Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application to the southeast United States and co-benefit of SO2 emission controls

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Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application to the southeast United States and co-benefit of SO2 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 prevalingly 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 (SEAC4RS) and ground-based (SOAS) observations over the southeast US in summer 2013 using the GEOS-Chem chemical transport model. Emissions of nitrogen oxides (NOx ≡ NO + NO2) over the southeast US are such that the peroxy radicals produced from isoprene oxidation (ISOPO2) react significantly with both NO (high-NOx pathway) and HO2 (low-NOx 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 epoxidiols (IEPOX, 58 % of isoprene SOA) from the low-NOx pathway and glyoxal (28 %) from both low- and high-NOx pathways. This speciation is consistent with observations of IEPOX SOA from SOAS and SEAC4RS. 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 NOx emissions decrease (favoring the low-NOx pathway for isoprene oxidation), but decrease more strongly as SO2 emissions decrease (due to the effect of sulfate on aerosol acidity and volume). The US Environmental Protection Agency (EPA) projects 2013–2025 decreases in anthropogenic emissions of 34 % for NOx (leading to a 7 % increase in isoprene SOA) and 48 % for SO2 (35 % decrease in isoprene SOA). Reducing SO2 emissions decreases sulfate and isoprene SOA by a similar magnitude, represent-
ing a factor of 2 co-benefit for PM$_{2.5}$ from SO$_2$ emission controls.

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$_x$ = 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, b). 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 and the SEAC$^4$RS science team, 2016; SEAC$^4$RS Archive, 2015).

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$_x$ 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).
in mass percent, unless stated otherwise. Reactive ISOPO$_2$ to isoprene SOA precursors are described below. 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 gray 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 a dashed line is the mean atmospheric yield of 3.3 % for the southeast US determined in our study.

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, b) 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).

The NO reaction pathway is 7 mol % (yield on a molar basis). Krechmer et al. (2015) report a 2.5 mol % yield of C$_5$-LVOC from ISOPOOH but we underestimate the observed IEPOX SOA concentrations in SOAS and SEAC4RS (Sect. 4).

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 (Sect. 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., 2015a).
Minor channels for ISOPO$_2$ are isomerization and reaction with RO$_2$. Isomerization forms hydroperoxy aldehydes (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 Stavrkou 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 alkyl nitrates (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 \( \gamma \) as given by Anttila et al. (2006) and Gaston et al. (2014):

\[
\gamma = \frac{1}{\alpha} + \frac{3\omega}{4rRT H^+ k_{aq}}. \quad (1)
\]

Here \( \alpha \) is the mass accommodation coefficient (taken as 0.1 for all immediate SOA precursors in Fig. 2), \( \omega \) is the mean gas-phase molecular speed (cm s\(^{-1}\)), \( r \) is the aqueous particle radius (cm), \( R \) is the universal gas constant \((0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})\), \( T \) 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 \((\text{s}^{-1})\) 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 constant formulation is from Eddingsaas et al. (2010),

\[
k_{aq} = k_{H^+} [H^+] + k_{nuc} [\text{nuc}] [H^+] + k_{\text{HSO}_4^-} [\text{HSO}_4^-], \quad (2)
\]

and includes three channels: acid-catalyzed ring opening followed by nucleophilic addition of \( \text{H}_2\text{O} \) \((k_{H^+} \text{ in M}^{-1} \text{s}^{-1})\) leading to methyltetros, acid-catalyzed ring opening followed by nucleophilic addition of sulfate and nitrate ions \((\text{nuc} \equiv \text{SO}_4^{2-} + \text{NO}_3^-, k_{nuc} \text{ in M}^{-2} \text{s}^{-1})\) leading to organosulfates and organonitrates, and concerted protonation and nucleophilic addition by bisulfate, \( \text{HSO}_4^- (k_{\text{HSO}_4^-} \text{ in M}^{-1} \text{s}^{-1}) \), 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; Sumner et al., 2014). We use a daytime \( \gamma \) of \(2.9 \times 10^{-3}\) for glyoxal from Liggio et al. (2005) and a nighttime \( \gamma \) of \(5 \times 10^{-6}\) (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 \( \gamma \) \((2.9 \times 10^{-3})\) 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 \( \gamma \) for methylglyoxal to the ratio of effective Henry’s law constants: \( H^+ = 3.7 \times 10^3 \text{ M atm}^{-1} \) for methylglyoxal (Tan et al., 2010) and \( H^+ = 2.7 \times 10^7 \text{ M atm}^{-1} \) 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\(_5\)-LVO from ISOPPOOH oxidation and NT-ISOPN from isoprene reaction with NO\(_3\) have very low volatility and are assumed to condense to aerosols with a \( \gamma \) of 0.1 limited by mass accommodation. Results are insensitive to the precise value of \( \gamma \) since uptake by aerosols is the main sink for these species in any case.

Table 1 gives input variables used to calculate \( \gamma \) 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 \(1.2 \times 10^{-3} \text{ M}^{-1} \text{s}^{-1}\) (Eddingsaas et al., 2010) to \(3.6 \times 10^{-2} \text{ M}^{-1} \text{s}^{-1}\) (Cole-Filipiak et al., 2010). Values of \( k_{nuc} \) vary by 3 orders of magnitude from \(2 \times 10^{-14} \text{ M}^{-2} \text{s}^{-1}\) (Eddingsaas et al., 2010) to \(5.2 \times 10^{-1} \text{ M}^{-2} \text{s}^{-1}\) (Piletic et al., 2013). Reported values of \( H^+ \) vary by 2 orders of magnitude (Eddingsaas et al., 2010; Nguyen et al., 2014). We chose values of \( k_{H^+}, k_{nuc}, \) and \( H^+ \) to fit the SOAS and SEAC\(^4\)RS observations of to-
Table 2. Mean reactive uptake coefficients $\gamma$ of isoprene SOA precursors.$^a$

<table>
<thead>
<tr>
<th>Species$^b$</th>
<th>$\gamma$</th>
<th>pH dependence$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH &gt; 3</td>
<td>2 &lt; $\gamma$ &lt; 3</td>
</tr>
<tr>
<td>IEPOX</td>
<td>$4.2 \times 10^{-3}$</td>
<td>$8.6 \times 10^{-7}$</td>
</tr>
<tr>
<td>MEPOX</td>
<td>$1.3 \times 10^{-4}$</td>
<td>$2.7 \times 10^{-8}$</td>
</tr>
<tr>
<td>ISOPN$_p$</td>
<td>$1.3 \times 10^{-7}$</td>
<td>–</td>
</tr>
<tr>
<td>ISOPN$_d$</td>
<td>$5.2 \times 10^{-5}$</td>
<td>–</td>
</tr>
<tr>
<td>DHDN</td>
<td>$6.5 \times 10^{-5}$</td>
<td>–</td>
</tr>
<tr>
<td>GLYX</td>
<td>$2.9 \times 10^{-3,d}$</td>
<td>–</td>
</tr>
<tr>
<td>MGLY</td>
<td>$4.0 \times 10^{-7}$</td>
<td>–</td>
</tr>
<tr>
<td>C$_3$-LVOC</td>
<td>0.1</td>
<td>–</td>
</tr>
<tr>
<td>NT-ISOPN</td>
<td>0.1</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ 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 $\gamma$ 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. $^c$ 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 $5 \times 10^{-6}$.
produces ISOPO\(_2\) 7 mol % from the ISOPO\(_2\) + ozone, and 5 % with NO\(_3\). GEOS-Chem. 87 % of isoprene reacts with OH, 8 % with isomerization in the southeast US boundary layer as calculated by (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 \(k_{\text{het}}\) (s\(^{-1}\)) (Schwartz, 1986; Jacob, 2000):

\[
k_{\text{het}} = \frac{4 \pi r^2}{D_g} \left(1 + \frac{4}{\gamma \omega} \right) \frac{1}{n(r)dr},
\]

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 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 high-NO\(_x\) pathway 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 h, respectively. For both species, aerosol uptake is thus a minor sink competing with gas-phase photochemical loss. Although we have assumed here the fast gas-phase kinetics from Jacobs et al. (2013) for the IEPOX + OH reaction, this result would not change if we used the slower kinetics from Bates et al. (2014).

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 \(\gamma\) and to the aqueous aerosol mass concentration (in both cases, \(\gamma\) is small enough that uptake is controlled by bulk aqueous-phase rather than surface reactions). We find under SEAC\(^4\)RS conditions that \(\gamma\) for IEPOX is mainly controlled by the H\(^+\) concentration (\(k_{\text{H}^+}[\text{H}^+]\) in Eq. 2), with little contribution from nucleophile-driven and HSO\(_4^−\)-driven channels, although this is based on highly uncertain rate constants (Sect. 2). Consistency with SOAS and SEAC\(^4\)RS observations will be discussed below.

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 iso-
Figure 3. Relationship of organic aerosol (OA) and formaldehyde (HCHO) concentrations over the southeast US in summer. The figure shows scatter plots of SEAC4RS aircraft observations of OA concentrations in the boundary layer (< 2 km) vs. HCHO mixing ratios measured from the aircraft (left), and column HCHO ($\Omega_{HCHO}$) retrieved from OMI satellite observations (right). Individual points denote data from individual SEAC4RS flight days (8 August–10 September), averaged on the GEOS-Chem grid. OMI data are for SEAC4RS 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 (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.

Prech et al. estimated that isoprene SOA yield in that simulation was only 1.1 %. The observed correlation of OA with HCHO in SEAC4RS 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 SEAC4RS aircraft payload included measurements of OA from an Aerodyne High-Resolution Time-of-Flight 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 SEAC4RS from the Ozone Monitoring Instrument (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 ($2.8 \pm 0.3$ µg m$^{-3}$ ppbv$^{-1}$, vs. $3.0 \pm 0.4$ µg m$^{-3}$ 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 ($2.0 \pm 0.3$ µg m$^{-3}$ 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 $\sim 40$ % 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 m$^{-3}$ (mean AMS OA is $5.8 \pm 4.3$ µg m$^{-3}$; model OA is $4.7 \pm 4.4$ µg m$^{-3}$). 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 SEAC4RS.

Figure 4 shows time series of the isoprene SOA components IEPOX SOA and C$_3$-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$_3$-LVOC SOA are on average 17 and 2 % of total AMS OA, respectively (Hu et al., 2015;
The model reproduces mean IEPOX SOA and C5-LVOC SOA without bias, supporting the conclusion that IEPOX is the dominant contributor to isoprene SOA in the southeast US (Fig. 2).

Figure 5 shows the relationships of daily mean IEPOX SOA and sulfate concentrations at Centreville and in the SEAC4RS boundary layer. The same factor analysis method was used to derive IEPOX SOA in SEAC4RS 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 may form by 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. The correlation of IEPOX SOA and sulfate in the model is because increasing sulfate drives an increase in aqueous aerosol volume and acidity. Although dominance of the H\(^+\)-catalyzed channel is sensitive to uncertainties in the rate constants (Sect. 2), measurements from the PALMS (Particle Analysis by Laser Mass Spectrometry) instrument during SEAC4RS (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).

Correlation between IEPOX SOA and sulfate is also apparent in the spatial distribution of IEPOX SOA, as observed by the SEAC4RS 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 ± 2.4 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 SEAC4RS 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 SEAC4RS 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 Environmental Protection Agency (EPA) projects that US anthropogenic emissions of NOx and SO2 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 NOx and SO2 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 NOx emission by 34% decreases the mean NO concentration by only 23%, in part because decreasing OH increases the NOx lifetime and in part because decreasing ozone increases the NO/NO2 ratio. There is no change in HO2. We find a 10% decrease in the high-NOx pathway and a 6% increase in the low-NOx pathway involving ISOPO2 + HO2. Aerosol sulfate decreases by 2% and there is no change in [H+] at the boundary layer in summer. Reducing SO2 emission by 48% decreases SO2 concentration by 50%. 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 SO2 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 SO2 emission reductions is similar (~30%) and uptake of IEPOX SOA is proportional to the product of the two (Sect. 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 SO2 emissions are more effective than NOx emissions at reducing IEPOX SOA in the southeast US. Remarkably, we find that reducing SO2 emissions decreases sulfate and isoprene SOA with similar effectiveness (Fig. 7). With sulfate contributing ~30% of present-day PM2.5 in the southeast US and isoprene SOA contributing ~25% (Kim et al., 2015), this represents a factor of 2 co-benefit on PM2.5 from reducing SO2 emissions.

6 Conclusions

Standard mechanisms for the 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 (SEAC4RS) observations over the southeast US in summer 2013.

Our mechanism includes different channels for isoprene SOA formation by the high-NOx pathway, when the isoprene peroxy radicals (ISOPO2) react with NO, and in the low-NOx pathway where they react mostly with HO2. The main SOA precursors are found to be isoprene epoxide (IEPOX) in the low-NOx pathway and glyoxal in the high- and low-NOx 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-NOx pathway is 5 times more efficient than the high-NOx pathway for isoprene SOA pro-
duction. Under southeast US conditions, IEPOX and glyoxal account respectively for 58 and 28 % of isoprene SOA.

Our model simulates the observations and variability of IEPOX SOA at the surface and from aircraft well. The observations show a strong correlation with sulfate that we reproduce in the model. We find this 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.

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