Response to reviewers for the paper "Volatility and lifetime against OH heterogeneous reaction of ambient Isoprene Epoxydiols-Derived Secondary Organic Aerosol (IEPOX-SOA)" by Weiwei Hu et al.

We appreciate the reviewer's comments and support for publication of this manuscript after minor revisions. Following the reviewer's suggestions, we have carefully revised the manuscript. To facilitate the review process, we have copied the reviewer comments in black text. Our responses are in regular blue font. We have responded to all the referee comments and made alterations to our paper **(in bold text).**

Anonymous Referee #1

General Comments

R1.0. This is a very interesting study about the volatility and lifetime of IEPOX-derived SOA. As the authors point out in the manuscript, studies on heterogeneous reactions of ambient SOA with hydroxyl radicals are missing. This work presents a well-conduct series of ambient measurements and box models that provide supporting evidences for their findings. The study is technically well done and the paper is well written. I think it is suitable for publication in ACP after few minor revisions. My major comment is on the determination of the IEPOX-derived SOA lifetime as discussed below.

A1.0: We thank the reviewer for his/her review and useful comments. All of the items mentioned here are addressed in response to the more specific comments below.

R1.1. Line 70: The authors should consider adding the references and not only cite their previous work. Add these references: Robinson et al., 2011; Budisulistiorini et al., 2013; 2015; Chen et al., 2015, Xu et al., 2015

A1.1: The sentence in question states "IEPOX-SOA [...] can account for 6-34% of total OA over multiple forested areas across the globe range". Hu et al., 2016 was the paper that summarized all the results and showed that IEPOX-SOA is globally important and positively correlated with modeled gas-phase IEPOX. Thus we think the citation of this sentence is correct. The other references suggested by the reviewer are cited in different parts of our paper, as appropriate for each instance. There are also numerous citations in Hu et al., 2015, beyond those proposed by the reviewer here. For clarity we have revised that text to read:

Line 68-70: "IEPOX-SOA measurements in field studies show that it can account for 6-34% of total OA over multiple forested areas across the globe, with important impacts on the global and regional OA budget (Hu et al., 2015 and references therein)."

R1.2. Line 72: Add Riedel et al., 2015

A1.2: Added.

R1.3. Line 82: Similar comment as Line 70, add references: Robinson et al., 2011; Lin et al.,2012; Budisulistiorini et al., 2013

A1.3: Hu et al., 2015 is the only paper that (to our knowledge) has proposed the use of f_{82} as a real-time tracer for estimating IEPOX-SOA mass concentration, which is what the sentence states. The other references suggested by the reviewer had already been cited above this sentence where they were relevant. Adding them to this sentence would be incorrect and confusing. Thus, this text has not been changed.

R1.4. Line 85: Add reference: Kroll et al., 2015

A1.4: We agree with reviewer's suggestion. Note that Kroll et al., 2015 has already been cited in the ACPD version of this study to support the volatilization of aerosol products. The updated text reads:

"which also showed that OH oxidation led to formation of volatile products escaping to the gas phase (Kessler et al., 2010; Kroll et al., 2015)"

R1.5. Line 114: How did temperature affect the reactivity of IEPOX-derived SOA? Indeed as shown by Lai et al. (2015), small changes in the temperature (20C-30C) could impact OH heterogeneous oxidation.

A1.5: In Lai et al. (2015) k_{OH} increases with temperature. However, in SOAS k_{OH} increases with RH (Figure 6), which we interpret as being mainly due to the increase in surface area due to water uptake. Ambient temperature is inversely correlated with RH, so the apparent trend in our study is that k_{OH} *decreases* as temperature *increases*, which on the surface is the opposite effect than Lai et al. (2015) reported. There are many differences between the two studies (different species, lab vs field, particles on a sample holder vs suspended, etc.), and importantly it is not possible to isolate the effect of temperature from those of other variables in our ambient study. Thus we have added the following text recommending further study of this topic:

Line 464-467: **"An effect of temperature on k_{OH} was not apparent in our study. Lai et al. (2015) reported a significant effect for a laboratory study with a pure compound. We recommend that this issue is explored further in the laboratory using pure IEPOX-SOA."**

R1.6. Line 125: Why did the authors limit the range of OH exposures from 10e+10 – 10e+13 molecule cm-3? Indeed, as previously reported and discussed below, OH uptake and heterogeneous oxidation is impacted by the concentration of OH radicals (Arangio et al., 2015).

A1.6: First of all, we have to clarify that the units for OH exposure are molec. cm^{-3} s, not molec cm^{-3}. The range of OH exposure of 10^{10}-10^{13} molecule cm^{-3} s corresponds to 0.1 day to several months equivalent aging time, which is the range over which it is important to investigate atmospheric aerosol chemistry. We modified the main text for clarity to read:

Line135-143: **"A large range of OH exposures (10^{10}-10^{13} molec. cm^{-3} s) can be achieved by varying UV light intensity, equivalent to several hours to several weeks of photochemical aging of ambient air (assuming a 24-hr average OH=1.5×10^{6} molec. cm^{-3}; Mao et al., 2009). Thus we believe that the range of OH exposures (10^{10}-10^{13} molec. cm^{-3} s) covered by our study is the relevant range for the atmosphere. We note that OH radical concentration can be calculated as the ratio of the OH exposure (10^{10}-10^{13} molec. cm^{-3} s) and the residence time (200 s). The calculated OH radical concentration in our flow reactor is between 5×10^{7}**

to 5×10^{10} molec. cm^{-3}. The lower range of OH radical concentration is comparable to the higher end of observed ambient OH concentrations (Mao et al., 2009).”

R1.7. Line 154: The authors mentioned other type of oxidants, such as O3 and NO3. If they performed some experiments using different oxidants, it would be interesting to discuss the reactivity of these oxidants (especially NO3) and compare the results with OH radicals. Could the authors provide additional experimental information for the production of NO3 radicals in the OFR?

A1.7: We indeed conducted ambient OFR experiments with O_3 and NO_3, in addition to OH during the SOAS study. However, the results from those experiments greatly exceed the scope of this paper, and will be presented in future publications. For example, we are close to submitting a stand-alone paper that reports results of OFR experiments with O_3 and NO_3 for a different field study, and that paper has over 40 pages of text and 10 figures.

R1.8. Line 155: The authors mentioned that they used different methods (i.e. OFR 185 and OFR 254?) but decided to present only results from one. Could they explain the reasons and add some information and/or comparison between both methods?

A1.8: This is incorrect. All experiments reported here were done with the OFR185 method, as clearly stated in Line 155 of the ACPD paper. In fact, the words “OFR 254” do not appear in our paper at all. We refer the reviewer to the work of Palm et al. (ACP 2016) who presented a comparison of results from the OFR185 and OFR254 methods for the BEACHON-RoMBAS study. Our conclusion from that and other studies is that although the results are similar, the OFR185 method is preferable, especially for ambient studies, and thus that was the method used during SOAS. The main text has been modified to reflect this:

Line 162-165: “A comparison of results from the OFR185 and OFR254 methods for a study at a pine forest was presented by Palm et al. (2016), showing similar SOA formation by both methods. Their results, together with other model studies (Peng et al., 2015) showed that the OFR185 method is preferable for ambient studies, and thus that was the method used during SOAS.”

R1.9. Line 168-170: The authors mentioned that during the dry season SOA were significantly influenced by biomass burning. This statement is supported by neither references nor experimental data. Additional information is needed to evaluate the importance of BBOA in OA. In addition, how do the authors expect the presence of BBOA to impact the IEPOX-SOA aging?

A1.9: The presence of BBOA was very obvious during the dry season. We have added a reference to Martin et al. (ACP 2016) which discusses this issue for the GoAmazon study.

We have added the following text in Line 435-438 to address the second point:

"The higher aerosol concentrations from biomass burning during the Amazon study did not appear to cause any major differences in the observed OH uptake. This may be due to the mostly liquid state of the ambient particles in both studies, which will be discussed in detail below (Bateman et al., 2015; Pajunoja et al., 2016)."

R1.10. Line 192: Similar comment as line 82, add the references.

A1.10: Several references have been added.

"(Robinson et al., 2011; Lin et al., 2012; Allan et al., 2014; Hu et al., 2015)".

R1.11. Lines 203-204: Riedel et al. (2016) have recently reported bulk laboratory measurements and determined the reaction rate constants of IEPOX-SOA products from the reactive uptake of IEPOX. The authors didn't consider this study and only use a global rate constant. The rates constants proposed by Riedel et al. (2016) should be added in the model and results from both approaches should be compared in the paper.

A1.11: In our paper we use the model of the uptake of gas-phase IEPOX to form IEPOX-SOA to show that it is negligible in the reactor, and thus that our measurements can be directly interpreted as the heterogeneous oxidation of IEPOX-SOA in the aerosol. The conclusion that IEPOX-SOA formation is negligible is strengthened if we consider the timescale of IEPOX-SOA formation in Riedel et al (2016). We have added the following text to the paper to clarify this issue:

Line 386-389: **“If the more detailed IEPOX-SOA formation model of Riedel et al. (2016) were used, the modeled IEPOX-SOA formation would be significantly lower, due to the consideration of the kinetics of IEPOX-SOA formation. That reinforces our conclusion that IEPOX-SOA formation in the reactor was negligible.”**

R1.12. Lines 270-271: At which temperature did the authors perform these evaporation experiments?

A1.12: We did not perform evaporation experiments in this part of the study, but estimated the isothermal evaporation loss upon dilution, based on the volatility distribution estimated from the thermodenuder (TD) measurements, using Eq 1.

To clarify, the original sentence “Using the volatility distributions determined from the TD, the fractional losses for both OA and IEPOX-SOA due to evaporation upon dilution can be estimated” was revised to read:

Line 279-281: **“It is of high interest to estimate the fractional losses for both OA and IEPOX-SOA due to isothermal evaporation upon dilution. These losses can be estimated using the volatility distributions estimated from the TD measurements.”**

R1.13. Lines 295-296: Riva et al. (2016) have shown that IEPOX reactive uptake could be significantly reduced by the presence of organic on seed aerosols. The authors should add this reference and also discuss this potential impact in their model.

A1.13: The result of reduced IEPOX uptake due to organic coatings was already reported by Gaston et al. (2014), and it was incorporated in their model, which we use here. We also show (Fig. S16) that even if the reduced uptake is neglected, IEPOX-SOA formation is still negligible. Therefore, we have not changed the paper in response to this comment, other than to add a citation to Riva et al. (2016) when discussing the slower uptake due to organic coatings in Line 314.

R1.14. Lines 321-323: The authors should better justify the average molar yield used in the model regardless to Riedel et al. (2016).

A1.14: We are not totally clear of what the reviewer means by "regardless to Riedel et al." The molar yield used is supported from a literature reference of an experimental study. See response R1.11 for further details on this issue.

R1.15. Line 335: The authors mentioned on Line 125 that the OPR was operated using an OH concentration of 10e+10 – 10e+13 molecule cm-3. At different places in the article, the authors refer to different ranges. This is confusing, thus it needs to be clarified.

A1.15: The reviewer appears to confuse OH concentrations (molec cm^{-3}) with OH exposures (integral of OH x time, units of molec. cm^{-3} s). Both quantities are related, and are relevant for different reasons. See response to comment A1.6 for further details and text modified for clarity.

R1.16. Lines 343-347: As it is written in the article, the authors point out that the limitation of the reactive uptake of IEPOX is due to the acidity of the particles. Is it only due to the acidity, or the surface area, or both? Could the authors provide the surface area before and after injection of H2SO4 particles?

A1.16: The increased surface areas indeed played a role for the enhanced IEPOX-SOA formation in the OFR, however its role is minor compared to that of the acidity changing. Following the reviewer's suggestion, we have modified the main text to read:

Line 374-378: **"The increased surface area and acidity from added H_2SO_4 seed both help accelerate IEPOX reactive uptake, although acidity plays a more important role. If we use in the model the ambient surface area and pure H_2SO_4 the lifetime of IEPOX uptake is ~10 min, while if we assume the ambient acidity and the same surface area as 100 µg m^{-3} of pure H_2SO_4, the lifetime is 1.1 h."**

R1.17. Lines 359-360: The statement, "oligomer decomposition could be fast in the ambient air", is not clear and a bit speculative. Could the authors provide more information and/or references to support this statement?

A1.17: This is indeed speculative, as this possible process has not been reported in the literature. The main idea here is to emphasize that even if fast decomposition of IEPOX-SOA oligomers happened in the ambient air, the decomposition would not have played an important role for IEPOX-SOA loss in the flow reactor because the residence time of aerosols in the OFR is low (3 min). Thus, to clarify, the text has been revised to read:

Line 392-397: **"Oligomer decomposition followed by evaporation is very likely negligible in the flow reactor residence time scale of 3 min. However, this process could be more important in ambient air, and if fast, could influence the IEPOX-SOA lifetime. No results for oligomer decomposition rates or extents for IEPOX-SOA have been reported in the literature, to our knowledge. Thus, further research on this topic is recommended."**

R1.18. Lines 499-500 and general comment: Here the authors mentioned that they have estimated an OH yield based on range of OH concentrations of 10e+7 – 10e+10 molecule cm-3. However, in the experimental section, the range used was 10e+10 – 10e+13 molecule cm-3. Therefore, it is not clear if the yield was determined from extrapolation in the model or from measurements. If it is from extrapolation, how reliable is the yield proposed in this study since different studies have shown that OH yield is dependent on the concentration of OH radicals?

A1.18: Again this appears to be a confusion between OH concentrations and exposures, see response A1.6.

R1.19. In addition, the authors mentioned that they have investigated the impact of OH concentrations on OH yield. Regardless the previous studies, this set of experiments was conducted in a substantially small range to make a conclusion in the dependence of OH yields on OH concentration. Therefore, it appears to be overreached to propose such conclusions, and the question of the larger reactivity of IEPOX-derived SOA using a lower concentration of OH radicals remains present.

A1.19: Our OFR study used a OH concentration range of 1000, which is similar to that used in other numerous laboratory studies listed in Table 1. E.g., Che et al., 2009; Smith et al., 2009; Kessler et al., 2010; Kessler et al., 2012; Slade and Knopf, 2014. The lower range of OH radical concentration in our study is also comparable to the higher end of observed ambient OH concentrations (Mao et al., 2009), see revised text in A1.6. However, it is important to note that our results for γ_{OH} do not cover the range of atmospheric OH levels. We have added the following text to the paper to clarify this point:

Line 558-560: **"We note that our experiments do not rule out some dependence of γ_{OH} on OH at lower OH levels in the atmosphere."**

Technical comments:

R1.20. Line 140: O3: subscript "3"

A1.20: Corrected

R1.21. Line 141: s-1: superscript "-1"

A1.21: Corrected

R1.22. Line 277: typo error. "isis" should be "is"

A1.22: Corrected

R1.23. Lines 324/366: acidic NH4HSO4 should be either acidic (NH4)2SO4 or NH4HSO4

A1.23: Revised to be "acidic $(NH_4)_2SO_4$" and "acidified $(NH_4)_2SO_4$ seed"

R1.24. Line 418: > 10–14 should be 10-14

A1.24: Corrected

Anonymous Referee #2

General Comments

R2.0. This paper describes detailed field measurements of "IEPOX-SOA", secondary organic aerosol deriving the reactive uptake IEPOX, a major product of isoprene oxidation. Key results include evidence that IEPOX-SOA is quite low in volatility, suggesting the importance of accretion products (consistent with other recently-published work), and measurements of the rate of atmospheric degradation of IEPOX-SOA material (which is a fundamentally new result). These are important results, and overall this is a solid study of general interest to the atmospheric chemistry community. It is certainly publishable in ACP; first, I have a number of detailed comments, listed below, that should be addressed prior to publication.

A2.0: We thank the reviewer for his/her review and useful comments. All of the items mentioned here are addressed in response to the more specific comments below.

R2.1. 246-263 (and elsewhere): There manuscript makes repeated reference to the IEPOX-SOA compounds being oligomers. However, it seems to me that other accretion products (namely organosulfates) could also explain much of the data (such as the low volatility of the compounds). The authors should either explain why they organosulfate formation is unlikely, or change the language throughout the paper to reflect this possibility.

A2.1: Here, we include the IEPOX organosulfate as part of IEPOX-SOA. As reported in the ACPD version of this paper (L234-236), the IEPOX organosulfate accounts for 24% of total IEPOX-SOA. We have added the following text to the manuscript to address this point:

Line 260-266**: "Although the IEPOX organosulfate may have lower volatility than estimated in Fig. 1D, it only accounts for 24% of total IEPOX-SOA (Hu et al., 2015) and thus it cannot be the only reason for the low volatility of the bulk of IEPOX-SOA. For reference, only 5% of the total sulfate is due to the IEPOX organosulfate, with the rest being inorganic sulfate consistent with other results from the SE US in Summer 2013 (Liao et al., 2015). Indeed, the thermogram of total sulfate is very different from that of IEPOX-SOA (Fig. 1a and Fig.2a)."**

R2.2. Figs 1-2: A comparison with the sulfate thermogram would be helpful here for context.

A2.2: As discussed in A2.1, only 5% of the total sulfate is due to the IEPOX organosulfate, and indeed the two thermograms are quite different. This has been added to Figure 1A and Figure 2A as shown below.

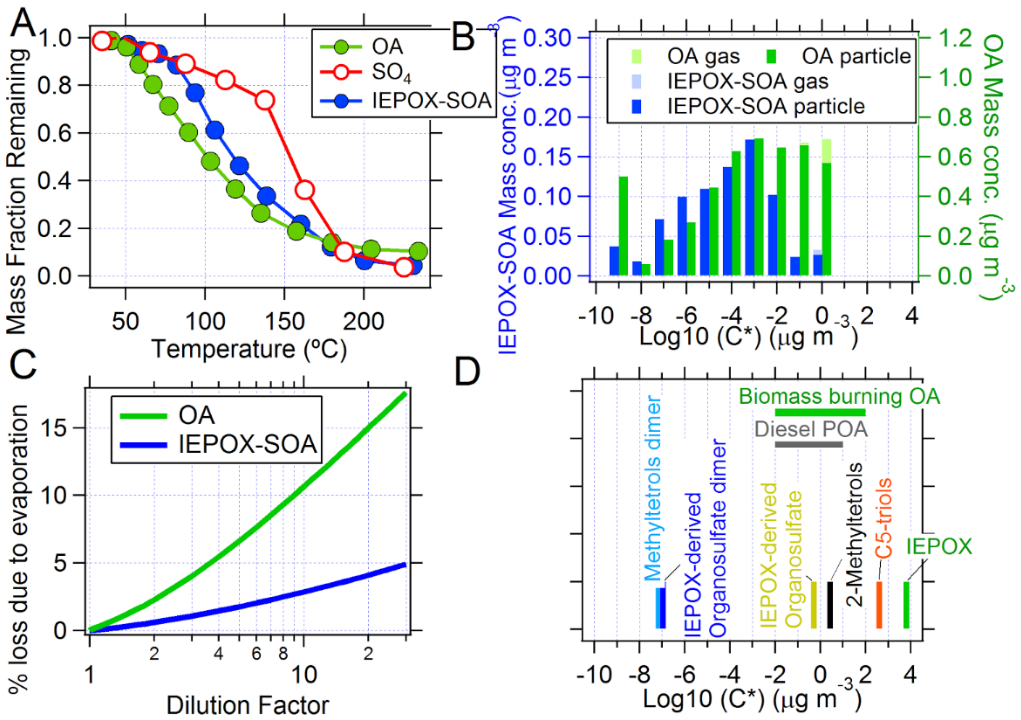

Figure 1 (a) Mean mass fraction remaining of IEPOX-SOA, OA and SO_4 versus temperature in TD ("thermograms") during SE US study. (b) Volatility distributions of IEPOX-SOA and OA estimated from TD thermograms (see text). Bars are offset for clarity and were both calculated for integer log(*C**) values. (c) Evaporation losses of IEPOX-SOA and OA as a function of dilution factors. (d) Volatility of typical IEPOX-SOA molecular species in the aerosol phase based the on SIMPOL group contribution method (Pankow and Asher, 2008). The reduction in vapor pressure upon addition of a nitrate group was used to estimate the effect of the sulfate group, due to lack of SIMPOL parameters for the latter, and the derived *C** may be overestimated for this reason.

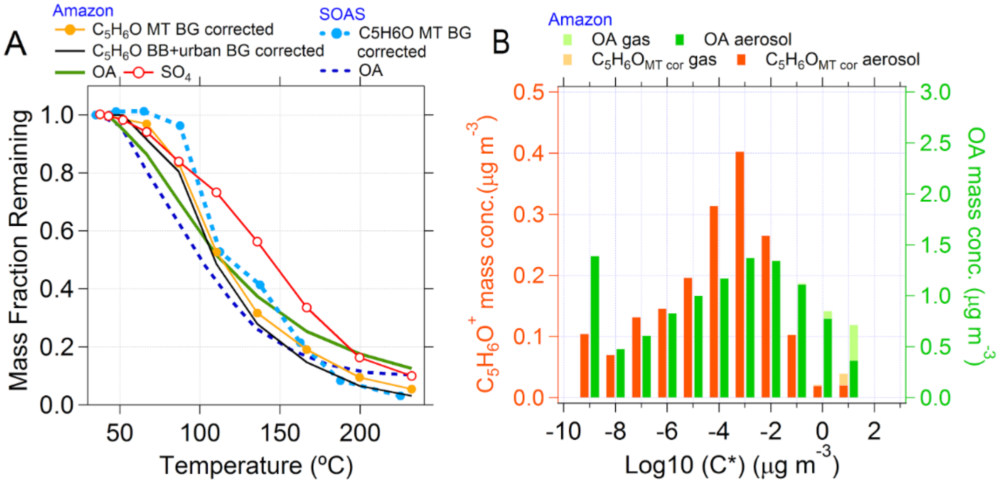

Figure 2 (a) Thermogram of OA, SO_4 and background-corrected $C_5H_6O^+$ ion in the SE US and Amazon studies. (b) Volatility distributions of $C_5H_6O^+$ and OA estimated based on TD thermograms from the Amazon study.

R2.3. 273-276: These two possibilities seem closely related to me. The “real” volatility distribution (from physical volatilization only) is irrelevant if the room temperature evaporation is governed by chemical decomposition to more volatile monomers. The TD is measuring “effective volatility”, which takes into account both physical evaporation and oligomer decomposition; this effective volatility (at atmospheric temperatures at least) is what matters for phase partitioning in the atmosphere. Therefore I’m not sure it’s correct to say this approach is overestimating the volatility distribution.

A2.3: We respectfully disagree. The volatility distribution of the molecules present in the aerosol at any given time depends on their molecular identity. That distribution may indeed be even lower than estimated in Fig. 1b, if some of the oligomers are decomposing in the thermal denuder, and thus evaporating at lower temperatures than would be needed to evaporate the intact oligomer. Lopez-Hilfiker et al. (2016) has shown molecular evidence that this process is indeed occurring with a related thermal desorption mass spectrometric instrument during SOAS. Thus we do believe that the sentence starting with **“One is that…”** is indeed correct.

The effect of oligomer decomposition under ambient conditions would be more complex, when the airmass is undergoing dilution. As the gas-phase is depleted of monomers by dilution, some of the molecules comprising the oligomers would not return to the particle phase after evaporation. However, the volatility distribution of the molecules present in the particle phase would still be similar to that measured in SOAS (assuming all oligomers have consistent rates).

Thus we believe that text **(“One is that the real volatility distribution of IEPOX-SOA is likely even lower, since the TD results are thought to be affected by oligomer decomposition upon heating. The other one is that this calculation neglects the effect of possible decomposition of oligomers into monomers in ambient air.”)** is correct, and that both possibilities are distinct and both need to be considered, and have made no changes in response to this comment.

R2.4. 279-280: The Vaden reference may be describing a very different effect, namely slow evaporation of monomers out of low-viscosity (and very dry) particles.

A2.4: Our understanding of the α-pinene SOA debates is that oligomers are thought to comprise a large fraction of the particle mass. However, the possibility suggested by the reviewer is also plausible. We have modified this sentence to read as:

Line 296-298: **"E.g. Vaden et al (2011) reported that it took 24 h to evaporate 75% of α-pinene SOA (although it is possible that processes other than oligomer decomposition were important for determining the timescale of those experiments)."**

R2.5. 314-316: Here it is argued that wall loss of IEPOX cannot happen because of the high saturation vapor pressure of the molecule. But this is the wrong quantity to use, since IEPOX condenses almost entirely via reactive uptake. (If saturation vapor pressure is what determined IEPOX condensation, there'd be no such thing as IEPOX-SOA!) It is highly likely that there is reactive uptake to the walls, since there's probably a reasonable amount of sulfate (aqueous, likely quite acidic) from previous deposition. This effect needs to be included in these calculations.

A2.5: We still believe that IEPOX loss to the walls of the OFR is negligible. We have added the following text to the paper to explain this point further:

Line 351-355: **"We can estimate the timescale of IEPOX loss rate to the walls by assuming that the walls are covered by a layer of deposited ambient aerosol. We combine the 1st order rate of collision of gas molecules with the walls (400 s; Palm et al., 2016) and the uptake coefficient for IEPOX-SOA in ambient aerosols (γ_{IEPOX} = 0.009) to estimate a timescale of IEPOX loss to the walls of 12.3 h, which is negligible compared to residence time of IEPOX (~200s) in the OFR. Even if the walls were covered by sulfuric acid (γ_{IEPOX} = 0.082), the timescale of loss would be 1.4 h."**

R2.6. 351-354: This is an important definition, because it specifically excludes reactions that lead to the reaction of IEPOX-SOA components without major changes to the PMF factor (namely, with little change to m/z 82). This should be mentioned explicitly, as should the implication that these rates and uptake coefficients may be lower limit values.

A2.6: We have added the following text to clarify the issues raised in this point:

Line 386-389: **"Note that the rate derived here may be a lower limit for individual molecular components of IEPOX-SOA, if e.g. it takes two or more OH reactions for their AMS spectrum to no longer resemble that of IEPOX-SOA."**

R2.7. 378: "IEPOX-SOA" should be in brackets to signify concentrations (as written, the left side of formula looks like IEPOX minus SOA/IEPOX minus SOAo).

A2.7: Revised as suggested.

R2.8. 379-384: "ith OH exposure step" is an unusual (and to me, confusing) way to describe chemical kinetics. A better way to word this is in terms of the integrated OH exposure, up to some reaction time t.

A2.8: We prefer to keep this as is, because in our experiments we change $OH_{exp,i} = [OH]_i \times \Delta t$ by changing $[OH]_i$ while keeping Δt constant. However, we have simplified the expression by replacing Δt_i by Δt, since that parameter is constant and does not change.

R2.9. 411-412: the paper cited here (Slade and Knopf 2014) did not attribute the RH effect to differences in surface area, as stated. The effect described really derives from the surface-area-to-volume ratio, which is well known to have an influence on the kOH value; Robinson 2006 may be the more appropriate reference here. (Though it may have been derived even before then?)

A2.9: We are unsure about which Robinson 2006 paper the reviewer is referring to, and a full citation is not provided. In any case the effect described by the reviewer is not what we believe is going on in our experiments. For particles of constant composition, indeed a higher surface/volume ratio will increase k_{OH}. However, as the ambient particles take up water, the surface/volume ratio *decreases*. We believe that the rate goes up because the added material (water) does not react with OH. Thus the surface area increase leads to more OH being taken up into the particle, but the mass of organic species that can react with that OH does not change. We found two papers from Allen Robinson et al. from 2006, but neither of them discusses the effect of water uptake on heterogeneous k_{OH}.

However, it is correct that Slade and Knopf, who worked in a different regime at much lower RH, attributed the effect to a different physical mechanism (high viscosity) which is not relevant for our studies, and thus we have removed that reference.

We are not aware of any previous paper reporting an RH effect for the reasons we stated in the paper, and thus that sentence does not have any literature reference in the revised version of our paper.

R2.10. 480-484: This is a long, wordy way to argue that the V/SA ratio is equal to D/6, and that the assumption that the reacted species is well-mixed (with the mass fraction the same at the surface and in the bulk) simplifies the calculations. These have been inherent to all heterogeneous oxidation studies going back to at least Robinson et al (2006), so probably does not need to be included here.

A2.10: We have simplified this text to read:

"We assume IEPOX-SOA is uniformly mixed with the other aerosol species (both in the surface and volume), and independent of particle size. Then for a spherical particle V_{total}/S_{total} is equal to $d_{surf}/6$, where d_{surf} is defined as surface-weighted particle diameter."

We cannot find this stated in the Robinson papers we know of, so we have not cited that paper for this point.

R2.11. 494-496: Based on the paper cited, and the text immediately following (lines 497-498), the authors appear to be arguing that this implies a role of oxidative processing of the IEPOX within the aqueous phase. But organosulfate formation (or even the catalytic promotion of IEPOX uptake by sulfate) would also seem to be a reasonable explanation for this effect, with no additional oxidation required.

A2.11: The text in those lines refers to the observed carbon oxidation state (OS_C) of IEPOX-SOA in different situations. Indeed, ambient IEPOX-SOA has a higher average OS_C than that freshly formed in chambers. Organosulfate formation does not affect OS_C, and thus it is not a plausible explanation for this effect. Uptake of IEPOX at a faster rate would form more fresh IEPOX-SOA, but not change its OS_C. Thus we have not changed the text in response to this comment.

R2.12. 514-517: Probably more important than changes to gamma at higher [OH] is changes at lower (atmospherically relevant) [OH]. This effect has been observed previously [Che, et al. 2009, PCCP 11, 7885–7895].

A2.12: The values of γ_{OH} reported by Che et al. only varied by 10% over the range [OH] = 1-7 x 10^8 molec. cm^{-3}, without a clear trend (their Table 1). Thus this variation is likely due to experimental uncertainty in those experiments. In the previous response (A1.19) we clarified that we did not cover the ambient OH concentration range in our experiments. We have added the following text to the paper to further clarify this point:

Line 558-560: **"We note that our experiments do not rule out some dependence of γ_{OH} on OH at lower OH levels in the atmosphere. However, Che et al. (2009) found no effect of OH on γ_{OH} for squalane particles in the range 1-7 x 10^8 molec. cm^{-3}."**

R2.13. 518: this statement appears to be directly contradicted in line 546.

A2.13: There is no contradiction, but to avoid confusion we have clarified the text in Line 556-558 to read:

"A possible explanation is that in our study OH uptake occurs on liquid particles, resulting on fast OH diffusion into the particle bulk, and causing OH uptake not to be limited by surface adsorption."

R2.14. Figure 3: An extra pathway should be included, since the SOA "yield" from Riedel et al was used (lines 319-325). This small yield implies that most (_90%) of the IEPOX reactive uptake leads to non-SOA (i.e., gas-phase) products, different from those generated by OH reaction; the formation of these should be therefore included in the figure as well.

A2.14: This is a good suggestion. Figure 3 has been revised to address this point, and it is reproduced below:

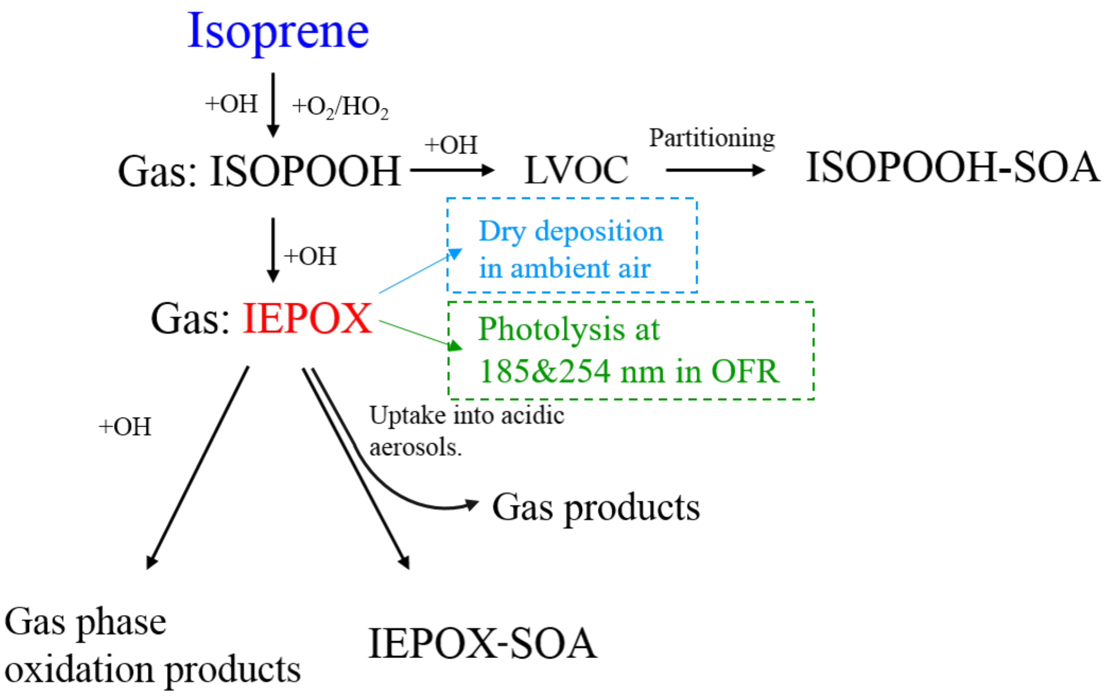

Figure 3 Mechanism diagram of gas-phase IEPOX model in ambient and OFR conditions. ISOPOOH-SOA refers to SOA formed through gas-particle partitioning of low-volatile VOCs from oxidation of isoprene 4-hydroxy-3-hydroperoxide (4,3-ISOPOOH) under low-NO conditions (Krechmer et al., 2015).

R2.15. Figure 7: The caption (or legend) should explain what the different symbols mean.

A2.15: This information was already included by using the axis colors. However, for further clarity we have also added a legend to Figure 7. Please see the revised Figure 7 below:

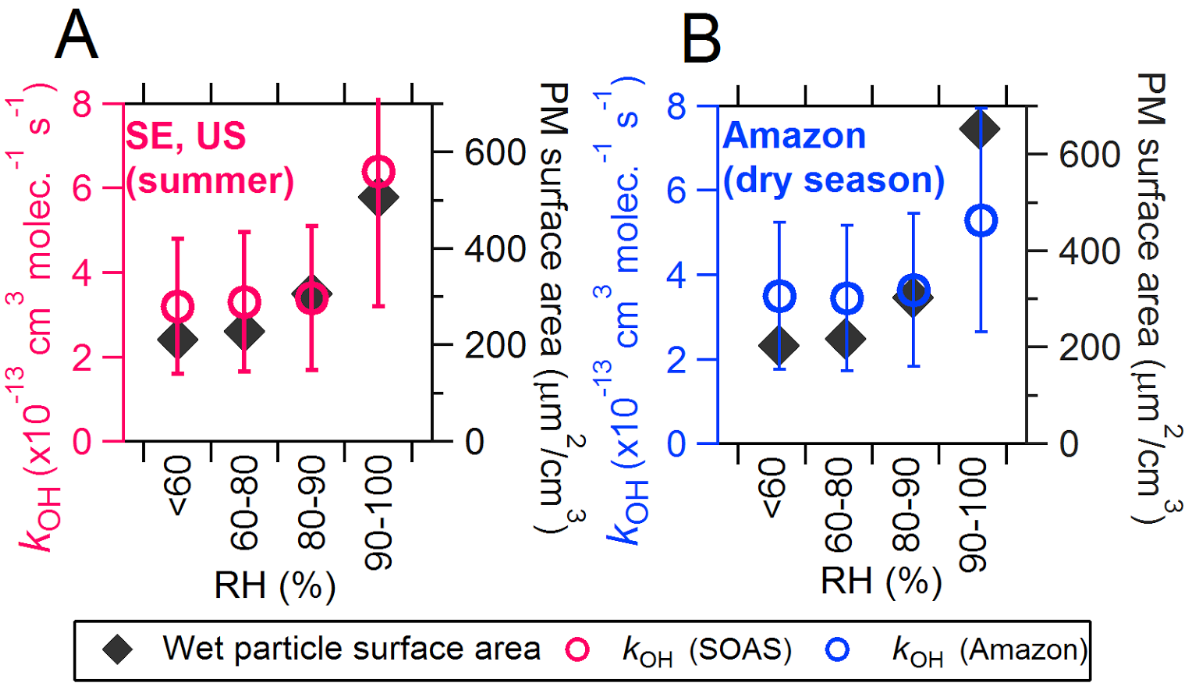

Figure 7 Estimated k_{OH} of IEPOX-SOA vs. ambient RH during the SOAS and Amazon studies. The ambient wet particle surface areas in both studies are shown on the right axis.

Volatility and lifetime against OH heterogeneous reaction of ambient Isoprene Epoxydiols-Derived Secondary Organic Aerosol (IEPOX-SOA)

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Abstract

Isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) can contribute substantially to organic aerosol (OA) concentrations in forested areas under low NO conditions, hence significantly influencing the regional and global OA budgets, accounting for example for 16-36% of the submicron OA in the SE US summer. Particle evaporation measurements from a thermodenuder show that the volatility of ambient IEPOX-SOA is lower than that of bulk OA and also much lower than that of known monomer IEPOX-SOA tracer species, indicating that IEPOX-SOA likely exists mostly as oligomers in the aerosol phase. The OH aging process of ambient IEPOX-SOA was investigated with an oxidation flow reactor (OFR). New IEPOX-SOA formation in the reactor was negligible, as the OFR cannot accelerate processes such as aerosol uptake and reactions that do not scale with OH. Simulation results indicate that adding ~100 µg m^{-3} of pure H_2SO_4 to the ambient air allows to efficiently form IEPOX-SOA in the reactor. The heterogeneous reaction rate coefficient of ambient IEPOX-SOA with OH radical (k_{OH}) was estimated as $4.0 \pm 2.0\times10^{-13}$ cm^3 $molec^{-1}$ s^{-1}, which is equivalent to more than a 2-week lifetime. A similar k_{OH} was found for measurements of OH oxidation of ambient Amazon forest air in an OFR. At higher OH exposures in the reactor ($>1\times10^{12}$ molec. cm^{-3} s), the mass loss of IEPOX-SOA due to heterogeneous reaction was mainly due to revolatilization of fragmented reaction products. We report for the first time OH reactive uptake coefficients (γ_{OH}=0.59±0.33 in SE US and γ_{OH}=0.68±0.38 in Amazon) for SOA under ambient conditions. A relative humidity dependence of k_{OH} and γ_{OH} was observed, consistent with surface area-limited OH uptake. No decrease of k_{OH} was observed as OH concentrations increased. These observation of physicochemical properties of IEPOX-SOA can help to constrain OA impact on air quality and climate.

1 Introduction

Organic aerosol (OA), which comprises 10-90% of ambient submicron aerosol mass globally, has important impacts on climate forcing and human health (Kanakidou et al., 2005; Zhang et al., 2007; Hallquist et al., 2009). However, quantitative predictions of OA mass concentrations often fails to match the real ambient measurements by large factors, (e.g.Volkamer et al., 2006; Dzepina et al., 2011; Tsigaridis et al., 2014). Improved characterization of the properties and lifetime of OA is needed to better constrain OA model predictions.

Isoprene is the most abundant non-methane hydrocarbon (NMHC) emitted into the Earth's atmosphere (Guenther et al., 2012). Many studies in the past decade have shown that the reaction products of isoprene-derived epoxydiols (IEPOX), formed under low NO conditions (Paulot et al., 2009), can contribute efficiently to secondary OA (SOA) via reactive uptake of gas-phase IEPOX onto acidic aerosols (Eddingsaas et al., 2010; Froyd et al., 2010; Surratt et al., 2010; Lin et al., 2012; Liao et al., 2015). IEPOX-SOA measurements in field studies show that it can account for 6-34% of total OA over multiple forested areas across the globe, with important impacts on the global and regional OA budget (Hu et al., 2015 and references therein). Although the formation of IEPOX-SOA from gas-phase IEPOX has been investigated in many laboratory studies (e.g. Eddingsaas et al., 2010; Lin et al., 2012; Gaston et al., 2014; Riedel et al., 2015), the lifetime and aging of IEPOX-SOA in the aerosol phase is still mostly unexplored in the literature.

IEPOX-SOA can be measured by multiple methods. Gas chromatography/mass spectrometry (GC/MS) or liquid chromatography/mass spectrometry (LC/MS) of filter extracts can be used to measure some IEPOX-SOA species (accounting for 8-80% of total IEPOX-SOA depending on the study, Lin et al., 2012; Budisulistiorini et al., 2015; Hu et al., 2015). Recently, several studies have shown that factor analysis of real-time aerosol mass spectrometer (AMS) data provides a method to obtain the total amount, overall fraction contribution, and properties of IEPOX-SOA (Robinson et al., 2011; Budisulistiorini et al., 2013; Chen et al., 2015). The $C_5H_6O^+$ ion at *m/z* 82 in AMS spectra, arising from decomposition and ionization of molecular IEPOX-SOA species, has also been suggested as a proxy for real-time estimation of IEPOX-SOA (Hu et al., 2015).

Heterogeneous reaction of OA with hydroxyl radicals (OH) is a contributor to aerosol aging and significantly influences aerosol lifetime (George and Abbatt, 2010; George et al., 2015; Kroll et al., 2015). To describe the aging process, OA reaction rate coefficients with OH radicals (k_{OH}), or alternatively uptake coefficients of OH (γ_{OH}), defined as the fraction of OH collisions with a compound that result in reaction, have been reported for numerous laboratory studies. Values of effective γ_{OH} ($\leq$0.01 to $\geq$1) also can vary significantly under different reaction conditions, such as different OA species (George and Abbatt, 2010), temperature and humidity (Park et al., 2008; Liu et al., 2012; Slade and Knopf, 2014), OH concentrations (Slade and Knopf, 2013; Arangio et al., 2015), and particle phase state or coatings (McNeill et al., 2008; Arangio et al., 2015). Most of the studies that have reported k_{OH} and γ_{OH} are based on laboratory experiments, with few experimental determinations of k_{OH} based on field measurements under ambient conditions (Slowik et al., 2012; Ortega et al., 2016), while no γ_{OH} has been reported based on field studies to our knowledge.

During the Southern Oxidant and Aerosol Study (SOAS), 17% of ambient OA was estimated to be IEPOX-SOA (Hu et al., 2015). In this study, ambient gas and aerosol species were sampled through an oxidation flow reactor (OFR) and a thermodenuder (TD) to investigate heterogeneous oxidation and evaporation of ambient IEPOX-SOA, respectively. These systems included an AMS and other on-line instruments measuring both gas and aerosol species inflow and outflow. A simplified box model is used to investigate the fate of gas-phase IEPOX under ambient and OFR conditions. The potential of evaporation to impact the lifetime of IEPOX-SOA was evaluated. The heterogeneous reaction rate coefficient (k_{OH}) and OH uptake coefficient (γ_{OH}) of IEPOX-SOA with OH radicals are estimated from the OFR data. IEPOX-SOA aging during the dry season of 2014 in central Amazonia as part of the Green Ocean Amazon (GoAmazon2014/5, IOP2) experiment, using the same OFR experimental setup, was compared to the SOAS results.

2 Experimental method

2.1 Background and instrumentation

The SOAS study (hereafter refer to “SE US study”) took place in the SE US in the summer (June 1− July 15) of 2013. Results shown here are from the SEARCH Centreville Supersite (CTR) in a mixed forest in Alabama (32.95° N, 87.13°W; Hansen et al., 2003). The average

(±standard deviation) temperature and relative humidity (RH) of ambient air were 25±4℃ and 83±18%, respectively (Fig. S1). Biogenic volatile organic compounds (BVOCs) were highly abundant with average isoprene and monoterpene concentrations of 3.3±2.4 ppb and 0.7±0.4 ppb, respectively, and they displayed clear diurnal variations (Fig. S1). Isoprene showed a broad mid-afternoon peak (~5.8 ppb), and monoterpenes peaked during the nighttime and early morning (~0.9-1.0 ppb). Chemically-resolved mass concentrations of submicron non-refractory aerosol (PM_1) were measured by a high-resolution time-of-flight AMS (HR-ToF-AMS, Aerodyne Research Inc., DeCarlo et al., 2006) at a time resolution of 2 min. Detailed information about AMS setup, operation and data analysis is given in the supporting information and as well as in Hu et al. (2015).

A "Potential Aerosol Mass" oxidation flow reactor (OFR) was used to investigate OA formation/aging from ambient air over a wide range of OH exposures (10^{10}-10^{13} molec. cm^{-3} s). This field-deployable OFR provides a fast and direct way to investigate oxidation processes of ambient gas and aerosol with OH radicals under low-NO chemistry (Kang et al., 2007; Lambe et al., 2011; Li et al., 2015a; Peng et al., 2015; Ortega et al., 2016; Palm et al., 2016). The OFR is a cylindrical vessel (~13 L) with an average residence time of ~180-220 s in this study, depending on the flow rates of sampled ambient air (3.5-4.2 L min^{-1}) (Fig. S2-S3). In the "OFR185" method of OH production used in this study, two low-pressure mercury lamps inside the OFR produce UV radiation at 185 and 254 nm (Peng et al., 2015). OH radicals were generated when the UV light initiated O_2, H_2O, and O_3 photochemistry (Li et al., 2015a).

A large range of OH exposures (10^{10}-10^{13} molec. cm^{-3} s) can be achieved by varying UV light intensity, equivalent to several hours to several weeks of photochemical aging of ambient air (assuming a 24-hr average OH=1.5×10^6 molec. cm^{-3}; Mao et al., 2009). Thus we believe that the range of OH exposures (10^{10}-10^{13} molec. cm^{-3} s) covered by our study is the relevant range for the atmosphere. We note that OH radical concentration can be calculated as the ratio of the OH exposure (10^{10}-10^{13} molec. cm^{-3} s) and the residence time (200 s). The calculated OH radical concentration in our flow reactor is between 5×10^7 to 5×10^{10} molec. cm^{-3}. The lower range of OH radical concentration is comparable to the higher end of observed ambient OH concentrations (Mao et al., 2009).

OH exposures in the OFR were calculated by the real-time decay of CO added to the ambient air in the OFR (1-2 ppm; OH reactivity≈5-10 s^{-1}). The empirical estimation of OH exposure based on the OFR output parameters O_3, water, and ambient OH reactivity (15 s^{-1}) showed good agreement with that calculated from CO decay as shown in Fig. S4 (2015a). The uncertainty of calculated OH exposures in the OFR was estimated as 35% based on regression analysis (Li et al., 2015a; Peng et al., 2015).

The average wall loss corrections for OA in OFR during the SE US study is 2±0.7%. This wall loss is estimated by comparing the ambient OA concentrations to those concentrations after the OFR when the UV lights were off and no oxidant was present (other than ambient O_3).

A TD was used to investigate the volatility of ambient OA and IEPOX-SOA. The temperature in the TD increased linearly during the heating period (from 30℃ to 250℃ over 60 min) and then cooled down to 30℃ for 60 min. More detailed information on the TD technique and instrumentation can be obtained elsewhere (Faulhaber et al., 2009; Huffman et al., 2009a; Huffman et al., 2009b).

A typical sampling cycle during SE US study took a total of 24 min, sequentially sampling ambient (4 min), TD (4 min), ambient (4 min), OFR with OH radicals as oxidant (4 min), ambient (4 min), and OFR with other types of oxidation (e.g., O_3 or NO_3 as oxidants; 4 min), as illustrated in the diagram in Fig. S2. Only OFR data for OH oxidation using OFR185 method is presented here. A comparison of results from the OFR185 and OFR254 methods for a study at a pine forest was presented by Palm et al. (2016), showing similar SOA formation by both methods. Their results, together with modeling studies (Peng et al., 2015; Peng et al., 2016) showed that the OFR185 method is preferable for ambient studies, and thus that was the method used during SOAS. UV light intensities in the OFR were changed immediately after sampling the second OFR outflow for each cycle. Thus, oxidant concentrations in the OFR had sufficient time (at least 12 min, i.e. 3-4 flow e-folding times) to stabilize before the next OFR sampling interval. The air from each sampling mode was sampled by the AMS, a scanning mobility particle sizer (for measuring particle number size distributions; SMPS, TSI Inc.), and several other instruments to measure related gas phase species, e.g., VOCs from proton-transfer-reaction mass spectrometer (PTR-MS), O_3, CO and H_2O (Table S1).

Measurements collected during the second Intensive Operating Period (IOP2) of the Green Ocean Amazon (GoAmazon2014/5, hereinafter "Amazon study") Experiment (Martin et al., 2016), which took place in the dry season of central Amazonia, are also presented here. The region has high isoprene and monoterpene emissions (Karl et al., 2007; Martin et al., 2010). In this analysis, data from the "T3" ground site (3.213 S, 60.599 W), a rural location 60 km west of Manaus (Pop. 2 million) in the dry season (Aug. 15 to Oct. 15, 2014) are also shown. Unlike SE US study, the aerosols in dry season of Amazon study were heavily influenced by biomass burning (Martin et al., 2016), thus providing a difference dataset to investigate IEPOX-SOA heterogeneous reaction. The instrument setup, OFR settings, sampling schemes and data processing were similar to those for SE US study.

2.2 IEPOX-SOA identification

We classified ambient OA using positive matrix factorization (PMF) on the time series of peak-fitted, high-resolution organic spectra measured by the AMS (Ulbrich et al., 2009). A factor corresponding to ambient IEPOX-SOA was assigned based on its spectral features (e.g. prominent $C_5H_6O^+$ ion at *m/z* 82), and strong correlation with hourly or daily-measured 2-methyltetrols (R=0.79), an oxidation product of isoprene oxidation via the IEPOX pathway (Surratt et al., 2010; Hu et al., 2015), as well as with sulfate (R=0.75), which facilitates IEPOX-SOA formation through direct reactions or nucleophilic effects (Nguyen et al., 2014a; Liao et al., 2015). Unconstrained PMF analysis often fails when the factor fractions become too small (<5%), e.g., as is for the IEPOX-SOA at higher OH exposures in the OFR in this study (Ulbrich et al., 2009). To overcome this, a more advanced algorithm, the Multilinear Engine (ME-2) (Paatero, 2007; Canonaco et al., 2013), was applied through the recently implemented Source Finder (SoFi, Canonaco et al., 2013). In SoFi, the mass spectrum of the IEPOX-SOA factor was constrained based on the ambient spectrum of IEPOX-SOA from conventional PMF, and the concentrations of IEPOX-SOA factors were retrievable even at low concentrations. More information can be found in Supp. Info. (Sect. 2 and Fig. S5-S9). Here after we will call IEPOX-SOA PMF factor to be IEPOX-SOA for abbreviation.

In this study, $C_5H_6O^+$ data directly measured from AMS is used as a complementary tool to examine/interpret the analysis results from IEPOX-SOA PMF factor, since both lab and ambient results have shown $C_5H_6O^+$ is a very good tracer for IEPOX-SOA (Robinson et al., 2011; Lin et al., 2012; Allan et al., 2014; Hu et al., 2015). Analyzing $C_5H_6O^+$ is an easy alternative method to evaluate the physicochemical evolution of IEPOX-SOA, that avoids the uncertainties related to PMF analysis, and thus provides further confidence in the results. This is especially true when periods where the OA is dominated by IEPOX-SOA are analyzed.

2.3 Box model to simulate gas-phase IEPOX

The chemistry of OH oxidation in the OFR is typical of low-NO conditions with HO_2 being the dominant reaction partner of RO_2 radicals due to the greatly elevated HO_2 concentrations and the very short lifetime of NO and NO_x in OFR (Li et al., 2015a; Peng et al., 2015). A box model (KinSim 3.2 in Igor Pro. 6.37) was used to simulate the fate of gas-phase IEPOX under both ambient and OFR conditions, as shown in Fig. 3 (Paulot et al., 2009; Xie et al., 2013; Bates et al., 2014; Krechmer et al., 2015). A detailed description, including reactions and parameters in the model, pH-dependent uptake coefficient of IEPOX onto aerosols (γ_{IEPOX}), aerosol surface area calculations and estimated photolysis of IEPOX, can be found in Supp. Info. Section 3 (Table S2-3 and Fig. S10-14).

3 Results and discussion

3.1 Low Volatility of IEPOX-SOA

TDs are widely used to investigate the volatility distribution of OA in ambient air (e.g. Faulhaber et al., 2009; Cappa and Jimenez, 2010). IEPOX-SOA evaporates more slowly upon heating (Fig. 1a) than total OA over a very wide range of TD temperatures (<170℃), indicating that IEPOX-SOA has a lower volatility than bulk OA. Consistent with that result, a lower volatility of the IEPOX-SOA tracer $C_5H_6O^+$ in both SE US and Amazon studies was also found (Fig. 2).

The volatility distributions of IEPOX-SOA and OA were estimated following the method of Faulhaber et al. (2009), based on calibration of the relationship between TD temperature and organic species saturation concentration at 298 K (C*). Similar methods have been developed for other thermal desorption instruments (e.g., Chattopadhyay and Ziemann, 2005; Lopez-Hilfiker et al., 2016). The volatility distribution of IEPOX-SOA (Fig. 1b) shows mass peaks at $C^*=10^{-4}-10^{-3}$ μg m^{-3}, which are much lower than those of diesel POA ($C^*=10^{-2}$ -1 μg m^{-3}) and biomass-burning POA ($C^*=10^{-2}$-100 μg m^{-3}, Fig. 1d) at various OA concentrations (1-100 μg m^{-3}). Those types of POA are reported to be semivolatile (Cappa and Jimenez, 2010; Ranjan et al., 2012; May et al., 2013). The estimated distribution implies that very little of the ambient IEPOX-SOA was actively partitioning to the gas phase during SE US study (Fig. 1b). Although we cannot rule out some chemical changes during TD heating, this conclusion is dictated by the data at the lowest TD temperatures, when such chemistry is less likely. Lopez-Hilfiker et al. (2016) have shown that oligomer decomposition for IEPOX-SOA upon heating at ~90℃ was important during SE US study, but that process will only make the measured volatility of IEPOX-SOA in TD higher than it should be. This reinforces our conclusion about the low volatility of ambient IEPOX-SOA, consistent with the independent results of Lopez-Hilfiker et al. (2016).

Several molecular species (e.g., 2-methyltetrols, C_5-alkene triols, IEPOX organosulfate and its dimer) comprising IEPOX-SOA have been characterized both in field and chamber studies (Surratt et al., 2010; Lin et al., 2012; Budisulistiorini et al., 2013; Liao et al., 2015). At the CTR site during the SE US study, 2-methyltetrols, C_5-alkene triols and IEPOX organosulfate measured by GC/MS and LC/MS in the particle phase accounted for an average of 80% (individually 29%, 28% and 24%, respectively) of total IEPOX-SOA factor mass (Hu et al., 2015). The volatilities of these IEPOX-SOA molecular species was estimated based on SIMPOL group contribution method (Pankow and Asher, 2008). The species reported to comprise most of IEPOX-SOA have relatively high C^* (2-methyltetrol=2.7 μg m^{-3}; C_5-alkene triols=400 μg m^{-3}, and IEPOX organosulfate=0.5 μg m^{-3}). The alkene triols in ambient air during SE US study (where average OA mass concentration was 3.6 μg m^{-3}) should have been almost completely in the gas phase (>98%), while 43% and 12% of the methyltetrol and organosulfate should have been in the gas-phase, respectively. The C^* of those monomer species is much higher than for the bulk IEPOX-SOA ($C^*= 10^{-6}$ -10^{-2} μg m^{-3}) that they are thought to comprise. On the other hand, the estimated C^* of a hypothetical methyltetrol molecular dimer (~10^{-7} μg m^{-3}) is significantly lower than that of most of the bulk IEPOX-SOA (Fig. 1d). This suggests that IEPOX-SOA may exist as oligomers in the aerosol phase, but that the oligomers were not evaporating as oligomers, rather decomposing and evaporating as monomer species at temperatures intermediate with those corresponding to the C^* of the monomers and the dimers, consistent with results of Lopez-Hilfiker et al. (2016). Although the IEPOX organosulfate may have lower volatility than estimated in Fig. 1D, it only accounts for 24% of total IEPOX-SOA (Hu et al., 2015) and thus it cannot be the only reason for the low volatility of the bulk of IEPOX-SOA. For reference, only 5% of the total sulfate is due to the IEPOX organosulfate, with the rest being inorganic sulfate consistent with other results from the SE US in Summer 2013 (Liao et al., 2015). Indeed, the thermogram of total sulfate is very different from that of IEPOX-SOA (Fig. 1a and Fig. 2a).

Further evidence supporting low volatility and strong oligomerization of IEPOX-SOA molecular species has also been reported. Lin et al. (2014) showed oligomers as part of IEPOX-

SOA in filter-based LC/MS measurement at three sites (including CTR) during SE US study. Some of the oligomers were separated by mass units of 100 ($C_5H_8O_2$) and 82 (C_5H_6O), which would be consistent with C_5-alkene triol ($C_5H_{10}O_3$) and methyltetrol ($C_5H_{12}O_4$) oligomerization though dehydration reactions (-H_2O or 2 H_2O), or with other reactions resulting in similar products. Results from online gas-particle partitioning measurements at the same site during this study have shown that the measured particle-phase fractions (F_{p}, negatively correlated with $C*$) of ambient IEPOX-SOA tracers (e.g., 2-methyltetrols and C_5-alkene triols) are much higher than expected based on the species vapor pressures, consistent with these tracers being formed during GC analysis by decomposition of larger molecules (likely oligomers) (Isaacman-VanWertz et al., 2016). Thus, the low volatility of IEPOX-SOA estimated from our TD data is consistent with multiple other measurements.

It is of high interest to estimate the fractional losses for both OA and IEPOX-SOA due to isothermal evaporation upon dilution. These losses can be estimated using the volatility distributions estimated from the TD measurements. This parameter can be quantified as (Cappa and Jimenez, 2010):

$$E_{loss} = 100\% \left[1 - \frac{C_{OA}(DF)}{C_{OA}(0)/DF}\right]. \qquad (1)$$

where E_{loss} is the fractional OA loss due to evaporation; $C_{OA}(0)$ is the initial organic mass concentration before dilution, and DF is the dilution factor applied. $C_{OA}(DF)$ is the OA concentration in equilibrium after dilution. Dilution factors varying from one to thirty were used here. The results are shown in Fig. 1c. After a 30-fold dilution, IEPOX-SOA mass loss due to evaporation is estimated to be ~5%, substantially lower than for total OA (17%). There are two uncertainties affecting this result. One is that the real volatility distribution of IEPOX-SOA is likely even lower, since the TD results are thought to be affected by oligomer decomposition upon heating. The other one is that this calculation neglects the effect of possible decomposition of oligomers into monomers in ambient air. If that process occurs on a timescale of e.g., 1day, it would lead to higher evaporated fractions than estimated here. The residence time of TD is ~10-15s, which may not be sufficient time for oligomer decomposition, especially at the lower temperatures that determined the upper end of the estimated volatility distribution. E.g. Vaden et al (2011) reported that it took 24 h to evaporate 75% of α-pinene SOA (although it is possible that processes other than oligomer decomposition were important for determining the timescale of those experiments). The kinetics of oligomer decomposition of IEPOX-SOA under ambient conditions should be further investigated to fully constrain its evaporation dynamics.

3.2 Fate of gas-phase IEPOX

IEPOX-SOA loadings exhibited a continuous decrease as OH exposure increases in the OFR. To interpret the observed decay of IEPOX-SOA in the OFR, we first need to understand whether additional IEPOX-SOA was formed in the OFR during SE US study. More details about the IEPOX-SOA decay will be discussed in Sect. 3.3. Here, the box model described above (Fig. 3) was used to simulate the fate of gas-phase IEPOX in OFR and ambient conditions, as shown in Fig. 4.

In ambient air, gas-phase IEPOX will either react with OH radicals to form more oxidized gas-phase products (e.g. hydroxyacetone) (Bates et al., 2014; Bates et al., 2015), be taken up onto acidic aerosol (Surratt et al., 2010), or be lost from the atmosphere by dry or wet deposition (Nguyen et al., 2015). Photolysis of IEPOX in ambient air should be negligible, since the epoxide and hydroxyl groups in IEPOX are photostable at visible or actinic UV wavelengths (Fleming et al., 1959). A model scenario accounting for organic resistance with slower IEPOX uptake than pure inorganic is applied to simulate the fate of gas-phase IEPOX (Gaston et al. 2014; Riva et al. 2016). This scenario is the most realistic assumption, since 67% of ambient aerosol is OA during SE US study (Fig. S15). Results from an alternative model assuming pure inorganic aerosols are shown in Supp. Info. The model predicts that the main pathway of gas-phase IEPOX removal in ambient air is aerosol-phase uptake during SE US study, where about 75% of IEPOX was taken up by the aerosol after one day under ambient conditions, because of the efficient uptake of gas-phase IEPOX onto acidic ambient aerosols (pH=0.8±0.5) at the CTR site (γ_{IEPOX}=0.009, lifetime~1.8 h). The rest of IEPOX was lost to dry deposition to the surface (16%), according to reported boundary layer of 1200 m and dry deposition rate of 3 cm s^{-1} (Nguyen et al., 2015), or to gas-phase reaction with OH (9%).

The fate of IEPOX sampled into the OFR differed from its fate in ambient air. Remaining unreacted and then leaving OFR or destruction in the gas phase completely dominate the fate of IEPOX under OFR conditions (Fig 4b). Negligible amounts of IEPOX (<1%) were taken up into the aerosol phase in the OFR. This is mainly because the lifetime of IEPOX aerosol uptake (γ_{IEPOX}=0.002; lifetime=7.0h) was much longer than the OFR residence time (200s). The lower

γ_{IEPOX} in OFR (0.002) than in ambient condition (0.008) was because of the higher pH of aerosol leading to a slower IEPOX uptake. Higher pH in OFR (1.35±0.6) than that in ambient (0.8±0.5) was because extra neutralized inorganic aerosol was formed in OFR. Photolysis of IEPOX in OFR is estimated to be very minor (less than 0.2%) (Fig. 4b and Table S3). Loss of IEPOX to the reactor walls is thought to be minor under the conditions of SE US study, given its high vapor pressure (Krechmer et al., 2015; Palm et al., 2016). We can estimate the timescale of IEPOX loss rate to the walls by assuming that the walls are covered by a layer of deposited ambient aerosol. We combine the 1st order rate of collision of gas molecules with the walls (400 s; Palm et al., 2016) and the uptake coefficient for IEPOX-SOA in ambient aerosols (γ_{IEPOX} = 0.009) to estimate a timescale of IEPOX loss to the walls of 12.3 h, which is negligible compared to residence time of IEPOX (~200s) in the OFR. Even if the walls were covered by sulfuric acid (γ_{IEPOX} = 0.082), the timescale of loss would be 1.4 h.

IEPOX-SOA mass concentrations formed in both ambient and OFR conditions were calculated as a function of OH exposure. For this estimate the molar mass of IEPOX-SOA and the SOA molar yield (φ_{SOA}) of IEPOX, defined as the sum of formed aqueous phase SOA tracer relative to the heterogeneous rate of gas-phase epoxide loss to particles (Riedel et al., 2015), are needed. Using the measured molecular composition of IEPOX-SOA (Hu et al., 2015), and assuming all species were present as dimers as discussed above, yields an average molar mass of bulk IEPOX-SOA of 270 g mol^{-1}. Laboratory uptake experiments showed the SOA molar yield of IEPOX is around 10-12% for acidic $(NH_4)_2SO_4$ (Riedel et al., 2015). A molar mass of 270 g mol^{-1} and φ_{SOA}=6% (to account for the dimerization) for IEPOX-SOA were applied here. In the OFR, the maximum modeled IEPOX-SOA mass concentrations were less than 12 ng m^{-3}, peaking at ~1 day OH exposure. The model-predicted IEPOX-SOA formation is equivalent to ~1% of the ambient IEPOX-SOA, indicating negligible IEPOX-SOA was formed in the OFR. If the more detailed IEPOX-SOA formation model of Riedel et al. (2016) were used, the modeled IEPOX-SOA formation would be significantly lower, due to the consideration of the kinetics of IEPOX-SOA formation. That reinforces our conclusion that IEPOX-SOA formation in the reactor was negligible. An upper limit of ~6% of the ambient IEPOX-SOA mass being formed in the OFR can be derived assuming that the particles are 100% inorganic, as shown in Fig. S17.

In addition to the box model results, we also have experimental evidence demonstrating negligible IEPOX-SOA formation in the OFR. During the Amazon study, standard additions of isoprene (50-200 ppb) were injected into ambient air at the entrance of the OFR, during a period when little SOA was formed from ambient precursors. After isoprene was exposed to varied OH exposures (~10^9-10^{12} molec. cm^{-3} s) in the OFR in the presence of ambient aerosols, no additional IEPOX-SOA formation was observed in the oxidized air exiting the OFR, as shown in Fig. 5. Even under optimum OH exposures (8-11×10^{10} molec. cm^{-3} s), where most of the isoprene and isoprene dydroxyhydroperoxide (ISOPOOH) are expected to be oxidized and before substantial decay of IEPOX-SOA occurs, no enhancements of IEPOX-SOA tracer $C_5H_6O^+$ ion abundance in OA spectra were observed. Consistent with our results, a laboratory flow tube study (residence time = 1 min) of low-NO isoprene oxidation in the presence of acidified inorganic seeds also reported negligible IEPOX-SOA formation (Wong et al., 2015). Those results highlight a key limitation of this type of OFR: processes that do not scale with OH and thus are not greatly accelerated in the reactor are not captured. This limitation can be removed by seeding the OFR with H_2SO_4 particles, which greatly accelerate IEPOX aerosol uptake. Simulation results (not shown) indicate that adding ~100 μg m^{-3} of pure H_2SO_4 to the ambient air allows to efficiently form IEPOX-SOA in the reactor. The increased surface area and acidity from added H_2SO_4 seed both help accelerate IEPOX reactive uptake, although acidity plays a more important role. If we use the ambient surface area and pure H_2SO_4 in the model the lifetime of IEPOX uptake is ~10 min, while if we assume the ambient acidity and the same surface area as 100 μg m^{-3} of pure H_2SO_4, the lifetime is 1.1 h.

3.3 Lifetime of IEPOX-SOA against OH oxidation

IEPOX-SOA loadings showed a continuous decrease as OH exposure increases in the OFR (Fig. 6a). Since negligible IEPOX-SOA mass was added in the OFR (Sect. 3.2), this decay should be due to the sum of all IEPOX-SOA loss processes. The loss of IEPOX-SOA is defined empirically here as the loss of the molecular structures that result on AMS spectral features of IEPOX-SOA (e.g., $C_5H_6O^+$ and $C_4H_5^+$ enhancements, Lin et al., 2012; Hu et al., 2015), such that an IEPOX-SOA component cannot be distinguished in constrained PMF analysis. Evaporation, photolysis and heterogeneous reaction with OH radicals are three possible loss pathways. Note that the rate derived here may be a lower limit for individual molecular components of IEPOX-SOA, if e.g. it takes two or more OH reactions for their AMS spectrum to no longer resemble that of IEPOX-SOA.

In principle some IEPOX-SOA could evaporate, if semivolatile molecules in equilibrium with it were oxidized by OH. As discussed above, IEPOX-SOA itself has low volatility and only a small fraction (~5%) may evaporate to the gas phase after dilution of a factor of 30. Oligomer decomposition followed by evaporation is very likely negligible in the flow reactor residence time scale of 3 min. However, this process could be more important in ambient air, and if fast, could influence the IEPOX-SOA lifetime. No results for oligomer decomposition rates or extents for IEPOX-SOA have been reported in the literature, to our knowledge. Thus, further research on this topic is recommended. Thus IEPOX-SOA evaporation is unlikely to contribute to the large observed IEPOX-SOA loss in the OFR (up to 90%).

Photolysis of IEPOX-SOA also cannot explain the large deceases of IEPOX-SOA in Fig. 6a. Washenfelder et al. (2015) reported that IEPOX-SOA during SOAS contributed negligibly to the aerosol absorption at 365 nm. Lin et al. (2014) reported a wavelength-dependent effective mass absorption coefficient (MAC) value of ~247 cm^2 g^{-1} at 254 nm for laboratory-generated IEPOX-SOA on acidified $(NH_4)_2SO_4$ seed. Using the MAC trend vs. wavelength and the measured data down to 200 nm we estimate an MAC of ~5200 cm^2 g^{-1} at 185 nm. Using those absorption efficiencies (and assuming an upper limit quantum yield of 1) we can derive an upper limit photolysis fraction of 1.5% of IEPOX-SOA in the OFR when neglecting other competing effects (e.g. OH oxidation, Table S3 and Fig. S18). In addition, the actual quantum yield may be much less than 1, as IEPOX-SOA molecular species contain mainly hydroxyl and carbonyl groups (Surratt et al., 2010; Lin et al., 2014). Interactions between these groups are thought to result in low quantum yields in the condensed phase (Phillips and Smith, 2014; Sharpless and Blough, 2014; Phillips and Smith, 2015; Peng et al., 2016). Therefore, photolysis of IEPOX-SOA should contribute negligibly to the observed IEPOX-SOA decay.

The observed decay of IEPOX-SOA in Fig. 6a must then be the result of heterogeneous reactions with OH radicals. This process can be quantitatively described as:

$$[IEPOX-SOA]_i/[IEPOX-SOA]_0 = e^{-k_{OH}\times OH_i\times\Delta t} = e^{-k_{OH}\times OH_{exp,i}} \qquad (2)$$

where $[IEPOX\text{-}SOA]_i$ is the IEPOX-SOA mass concentration after the i^{th} OH exposure step in the OFR. $[IEPOX\text{-}SOA]_0$ is the initial ambient IEPOX-SOA entering the OFR; $[IEPOX\text{-}SOA]_i/[IEPOX\text{-}SOA]_0$ is the mass fraction remaining of IEPOX-SOA in the OFR output, shown on Fig. 6a. OH_i is the average OH concentration of step i in the OFR, Δt is the real exposure time. $OH_{exp,i} = OH_i \times \Delta t$ is the OH exposure of step i. k_{OH} is the heterogeneous reaction rate coefficient between IEPOX-SOA and OH radicals.

Fitting the results in Fig. 6a with Eq. (2) results in a k_{OH} of $4.0 \pm 2.0 \times 10^{-13}$ cm^3 molec.$^{-1}$ s^{-1} The 1σ uncertainty was obtained by Monte Carlo simulation, from propagation of the errors of [IEPOX-SOA]$_i$/[IEPOX-SOA]$_0$ (9%) and the uncertainty of OH exposure (35%, Fig. S4). The uncertainty of [IEPOX-SOA]$_i$/[IEPOX-SOA]$_0$ was estimated as 9% from PMF analysis of OFR data (Hu et al., 2015).

A similar k_{OH} value (4.6×10^{-13} cm^3 molec.$^{-1}$ s^{-1}) was obtained by fitting the IEPOX-SOA tracer $C_5H_6O^+$ ion decay as a function of OH exposure during a period (June 26th, 14:00-19:00) when 80-90% of ambient OA was composed of IEPOX-SOA (Fig. S19-S20), which confirms the k_{OH} determined above.

For comparison, the average mass fraction remaining of IEPOX-SOA vs. OH exposure during the Amazon study is also shown in Fig. 6a. A similar k_{OH} value of $3.9 \pm 1.8 \times 10^{-13}$ cm^3 molec.$^{-1}$ s^{-1} was obtained. Despite differences between the SE and Amazon studies, the similarity of results from both studies increases our confidence in the derived value of the heterogeneous reaction rate coefficient. The higher aerosol concentrations from biomass burning during the Amazon study did not appear to cause any major differences in the observed OH uptake. This may be due to the mostly liquid state of the ambient particles in both studies (Bateman et al., 2015; Pajunoja et al., 2016), which will be discussed in detail below.

To investigate k_{OH} of OA, multiple experiments (usually with RH<30%) with laboratory-generated different types of OA have been conducted. The bulk of those OA in the lab usually had mobility particle sizes ranging from 100-300 nm (Table 1), similar to that of IEPOX-SOA in SE US (wet size=415 nm). The k_{OH} value of IEPOX-SOA determined here is similar to heterogeneous k_{OH} determined in those laboratory studies, including highly-oxidized OA (e.g. citric acid; $3.3 - 7.6 \times 10^{-13}$ cm^3 molec.$^{-1}$ s^{-1}) (Kessler et al., 2012), levoglucosan ($1.4 - 4.3 \times 10^{-13}$ cm^3 molec.$^{-1}$ s^{-1}) (Slade and Knopf, 2014), and pure erythritol (2.5×10^{-13} cm^3 molec.$^{-1}$ s^{-1}), which has a similar structure to the 2-methyltetrols in IEPOX-SOA (Kessler et al., 2010). A summary of k_{OH} in this study and other laboratory studies with additional experimental information for each study is shown in Table 1.

A dependence of k_{OH} on ambient RH was found in both the SE US and Amazon studies, with larger k_{OH} at high RH, especially above 90% RH (Fig. 7). This effect may be due to higher liquid water content, leading to a larger surface area that facilitates faster OH uptake to the aerosol phase and thus resulting in faster k_{OH} values. Accounting for liquid water content, the calculated particle surface areas show similar trends to $k_{OH,}$ in both studies, as shown in Fig. 7. The values of both parameters increase with RH (especially for RH>90%).

An alternative explanation for the measured RH dependence would be the influence of diffusion limitations. However, at the RH levels studied here (>40%), diffusion limitations of OH in the aerosol phase are thought to be negligible (calculated lifetime of bulk diffusion of OH radical < 1s). The diffusion coefficient of OH radical in liquid phase ($>10^{-14}$ m^2 s^{-1}) was obtained from other laboratory-generated OA (e.g. isoprene derived SOA, α-pinene derived SOA, levoglucosan particles) (Renbaum-Wolff et al., 2013; Arangio et al., 2015; Li et al., 2015b). Li et al. (2015b) reported that the diffusion of NH_3 on laboratory biogenic SOA is only slowed at much lower transition RH (10-40%) than that for liquid/solid phase transition (50-80%). This supports that under the conditions in SE and Amazon studies diffusion limitations should not play a role. An effect of temperature on k_{OH} was not apparent in our study. Lai et al. (2015) reported a significant effect for a laboratory study with a pure compound. We recommend that this issue is explored further in the laboratory using pure IEPOX-SOA.

The ambient lifetime of IEPOX-SOA due to the heterogeneous reaction with OH radicals was estimated to be more than 2 weeks (19±9 days) based on the average k_{OH} ($4.0\pm2.0\times10^{-13}$ cm^3 $molec.^{-1}$ s^{-1}), assuming an average ambient OH concentration of 1.5×10^6 molec. cm^{-3}. A similar lifetime can be estimated for the Amazon study. Longer lifetimes of 48 days in SE US study and 99 days in Amazon study were estimated when the observed average 24h OH concentration in both studies (0.6×10^6 molecule cm^{-3} in SE US and 0.3×10^6 molecule cm^{-3} in Amazon) were used (Krechmer et al., 2015). The long lifetime of IEPOX-SOA against heterogeneous oxidation is consistent with the estimated lifetime of total OA in urban and forested areas (Ortega et al., 2016; Palm et al., 2016), and also pure highly-oxidized OA (1-2 weeks) in laboratory studies (Kessler et al., 2010; Kessler et al., 2012).

3.4 Fate of Oxidized IEPOX-SOA mass

It is of interest to determine whether the mass of IEPOX-SOA continues to be present in the aerosol after OH heterogeneous oxidation, albeit as a different chemical form, or whether it evaporates from the particles. Functionalization reactions would favor the former, while fragmentation reactions would favor the latter (George et al., 2007).

At lower OH exposures (<1×10^{12} molec. cm^{-3} s) during daytime, SOA formation (non-IEPOX-SOA) was observed in the OFR (e.g., from monoterpene and sesquiterpenes oxidation, Fig. 6b), making it difficult to discern whether functionalization or fragmentation dominated for IEPOX-SOA losses. However, at OH exposures in the OFR above 1×10^{12} molec. cm^{-3} s, net SOA formation from ambient air was no longer observed. This is presumably due to organic vapors undergoing multiple generations of oxidation and fragmenting in the gas phase in the OFR (Palm et al., 2016). For that OH exposure range, changes of the aerosol phase should be dominated by heterogeneous reactions. In this regime, OA mass was lost at a rapid rate of ~6 % OA mass per 1×10^{12} molec. cm^{-3} s of OH exposure through volatilization. A very similar rate was observed for the IEPOX-SOA (~7% per 1×10^{12} molec. cm^{-3} s), which implies that the main loss mechanism of IEPOX-SOA at higher OH exposures is due to volatilization following fragmentation. In the period when 80-90% of OA was composed of IEPOX-SOA, the OA also showed an up to 70% mass loss (Fig. S20), confirming the conclusion that a high fraction of IEPOX-SOA was volatilized to the gas phase after heterogeneous reaction at higher OH exposures.

The aerosol mass losses of IEPOX-SOA and OA into gas phase are consistent with laboratory experiments of heterogeneous reaction of pure erythritol particles (a surrogate of the IEPOX-SOA tracer 2-methyltetrols, see Fig. 6b), which also showed that OH oxidation led to formation of volatile products escaping to the gas phase (Kessler et al., 2010; Kroll et al., 2015). We note however that IEPOX-SOA is mostly composed of oligomers, rather than monomers as with erythritol.

3.5 Estimation of reactive uptake coefficient (γ) of OH

By quantifying the removal of IEPOX-SOA in the aerosol phase, an effective reactive uptake coefficient of OH (γ_{OH}) on the aerosol in the OFR can be estimated. To our knowledge, this is the first time that γ_{OH} has been derived from measurements of ambient SOA aging.

The variable γ_{OH} can be calculated from k_{OH} per Smith et al. (2009):

$$\gamma_{OH} = \frac{4 \cdot k_{OH} \cdot V_{IEPOX-SOA} \cdot \rho_0 \cdot N_A}{\bar{c} \cdot S_{IEPOX-SOA} \cdot MW_{IEPOX-SOA}} = \frac{4 \cdot k_{OH} \cdot D_{surf} \cdot \rho_0 \cdot N_A}{\bar{c} \cdot MW_{IEPOX-SOA}}, \quad (3)$$

where k_{OH} is the heterogeneous reaction rate coefficient of IEPOX-SOA discussed above (4.2±2.1×10^{-13} cm^3 molec.$^{-1}$ s^{-1}); ρ_0 is density of aerosol in OFR, which is estimated as 1.46±0.49

g cm^{-3} based on the aerosol composition (Fig. S15). N_A is Avogadro's number; $\bar{c}$ is the mean speed of gas-phase OH radicals, calculated as $(8RT/\pi M)^{0.5}$ (R is the universal gas constant, T is the temperature in K, and M is the molar mass of the OH radical). The calculated $\bar{c}$ for OH (at 293 K) is 604 m s^{-1}. $MW_{IEPOX-SOA}$ is the molar mass of IEPOX-SOA. The estimated $MW_{IEPOX-SOA}$=270 g mol^{-1} was used here, which is similar to isoprene-SOA molar mass of 252 g mol^{-1} estimated from a separate flow tube study based on CCN measurement (King et al., 2010). An uncertainty of 30% is assigned to $MW_{IEPOX-SOA}$. $V_{IEPOX-SOA}$ and $S_{IEPOX-SOA}$ are the mean volume and surface areas of IEPOX-SOA. We assume IEPOX-SOA is uniformly mixed with the other aerosol species (both in the surface and volume), and independent of particle size. Then for a spherical particle V_{total}/S_{total} is equal to $d_{surf}/6$, where d_{surf} is defined as surface-weighted particle diameter. The dried surface-weighted aerodynamic size distribution of *m/z* 82 (background corrected), tracer of IEPOX-SOA (Hu et al., 2015), peaks around 400 nm (Fig. 8), which is equivalent to mobility size of ~274 nm. By applying the average particle size growth factor of 1.5 calculated from average kappa (0.27) and ambient RH (Nguyen et al., 2014b), the average d_{surf} of wet IEPOX-SOA is estimated as 410 nm; Similar method was applied to calculate d_{surf} of wet IEPOX-SOA in Amazon study, which is finally calculated to be 490 nm.

The average mass-weighted aerodynamic size distribution of *m/z* 82 in SOAS and Amazon (d_{va}=~500 nm and 600 nm) is consistent with that of sulfate (d_{va}=~450 nm and 510 nm), which may indicate sulfate control of the IEPOX uptake formation pathway (Xu et al., 2014; Liao et al., 2015; Marais et al., 2016). Both peaks of *m/z* 82 and sulfate were systematically larger than of total OA (d_{va}=~370 or 400 nm), suggesting the IEPOX-SOA formation in SE US and Amazon studies may be partially contributed by aqueous/cloud processing (Meng and Seinfeld, 1994). The systematically higher oxidation level of IEPOX-SOA in the ambient air than from chamber studies also support this conclusion (Chen et al., 2015; Hu et al., 2015).

Finally, γ_{OH} is estimated as 0.59±0.33 under a range of OH concentrations between 5×10^7-5×10^{10} molec. cm^{-3}, which is consistent with the range of γ_{OH} (0.37-0.77) calculated for highly oxidized OA in laboratory studies (Table 1). The uncertainty of γ_{OH} was estimated by MonteCarlo simulation, propagated from errors of each parameter in equation (2) (50% for k_{OH}, 30% for d_{surf}, 28% for ρ_0, and 30% for $MW_{IEPOX-SOA}$). When considering the apparent RH effect on k_{OH}, the estimated γ_{OH} varies between 0.34-1.19. The γ_{OH} above 1 at the highest RH range

(90-100%) might be due to secondary reactions of IEPOX-SOA in the more dilute liquid phase. The estimated γ_{OH} in Amazon study is around 0.68±0.38.

Ambient particles in both SOAS and GoAmazon were liquid as quantified by particle bounce experiments (Bateman et al., 2015; Pajunoja et al., 2016) and thus kinetic limitations to OH uptake in the OFR should not play a role (Li et al., 2015). In this study, we calculated γ_{OH} based on a wide range of OH concentrations (5×10^7 - 5×10^{10} molec. cm^{-3}). Several laboratory experiments suggest that OH uptake should obey the Langmuir–Hinshelwood (LH) kinetic mechanism, where γ_{OH} tends to lower under higher OH concentrations, because of a saturation of surface reactive sites at higher OH concentrations (George and Abbatt, 2010; Slade and Knopf, 2013). We have calculated k_{OH} at different OH exposure ranges (10^{10} to 10^{11}-10^{13} molec. cm^{-3} s^{-1}, Fig. S22). No obvious OH dependence of k_{OH} (γ_{OH}) was found above 3×10^9 molec. cm^{-3} (beyond where k_{OH} calculation is more robust), which suggests the γ_{OH} calculated in this study does not depend on OH concentration. A possible explanation is that in our study OH uptake occurs on liquid particles, resulting on fast OH diffusion into the particle bulk, and causing OH uptake not to be limited by surface adsorption. We note that our experiments do not rule out some dependence of γ_{OH} on OH at lower OH levels in the atmosphere. However, Che et al. (2009) found no effect of OH on γ_{OH} for squalane particles in the range 1-7 x 10^8 molec. cm^{-3}. More consideration of other factors (e.g., surface regeneration due to volatilization; aerosol phase influence) should be explored in future studies of the γ_{OH} for IEPOX-SOA.

4. Conclusions

We investigated volatility and aging process of IEPOX-SOA during the late spring and early summer of SE US and the dry season of central Amazonia with field-deployed thermodenuder and oxidation flow reactor. IEPOX-SOA had a volatility distribution much lower than those of the monomer tracers that have been reported as comprising most of its mass. Much of IEPOX-SOA likely exists as oligomers in the aerosol phase. The kinetics of decomposition of oligomers to monomers needs further investigation to fully constrain the lifetime of IEPOX-SOA against evaporation.

The formation of IEPOX-SOA in the field and in the OFR flow reactor was investigated. In contrast to the efficient IEPOX uptake in the ambient air, negligible IEPOX-SOA was formed in the OFR under OH oxidation, as the OFR as used here cannot accelerate processes such as aerosol uptake and reactions that do not scale with OH. Simulation results indicate that adding

~100 µg m^{-3} of pure H_2SO_4 to the ambient air would allow to efficiently form IEPOX-SOA in the reactor. Photolysis and evaporation of IEPOX-SOA in the OFR contributed negligibly to IEPOX-SOA loss. From the OFR results, we determined the lifetime of IEPOX-SOA through heterogeneous reaction with OH radicals (k_{OH}=$4.0\pm2.0\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} in SE US and $3.9\pm1.8\times10^{-13}$ cm^3 $molecule^{-1}$ s^{-1} in the Amazon) is equivalent to more than a 2-week photochemical aging lifetime (assuming OH = 1.5×10^6 molec. cm^{-3}). The mass lost at high OH exposures is mainly volatilized, rather than transformed into other aerosol species with different composition, which suggests fragmentation plays an important role during ambient aging process.

Values of effective γ_{OH} based on the measured IEPOX-SOA k_{OH} and other particle parameters were determined to be 0.59±0.33 in SE US and 0.68±0.38 in Amazon with no dependence on OH concentration over the range 5×10^7-5×10^{10} molecule cm^{-3}. This is the first time of γ_{OH} was estimated based on ambient SOA. Positive correlation between γ_{OH} and wet particle surface areas (RH dependent) suggest that OH uptake is surface area-limited. The substantially larger size distribution of IEPOX-SOA tracer *m/z* 82 and sulfate vs. bulk OA suggests that IEPOX-SOA formation in SE US study may be controlled by sulfate and/or influenced by cloud processing. However, the effect of aqueous processing under very dilute conditions relevant to clouds has not been investigated to our knowledge. Our results provide constraints on the sinks of IEPOX-SOA, which are useful to better quantify OA impacts on air quality and climate.

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Table 1 Summary of k_{OH}, γ_{OH} and different experiment parameters used in this study and other lab studies.

Species Name	$k_{OH}\times10^{12}$ (cm^3 molec.$^{-1}$ s^{-1})	γ_{OH}	OH conc.(molec.cm^{-3})	React. time	Particle Size (nm)	RH	References
IEPOX-SOA in SE US	0.40±0.20	0.59±0.33	10^7–10^{10}	~200s	415	~83%	(1)
IEPOX-SOA In SE US RH dependent	0.32	0.34	10^7–10^{10}	~200s	302	<60%	(1)
	0.33	0.39	10^7–10^{10}	~200s	328	60-80%	(1)
	0.34	0.46	10^7–10^{10}	~200s	380	80-90%	(1)
	0.64	1.19	10^7–10^{10}	~200s	525	90-100%	(1)
IEPOX-SOA in Amazon	0.39±0.19	0.68±0.38	10^7–10^{10}	~200s	490	~86%	(1)
IEPOX-SOA in Amazon RH dependent	0.35	0.45	10^7–10^{10}	~200s	363	<60%	(1)
	0.35	0.46	10^7–10^{10}	~200s	380	60-80%	(1)
	0.37	0.54	10^7–10^{10}	~200s	415	80-90%	(1)
	0.53	1.09	10^7–10^{10}	~200s	576	90%-100%	(1)
Highly oxidized organic species							
BTA[a]	0.76	0.51	~10^9-3×10^{11}	~37s	~130-145	30%	(2)
Citric acid	0.43	0.37	~10^9-3×10^{11}	~37s	~130-145	30%	(2)
Tartaric acid	0.33	0.40	~10^9-3×10^{11}	~37s	~130-145	30%	(2)
Erythritol	*0.25*	*0.77*	~1×10^9-2×10^{11}	~37s	~200	30%	(3)
Motor oil particles							
Diesel particles	0.4-34	0.1-8	0.6–40×10^6	4h	~300	10-75%	(4)
Nucleated motor oil particles	N/A	0.72	0-3×10^{10}	37s	~170	~30%	(5)
Biomass burning tracers							
Levoglucosan	0.31	0.91	~1×10^9-2×10^{11}	~37s	~200	30%	(3)
	0.14-0.43	0.21-0.65	10^8 to 10^9	N/A	120-267	0-40%	(6)
	N/A	0.15-0.6	10^7-10^{11}	<1 s	N/A	0%	(7)
Abietic acid	N/A	0.15-0.6	10^7-10^{11}	N/A	N/A	0%	(7)
Nitroguaiacol	N/A	0.2-0.5	10^7-10^{11}	N/A	N/A	0%	(7)
MNC[b]	0.04-0.16	0.07-0.22	10^8 to 10^9	N/A	203-307	0-26%	(6)
Other pure organic species							
Squalene	N/A	0.3±0.07	1×10^{10}	~37s	~160	30%	(8)
Squalene	1.8-1.9	0.49-0.54	1–7×10^8	1.5-3h	~220	30%	(9)
Palmitic Acid	N/A	0.8-1	1.4-3×10^{10}	10-17s	85-220	~16%	(10)

[a] 1, 2, 3, 4-Butanetetracarboxylic acid; [b] 4-methyl-5-Nitrocatechol

(1) This study; (2) (Kessler et al., 2012); (3) (Kessler et al., 2010); (4) (Weitkamp et al., 2008); (5) (Isaacman et al., 2012); (6) (Slade and Knopf, 2014); (7) (Slade and Knopf, 2013); (8) (Smith et al., 2009); (9) (Che et al., 2009); (10) (McNeill et al., 2008).

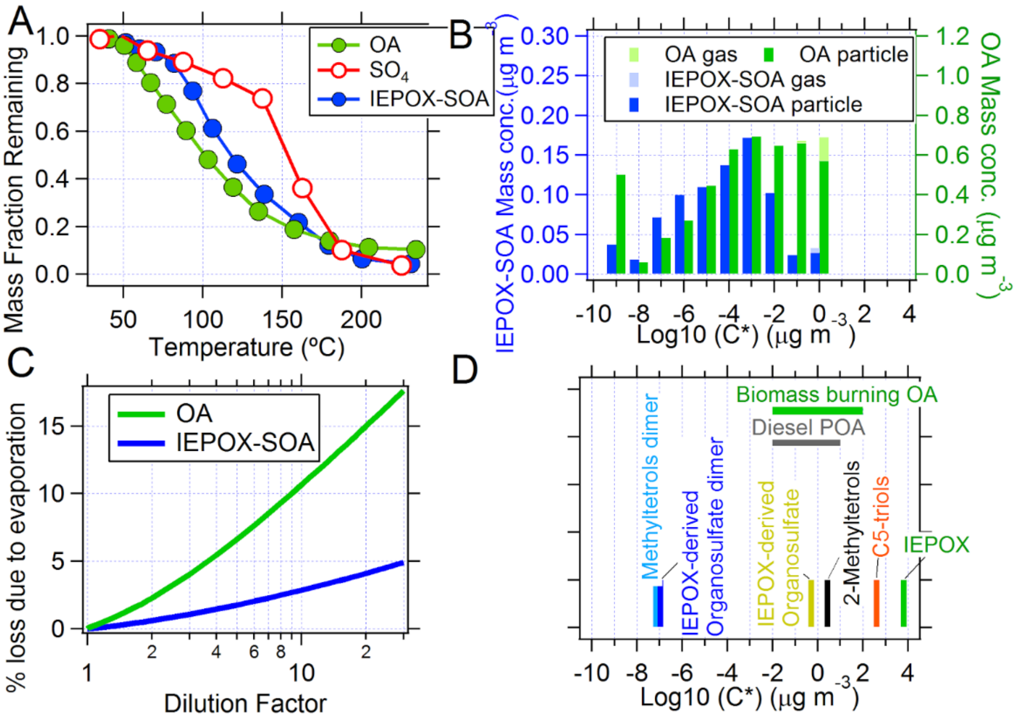

Figure 1 (a) Mean mass fraction remaining of IEPOX-SOA, OA and SO_4 versus temperature in TD ("thermograms") during SE US study. (b) Volatility distributions of IEPOX-SOA and OA estimated from TD thermograms (see text). Bars are offset for clarity and were both calculated for integer log(*C**) values. (c) Evaporation losses of IEPOX-SOA and OA as a function of dilution factors. (d) Volatility of typical IEPOX-SOA molecular species in the aerosol phase based the on SIMPOL group contribution method (Pankow and Asher, 2008). The reduction in vapor pressure upon addition of a nitrate group was used to estimate the effect of the sulfate group, due to lack of SIMPOL parameters for the latter, and the derived *C** may be overestimated for this reason.

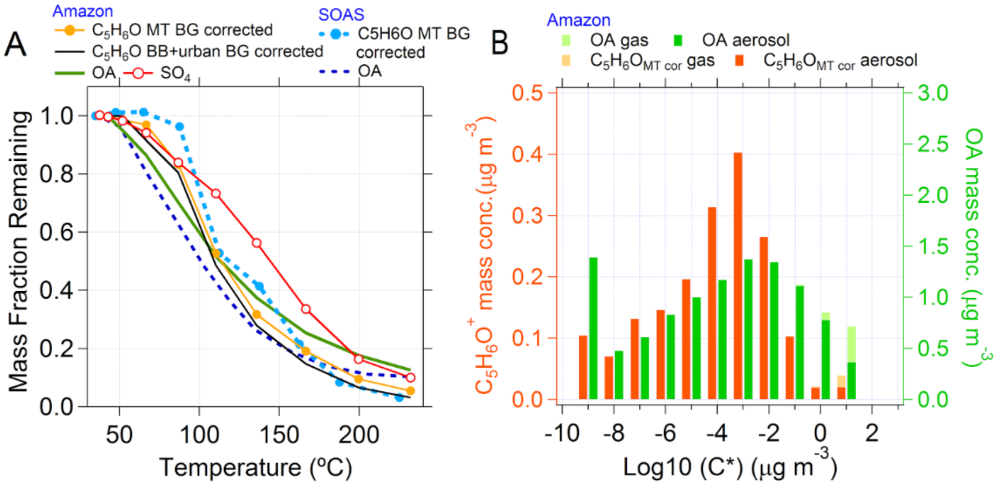

Figure 2 (a) Thermogram of OA, SO_4 and background-corrected $C_5H_6O^+$ ion in the SE US and Amazon studies. (b) Volatility distributions of $C_5H_6O^+$ and OA estimated based on TD thermograms from the Amazon study.

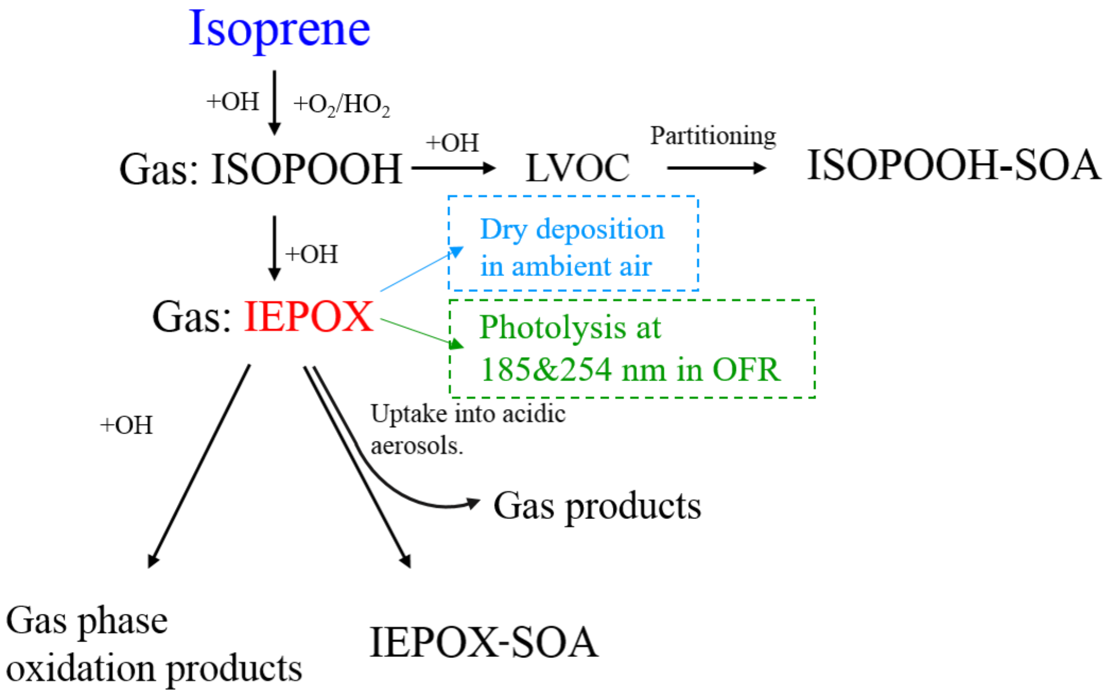

Figure 3 Mechanism diagram of gas-phase IEPOX model in ambient and OFR conditions. ISOPOOH-SOA refers to SOA formed through gas-particle partitioning of low-volatile VOCs from oxidation of isoprene 4-hydroxy-3-hydroperoxide (4,3-ISOPOOH) under low-NO conditions (Krechmer et al., 2015).

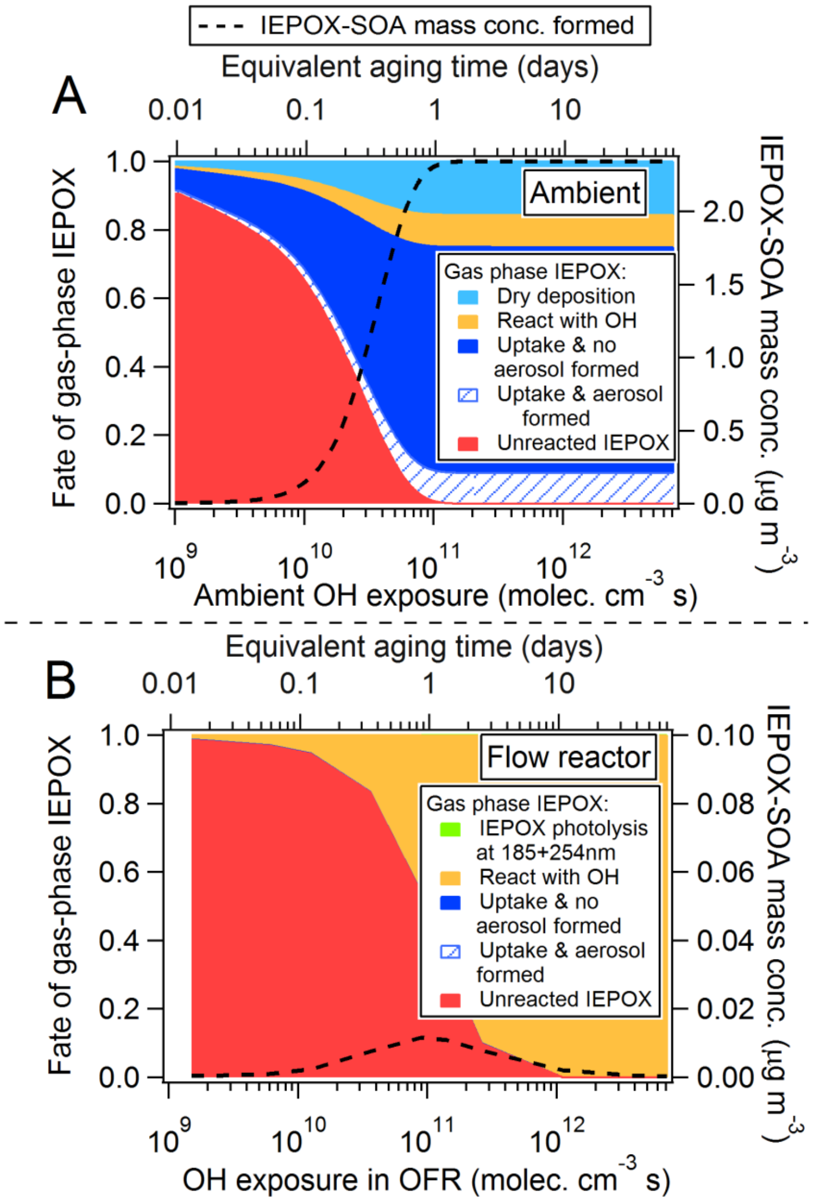

Figure 4 Modeled IEPOX fate (a) in ambient air and (b) oxidation flow reactor (OFR) conditions in SE US study. The uptake rate of gas-phase IEPOX onto aerosol is calculated by using the model of Gaston et al. (2014), and is mainly influenced by aerosol pH (estimated as 0.8 and 1.35 for ambient and OFR aerosol, respectively) and aerosol surface areas (300 and 350 µm^2/cm^3 for ambient and OFR aerosol, respectively). The calculated IEPOX-SOA mass concentrations are shown in Fig. 3. The OH exposures for both panels range 15 min-2 months of atmospheric equivalent age (at OH concentration=1.5×10^6 molec. cm^{-3}).

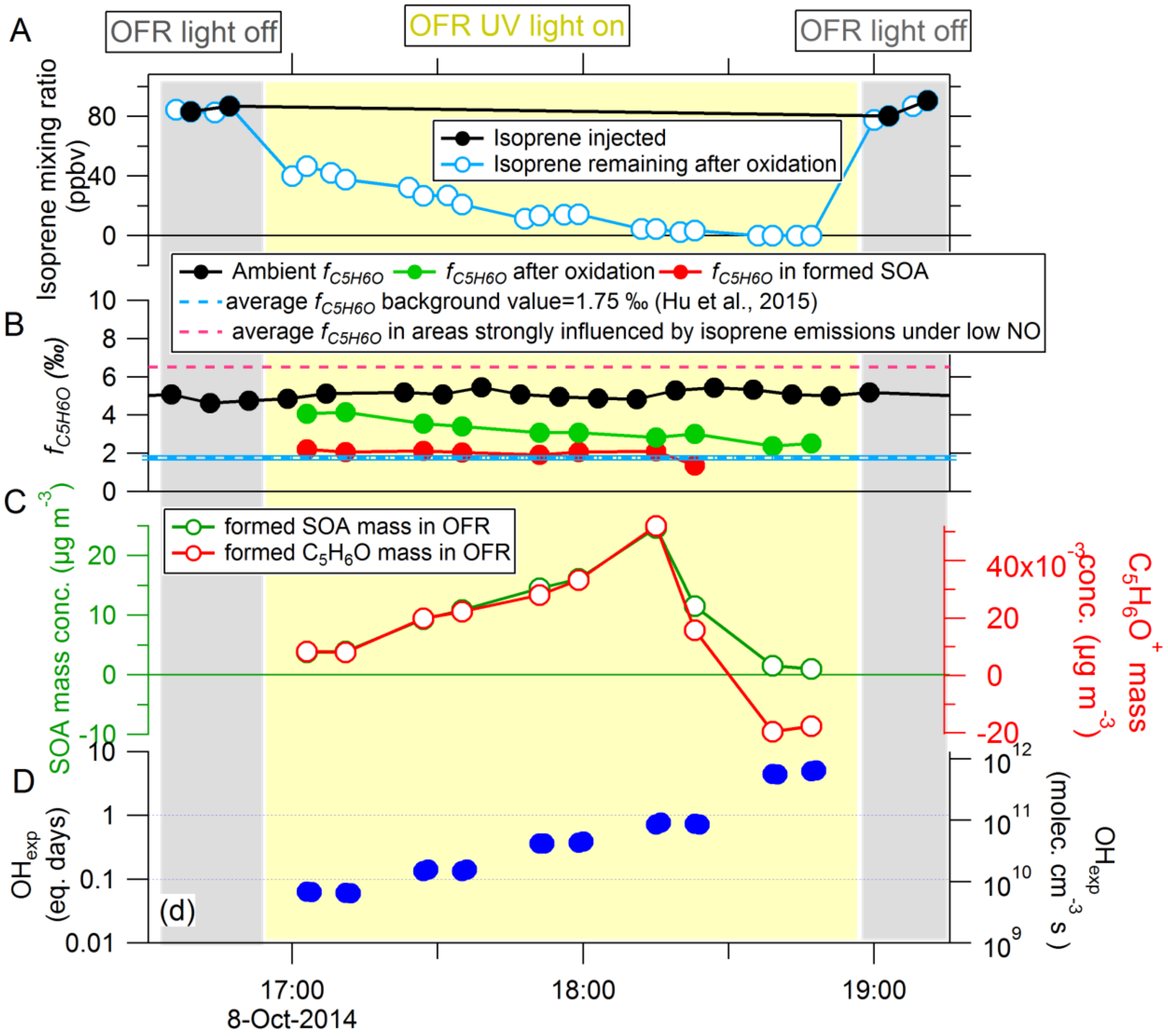

Figure 5. Isoprene standard addition experiment in ambient air during the GoAmazon2014/5 study. (a) Isoprene concentration injected and remaining after OFR. (b) Time series of ambient $f_{C_5H_6O}$, $f_{C_5H_6O}$ in OA after oxidation and $f_{C_5H_6O}$ in newly formed SOA from OFR oxidation. The average background value $f_{C_5H_6O}$=1.75‰ from urban and biomass burning emissions and $f_{C_5H_6O}$=6.5 ‰ from aerosol strongly influenced by isoprene emissions are also shown (Hu et al., 2015). (c) Time series of mass concentration of newly formed SOA (left axis) and $C_5H_6O^+$ (right axis). (d) Time series of equivalent aging time (left axis) and OH exposure in OFR (right axis). OH concentration=1.5×10^6 molec. cm^{-3} was assumed here to calculate equivalent OH aging times. The grey background indicates OFR light off period and light yellow is OFR light on period. Different OH exposures were achieved by varying the UV light intensity. Residence time in the OFR was about 200 s.

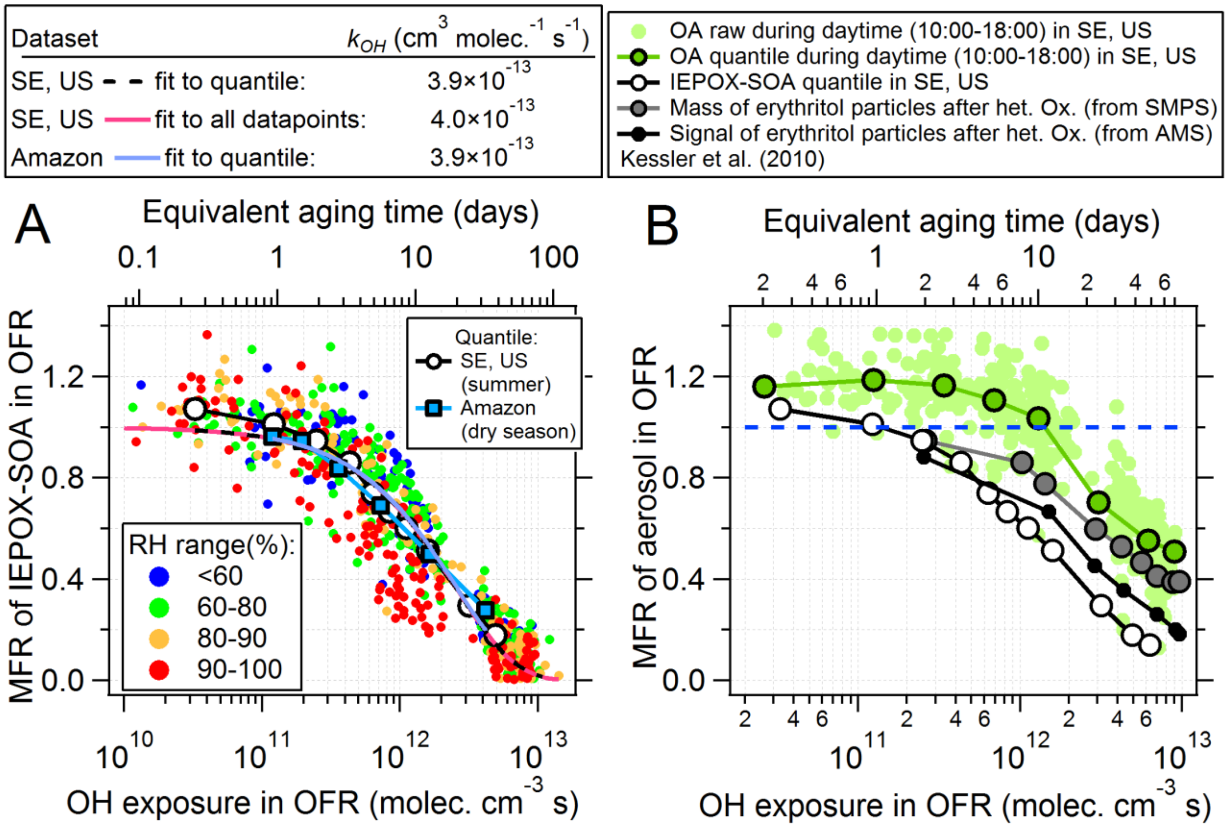

Figure 6 (a) Mass fraction remaining (MFR) of IEPOX-SOA in OFR output as a function of OH exposure during the entire SOAS and GoAmazon 2014/5 (dry season) studies. Individual datapoints from SOAS are color-coded by ambient RH. Similar data for GoAmazon 2014/5 are shown in Fig. S24. (b) Mass fraction of OA remaining in OFR output as a function of OH exposure in daytime (12:00-18:00) during SOAS. Also shown is the MFR of pure erythritol particles after heterogeneous oxidation as detected by SMPS and by AMS for reference (Kessler et al., 2010). Erythritol has a similar structure to the IEPOX-SOA tracers 2-methytetrols.

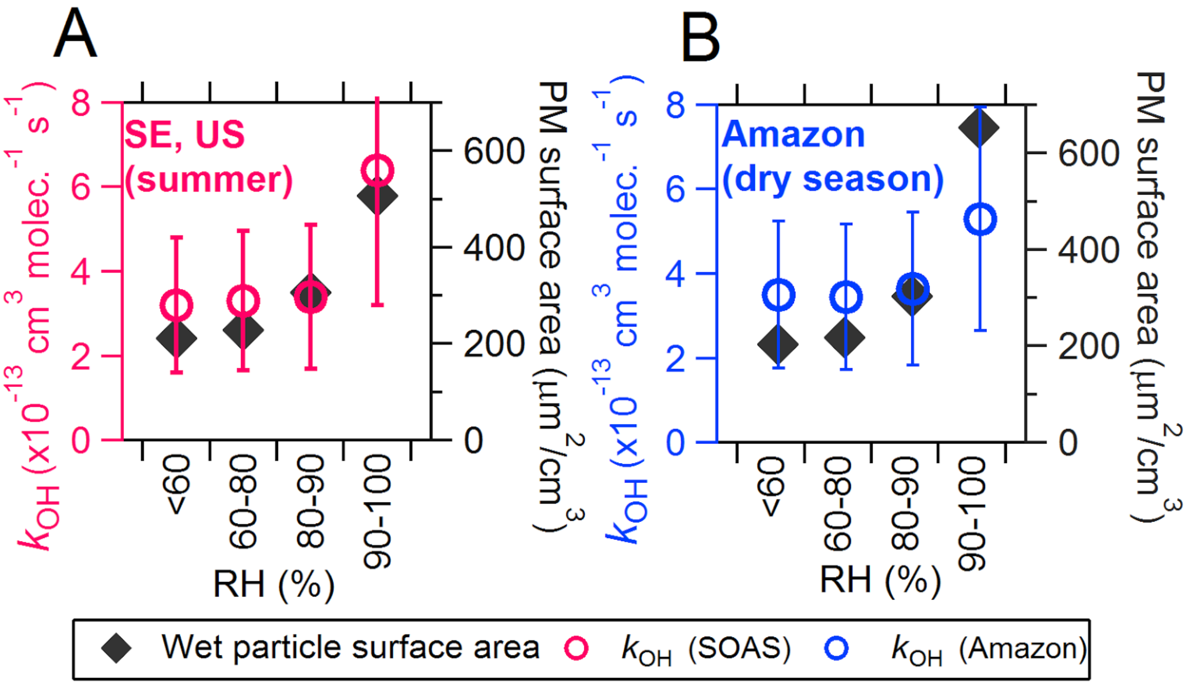

Figure 7 Estimated k_{OH} of IEPOX-SOA vs. ambient RH during the SOAS and Amazon studies. The ambient wet particle surface areas in both studies are shown on the right axis.

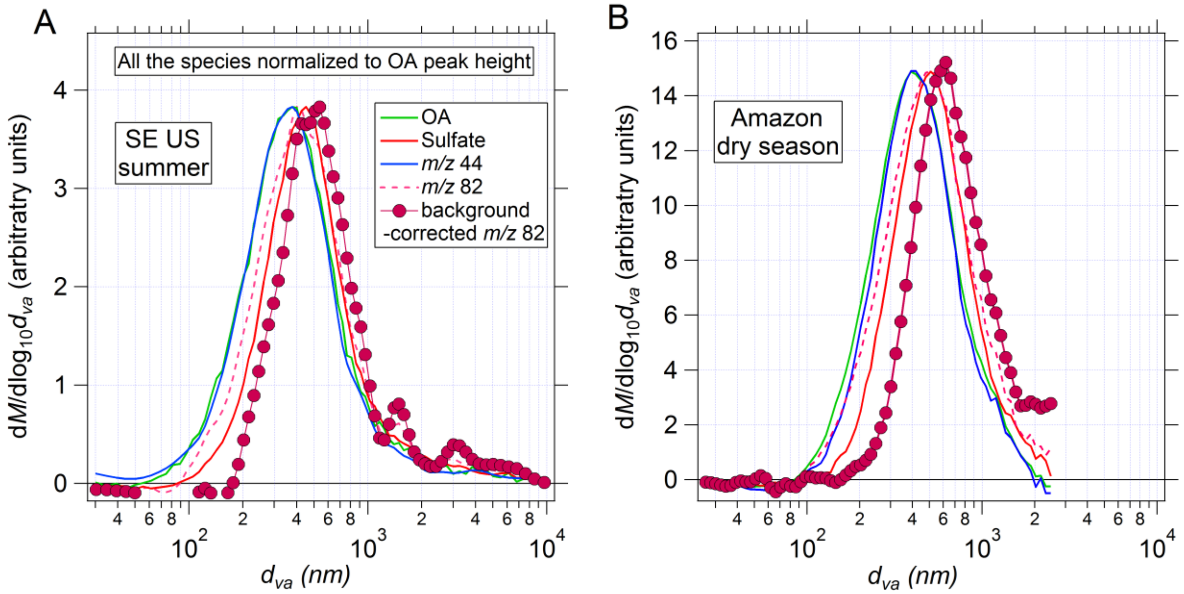

Figure 8. Average mass-weighted aerodynamic size distribution of OA, sulfate, *m/z* 44 and *m/z* 82 in (a) SE US and (b) Amazon. The mass size distribution of *m/z* 82 with background correction is also shown. The background correction method was introduced in Hu et al.(2015). Heights of all the size distributions are set to the same value for ease of visual comparison.