formed in the first OH oxidation step react with NO, the hydroperoxyl radical (HO_2), other peroxy radicals (RO_2), or undergo isomerization (Peeters et al., 2009). The NO reaction pathway (high-NO_x pathway) yields C_5 hydroxy carbonyls, methyl vinyl ketone, methacrolein, and first-generation isoprene nitrates (ISOPN). The first three products go on to produce glyoxal and methylglyoxal, which serve as SOA precursors. The overall yield of glyoxal from the high-NO_x pathway is 7 mol % (yield on a molar basis). Oxidation of ISOPN by OH and O_3 is as described by Lee et al. (2014). Reaction of ISOPN with OH produces saturated dihydroxy dinitrates (DHDN), 21 and 27 mol % from the beta and delta channels respectively (Lee et al., 2014), and 10 mol % isoprene epoxydiols (IEPOX) from each channel (Jacobs et al., 2014). We also adopt the mechanism of Lin et al. (2013) to generate C_4 hydroxyepoxides (methacrylic acid epoxide and hydroxymethylmethyl-α-lactone, both denoted MEPOX) from OH oxidation of a peroxyacylnitrate formed when methacrolein reacts with OH followed by NO_2. Only hydroxymethylmethyl-α-lactone is shown in Fig. 2.

The HO_2 reaction pathway for $ISOPO_2$ leads to formation of hydroxyhydroperoxides (ISOPOOH) that are oxidized to IEPOX (Paulot et al., 2009b) and several low-volatility products, represented here as C_5-LVOC (Krechmer et al., 2015). The kinetics of IEPOX oxidation by OH is uncertain, and experimentally determined IEPOX lifetimes vary from 8 to 28 h for an OH concentration of 1×10^6 molecules cm^{-3} (Jacobs et al., 2013; Bates et al., 2014). In GEOS-Chem we apply the fast kinetics of Jacobs et al. (2013) and reduce the yield of IEPOX from ISOPOOH from 100 to 75%, within the range observed by St. Clair et al. (2016), to address a factor of 4 overestimate in simulated IEPOX (Nguyen et al., 2015a). IEPOX oxidizes to form glyoxal and methylglyoxal (Bates et al., 2014). The overall glyoxal yield from the $ISOPO_2$ + HO_2 pathway is 6 mol %. Krechmer et al. (2015) report a 2.5 mol % yield of C_5-LVOC from ISOPOOH but we reduce this to 0.5 mol % to reproduce surface observations of the corresponding aerosol products (Section 4). Methyl vinyl ketone and methacrolein yields from the $ISOPO_2$ + HO_2 pathway are 2.5 and 3.8 mol %, respectively (Liu et al., 2013), sufficiently low that they do not lead to significant SOA formation.

Minor channels for $ISOPO_2$ are isomerization and reaction with RO_2. Isomerization forms hydroperoxyaldehydes (HPALD) that go on to photolyze, but products are uncertain (Peeters and Müller, 2010). We assume 25 mol % yield each of glyoxal and methylglyoxal from HPALD photolysis in GEOS-Chem following Stavrakou et al. (2010). Reaction of $ISOPO_2$ with RO_2 leads to the same suite of C_4-C_5 carbonyls as reaction with NO (C_5 hydroxy carbonyls, methacrolein, and methyl vinyl ketone) and from there to glyoxal and methylglyoxal.

Immediate aerosol precursors from the isoprene + OH oxidation cascade are identified in Fig. 2. For the high-NO_x pathway ($ISOPO_2$ + NO channel) these include glyoxal and methylglyoxal (McNeill et al., 2012), ISOPN (Darer et al., 2011; Hu et al., 2011), DHDN (Lee et al., 2014), MEPOX (Lin et al., 2013), and IEPOX (Jacobs et al., 2014). For the low-NO_x pathway ($ISOPO_2$ + HO_2 channel) aerosol precursors are IEPOX (Eddingsaas et al., 2010), C_5-LVOC (Krechmer et al., 2015, in which the aerosol-phase species is denoted ISOPOOH-SOA), glyoxal, and methylglyoxal. Glyoxal and methylglyoxal are also produced from the $ISOPO_2$ + RO_2 and $ISOPO_2$ isomerization channels.

Ozonolysis and oxidation by NO_3 are additional minor isoprene reaction pathways (Fig. 2). The NO_3 oxidation pathway is a potentially important source of isoprene SOA at night (Brown et al., 2009) from the irreversible uptake of low-volatility second-generation hydroxynitrates (NT-ISOPN) (Ng et al., 2008; Rollins et al., 2009). We update the gas-phase chemistry of Rollins et al. (2009) as implemented by Mao et al. (2013) to include formation of 4 mol % of the aerosol-phase precursor NT-ISOPN from first-generation alkylnitrates (Rollins et al., 2009). Ozonolysis products are volatile and observed SOA yields in chamber studies are low (< 1%; Kleindienst et al., 2007). In GEOS-Chem only methylglyoxal is an aerosol precursor from isoprene ozonolysis.

We implement uptake of isoprene oxidation products to aqueous aerosols using laboratory-derived reactive uptake coefficients (γ) as given by Anttila et al. (2006) and Gaston et al. (2014):

$$\gamma = \left[\frac{1}{\alpha} + \frac{3\omega}{4rRTH^{*}k_{aq}} \right]^{-1} \qquad (1).$$

Here α is the mass accommodation coefficient (taken as 0.1 for all immediate SOA precursors in Fig. 2), ω is the mean gas-phase molecular speed (cm s^{-1}), r is the aqueous particle radius (cm), R is the universal gas constant (0.08206 L atm K^{-1} mol^{-1}), T is temperature (K), H^* is the effective Henry's Law constant (M atm^{-1}) accounting for any fast dissociation equilibria in the aqueous phase, and k_{aq} is the pseudo first-order aqueous-phase reaction rate constant (s^{-1}) for conversion to non-volatile products.

Precursors with epoxide functionality, IEPOX and MEPOX, undergo acid-catalyzed epoxide ring opening and nucleophilic addition in the aqueous phase. The aqueous-phase rate constant formulation is from Eddingsaas et al. (2010),

$$k_{aq} = k_{\mathrm{H^+}}\left[\mathrm{H^+}\right] + k_{nuc}\left[nuc\right]\left[\mathrm{H^+}\right] + k_{HSO_4^-}\left[\mathrm{HSO_4^-}\right] \quad (2),$$

and includes three channels: acid-catalyzed ring opening followed by nucleophilic addition of H_2O ($k_{\mathrm{H^+}}$ in M^{-1} s^{-1}) leading to methyltetrols, acid-catalyzed ring opening followed by nucleophilic addition of sulfate and nitrate ions ($nuc \equiv SO_4^{2-} + NO_3^-$, k_{nuc} in M^{-2} s^{-1}) leading to organosulfates and organonitrates, and concerted protonation and nucleophilic addition by bisulfate, HSO_4^- (k_{HSO4-} in M^{-1} s^{-1}), leading to organosulfates.

Precursors with nitrate functionality ($-ONO_2$), ISOPN and DHDN, hydrolyze to form low-volatility polyols and nitric acid (Hu et al., 2011; Jacobs et al., 2014), so k_{aq} in Eq. (1) is the hydrolysis rate constant.

Glyoxal and methylglyoxal form SOA irreversibly by surface uptake followed by aqueous-phase oxidation and oligomerization to yield non-volatile products (Liggio et al., 2005; Volkamer et al., 2009; Nozière et al., 2009; Ervens et al., 2011; Knote et al., 2014). Glyoxal forms SOA with higher yields during the day than at night due to OH aqueous-phase chemistry (Tan et al., 2009; Volkamer et al., 2009; Summer et al., 2014). We use a daytime γ of 2.9 × 10^{-3} for glyoxal from Liggio et al. (2005) and a nighttime γ of 5 × 10^{-6} (Waxman et al., 2013; Sumner et al., 2014). The SOA yield of methylglyoxal is small compared with that of glyoxal (McNeill et al., 2012). A previous GEOS-Chem study by Fu et al. (2008) used the same γ (2.9 × 10^{-3}) for glyoxal and methylglyoxal. Reaction rate constants are similar for aqueous-phase processing of glyoxal and methylglyoxal (Buxton et al., 1997; Ervens et al., 2003), but H^* of glyoxal is about 4 orders of magnitude higher. Here we scale the γ for methylglyoxal to the ratio of effective Henry's law constants: $H^* = 3.7 \times 10^3$ M atm^{-1} for methylglyoxal (Tan et al., 2010) and $H^* = 2.7 \times 10^7$ M atm^{-1} for glyoxal (Sumner et al., 2014). The resulting uptake of methylglyoxal is very slow and makes a negligible contribution to isoprene SOA.

The species C_5-LVOC from ISOPOOH oxidation and NT-ISOPN from isoprene reaction with NO_3 have very low volatility and are assumed to condense to aerosols with a γ of 0.1 limited by mass accommodation. Results are insensitive to the precise value of γ since uptake by aerosols is the main sink for these species in any case.

Table 1 gives input variables used to calculate γ for IEPOX, ISOPN, and DHDN by Eqs. (1) and (2). Rate constants are from experiments in concentrated media, representative of aqueous aerosols, so no activity correction factors are applied. Reported experimental values of k_{H+} vary by an order of magnitude from 1.2 × 10^{-3} M^{-1} s^{-1} (Eddingsaas et al., 2010) to 3.6 × 10^{-2} M^{-1} s^{-1} (Cole-Filipiak et al., 2010). Values of k_{nuc} vary by 3 orders of magnitude from 2 × 10^{-4} M^{-2} s^{-1} (Eddingsaas et al., 2010) to 5.2 × 10^{-1} M^{-2} s^{-1} (Piletic et al., 2013). We chose values of k_{H+} and k_{nuc} to fit the SOAS and SEAC^{4}RS observations of total IEPOX SOA and IEPOX organosulfates, as shown in Section 4.

Table 2 lists average values of γ for all immediate aerosol precursors in the Southeast US boundary layer in summer as simulated by GEOS-Chem (Section 3). γ for IEPOX is a strong function of pH and increases from 1×10^{-4} to 1×10^{-2} as pH decreases from 3 to 0. The value of γ for MEPOX is assumed to be 30 times lower than that of IEPOX when the aerosol is acidic (pH < 4), due to slower acid-catalyzed ring opening (Piletic et al., 2013; Riedel et al., 2015). At pH > 4 we assume that γ for IEPOX and MEPOX are the same (Riedel et al., 2015), but they are then very low.

Isoprene SOA formation in clouds is not considered here. Acid-catalyzed pathways would be slow. Observations show that the isoprene SOA yield in the presence of laboratory-generated clouds is low (0.2-0.4%; Brégonzio-Rozier et al., 2015). Wagner et al. (2015) found no significant production of SOA in boundary layer clouds over the Southeast US during SEAC^{4}RS.

3. GEOS-Chem simulation and isoprene SOA yields

Several companion papers apply GEOS-Chem to interpret SEAC^{4}RS and surface data over the Southeast US in summer 2013 including Kim et al. (2015) for aerosols, Fisher et al. (2016) for organic nitrates, Travis et al. (2016) for ozone and NO_x, and Zhu et al. (2016) for HCHO. These studies use a model version with 0.25° × 0.3125° horizontal resolution over North America, nested within a 4° × 5° global simulation. Here we use a 2° × 2.5° global GEOS-Chem simulation with no nesting. Yu et al. (2016) found little difference between 0.25° × 0.3125° and 2° × 2.5° resolutions in simulated regional statistics for isoprene chemistry.

The reader is referred to Kim et al. (2015) for a general presentation of the model, the treatment of aerosol sources and sinks, and evaluation with Southeast US aerosol observations; and to Travis et al. (2016) and Fisher et al. (2016) for presentation of gas-phase chemistry and comparisons with observed gas-phase isoprene oxidation products. Isoprene emission is from the MEGAN v2.1 inventory (Guenther et al., 2012). The companion papers decrease isoprene emission by 15% from the MEGAN v2.1 values to fit the HCHO data (Zhu et al., 2016), but this is not applied here.

Our SOA simulation differs from that of Kim et al. (2015). They assumed fixed 3% and 10% mass yields of SOA from isoprene and monoterpenes, respectively, and parameterized SOA formation from anthropogenic and open fire sources as a kinetic irreversible process following Hodzic and Jimenez (2011). Here we use our new aqueous-phase mechanism for isoprene SOA coupled to gas-phase chemistry as described in Section 2, and otherwise use the semivolatile reversible partitioning scheme of Pye et al. (2010) for monoterpene, anthropogenic, and open fire SOA. Kim et al. (2015) found no systematic bias in detailed comparisons to OA measurements from SEAC^{4}RS and from surface networks. We find a low bias, as shown below, because the reversible partitioning scheme yields low SOA concentrations.

Organic aerosol and sulfate contribute most of the aerosol mass over the Southeast US in summer, while nitrate is negligibly small (Kim et al., 2015). GEOS-Chem uses the ISORROPIA thermodynamic model (Fountoukis and Nenes, 2007) to simulate sulfate-nitrate-ammonium (SNA) aerosol composition, water content, and acidity as a function of local conditions. Simulated aerosol pH along the SEAC^{4}RS flight tracks in the Southeast US boundary layer averages 1.3 (interquartiles 0.92 and 1.8). The aerosol pH remains below 3 even when sulfate aerosol is fully neutralized by ammonia (Guo et al., 2015).

We consider that the aqueous aerosol population where isoprene SOA formation can take place is defined by the sulfate aerosol population. This assumes that all aqueous aerosol particles contain some sulfate, and that all sulfate is aqueous. Clear-sky RH measured from the aircraft in the Southeast US boundary layer during SEAC^{4}RS averaged 72 ± 17%, and the corresponding values in GEOS-Chem sampled along the flight tracks averaged 66 ± 16%). These RHs are sufficiently high that sulfate aerosol can reliably be expected to be aqueous (Wang et al., 2008). The rate of gas uptake by the sulfate aerosol is computed with the pseudo-first order reaction rate constant k_{het} (s^{-1}) (Schwartz, 1986; Jacob, 2000):

$$k_{het} = \int_0^\infty 4\pi r^2 \left(\frac{r}{D_g} + \frac{4}{\gamma\omega} \right)^{-1} n(r)dr \qquad (3),$$

where D_g is the gas-phase diffusion constant (taken to be 0.1 $cm^2 s^{-1}$) and $n(r)$ is the number size distribution of sulfate aerosol (cm^{-4}). The first and second terms in parentheses describe the limitations to gas uptake from gas-phase diffusion and aqueous-phase reaction, respectively.

The sulfate aerosol size distribution including RH-dependent hygroscopic growth factors is from the Global Aerosol Data Set (GADS) of Koepke et al. (1997), as originally implemented in GEOS-Chem by Martin et al. (2003) and updated by Drury et al. (2010). The GADS size distribution compares well with observations over the eastern US in summer (Drury et al., 2010), including for SEAC^{4}RS (Kim et al., 2015). We compute $n(r)$ locally in GEOS-Chem by taking the dry SNA mass concentration, converting from mass to volume with a dry aerosol mass density of 1700 kg m^{-3} (Hess et al., 1998), applying the aerosol volume to the dry sulfate size distribution in GADS, and then applying the GADS hygroscopic growth factors. We verified that the hygroscopic growth factors from GADS agree within 10% with those computed locally from ISORROPIA.

Figure 2 shows the mean branching ratios for isoprene oxidation in the Southeast US boundary layer as calculated by GEOS-Chem. 87% of isoprene reacts with OH, 8% with ozone, and 5% with NO_3. Oxidation of isoprene by OH produces $ISOPO_2$ of which 51% reacts with NO (high-NO_x pathway), 35% reacts with HO_2, 8% isomerizes, and 6% reacts with other RO_2 radicals.

Glyoxal is an aerosol precursor common to all isoprene + OH pathways in our mechanism with yields of 7 mol % from the $ISOPO_2$ + NO pathway, 6 mol % from $ISOPO_2$ + HO_2, 11 mol % from $ISOPO_2$ + RO_2, and 25 mol % from $ISOPO_2$ isomerization. For the Southeast US conditions we thus find that 44% of glyoxal is from the $ISOPO_2$ + NO pathway, 24% from $ISOPO_2$ + HO_2, 8% from $ISOPO_2$ + RO_2, and 24% from $ISOPO_2$ isomerization.

The mean total yield of isoprene SOA computed in GEOS-Chem for the Southeast US boundary layer is 3.3%, as shown in Fig. 2. IEPOX contributes 1.9% and glyoxal 0.9%. The low-NO_x pathway involving $ISOPO_2$ reaction with HO_2 contributes 73% of the total isoprene SOA yield, mostly from IEPOX, even though this pathway is only 35% of the fate of $ISOPO_2$. The high-NO_x pathway contributes 16% of isoprene SOA, mostly from glyoxal. MEPOX contribution to isoprene SOA is small (2%) and consistent with a recent laboratory study that finds low SOA yields from this pathway under humid conditions (Nguyen et al., 2015b). The minor low-NO_x pathways from $ISOPO_2$ isomerization and reaction with RO_2 contribute 8% of isoprene SOA through glyoxal. The remainder of isoprene SOA formation (3%) is from nighttime oxidation by NO_3.

The dominance of IEPOX and glyoxal as precursors for isoprene SOA was previously found by McNeill et al. (2012) using a photochemical box model. Both IEPOX and glyoxal are produced photochemically, and both are removed photochemically in the gas phase by reaction with OH (and photolysis for glyoxal). The mean lifetimes of IEPOX and glyoxal against gas-phase photochemical loss average 1.6 and 2.3 h respectively for SEAC^{4}RS daytime conditions; mean lifetimes against reactive uptake by aerosol are 31 and 20 hours, respectively. For both species, aerosol uptake is thus a minor sink competing with gas-phase photochemical loss. The model yield of IEPOX SOA from IEPOX is 5% in the boundary layer, consistent with average yields from chamber experiments (4-10%) for aerosols with similar acidity to aerosols in the Southeast US (Riedel et al., 2015).

The dominance of gas-phase loss over aerosol uptake for both IEPOX and glyoxal implies that isoprene SOA formation is highly sensitive to their reactive uptake coefficients γ and to the aqueous aerosol mass concentration (in both cases, γ is small enough that uptake is controlled by bulk aqueous-phase rather than surface reactions). We find under SEAC^{4}RS conditions that γ for IEPOX is mainly controlled by the H$^+$ concentration (k_{H+}[H$^+$] in Eq. (2)), with little contribution from nucleophile-driven and HSO_4^--driven channels. This will be discussed below in comparison to SOAS and SEAC^{4}RS observations.

The 3.3% mean yield of isoprene SOA from our mechanism is consistent with the fixed yield of 3% assumed by Kim et al. (2015) in their GEOS-Chem simulation of the SEAC^{4}RS period, including extensive comparisons to OA observations that showed a 40% mean contribution of isoprene to total OA. We conducted a sensitivity simulation using the default isoprene SOA mechanism in GEOS-Chem based on reversible partitioning of semivolatile oxidation products onto pre-existing OA (Pye et al., 2010). The isoprene SOA yield in that simulation was only 1.1%. The observed correlation of OA with HCHO in SEAC^{4}RS supports our higher yield, as shown below.

4. Observational constraints on isoprene SOA yields

Isoprene is the largest source of HCHO in the Southeast US (Millet et al., 2006), and we use the observed relationship between OA and HCHO to evaluate the GEOS-Chem isoprene SOA yields. The SEAC^{4}RS aircraft payload included measurements of OA from an Aerodyne Aerosol Mass Spectrometer (HR-ToF-AMS; DeCarlo et al, 2006; Canagaratna et al, 2007) concurrent with HCHO from a laser-induced fluorescence instrument (ISAF; Cazorla et al., 2015). Column HCHO was also measured during SEAC^{4}RS from the OMI satellite instrument (González Abad et al., 2015; Zhu et al., 2016), providing a proxy for isoprene emission (Palmer et al., 2003; 2006).

Figure 3 (left) shows the observed and simulated relationships between OA and HCHO mixing ratios in the boundary layer. There is a strong correlation in the observations and in the model (R = 0.79 and R = 0.82, respectively). OA simulated with our aqueous-phase isoprene SOA mechanism reproduces the observed slope (2.8 ± 0.3 μg sm^{-3} ppbv^{-1}, vs. 3.0 ± 0.4 μg sm^{-3} ppbv^{-1} in the observations). Similarly strong correlations and consistency between model and observations are found with column HCHO measured from OMI (Fig. 3, right). The estimated error on individual OMI HCHO observations is about 30% (Millet et al., 2006).

Also shown in Fig. 3 is a sensitivity simulation with the default GEOS-Chem mechanism based on reversible partitioning with pre-existing organic aerosol (Pye et al., 2010) and producing a 1.1% mean isoprene SOA yield, as compared to 3.3% in our simulation with the aqueous-phase mechanism. That sensitivity simulation shows the same OA-HCHO correlation (R = 0.82) but underestimates the slope (2.0 ± 0.3 μg sm^{-3} ppbv^{-1}). The factor of 3 increase in our isoprene SOA yield does not induce a proportional increase in the slope, as isoprene contributes only ~ 40% of OA in the Southeast US. But the slope is sensitive to the isoprene SOA yield, and the good agreement between our simulation and observations supports our estimate of a mean 3.3% yield for the Southeast US.

Figure 3 shows an offset between the model and observations illustrated by the regression lines. We overestimate HCHO by 0.4 ppbv on average because we did not apply the 15% downward correction to MEGAN v2.1 isoprene emissions (Zhu et al., 2016). We also underestimate total OA measured by the AMS in the boundary layer by 1.1 μg sm^{-3} (mean AMS OA is 5.8 ± 4.3 μg sm^{-3}; model OA is 4.7 ± 4.4 μg sm^{-3}). The bias can be explained by our omission of anthropogenic and open fire SOA, found by Kim et al. (2015) to account on average for 18% of OA in SEAC^{4}RS.

Figure 4 shows time series of the isoprene SOA components IEPOX SOA and C$_5$-LVOC SOA at Centreville, Alabama during SOAS. AMS observations from Hu et al. (2015) and Krechmer et al. (2015) are compared to model values. IEPOX SOA and C$_5$-LVOC SOA are on average 17% and 2% of total AMS OA, respectively (Hu et al., 2015; Krechmer et al., 2015). The model reproduces mean IEPOX SOA and C$_5$-LVOC SOA without bias, supporting the conclusion that IEPOX is the dominant contributor to isoprene SOA in the Southeast US (Fig. 2). Low values on July 2-7, both in the observations and the model, are due to low temperatures suppressing isoprene emission.

Figure 5 shows the relationships of daily mean IEPOX SOA and sulfate concentrations at Centreville and in the SEAC^{4}RS boundary layer. The same factor analysis method was used to derive IEPOX SOA in SEAC^{4}RS as in SOAS, however the uncertainty is larger for the aircraft observations due to the much wider range of conditions encountered. There is a strong correlation between IEPOX SOA and sulfate, both in observations and the model, with similar slopes. Correlation between IEPOX SOA and sulfate has similarly been observed at numerous

Southeast US monitoring sites (Budisulistiorini et al., 2013; 2015; Xu et al., 2015; Hu et al., 2015). Xu et al. (2015) concluded that IEPOX SOA must form by acid-catalyzed nucleophilic addition of sulfate (sulfate channels in Eq. (2)) leading to organosulfates. However, we find in our model that the H^+-catalyzed channel ($k_{H+}[H^+]$ term in Eq. (2)) contributes 90% of IEPOX SOA formation throughout the Southeast US boundary layer, and that sulfate channels play only a minor role. Thus the correlation of IEPOX SOA and sulfate is not an indication of organosulfate formation but rather reflects the correlation of sulfate with aqueous aerosol volume and acidity. Measurements from the PALMS laser mass spectrometer during SEAC^{4}RS (Liao et al., 2015) show a mean IEPOX organosulfate concentration of 0.13 μg sm^{-3}, amounting to at most 9% of total IEPOX SOA. The organosulfate should be a marker of the sulfate channels because its hydrolysis is negligibly slow (Hu et al., 2011).

Formation of IEPOX SOA is nearly linear with k_{het} in Eq. (3) as aqueous aerosol is only a minor sink for IEPOX. IEPOX γ is sufficiently small (Table 2) that gas-phase diffusion and mass accommodation are not limiting processes. k_{aq} in Eq. (2) is dominated by the $k_{H+}[H^+]$ term as discussed above. It follows from combination of Eqs. (1), (2), and (3) that IEPOX SOA formation is proportional to $V[H^+]$, where V is the volume concentration of aqueous aerosol. An increased supply of sulfate as sulfuric acid increases both V and $[H^+]$, explaining the correlation between IEPOX SOA and sulfate.

Correlation between IEPOX SOA and sulfate is also apparent in the spatial distribution of IEPOX SOA, as observed by the SEAC^{4}RS aircraft below 2 km and simulated by GEOS-Chem along the aircraft flight tracks (Fig. 6). The correlation between simulated and observed IEPOX SOA in Fig. 6 is R = 0.70. Average (mean) IEPOX SOA is 1.4 ± 1.4 μg sm^{-3} in the observations and 1.3 ± 1.2 μg sm^{-3} in the model. The correlation between IEPOX SOA and sulfate is 0.66 in the observations and 0.77 in the model. IEPOX SOA concentrations are highest in the industrial Midwest and Kentucky, and in Louisiana-Mississippi, coincident with the highest sulfate concentrations sampled on the flights. We also see in Fig. 6 frequent observations of very low IEPOX SOA (less than 0.4 μg sm^{-3}) that are well captured by the model. These are associated with very low sulfate (less than 1 μg sm^{-3}).

The mean IEPOX SOA concentration simulated by the model for the $SEAC^4RS$ period (background contours in Fig. 6) is far more uniform than IEPOX SOA simulated along the flight tracks. This shows the importance of day-to-day variations in sulfate in driving IEPOX SOA variability. IEPOX SOA contributed on average 24% of total OA in the $SEAC^4RS$ observations, and 28% in GEOS-Chem sampled along the flight tracks and as a regional mean. With IEPOX SOA accounting for 58% of isoprene SOA in the model (Fig. 2), this amounts to a 41-48% contribution of isoprene to total OA, consistent with the previous estimate of 40% by Kim et al. (2015).

5. Effect of Anthropogenic Emission Reductions

The EPA projects that US anthropogenic emissions of NO_x and SO_2 will decrease respectively by 34% and 48% from 2013 to 2025 (EPA, 2014). We conducted a GEOS-Chem sensitivity simulation to examine the effect of these changes on isoprene SOA, assuming no other changes and further assuming that the emission decreases are uniform across the US.

Figure 7 shows the individual and combined effects of NO_x and SO_2 emission reductions on the branching pathways for isoprene oxidation, sulfate mass concentration, aerosol pH, and isoprene SOA in the Southeast US boundary layer in summer. Reducing NO_x emission by 34% decreases the mean NO concentration by only 23%, in part because decreasing OH increases the

NO_x lifetime and in part because decreasing ozone increases the NO/NO_2 ratio. There is no change in HO_2. We find a 10% decrease in the high-NO_x pathway and a 6% increase in the low-NO_x pathway involving $ISOPO_2 + HO_2$. Aerosol sulfate decreases by 2% and there is no change in $[H^+]$. The net effect is a 7% increase in isoprene SOA, as the major individual components IEPOX SOA and glyoxal SOA increase by 17% and decrease by 8%, respectively.

A 48% decrease in SO_2 emissions drives a 36% reduction in sulfate mass concentration, leading to a decline in aerosol volume (31%) that reduces uptake of all isoprene SOA precursors. The decrease in aerosol $[H^+]$ (26%) further reduces IEPOX uptake. Decline in aerosol volume and $[H^+]$ have a comparable effect on IEPOX SOA, as the change in each due to SO_2 emission reductions is similar (~30%) and uptake of IEPOX SOA is proportional to the product of the two (Section 4). IEPOX SOA and glyoxal SOA decrease by 45% and 26%, respectively, and total isoprene SOA decreases by 35%. Pye et al. (2013) included uptake of IEPOX to aqueous aerosols in a regional chemical transport model and similarly found that SO_2 emissions are more effective than NO_x emissions at reducing IEPOX SOA in the Southeast US. Remarkably, we find that reducing SO_2 emissions decreases sulfate and isoprene SOA with similar effectiveness (Fig. 7). With sulfate contributing ~30% of present-day $PM_{2.5}$ in the Southeast US and isoprene SOA contributing ~25% (Kim et al., 2015), this represents a factor of 2 co-benefit on $PM_{2.5}$ from reducing SO_2 emissions.

We examined whether this co-benefit from reducing SO_2 emissions can be seen in past decadal trends. Observations from monitoring networks in the Southeast US show that summertime OA and sulfate concentrations declined from 2003 to 2013 at rates of 3.9% a^{-1} and 7.4% a^{-1}, respectively, while wintertime OA showed no significant decrease (Kim et al., 2015). With isoprene accounting for 40% of OA in summer (Kim et al., 2015), and assuming no trend in other OA components on the basis of the wintertime data, we would infer a rate of isoprene SOA decrease of 9.8% a^{-1}. The observed trends thus seem to support a similar relative rate of decrease of sulfate and isoprene SOA over the past decade.

6. Conclusions

Standard mechanisms for formation of isoprene secondary organic aerosol (SOA) in chemical transport models assume reversible partitioning of isoprene oxidation products to pre-existing dry OA. This may be appropriate for dry conditions in experimental chambers but not for typical atmospheric conditions where the aerosol is mostly aqueous. Here we developed an aqueous-phase reactive uptake mechanism coupled to a detailed gas-phase isoprene chemistry mechanism to describe the reactive uptake of water-soluble isoprene oxidation products to aqueous aerosol. We applied this mechanism in the GEOS-Chem chemical transport model to simulate surface (SOAS) and aircraft (SEAC^{4}RS) observations over the Southeast US in summer 2013.

Our mechanism includes different channels for isoprene SOA formation by the high-NO_x pathway, when the isoprene peroxy radicals ($ISOPO_2$) react with NO, and in the low-NO_x pathway where they react mostly with HO_2. The main SOA precursors are found to be isoprene epoxide (IEPOX) in the low-NO_x pathway and glyoxal in the high- and low-NO_x pathways. Both of these precursors have dominant gas-phase photochemical sinks, and so their uptake by aqueous aerosol is nearly proportional to the reactive uptake coefficient γ and to the aqueous aerosol mass concentration. The γ for IEPOX is mostly determined by the rate of H^+-catalyzed ring opening in the aqueous phase.

Application of our mechanism to the Southeast US indicates a mean isoprene SOA yield of 3.3% on a mass basis. By contrast, a conventional mechanism based on reversible uptake of semivolatile isoprene oxidation products yields only 1.1%. Simulation of the observed relationship of OA with formaldehyde (HCHO) provides support for our higher yield. We find that the low-NO_x pathway is 5 times more efficient than the high-NO_x pathway for isoprene SOA production. Under Southeast US conditions, IEPOX and glyoxal account respectively for 58% and 28% of isoprene SOA.

Our model simulates well the observations and variability of IEPOX SOA at the surface and from aircraft. The observations show a strong correlation with sulfate that we reproduce in the model. This correlation was previously attributed to acid-catalyzed nucleophilic addition of sulfate as mechanism for IEPOX SOA formation but we find in the model that this pathway is minor. We find instead that the correlation of IEPOX SOA with sulfate is due to the effect of sulfate on aerosol pH and volume concentration, increasing IEPOX uptake by the H^+-catalyzed ring-opening mechanism. Low concentrations of sulfate are associated with very low IEPOX SOA, both in the observations and the model, and we attribute this to the compounding effects of low sulfate on aerosol $[H^+]$ and on aerosol volume.

The US EPA has projected that US NO_x and SO_2 emissions will decrease by 34 and 48% respectively from 2013 to 2025. We find in our model that the NO_x reduction will increase isoprene SOA by 7%, reflecting greater importance of the low-NO_x pathway. The SO_2 reduction will decrease isoprene SOA by 35%, due to decreases in both aerosol $[H^+]$ and volume concentration. The combined effect of these two changes is to decrease isoprene SOA by 32%, corresponding to a decrease in the isoprene SOA mass yield from 3.3% to 2.3%. Decreasing SO_2 emissions by 48% has similar relative effects on sulfate (36%) and isoprene SOA (35%).

Considering that sulfate presently accounts for about 30% of $PM_{2.5}$ in the Southeast US in summer, while isoprene SOA contributes 25%, we conclude that decreasing isoprene SOA represents a factor of 2 co-benefit when reducing SO_2 emissions. There is some evidence for this co-benefit in observed long-term trends of OA in the Southeast US over the past decade.

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TABLES

Table 1. Constants for reactive uptake of isoprene SOA precursors [a]

Species [b]	H^* [M atm^{-1}]	$k_{\mathrm{H+}}$ [M^{-1} s^{-1}]	k_{nuc} [M^{-2} s^{-1}]	$k_{\mathrm{HSO4-}}$ [M^{-1} s^{-1}]	k_{aq} [s^{-1}]
IEPOX	3.3×10^7 [c]	3.6×10^{-2} [d]	2.0×10^{-4} [e]	7.3×10^{-4} [e]	Equation (2)
ISOPN$_\beta$ [f]	3.3×10^5 [g]	–	–	–	1.6×10^{-5} [h]
ISOPN$_\delta$ [f]	3.3×10^5 [g]	–	–	–	6.8×10^{-3} [h]
DHDN	3.3×10^5 [g]	–	–	–	6.8×10^{-3} [i]

[a] Effective Henry's law constants H^* and aqueous-phase rate constants used to calculate reactive uptake coefficients γ for isoprene SOA precursors IEPOX, ISOPN$_\beta$, ISOPN$_\delta$, and DHDN following Eqs. (1) and (2). Calculation of γ for other isoprene SOA precursors in Fig. 2 is described in the text.

[b] See Fig. 2 for definition of acronyms.

[c] Nguyen et al. (2014).

[d] Cole-Filipiak et al. (2010).

[e] Eddingsaas et al. (2010).

[f] ISOPN species formed from the beta and delta isoprene oxidation channels (Paulot et al., 2009a) are treated separately in GEOS-Chem.

[g] By analogy with 4-nitrooxy-3-methyl-2-butanol (Rollins et al., 2009).

[h] Jacobs et al. (2014).

[i] Assumed same as for ISOPN$_\delta$ (Hu et al., 2011).

Table 2. Mean reactive uptake coefficients γ of isoprene SOA precursors [a]

Species [b]	γ	pH dependence [c]			
		pH > 3	2 < pH < 3	1 < pH < 2	0 < pH < 1
IEPOX	4.2×10^{-3}	8.6×10^{-7}	2.0×10^{-4}	1.1×10^{-3}	1.0×10^{-2}
MEPOX	1.3×10^{-4}	2.7×10^{-8}	6.4×10^{-6}	3.6×10^{-5}	3.2×10^{-4}
$ISOPN_\beta$	1.3×10^{-7}	–			
$ISOPN_\delta$	5.2×10^{-5}	–			
DHDN	6.5×10^{-5}	–			
GLYX	2.9×10^{-3}, [d]	–			
MGLY	4.0×10^{-7}	–			
C_5-LVOC	0.1	–			
NT-ISOPN	0.1	–			

[a] Mean values computed in GEOS-Chem for the Southeast US in summer as sampled along the boundary-layer (< 2 km) SEAC^{4}RS aircraft tracks and applied to aqueous aerosol. The reactive uptake coefficient γ is defined as the probability that a gas molecule colliding with an aqueous aerosol particle will be taken up and react in the aqueous phase to form non-volatile products.

[b] See Fig. 2 for definition of acronyms.

[c] γ for IEPOX and MEPOX are continuous functions of pH (Eq. (2)). Values shown here are averages for different pH ranges sampled along the SEAC^{4}RS flight tracks. Aqueous aerosol pH is calculated locally in GEOS-Chem using the ISORROPIA thermodynamic model (Fountoukis and Nenes, 2007).

[d] Daytime value. Nighttime value is 5×10^{-6}.

FIGURES

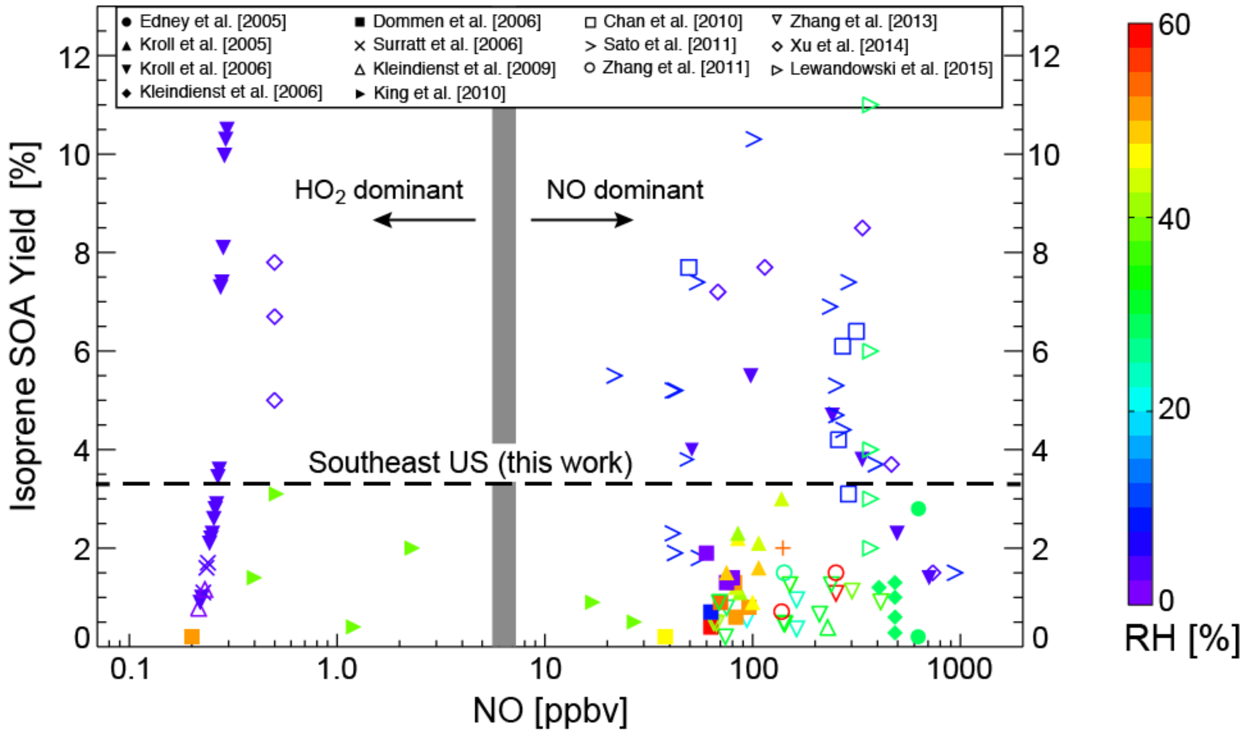

Figure 1. Yields of secondary organic aerosol (SOA) from isoprene oxidation as reported by chamber studies in the literature and plotted as a function of the initial NO concentration and relative humidity (RH). Yields are defined as the mass of SOA produced per unit mass of isoprene oxidized. For studies with no detectable NO we plot the NO concentration as half the reported instrument detection limit, and stagger points as needed for clarity. Data are colored by relative humidity (RH). The thick grey line divides the low-NO$_x$ and high-NO$_x$ pathways as determined by the fate of the ISOPO$_2$ radical (HO$_2$ dominant for the low-NO$_x$ pathway, NO dominant for the high-NO$_x$ pathway). The transition between the two pathways occurs at a higher NO concentration than in the atmosphere because HO$_2$ concentrations in the chambers are usually much higher. Also shown as dashed line is the mean atmospheric yield of 3.3% for the Southeast US determined in our study.

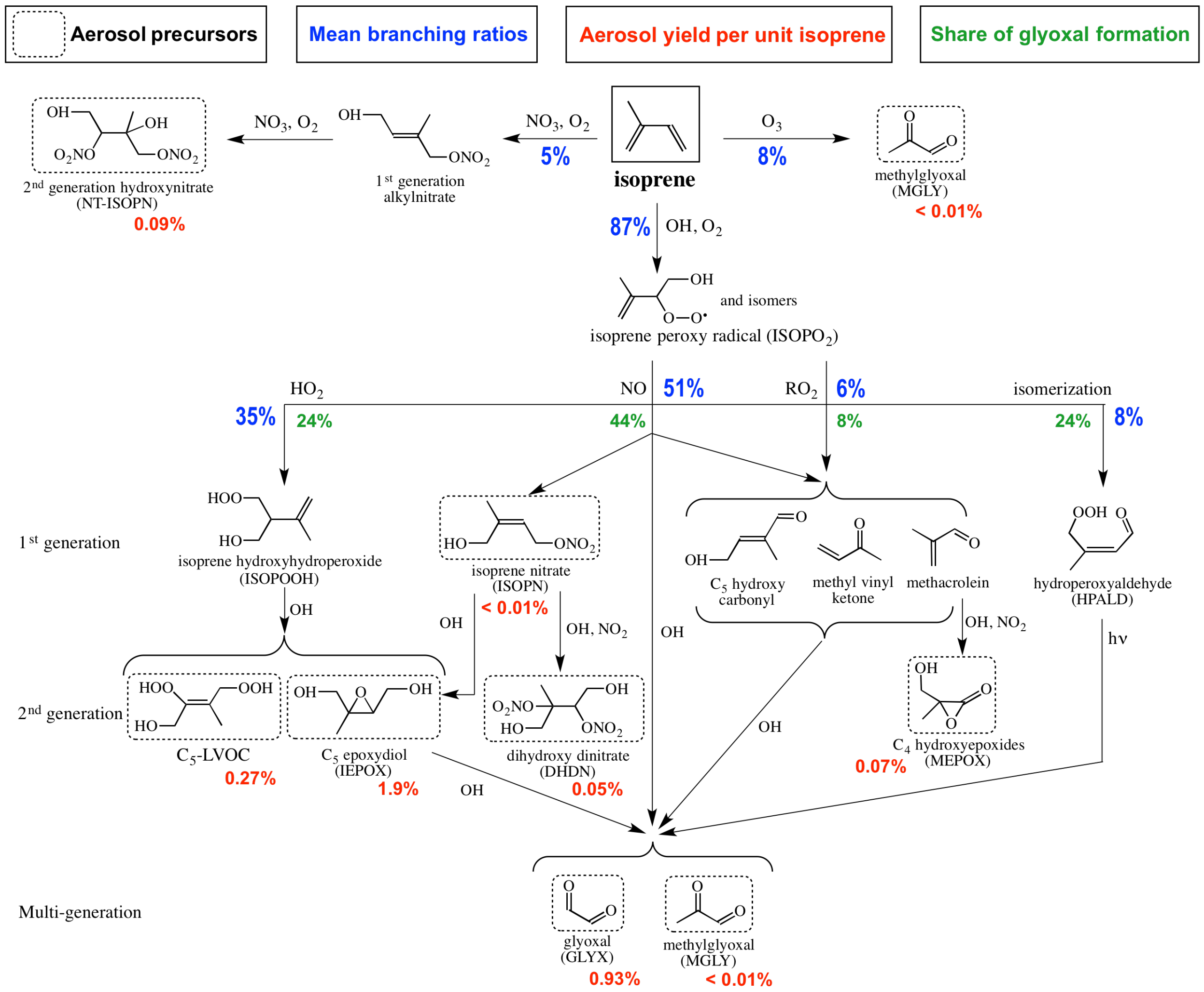

Figure 2. Gas-phase isoprene oxidation cascade in GEOS-Chem leading to secondary organic aerosol (SOA) formation by irreversible aqueous-phase chemistry. Only selected species relevant to SOA formation are shown. Immediate aerosol precursors are indicated by dashed boxes. Branching ratios and SOA yields (aerosol mass produced per unit mass isoprene reacted) are mean values from our GEOS-Chem simulation for the Southeast US boundary layer in summer. The total SOA yield from isoprene oxidation is 3.3% and the values shown below the dashed boxes indicate the contributions from the different immediate precursors adding up to 3.3%. Contributions of high- and low-NO_x isoprene oxidation pathways to glyoxal are indicated.

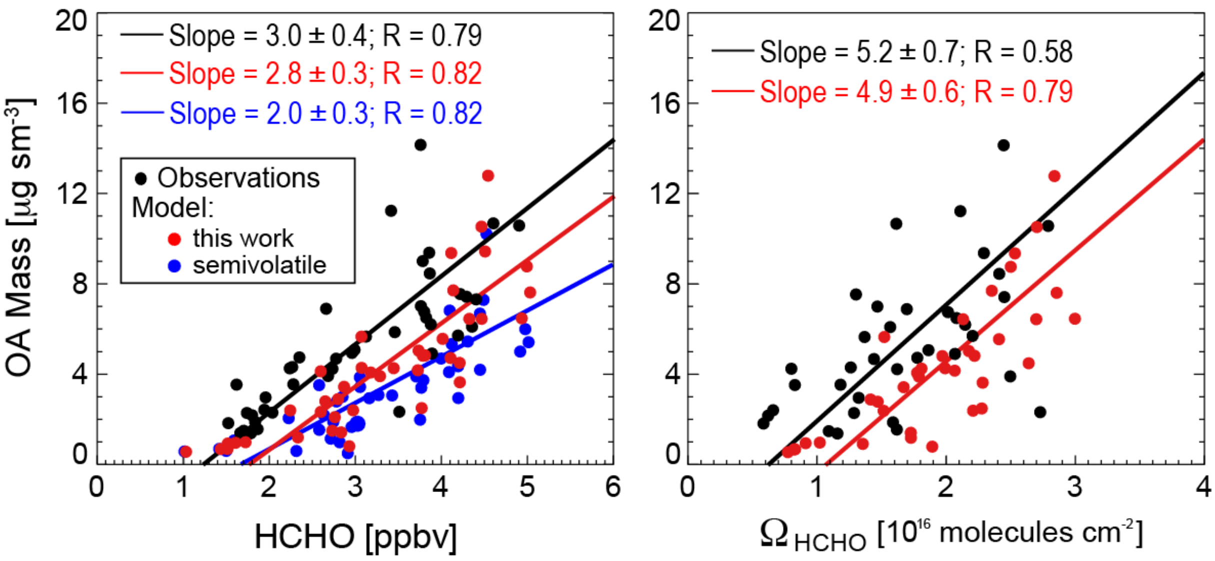

Figure 3. Relationship of organic aerosol (OA) and formaldehyde (HCHO) concentrations over the Southeast US in summer. The figure shows scatterplots of SEAC^{4}RS aircraft observations of OA concentrations in the boundary layer (< 2 km) vs. HCHO mixing ratios measured from the aircraft (left), and column HCHO (Ω_{HCHO}) retrieved from OMI satellite observations (right). Individual points are data from individual SEAC^{4}RS flight days (August 8 - September 10), averaged on the GEOS-Chem grid. OMI data are for SEAC^{4}RS flight days and coincident with the flight tracks. GEOS-Chem is sampled for the corresponding locations and times. Results from our simulation with aqueous-phase isoprene SOA chemistry are shown in red, and results from a simulation with the Pye et al. (2010) semivolatile reversible partitioning scheme are shown in blue. Aerosol concentrations are per m^3 at standard conditions of temperature and pressure (STP: 273 K; 1 atm), denoted sm^{-3}. Reduced major axis (RMA) regressions are also shown with regression parameters and Pearson's correlation coefficients given inset. 1σ standard deviations on the regression slopes are obtained with jackknife resampling.

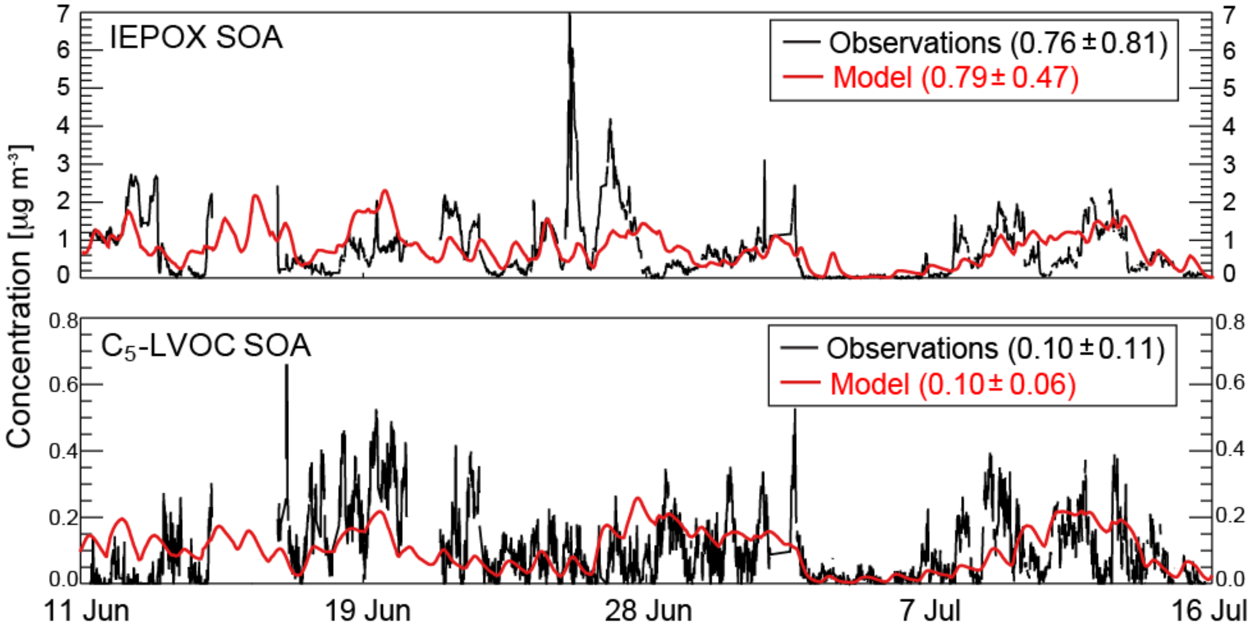

Figure 4. Time series of the concentrations of isoprene SOA components at the SOAS site in Centreville, Alabama (32.94°N; 87.18°W) in June-July 2013: measured (black) and modeled (red) IEPOX SOA (top) and C_5-LVOC SOA (bottom) mass concentrations. Means and 1σ standard deviations are given for the observations and the model.

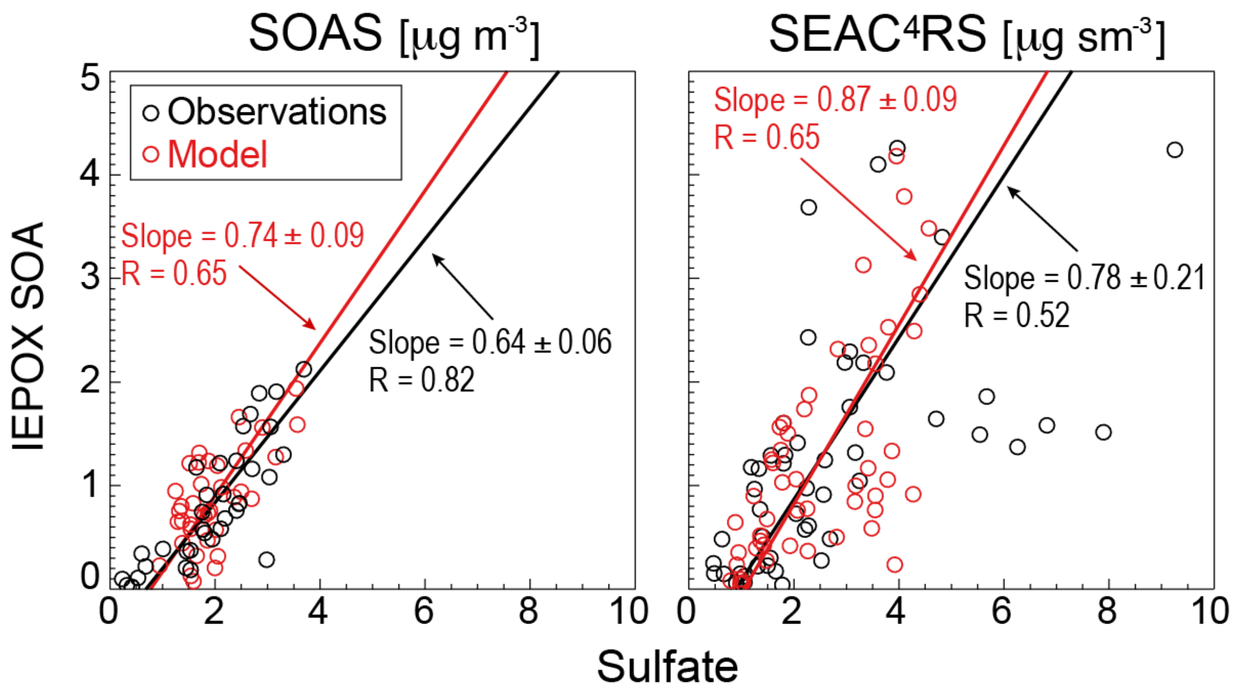

Figure 5. Relationship of IEPOX SOA and sulfate concentrations over the Southeast US in summer. Observed (black) and simulated (red) data are averages for each campaign day during SOAS (left), and boundary layer averages (< 2 km) for 2° × 2.5° GEOS-Chem grid squares on individual flight days during SEAC^{4}RS (right). RMA regression slopes and Pearson's correlation coefficients are shown. 1σ standard deviations on the regression slopes are obtained with jackknife resampling.

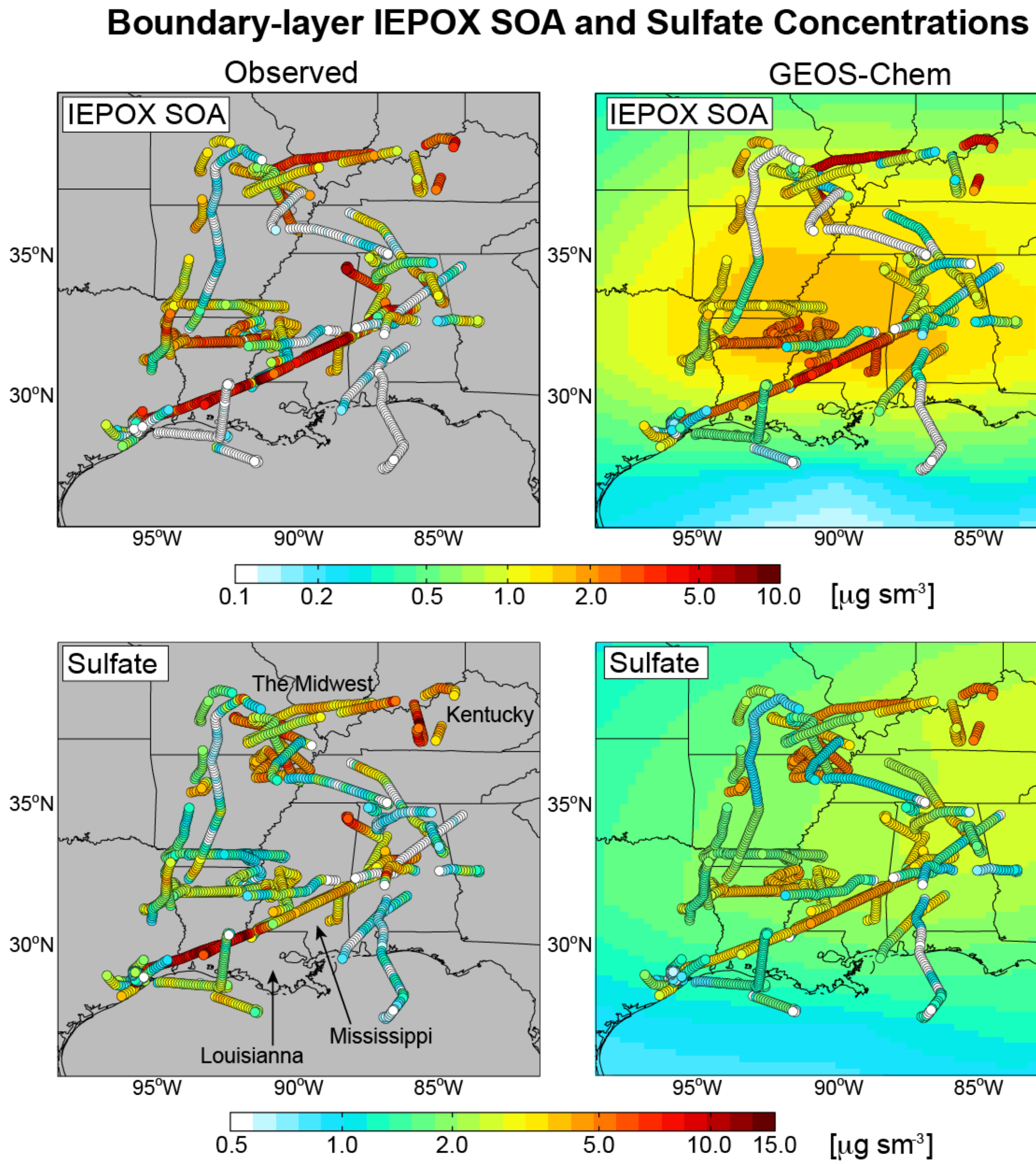

Figure 6. Spatial distributions of IEPOX SOA and sulfate concentrations in the boundary layer (<2 km) over the Southeast US during SEAC^{4}RS (August-September 2013). Aircraft AMS observations of IEPOX SOA (top left) and sulfate (bottom left) are compared to model values sampled at the time and location of the aircraft observations (individual points) and averaged during the SEAC^{4}RS period (background contours). Data are on a logarithmic scale.

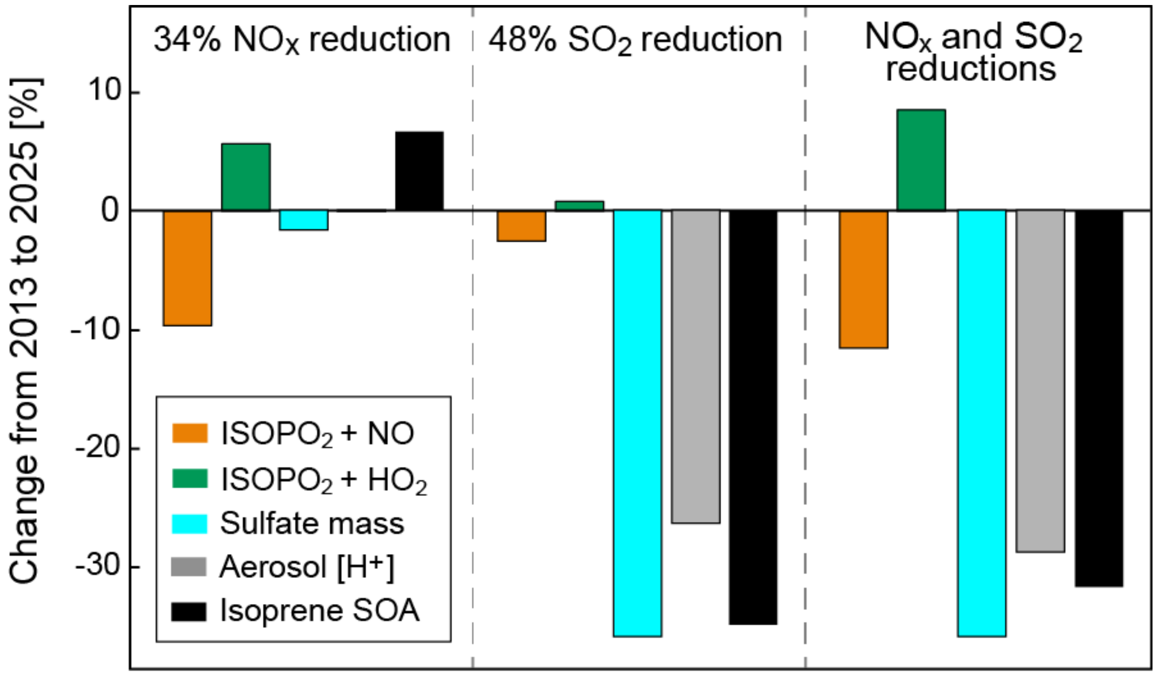

Figure 7. Effect of projected 2013-2025 reductions in US anthropogenic emissions on the formation of isoprene secondary organic aerosol (SOA). Emissions of NO_x and SO_2 are projected to decrease by 34% and 48%, respectively. Panels show the resulting percentage changes in the branching of $ISOPO_2$ between the NO and HO_2 oxidation channels, sulfate mass concentration, aerosol $[H^+]$ concentration, and isoprene SOA mass concentration. Values are summer means for the Southeast US boundary layer.