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Organic aerosol formation from the reactive uptake of isoprene epoxydiols (IEPOX) onto non-acidified inorganic seeds

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Dear Prof. McNeill,

We received two sets of reviewer comments in December 2013. We thank the reviewers for their helpful feedback. We have carefully answered each comment in the revised version of our manuscript and provided a detailed list of revisions below in the response letter. For your convenience, we have reproduced the reviewer comments in black and our author comments are presented in blue. We have uploaded the revised version of our manuscript. All authors have read and approved the suggested changes.

On behalf of my co-authors,

A handwritten signature in black ink, appearing to read 'Tran Nguyen', with a stylized flourish at the end.

Tran Nguyen

## Anonymous Reviewer #1

### General comments

This manuscript describes environmental chamber experiments aimed at investigating the potential reactive uptake of isoprene-derived epoxides (IEPOX) onto a number of non-acidic aerosol seed particles under conditions of varying pH and relative humidity (RH). The main finding of the work is that IEPOX undergoes reactive uptake onto wet aerosol seeds comprised on ammonium salts, while no reactive uptake is observed when the aerosol seeds are dry or when non-ammonium salts (such as sodium) are present. These results are important in that they suggest an atmospheric mechanism by which IEPOX may undergo reactive uptake in a manner which is only weakly correlated to particle pH, a somewhat baffling conclusion reached from previous field studies. The ammonium-catalyzed mechanism proposed here is also novel for epoxide chemistry, and the work also raises the intriguing possibility of amine reactivity with IEPOX. The findings are relevant to the construction of accurate chemical mechanisms for the formation of isoprene-derived SOA. The work has been carefully planned and executed, and the manuscript is clearly written. For these reasons, this study is quite appropriate for Atmospheric Chemistry and Physics.

We thank the reviewer for the insightful feedback that has been helpful in improving the clarity of the manuscript. We've responded to the specific comments below and made the suggested revisions to the text.

### Specific comments

p. 27684, line 24: Are the experimentally determined MS response factors (1.8) identical to the calculated dipole-polarizability MS response factors (1.4) to within the uncertainty of the measurement?

The definition of MS response ratio between species *a* and *b* were calculated in Paulot et al (2009b) as  $R = S_a / [S_a + S_b]$ , where *S* is the sensitivity of the species in CIMS. Our response ratio is calculated as  $R = S_a / S_b$ . If we calculate *R* from the theoretical dipole-polarizability approach described in Paulot et al. using the second definition, the response ratio is 1.6 (as quoted in Bates et al, JPCA 2014). This brings the theoretical response ratio within the uncertainty of the measurement of the experimentally-determined 1.8 ratio. We have corrected our error in describing the Paulot et al (2009b) number in the text so that it is directly comparable and added the following text after the response factor is mentioned in Section 2.2.1:

*“The difference between the two ratios is within the error of the sensitivity determination.”*

Figure 2: Why is the OA/IEPOX coefficient plotted on a log scale vs. LWC?

The log scale showed the 100%/-50% error bars as symmetric, so the data is easier to visualize than on a linear scale. We have reduced the range of the y-axis to eliminate most of the blank space.

Equation 1 suggests that there should be an inverse relationship.

We do observe an inverse relationship of  $\Phi_{\text{OA/IEPOX}}$  with  $P_{\text{LWC}}$ . Equation 1  $\{\Phi_{\text{OA/IEPOX}} = (C_{\text{OA}}/C_{\text{IEPOX}})/[10^6 \cdot R \cdot T \cdot P_{\text{LWC}}]\}$  suggests that if  $C_{\text{OA}}/C_{\text{IEPOX}}$  is constant, higher  $P_{\text{LWC}}$  will cause a decrease in  $\Phi_{\text{OA/IEPOX}}$ . If this were an equilibrium case (which is it not),  $C_{\text{OA}}/C_{\text{IEPOX}}$  would be proportional to  $P_{\text{LWC}}$ , thus keeping  $\Phi_{\text{OA/IEPOX}}$  constant (then  $\Phi = K_H$ ). However, in this non-equilibrium process,  $C_{\text{OA}}/C_{\text{IEPOX}}$  is dependent on

both the amount of water available (Henry's partitioning) and the reaction kinetics which are dependent on the activities of the inorganic ions. The activities of the ions control the extent of Reactions 2 – 4 (i.e., inverse relationship with  $P_{LWC}$ ) and the physical partitioning of the IEPOX controls Reaction 1 (direct relationship with  $P_{LWC}$ ), so the overall effect is difficult to predict *a priori*.

p. 27691, line 12: I assume that the pH for the hydrated AS is somewhat acidic due to the bisulfate/sulfate acid dissociation process. This should be explicitly stated.

We have added the following underlined text under Section 3.1.2, "Particle Acidity," to explicitly mention this point that was previously implied (new text is bolded):

*"Solutions of AS without additives had pH ~ 5.5 before atomization because, although no strong acid was present,  $H^+$  is expected to be present in small quantities based on the dissociation equilibria of inorganics, **such as the bisulfate/sulfate dissociation, and dissolution of  $CO_2$ .**"*

p. 27693, line 2: The actual  $k_{H^+}$  value ( $0.036 M^{-1} s^{-1}$ ) for IEPOX-4 has been experimentally determined by Cole-Filipiak et al. (ES&T, 44, 6718-6723, 2010).

Thank you for pointing to this omission. We added the citation to Cole-Filipiak et al (2010) and the following text (new text is bolded):

*"Eddingsaas et al. (2010) estimated  $k_{H^+} \sim 5 \times 10^{-2} M^{-1} s^{-1}$  and Cole-Filipiak et al. (2010) **determined  $k_{H^+} = 3.6 \times 10^{-2} M^{-1} s^{-1}$  for IEPOX.**"*

p. 27693, line 5: Since this work identifies  $NH_4^+$  as the catalyst for IEPOX uptake, I wonder why the authors did not carry out experiments at different  $NH_4^+$  concentrations in order to ascertain whether the kinetics of the IEPOX uptake was catalyst-limited or nucleophile-limited. The subsequent discussion of differences in reactivity observed for different nucleophiles implies the latter, but this issue is not specifically discussed.

We are in the process of doing kinetic studies on IEPOX +  $NH_4^+$  via NMR, similar to the experiments discussed in Eddingsaas et al (2010). These measurements are non-trivial due to the high salt content of the solutions, the long timescales of the measurements (because  $NH_4^+$  is a weaker catalyst than  $H^+$ , as discussed on Page 27682, lines 27-28), and the advanced techniques involved (water suppression NMR). As such, the results are ongoing and will be discussed in an upcoming manuscript.

We are fairly certain we are in a nucleophile-limited regime because different nucleophiles affect the reactivity (as the reviewer pointed out) and because pH does not significantly impact the reaction (i.e., removing some of the catalyst activity, in this case  $H^+$ , does not make too much of a difference.) We added the following text in the Summary section:

*"The weak dependence on pH and the strong dependence on nucleophile activity and particle liquid water suggest that the IEPOX reactions in hydrated ammonium salts are nucleophile-limited, rather than catalyst-limited"*

p. 27694, line 14: It is interesting that the results seem to show that  $Cl^-$  is a relatively poor nucleophile under the experimental conditions. While it is certainly possible that  $SO_4^{2-}$  is a better nucleophile than  $Cl^-$  under these conditions,  $Cl^-$  is well known to be a better nucleophile than  $H_2O$ . Since it is reported that

no organochloride products were detected, it makes me wonder how much tetrol was produced under these conditions. I realize that the authors did not detect and quantify tetrol products in this study, but it might be useful to add a brief discussion of this issue.

We agree that this is worth discussing in more detail. Regarding the formation of tetrols, they are the thermodynamically-favored product (Darer et al, 2011) and so it should not necessarily follow that if H<sub>2</sub>O is the poorest nucleophile that tetrols would be the least abundant compound in solution. Over time, even at moderate pH, compounds like organosulfates, organonitrates, and perhaps organochlorides will be converted to tetrols through hydrolysis.

Regarding why organochlorides were not observed, and whether it has implications on the nucleophilicity of Cl<sup>-</sup> in this system, we have considered the following possibilities:

- (1) Are the organochlorides produced, but we are not measured well using AMS? The EI source of the AMS should be able to ionize all the organic compounds, so the issue would lie in whether we can tell organic chlorine peaks from inorganic chlorine. The C-Cl bond is stronger than C-N bonds (~80 kcal/mol vs. ~70 kcal/mol, respectively), and we see organonitrates in the AMS as C<sub>c</sub>H<sub>h</sub>N<sub>1-2</sub>O<sub>o</sub><sup>+</sup> and C<sub>c</sub>H<sub>h</sub>N<sub>1-2</sub><sup>+</sup> fragments. So it should be possible to witness the same fragments with Cl instead of N in the AMS (C<sub>c</sub>H<sub>h</sub>Cl<sup>+</sup> for example), if they exist. For the NH<sub>4</sub>Cl + IEPOX experiments, we have tried to look for the C-Cl containing fragment, suggested by Hayes et al (2013) to be CCl<sup>+</sup>, C<sub>2</sub>HCl<sup>+</sup>, CCl<sub>2</sub><sup>+</sup>, C<sub>2</sub>Cl<sub>2</sub><sup>+</sup>, C<sub>2</sub>HCl<sub>2</sub><sup>+</sup>, CHOC<sub>2</sub><sup>+</sup>, but did not find any evidence of these peaks.
- (2) Are the organochlorides produced, but they evaporate in the diffusion drier prior to being sampled with the AMS? Organochlorides may be more volatile than the equivalent alcohol because the Cl group does not form hydrogen bonds with the solvent. For example, 2-chloro-2methylbutane (T<sub>boil</sub> ~ 85 C) has a lower boiling point compared to 2-hydroxy-2methylbutane (T<sub>boil</sub> ~ 102 C). If this is the case, we may be underestimating the total organic mass from the NH<sub>4</sub>Cl experiments compared to the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> experiments.
- (3) Are the organochlorides produced, but they are not stable in the aerosol water? Darer et al (2011) demonstrated that tertiary organosulfates and polyols were stable in water, even at low pH. However, tertiary organonitrates get converted to polyols (hydrolysis) and organosulfates (nucleophilic substitution) in a relatively short time, and the hydrolysis is seemingly pH-independent. There is no such data on organochlorides, but it may be possible that they are hydrolyzed or are involved in other nucleophilic substitution reactions because the chloride anion is a relatively good leaving group. If this is the case, we might slightly underestimate the total organic mass from the NH<sub>4</sub>Cl experiments compared to the (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> experiments because Cl<sup>-</sup> (35 g/mol) is heavier than OH<sup>-</sup> (19 g/mol).

We have added the citation to Darer et al (2011) in the text, and the following discussion at the end of Section 3.2.1. "Cation and anion substitutions":

*"Further, gas-phase organochlorides were not observed by the CIMS. It is possible that organochlorides are produced but are easily hydrolyzed in the aerosol liquid water due to the relatively-good leaving group ability of Cl<sup>-</sup>, i.e., the hydrolysis behavior of organochlorides is more similar to that of tertiary organonitrates than that of organosulfates (Darer et al., 2011). It is also possible that organochlorides are preferentially evaporated in the diffusion drier because*

*they might be more volatile than organosulfates or polyols. In both situations, but more so the latter, the total organic mass from the NH<sub>4</sub>Cl experiments would be underestimated by ToF-AMS. Although we did not quantify tetrols and other polyols in this work, it is expected that they are present in substantial quantities because they are the thermodynamically-preferred products in the epoxide ring-opening reactions.*

p. 27695, line 16: With the Henry's Law coefficient in hand, it would be useful to provide a quick estimate of the extent of IEPOX physical partitioning under typical atmospheric conditions. Is it important at all?

If one assumes 2 ppb ( $2 \times 10^{-9}$  atm) as an average IEPOX mixing ratio (which is realistic for the BEARPEX 2009 campaign), particle liquid water  $\sim 10 \mu\text{g m}^{-3}$ , and  $K_H = 3 \times 10^7 \text{ M atm}^{-1}$  (+ 100%, - 50%), we obtain **0.04 – 0.14  $\mu\text{g m}^{-3}$  IEPOX<sub>(aq)</sub>**.

Given that the average organic aerosol mass at BEARPEX 2009 was  $3.7 \mu\text{g m}^{-3}$  (Zhang et al, 2010), the condensed-phase IEPOX from physical partitioning alone can contribute up to 4% to the OA mass for this assumed liquid water content. The physical partitioning becomes more important in areas like the Southeast US where there is high liquid water content coupled to high isoprene emissions.

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aerosol (SOA) formation from 2-methyl-3-buten-2-ol (MBO) in the atmosphere. *Environ. Sci. Technol.* 2012, 46 (17), 9437-9446.

## Anonymous Reviewer #2

### Overall Comment and Recommendation:

Nguyen et al. conducts a series of new dark reactive uptake experiments in the Caltech smog chambers using synthetic cis- and trans- $\beta$ -IEPOX. This study basically follows the experimental approach of the UNC group (Lin et al., 2012, ES&T; Zhang et al. 2012, ACP); specifically, the Caltech group adapts synthetic procedures outlined in Zhang et al. (2012, ACP) to make cis- and trans- $\beta$ -IEPOX to conduct a series of dark reactive uptake experiments in the presence of seed aerosol. The biggest difference in this new study compared to the previous UNC group studies is that the authors explore the effect of seed composition and relative humidity, which hasn't been fully examined in prior studies. Importantly, the results of Nguyen et al. are consistent with dry experiments conducted by Lin et al. (2012, ES&T). For example, Nguyen et al. directly analyzes the IEPOX derived SOA generated in their experiments using the HR-AMS instrument. Similarly to Lin et al. (2012) (where this prior study collected filters from their dark reactive uptake experiments of  $\beta$ - and d-IEPOX and then extracted and re-aerosolized these extracts into a HR-AMS), this study also found a strong ion signal at m/z 82 in the AMS dataset. Consistent with both Lin et al (2012, ES&T) and Budisulistiorini et al. (2013, ES&T), this ion has now been proposed to be directly linked to IEPOX reactive uptake chemistry and has been resolved from PMF analyses of OA collected from isoprene-rich regions (Budisulistiorini et al., 2013, ES&T; Slowik et al., 2011, ACP; Robinson et al., 2011, ACP). Furthermore, OA formation was not observed from IEPOX in the presence of seed aerosol under dry conditions, which is again consistent with previous work. The most notable finding from this new study is that OA formation from IEPOX is observed from both cis- and trans- $\beta$ -IEPOX only on wet ammonium salt seed aerosols, where as no significant uptake is observed on seed aerosols that are dry or contain no ammonium salts. These new findings are important and warrant publication in Atmospheric Chemistry and Physics, especially since they show that OA formation from IEPOX depends on coupled relationship between inorganic composition and liquid water content of pre-existing aerosol. I want to stress here to the authors and the Editors that I fully concur with Reviewer 1's comments and I won't repeat these here, but they should be fully addressed before publication. In addition, I have a number of specific comments that should be addressed by the authors before publication of this manuscript.

We thank the reviewer for the detailed comments. There appears to be confusion about some parts of the manuscript, which we clarify in the comments below.

### Specific Comments:

#### 1.) Importance of [H<sup>+</sup>]:

The authors need to be extremely careful in concluding that [H<sup>+</sup>] doesn't seem to matter as much as [NH<sub>4</sub><sup>+</sup>] in the atmosphere. First, field measurements by Lin et al. (2013, ACP) and Budisulistiorini et al. (2013, ES&T) acknowledged the likely fact that the IEPOX-derived SOA products could form upwind and over the course of transport to their respective field sites. Thus, the aerosol likely became more neutralized (based on charge balance estimated by either IC or AMS analyses) over transport time. Thus, there was likely a weak correlation of the IEPOX-derived SOA to model estimated [H<sup>+</sup>] for this reason. I bring this up since the neutralization issue from previous field studies seems to be a major motivation for this new study. In addition, in the study by Lin et al. (2013), high volume PM<sub>2.5</sub> samplers were used. As

the authors know, high-volume samplers do not use denuders of any kind and also use quartz filter media. As a result, it is possible that gases (inorganic and organic) adsorb on these filters over sampling time to make charge balance appear to be neutralized. Finally, I remind the authors of the Surratt et al. (2007, ES&T) study on organosulfate formation from isoprene under low-NO conditions. Please refer to Figure 2B. As the authors know from this study, IEPOX (although not known at the time in 2007) was RAPIDLY consuming the inorganic sulfate in the seed aerosol (as measured by PILS-IC) to create the IEPOX-derived organosulfates. In fact, more than 50% of the initial inorganic sulfate as measured for the seed aerosol was consumed in just a few hours (more than wall loss alone could explain)! Thus, if you are someone in the field making IC measurements from filters, what you will likely find is that  $[\text{NH}_4^+]$  appears to be in high abundance compared to  $[\text{H}^+]$ , and thus, the aerosol appears to be fully neutralized. These issues are MAJOR caveats to what the authors are strongly proposing here, and I think more caution is warranted in the discussion and conclusions about the potentially important role of  $[\text{H}^+]$ . I still don't think there is enough data (yet) to discount the need of  $[\text{H}^+]$ . The point I'm trying to make here is that measuring the aerosol acidity that gaseous IEPOX encounters in the field is not as straightforward as it may seem. This is always estimated at the site at where the aerosol is collected, but the reality is that upwind of the site the IEPOX partitioning and acid-catalyzed reactions in the particle-phase are kinetically limited and are occurring over the entire transport time.

We did not mean to imply that catalysis by  $\text{NH}_4^+$  is sufficient to explain atmospheric observations – clearly  $\text{H}^+$  is a significant part of the aerosol chemistry of IEPOX. We went back through the text to ensure that we were careful not to dismiss the role of  $\text{H}^+$  in the dark reactive uptake of IEPOX.

Please see below for the manuscript text where we mention the strong catalytic effect of  $\text{H}^+$  on the IEPOX ring opening:

**Page 27680, lines 5 – 14:** *“The mechanism for OA production from IEPOX has been proposed as ring-opening of the epoxide group, activated by proton transfer from a strong acid such as sulfuric acid ( $\text{H}_2\text{SO}_4$ ), followed by nucleophilic addition of available .... This proposed mechanism has been corroborated by chamber investigations of particle acidity effects on OA formation (Surratt et al., 2007; Lin et al., 2012), wherein dry acidic seeds ( $\text{MgSO}_4 : \text{H}_2\text{SO}_4, 1 : 1$ ) prompted strong reactive uptake behavior from epoxides (Paulot et al., 2009b), compared to negligible uptake for dry, non-acidified seeds.”*

In this study, we suggest that in addition to  $\text{H}^+$  (not instead of),  $\text{NH}_4^+$  can activate the ring opening of IEPOX in an atmospherically relevant aerosol with liquid water present. Although  $\text{NH}_4^+$  is a weaker catalyst for the ring opening reaction, it may be as efficient as  $\text{H}^+$  in the reaction for the sole reason that there is so much  $\text{NH}_4^+$  in the atmosphere (e.g., their *effective* rates are similar). Below, please note the instances where we state that **both  $\text{H}^+$  and  $\text{NH}_4^+$**  may contribute to IEPOX-derived OA:

**Page 27692, lines 26 - 27:** *“...the comparison shows that a solution of high  $\text{H}^+$  activity and a solution of high  $\text{NH}_4^+$  activity may both lead to a relatively-similar reactive uptake.”*

**Page 27692, lines 10 - 11:** *“The dual reactivities of  $\text{H}^+$  and  $\text{NH}_4^+$  toward IEPOX is expected to be important in nature, as  $\text{NH}_4^+$ -based seeds are abundant.”*



**Abstract:** “Experiments and models aimed at understanding OA production from IEPOX, or other epoxides, should consider the  $\text{NH}_4^+$  activity, in conjunction with  $\text{H}^+$  activity (i.e., particle acidity)…”

We have stated in the text that  $\text{NH}_4^+$  can be important in the ring opening of IEPOX **only when the acid content is low**. This is because of the kinetic competition between  $\text{H}^+$  and  $\text{NH}_4^+$ , and perhaps also because there may be a different pH range when  $\text{NH}_4^+$  is effective as a catalyst. Please see below for the text were we describe this:

**Page 27692, lines 1 – 4:** “The data suggest that when  $[\text{H}^+]$  is small,  $\text{NH}_4^+$  may activate reactions leading to OA formation, similarly to its catalytic activity toward glyoxal (Noziere et al., 2009), methylglyoxal (Sareen et al., 2010), and other carbonyls (Nguyen et al., 2013; Bones et al., 2010).”

**Page 27692, lines 5 – 8:** “Interestingly,  $\text{pH} > 4$  is the range where  $\text{NH}_4^+$  catalysis is most efficient. This is demonstrated by a stable reactivity of the  $\text{NH}_4^+$ -catalyzed reaction to generate brown carbon from limonene SOA at  $\text{pH}$  4–9, but a sharp decline of reactivity below  $\text{pH}$  4 (Nguyen et al., 2012). As the  $\text{H}^+$  and  $\text{NH}_4^+$  ions are reactive toward organics in low-moderate and moderate-high  $\text{pH}$  ranges, respectively, the resulting  $\text{pH}$  dependence may appear to be weak in AS-containing seeds.”

**Page 27699, lines 15 – 16:** “Our results offer an alternate explanation to the abundance of IEPOX-derived OA tracers when the free  $\text{H}^+$  acidity in particles is modeled to be low...”

In summary, we believe there is no disagreement between our understanding of the importance of  $\text{H}^+$  in the IEPOX chemistry and that of the reviewer.

2.) Questions about estimation of aerosol pH:

- a) The authors estimate a particle pH of “-10” for  $\text{MgSO}_4 + \text{H}_2\text{SO}_4$  under dry conditions ( $\text{RH} < 5\%$ ) in Lin et al. (2012). I am not sure if they estimate this based on the properties of bulk aerosol solutions (0.06M  $\text{MgSO}_4 + \text{H}_2\text{SO}_4$ ). If so, this is likely not accurate. If one uses IC data collected from these aerosol experiments, the aerosol pH is around 1.10 (estimated by isorropia) under dry acidic conditions.

In the manuscript, we mentioned that we did not estimate this based on the bulk stoichiometry; the text that describes the estimation of pH based on the activity of  $\text{H}^+$  in aerosol liquid water is found on Page 27692, lines 14-20, which was estimated first using the available hygroscopicity data.

**Page 27692, lines 14 – 20:** “Assuming a growth factor of 1.15, and taking into consideration the inorganic seed mass concentration, we calculated  $P_{\text{LWC}}$  for the mean results in Lin et al. (2012), shown in Table 1. The AIOMFAC Model (Zuend et al., 2008, 2011) was used to estimate the pH based on the molal activity of  $\text{H}^+$  in the  $\text{MgSO}_4 : \text{H}_2\text{SO}_4$  (1 : 1) particle.”

AIOMFAC is a good tool for at estimating activities of  $\text{H}^+$  in  $\text{MgSO}_4 \cdot \text{H}_2\text{SO}_4$  seeds under dry conditions. If one considers that the seed is half sulfuric acid by volume, and there is only the water that the hygroscopic  $\text{H}_2\text{SO}_4$  pulls from the gas-phase, then the solution is very close to “neat” sulfuric acid, which

is has pH ~ -12. AIOMFAC produces a value of -10, which appear to be reasonable given the uncertainties in all estimates. The ISORROPIA estimates from IC data will have its own sources of error from the particle extraction, assumed dilution,  $H^+$  measurement by IC, and the assumption of  $P_{LWC}$ . We must not forget that these are both models, and may both be only as good as the data that is available to them.

Independent of whether the pH is -10 or 1, the main point that we wanted to make is that that the pH of  $H_2SO_4:MgSO_4$  particles under dry conditions is ***much lower*** than for that of non-acidified  $(NH_4)_2SO_4$  under humid conditions and yet, the uptake is similar.

We have added the following disclaimer in Section 3.1.2 (Particle acidity)

*“As the pH values of the particles in this work are derived using inorganic models, the values obtained may include any uncertainties inherent in the models, including uncertainties in the gas/particle partitioning of  $NH_3$ , hygroscopicity of salts, and/or acid dissociation equilibria.”*

b) Related to all of this, I'm curious as to why the AMS was not used to measure aerosol acidity as  $NH_4^+$  measured/ $NH_4^+$  neutralized? This seems very straightforward to do for these experiments. How would these values relate to your OA formation? As the authors know, the  $NH_4^+$  measured/ $NH_4^+$  neutralized is a measurement of degree of neutralization, which could be useful to determine more- or less-acidic periods. Aerosol acidity is indicated by  $H^+$  (nmol/m<sup>3</sup>) which is the difference between  $NH_4^+$  measured in the particles and concentrations of  $SO_4^{2-}$ ,  $NO_3^-$ , and  $Cl^-$ . Estimating those values from AMS measurements might give information on the evolution of acidity on the aerosol over the course of experiments.

For the experiments done here, and perhaps in general, charge balance of the ions measured by AMS is not necessarily a good indicator of particle acidity in the aerosol water for the following reasons:

1. The charge balance technique estimates the molar concentration of free  $H^+$  in volume of air and not in liquid water. We can couple the information we have on liquid water to get an activity of  $H^+$  (in order to calculate a pH), but we soon run into another limitation: the charge balance technique ignores the equilibrium between  $H^+$  and  $HSO_4^-$ . Thus, one makes an assumption that  $HSO_4^-$  is not important, which may not be true in the ammonium sulfate particles. Related to this, Reviewer #1 points out that the  $HSO_4^-$  to  $SO_4^{2-}$  dissociation may be responsible for most of the acidity in the wet AS seeds (we have added a statement about this). In the field, the inhomogeneity of the atmospheric particles introduces more potential issues because of the buffering effect from various inorganic ions, e.g., sea salt and sulfate (Keene et al, 1998).
2. For some experiments that used refractory materials like NaCl, estimating ionic concentration with AMS is not an option. AMS cannot measure  $Na^+$  or  $Cl^-$  ions accurately because at the 600 degC temperature of the vaporization plate, these ions will not enter the gas phase quantitatively.
3. In the lab, we added NaOH as a base in some of our  $(NH_4)_2SO_4$  experiments. For these experiments, one cannot tell the acidity by measuring  $NH_4^+$  and  $SO_4^{2-}$  content in the AMS alone. One problem is that we do not know how the  $OH^-$  changes the inorganic nitrogen content of the particles. On the one hand, if all of the nitrogen stays in the aqueous phase,

AMS detects them all at the same subset of ionic peaks, implying that the acidity is the same, with or without added NaOH. On the other hand, OH<sup>-</sup> causes the equilibrium of NH<sub>4</sub><sup>+</sup> ⇌ NH<sub>3</sub> to be shifted to NH<sub>3</sub>, which upon drying may leave the particle phase. This will lead to a low NH<sub>4</sub><sup>+</sup> to SO<sub>4</sub><sup>2-</sup> ratio to be determined by the AMS. Thus, the particles would be interpreted as “acidic” when, in reality, it is a very basic solution in the deliquesced particle. In both cases, the charge balance technique will lead to an erroneous conclusion.

We believe that modeling the activity of H<sup>+</sup> using AIM or AIOMFAC gives a better representation of reality as these models can explicitly treat the aqueous ionic equilibrium, gas-particle partitioning of ammonia, and particle water. Also, it is clear from AMS that the ammonium to sulfate ratio did not change throughout the course of the experiment and thus the relative “acidity” is expected to be the same throughout.

c) Lastly, I know the Caltech group has a PILS-IC system. I’m curious as to why this was not utilized as well to directly measure inorganic ions. This would seem useful as inputs into your model estimations of aerosol acidity.

We have a PILS available but it was not coupled to an IC system. IC work was not performed in this study.

d) I would suggest the authors add a section in the experimental section to more clearly describe how the aerosol acidity was estimated in each experiment instead of burying this information in the discussion sections. Would they agree?

We described our method of estimating the particle acidity, including the literature sources where some of the estimations came from, in Section 3.1.2 which is titled “Particle Acidity.” We believe this is an appropriate location in the manuscript for the information because these values were calculated, not experimentally measured.

I think directly measuring the inorganic ions over the course of the experiment should have been done in feeding the models. I’m not quite sure if this was done or if instead the initial composition of the atomization solution was used.

Yes, ions were measured with AMS throughout the course of the experiment. We have added a statement to clarify this in Section 2.2.2. “Aerosol mass spectrometry (AMS)”

*“The ToF-AMS monitored the content of ammonium (NH<sub>4</sub><sup>+</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>) and other non-refractory ions throughout the course of the experiment. The ammonium to sulfate ratio did not change over the course of the experiment.”*

3.) Question about the number of experiments:

How many experiments were conducted from the NaCl and Na<sub>2</sub>SO<sub>4</sub> seed aerosol experiments? This wasn’t clear from Table 1. Furthermore, from Table 1, it appears that each condition of RH and seed aerosol type has been examined once by the authors. Have these conditions been repeated to confirm trends you have observed in the data? This was unclear from the main text.

Experiments with most of the seed types and RH conditions were performed more than once, and the uptake behaviors of repeated trials were reproducible within 15%. Specifically, for the ammonium sulfate cases, the 85-86% RH conditions were repeated three times, the 40% RH conditions were repeated twice, the dry conditions were repeated 3 times, the ~ 50% condition was performed once. The error margins we quoted are from estimated experimental error, and are larger than the precision uncertainty derived from repeated experiments. We have added the following sentence to the Experimental Section:

*“Most of the experimental conditions were repeated and were found to be reproducible within 15%. We expect systematic error to dominate over the error of precision in this work.”*

4.) Drying aerosol from the wet chamber before AMS detection: How might the drying process before AMS detection affect the type of composition and abundance observed by this technique? Do the authors foresee any reaction occurring during this process?

We have discussed the effect of drying on the AMS detection of composition and abundance in the manuscript text – please see below:

*Page 27686, lines 5 – 8: “It is expected that drying the particles may introduce particle or organic line losses in the drier tube and change the particle bounce characteristics on the AMS vaporizer plate. These perturbations may be corrected by applying a collection efficiency (CE) factor.”*

*Page 27695, lines 5-8: “It is likely that the dissolved, but un-reacted, IEPOX was removed from the condensed phase upon particle drying, which would lead to no observed OA mass in the ToF-AMS data throughout the duration of the experiment.”*

We do expect reactions between ammonium and organics from the drying process, as has been demonstrated in the past (Nguyen et al, JGR 2012, DeHaan et al, EST 2011). However, as evaporation of aerosols is so common in nature, these reactive changes are not unrealistic. We added the following at the end of Section 2.2.2. “Aerosol mass spectrometry (AMS) (along with the relevant citations):

*“Further, it is expected that drying particles, relevant to the hydration/evaporation cycles of aerosols in nature, may lead to enhanced interactions between organic and inorganic compounds (De Haan et al., 2011, Nguyen et al., 2012), irreversibly forming OA.”*

5) What aerosol acidity do you estimate when comparing the DMA data to the AMS data??

We don't estimate acidity based on either DMA or AMS data. As mentioned, we use E-AIM and AIOMFAC to estimate H<sup>+</sup> activity in the particle water.

6.) Need of charcoal denuder: It isn't clear in the text exactly why the charcoal denuder was used in this study before filter collection. Was this really used to remove gaseous IEPOX from the air stream before filter collection? If so, why was this done? Please clarify in the experimental section.

There is no perfect representation of OA composition after filter collection. If one uses a charcoal denuder, one may strip semivolatiles from the condensed phase that might have otherwise been present in

the OA. The composition is still relevant to the OA; but may underrepresent the total mass and product distribution. On the other hand, by not using a denuder, the total organic mass and oligomeric/oxidized composition of the OA may be overrepresented. This is because filter sampling without a denuder forces semivolatile and volatile gasses through the filter medium for hours alongside any oxidants that may be present, which may cause side chemistry to happen that may not be atmospherically-relevant. We chose to err on the side of underrepresenting the condensed phase products to analyzing products that may have not actually been in the suspended OA.

6.) Potential formation of a N-containing IEPOX-derived SOA constituent: Why was the ESI source not also operated in the positive ion mode to detect the "potential" amine-containing products? This seems like a straightforward experiment to do. I'm not convinced by the AMS data alone that these products even matter. Since ESI operated in the positive ion mode is sensitive to basic species (such as the proposed product in Scheme 2), I would expect you to be able to observe the proposed amine-derived product. Until then, I think these are fairly tentative. Along with this, molecular identification of SOA products is one of the weakest aspects of this study and would provide further credibility to the tentatively proposed pathways.

The large ammonium content of the samples made the ESI positive mode data difficult to interpret, in that ammoniated non-amine products ( $M + NH_4^+$  ions) can be mistaken for actual amines (where the C-N are covalently bonded instead of weakly complexed). As this was not the point of the paper, but merely an interesting observation, we opted to not include data that we cannot conclusively interpret. Therefore, only the ESI negative mode was used, as previous measurements can be used as a benchmark for assigning peaks.

We are not suggesting that amines from IEPOX are important globally in this paper, and further we refer to the reaction as a "*minor possibility*" (Page 27697, lines 9 – 11). However, it is worth noting that there is some evidence that these products are forming, and not much is known about this reaction pathway. We agree that the identification is tentative, and have added the following bolded text to clarify this:

***"The identification of amines is tentative; however, to the best of our knowledge, this is the first suggestion of amine formation from IEPOX."***

7.) Abstract and elsewhere:

The authors must be careful in saying neutralized conditions. Even with ambient aerosols, the aerosol pH is likely not 7. Usually it is somewhere between 4-5. Related to this, should you really use "non-acidified" in your title? Maybe it is better to remove this word in order to prevent readers from thinking you are using non-acidic particles. In most cases, the pH is below 4 (as shown in Table 1).

We stand by our decision to use "non-acidified" as a description of the seeds. We are careful not to use the word "neutral," a word used in previous literature (e.g., in the papers the reviewer mentions) to describe the same type of seeds. In this case, the seeds are not purposefully acidified (hence "non-acidified"). The pH range of 3.5 - 4 is considered weakly acidic in chemistry, and this pH range is relevant in the atmosphere.

8.) Addition of NaOH to seed aerosols:

I'm still confused by this experiment. The reason for this confusion is you say the pH of your atomizing solution was 7, but the model estimated aerosol pH is really 5.5. You likely saw substantial OA formation due to the aerosol really being slightly acidic in the chamber and the water content being high.

The pH is higher for the NaOH case than the non-NaOH case, so a similar uptake is taken to mean that pH did not play a large role. Unfortunately, the available inorganic models (E-AIM, AIOMFAC, etc.) do not currently treat NaOH explicitly so the best we can do is estimate the pH based on the AS-only seeds. We chose to overestimate how acidic the aerosol is in order to not overstate the differences in pH. The real value may be between 5.5 and 7, which is something we are clear about as we do not know that the pH is “really 5.5”.

Thus, can you really conclude that  $[H^+]$  really doesn't matter as much as  $[NH_4^+]$ ?

That is not our general conclusion, certainly not for every inorganic/IEPOX system. We have stated explicitly that, in an absolute sense,  $H^+$  is a better catalyst for IEPOX ring-opening than  $NH_4^+$  (we estimate the rate coefficient is at least 100 times faster for  $H^+$ ). However, in ammonium sulfate particles, we believe  $[H^+]$  does not make much of a difference because the system is *not catalyst-limited* due to so much ammonium being present. If the  $H^+$  or  $NH_4^+$  is truly catalytic, then changing either of their concentrations will make much less impact than changing the sulfate activity. The catalyst that is in excess (which will likely be ammonium in the atmosphere) will shield the effect of the other catalysts in the system.

9a.) Related to # 8 above, I don't quite understand why they did not observe uptake with  $Na_2SO_4$  seed. As shown in Figure 4, they definitely did not see uptake with NaCl and  $Na_2SO_4$  seeds, but the difference between  $NH_4Cl$  and  $(NH_4)_2SO_4$  seeds is significant as well.

The explanations are available in Section 4 “Summary and atmospheric implications.” As mentioned in the text, we did not observe uptake with  $Na_2SO_4$  seeds because no catalyst (e.g., ammonium) was present to initiate the reactions shown in R1-R4, even though a good nucleophile was present. For  $Na_2SO_4$  seeded experiments, there is likely some  $H^+$  present, but still no IEPOX uptake was observed. This is likely because at near-neutral acidity, the activity of  $H^+$  is not enough to catalyze IEPOX ring-opening on the timescale of the experiment. We observed small uptake with  $NH_4Cl$  seeds because a good catalyst was present, but a relatively poorer nucleophile was present. And none of the reactions will happen on any of the seeds if no water is present.

9b) It looks to me that both  $NH_4^+$  and  $SO_4^{2-}$  are necessary. They cannot really conclude only on the importance of  $NH_4^+$ . There is likely some interaction between  $NH_4^+$  and  $SO_4^{2-}$  to cause the huge OA formation, and also the  $H^+$  also matters.

Correct, our conclusion is that a catalyst ( $NH_4^+$  and  $H^+$ ), a nucleophile ( $SO_4^{2-}$ , etc.) and particle liquid water are all necessary. We do not imply or explicitly state in the text otherwise, please see below for the manuscript text that supports this message:

**Page 27698, lines 21 – 22:** “Only when  $P_{LWC}$ ,  $NH_4^+$  activity, and  $SO_4^{2-}$  activity are all significant, as in the case of hydrated  $(NH_4)_2SO_4$  seeds, is the OA formation efficient and prompt.”

Scheme 2 also shows clearly that we suggest the interaction of the  $\text{H}^+/\text{NH}_4^+$  with nucleophiles like  $\text{SO}_4^{2-}$  is responsible for OA formation from IEPOX. We do not believe that only  $\text{NH}_4^+$  matters in this system, and have not dismissed the importance of sulfate nor  $\text{H}^+$  in this manuscript.

10.) Figure 3:

In Figure 3, I think the data point is not enough to conclude that the reactive partitioning coefficient is low at atmospheric relevant pH. First, the modeled pH was not fully examined. In addition, there is no data point between pH 4-5.5, which is more representative of the real atmosphere. I think the authors need to at least provide one more data point there to show the consistency.

We do not conclude that the reactive partitioning of IEPOX is low at atmospherically-relevant pH – quite the opposite. At atmospherically relevant pH, if the ammonium activity is also high, we find that the uptake is substantial, rivaling that of the highly-acidified seeds. As the reviewer is in agreement with us on this point, we did not make changes.

Regarding whether or not the modeled pH was fully-examined, E-AIM and AIOMFAC are reasonably well-established models to estimate particle pH. The method of modeling pH has been examined by a number of papers, some of which we have cited. Further, as we mentioned in Comment #2, the method may be more accurate than the AMS charge balance method.

Minor Comment:

1.) References: I noted there are references cited in the main text but the details of these references are missing in the reference section. For example, Surratt et al. (2007) was cited in the main text but not in the references section.

We are puzzled by this comment. There was only one Surratt et al (2007) cited in the text (**Page 27680, line 11**), and this citation was included in the references section (**Page 27706, lines 21 – 23**).

### References:

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- Nguyen, T. B.; Lee, P. B.; Updyke, K. M.; Bones, D. L.; Laskin, J.; Laskin, A.; Nizkorodov, S. A., Formation of nitrogen- and sulfur-containing light-absorbing compounds accelerated by evaporation of water from secondary organic aerosols. *J. Geophys. Res.* 2012, 117 (D1), D01207; doi:10.1029/2011JD016944