Anonymous Referee #2

Major Comments:

1. **The role of LWC and [H+] on isoprene SOA formation**
   Referee's Comment 1a: 'The use of $[H^+]$ or fractional free sulfate (FFS) as an indicator of particle acidity is puzzling. It is because particle acidity (pH) represents the hydrogen ion activity in an aqueous solution, which depends not only on $[H^+]$ (in unit of ug/m^3 air or $nmol/m^3$ air), but also LWC. Using $[H^+]$ as particle acidity is problematic and introduces a lot of confusion in the discussion. For example, p33138 line 12-13, YSOA decreases with increasing RH is a result of increase in pH, instead of reduction in $[H^+]$ ($ug/m3$ air) as stated in the manuscript. Same argument applies for FFS, which is essentially an ion balance method. Please refer to Hennigan et al. (2015) and Guo et al. (2015) for more discussions on particle acidity. Also, many recent studies have moved beyond ion balance or $[H^+]$, and calculated particle pH when discussing the role of particle acidity on isoprene SOA formation. Therefore, I strongly suggest the authors to use particle pH throughout the manuscript."

   Referee's Comment 1b: "The role of sulfate should be discussed explicitly in the manuscript, considering the following reasons. Firstly, sulfate drives both LWC and particle acidity. Secondly, organosulfate accounts for about 1/3 of total sulfate in the model (p 33136, line 9), which suggests the important role of sulfate as nucleophile. Thirdly, recent ambient measurements have repeatedly observed good correlation between isoprene SOA via IEPOX uptake and sulfate, which suggests that sulfate plays an important role in this process."

   Referee's Comment 1c: "I agree with that particle acidity plays an important role in isoprene SOA formation, especially via IEPOX uptake. However, one needs to be careful when interpreting the effects of particle acidity on isoprene SOA formation from laboratory studies, because sulfate is confounding in many studies. For example, the authors cite Lewandowski et al. (2015) to support the importance of $[H^+]$ (p33142 line 15). However, in Lewandowski et al. (2015), sulfate correlates perfectly with $[H^+]$, so that it is difficult to argue if the yield enhancement is due to $[H^+]$ or sulfate. I strongly suggest that the authors should carefully discuss the confounding effects and provide insights about the role of sulfate, particle acidity (pH), and LWC based on the model simulations."

   Referee's Comment 1d: 'The authors should calculate the pH and compare it to ambient measurements in (Xu et al., 2015; Budisulistiorini et al., 2015). Since H2SO4 is used in the study, the particle pH should be lower or comparable with ambient pH. This suggests that isoprene SOA formation (via IEPOX uptake) in this study should not be limited by particle acidity, which is similar to ambient observations.'

   a. **Response to 1a-1d:**
      In the manuscript $[H^+]$ has units of (mol of $[H^+]$/L of aerosol) and not (mol $[H^+]/m^3$ of air), which seems to the source of the confusion and should have been more clear. Therefore, the pH is simply the negative log_{10} of the $[H^+]$ used

throughout the manuscript, and the discussion on p33138 line 12-13 is correct as increasing the RH does lead to a reduction in $[H^+]$.

Guo et al. (2015) analyzed particle mass concentrations and the associated pH at one site of the Southern Oxidant and Aerosol Study (SOAS). The authors state that 'a simple ion balance or NH_4^+/SO_4^{2-} molar ratio or per-volume-air concentration of aerosol hydronium ion (H^+_{air}) cannot be used as a proxy for pH in the particle,' because it does not account for fluctuations in aerosol liquid water content (LWC) and the impact on pH. We completely agree with the conclusions of this paper, and use the same approach as the authors to calculate particle acidity within UNIPAR. The authors measure the inorganic ion concentration using a PILS-IC, and then input this data into an inorganic thermodynamic model to calculate particle pH. We use exactly the same approach with PILS-IC concentrations of SO_4^{2-} and NH_4^+ input into an inorganic thermodynamic model within UNIPAR. The only difference is that we use inorganic thermodynamic model E-AIM while ISORROPIA-II is used in Guo et al. (2015).

Furthermore, the pH of acidic aerosols in our study fall within the range of pH measured by the authors for the S.E. U.S. In Guo et al. (2015) the median predicted pH was 0.94 with a minimum and maximum pH of -0.94 and 2.23, respectively. While the acidic seeds in our study were created from H_2SO_4 solution before sunrise while RH is high, NH_3 (g) produced from the chamber walls immediately starts to titrate the seeds and increase the pH. Also, the formation of SOA dilutes particle $[H^+]$ as the isoprene SOA are single mixed phase, and the formation of *OS* consumes inorganic SO_4^{2-}. Therefore, our seeds are quickly titrated and are similar in pH to those of the S.E. U.S. For example, the acidic seeds in Experiment SA2 start at a predicted pH of -0.74 and end at pH of 0.63. In order to illustrate this, a new figure has been added to the manuscript and copied below (Fig. 1).

As can be seen, the pH rapidly increases with the formation of OS and by titration with ammonia. Also, the model does a good job at predicting the OS formation measured by the C-RUV method. Therefore, while the lack of clarification on the units of $[H^+]$ in the original manuscript hindered the
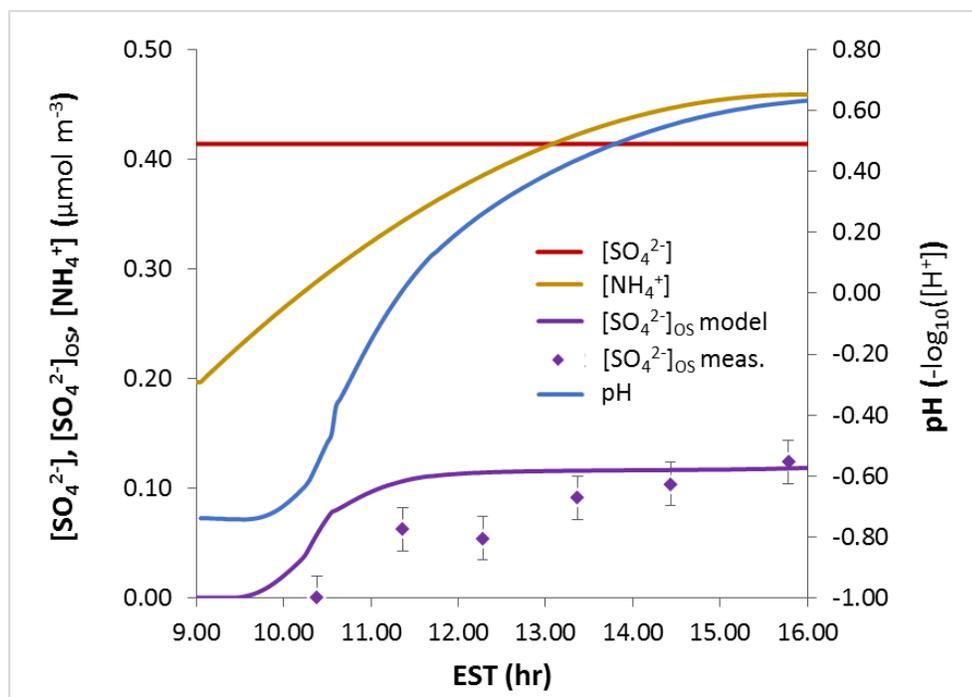
Figure 1. Time profiles of the total inorganic sulfate ($[SO_4^{2-}]$) and ammonium ($[NH_4^+]$) concentrations from Experiment SA2, along with the measured and model predicted concentrations of the sulfate associated with organosulfates (OS) ($[SO_4^{2-}]_{OS}$), and the predicted particle pH.

interpretation, our approach is in line with the current state of the research regarding particle acidity.

However, we still believe that using fractional free sulfate (FFS) and RH in Figure 5 (of the original manuscript) instead of pH provides for a clearer visualization of the impact of inorganic composition and LWC on isoprene SOA formation. As stated by Guo et al. (2015), 'measurement of pH is highly challenging, and so indirect proxies are often used to represent particle acidity,' such as the ion-balance method. We provide FFS along with the RH, which are the inputs that the authors of that study used to estimate pH within a thermodynamic model. Measurements of RH, $[SO_4^{2-}]$ and $[NH_4^+]$ are widely available and easy to produce, unlike pH, and can be used to estimate pH within ISORROPIA or E-AIM. Therefore, we believe our figure and associated discussion more clearly show the dynamics of how isoprene SOA yield relates to $[H^+]$ and LWC, and will be easier to use in future studies by a larger number of research groups.

In addition to adding a figure, the manuscript has been modified to clarify the units of $[H^+]$, to use pH instead of $[H^+]$ where appropriate in the discussion, to compare the range of pH to ambient aerosol, and to more carefully discuss the role of SO_4^{2-}, LWC, and pH.

The following was added to the end of section 3.2 along with added units of [H⁺] after first mention.

"$[H^+]$ is used throughout the manuscript to describe particle acidity and has units of mol H^+ / L of aerosol. Therefore, $[H^+]$ will change with variation in LWC and total aerosol mass (SOA formation), and the pH is simply the negative log of $[H^+]$. $[H^+]$ is not to be confused with H^+_{air}, which has been used in previous studies of the impact of acidity on isoprene SOA formation and has units of mol H^+/m^3 of air. H^+_{air} does not account for changes in particle volume and is not representative of particle pH (Guo et al., 2015)."

The end of Section 4.2 has been modified as follows:

"Y_{SOA} is also dynamically related to inorganic compositions. SOA formation in the absence of inorganic seed is primarily a function of the characteristics of $i_{m,n}$ and the impact of LWC on isoprene SOA is minimal. However, under ambient conditions SOA will typically be formed in the presence of inorganic aerosol. Variations in the inorganic aerosol composition ($[SO_4^{2-}]$ and $[NH_4^+]$) and RH lead to significant changes in LWC and pH. At high LWC, the total volume of absorptive mass (M_{mix}) increases allowing for hydrophilic $i_{m,n}$ to partition into the aerosol in significant amounts and engage in aerosol phase reaction. Additionally, highly reactive species such as IEPOX will react to rapidly form SOA in the presence of $[H^+]$ as a function of pH (Gaston et al., 2014). In Fig 6 the simulated Y_{SOA} is plotted as a function of the fractional free sulfate (FFS), ($[SO_4^{2-}]-0.5[NH_4^+])/[SO_4^{2-}]$), and RH. Unlike pH, which is very difficult to measure, $[SO_4^{2-}]$, $[NH_4^+]$, and RH data are widely available and easy to measure, which is why FFS and RH were used. Using an ion balance such as FFS alone has been shown to be not representative of actual particle pH (Guo et al., 2015), but providing both FFS and RH allow for estimation of pH within an inorganic thermodynamic model and ease of use by future studies.

It is difficult to decouple the effects of SO_4, LWC and pH since SO_4 ultimately influences both LWC and pH, but Fig 6 can be used to help elucidate the influence of these effects in UNIPAR. For AS seed (FFS=0.0), SO_4 is entirely titrated by ammonia and the lowest Y_{SOA} occurs below the ERH. As the RH increases, AS becomes deliquesced and the LWC gradually rises leading to an increase in Y_{SOA}. This is true for the predictions at all small values of FFS due to the increase in the total volume of absorptive mass (M_{mix}) allowing for hydrophilic $i_{m,n}$ to partition into the aerosol in significant amounts and engage in aerosol phase reactions. However, as the amount of $[NH_4^+]$ decreases (FFS < 0.7), the effect of increasing LWC reverses, and Y_{SOA} decreases with increasing LWC due to the dilution of $[SO_4^{2-}]$ and the resulting increase in pH. If RH is held constant, varying FFS allows for investigation of the effect of pH on Y_{SOA}. Increasing FFS or decreasing pH leads to a rapid increase in Y_{SOA} at all RH due to an increase in the SOA formation from the acid catalyzed reactions of species

such as IEPOX. Therefore, SO$_4$ modulates Y_{SOA} within UNIPAR by controlling LWC and [H$^+$] which influence $k_{AR,i}$. The consumption of SO$_4$ by OS formation is accounted for in UNIPAR through a reduction in acidity (Fig 4), but the role of SO4 as a nucleophile is not directly accounted for currently. Overall, the Y_{SOA} is predicted to be much more sensitive to pH than LWC, but dynamically related to both."

2. **Referee's Comment:** 'Many studies have developed models to evaluate the isoprene SOA formation via different pathways from lab scale to global scale, which should be discussed in the manuscript (Pye et al., 2013; McNeill et al., 2012; Lin et al., 2012; Gaston et al., 2014).'

   Response: Comment #1 by Referee #1 was very similar. Please find the response to Comment #1 by Referee #1.

3. **Referee's Comment:** 'The photooxidation of VOC is predicted explicitly offline and then the concentrations are set at the peak HO$_2$/NO ratio. This treatment is problematic since the gas phase composition changes dramatically with time. In Figure S2, modelled O3 and NOx do not agree with the measurements, which are probably due to the gas phase treatment. The authors need to test the sensitivity of modeled SOA to the gas phase treatment. I mean, if setting the gas phase concentrations at a different time, how would the modeled SOA change? I want to point out that the agreement between measured and predicted SOA is mainly due to the tuning parameter y in Eq. (7).'

   Response:
   Figure S2 shows the explicit gas phase simulation of our experimental data using the Master Chemical Mechanism v3.2 (MCM) within a kinetic solver. All of the offline gas phase simulations are performed explicitly. Then, using the explicit concentrations of each product from the gas phase simulations, the stoichiometric mass coefficients of each lumping group are calculated at the point of the maximum HO$_2$/NO. Therefore, the difference between the measured and predicted NO$_x$ and O$_3$ is not due to the concentrations being fixed in the gas phase simulation, because they aren't, but because of inaccuracy of MCM for our experimental conditions. While MCM is the best available tool for explicit gas phase modeling, it is far from perfect as is discussed in the limitations section of the manuscript. For example, the in the case of aromatic hydrocarbons additional OH radicals must be added in order to fit the VOC consumption. Isoprene does not require addition OH radicals, but possibly still has some error. We use MCM because it is the best available tool for providing explicit concentrations and product structures that we utilize for lumping.
   As far as, when the gas phase concentrations are fixed, we chose the maximum HO$_2$/NO ratio as it represents a shift in RO$_2$ chemistry that corresponds with the formation of products that are known to form isoprene SOA. Furthermore, the maximum HO$_2$/NO corresponds with the period of the majority of the isoprene SOA formation. Therefore, lumping at this time is the most

representative of the gas phase composition when SOA is forming. Lumping earlier in the photooxidation or later would yield less and more isoprene mass, respectively, due to the gas phase being composed of less and more oxidized products. We feel the current approach is effective and the best way to represent the gas phase composition at the time of SOA formation. However, we believe that SOA model may be much improved when the gas-phase reactions are explicitly simulated without lumping and applied to online aerosol model in the future.

4. **Referee's Comment:** 'In Eq. (6), do the authors consider the aerosol phase reaction between two species or species in two different bins?'

    a. Response:

        For the determination of reaction rate constant of organics, please also find the responses to Comments 1 and 6 from Reviewer 1. Like RO_2 chemistry, the cross reaction in aerosol phase is complex. The aerosol phase reaction rate is calculated using a self-dimerization reaction approach, and so the amount of OM_{AR} formed from each lumping group in each time step is calculated as the product of the concentration of that lumping group in the aerosol phase ($C_{mix,i}'$, mol L^{-1}) and the aerosol phase reaction rate constant, $k_{AR,i}$. The description of the equation was modified in the manuscript to add the word 'self-' as is shown below:

        "the OM_{AR} formation of i is estimated in UNIPAR assuming a second-order self-dimerization reaction as is shown in Eq. (4)"

5. **Referee's Comment:** 'In the model, OM_{AR} is calculated before OM_p. Does the calculation order affect the model results? It is surprising that even in the absence of seed, OMAR is much larger than OMP (p33135, line 22-24), considering the particle acidity is low without the seed. What are the products in OM_{AR} without seed? Is this conclusion affected by the calculation order of OMAR and OMP?'

    a. Response:

        The order of the OM_{AR} and OM_P module does not significantly affect the model results because the model iterates the concentration of each species in the aerosol phase in each module. The contribution of OM_{AR} in the absence of seeds is attributable to organic-organic oligomerization reactions. Referee #1 asked a similar question and this was discussed in detail in the response to Comment #1 by Referee #1, but in summary, oligomers have been shown to comprise the majority of the SOA mass of isoprene in the absence of inorganic seeds and in the presence of dry inorganic seeds (Nguyen et al., 2010; Surratt et al., 2006). The high volatility of isoprene SOA products means that partitioning cannot account for the SOA mass formation observed, and thus aerosol phase reactions are important even in the absence of a liquid inorganic phase. UNIPAR utilizes the

same predictive model (Eq. 7 in the manuscript) to determine the aerosol phase reaction rate constant, $k_{AR,i}$, of each lumping species, i, in the absence of seed or in the presence of effloresced inorganic salt, except terms associated with the inorganic liquid phase approach zero, and $k_{AR,i}$ is just a function of the reactivity of i.

The prediction that the majority of mass is contributed by aerosol phase reactions in the absence of seed agrees with the measurements of Surratt et al. (2006), in which the majority of SOA mass was from high MW species with 61% of this mass from organic peroxides. For Exp. ISO1, UNIPAR predicts that 70% of the total SOA mass is from lumping group 3OSp-M (products with both a carbonyl and alcohols, Figure S3). At the VOC/NO$_x$ ratio of ISO1 (17), 3OS$_p$-M is comprised almost entirely of organic peroxides with the MCM products C510OOH (~40%), C57OOH (~27%), C58OOH(~15%) and HMACROOH(11%) making up approximately 93% (structures shown below). Therefore, the predicted

|C510OOH|C57OOH|C58OOH|HMACROOH|
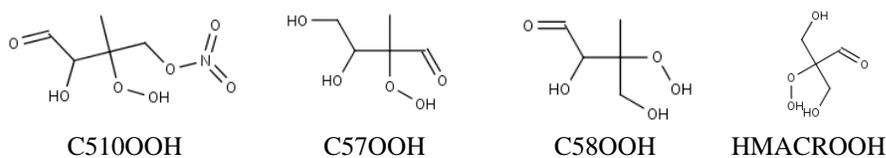
SOA composition of UNIPAR in the absence of seed correlates well with the measured composition of Surratt et al. (2006) for low NO$_x$ isoprene SOA.

Section 4.1 was updated to reflect these changes as is shown below:

"   The ability of UNIPAR to simulate the SOA formation from isoprene photooxidation in the presence and absence of acidic inorganic seeds under low initial VOC/NO$_x$ was determined through comparison of the simulated OM$_T$ and experimental OM formation (OM$_{exp}$). All OM$_{exp}$ were corrected for particle wall loss. Figure 3 shows measured and predicted SOA formation in the presence and absence of SA at initial VOC/NO$_x$ of ~17 for ISO1 and SA1 and 32 for ISO2 and SA2. The experiments performed in the absence of inorganic seed (ISO1 and ISO2) are used to test the prediction of organic-organic oligomerization reactions by UNIPAR. SOA formation is reasonably predicted in the absence of an inorganic aqueous phase at both experimental conditions with a maximum SOA yield ($Y_{SOA} = \Delta OM_{exp}/\Delta Iso$) of 0.025 and 0.007 for ISO1 and ISO2, respectively. These SOA yields are similar to those of reported literature values for isoprene in the absence of acidic seeds (Dommen et al., 2006). The model marginally overestimates the SOA formation in beginning of each chamber run, but the modeled OM$_T$ falls within the range of error of OM$_{exp}$ once the rate of SOA formation stabilizes and reaches a maximum. OM$_{AR}$ makes up the majority of OM$_T$ (>65% in ISO1 and ISO2) which agrees with the work of Nguyen et al. (2010) and Surratt et al. (2006) who analyzed the composition of isoprene SOA formed in the absence of an inorganic aqueous phase and found that the majority of SOA mass was from oligomeric structures. Furthermore, UNIPAR predicts that

6. **Referee's Comment:** 'More model vs measurements plots should be included in order to better evaluate the model performance. For example, the modeled [H^+] and [SO_4^{2-}]$_{OS}$ should be compared to the measurements (by C-RUV) in the format of time series or scatter plot.'

    Response: Based on your comment a new Figure was added to the manuscript and was used in the response to Comments 1a-1d above (Fig. 1). The following discussion of the figure was added to the manuscript in section 4.1

    "In addition to OM_T, O:C and [SO_4^{2-}]$_{OS}$ were also predicted using the model. The predicted [SO_4^{2-}]$_{OS}$ is important due to both the formation of additional OM_{AR} and the consumption of SO_4^{2-} that leads to an increase in particle pH. In exp. SA2, *[SO_4^{2-}]$_{OS}$* was measured using the C-RUV method allowing for comparison to the model (refer to Sect. 2 for C-RUV method description). Figure 4 shows time series of the model predicted and measured [SO_4^{2-}]$_{OS}$ along with the total [SO_4^{2-}] and [NH_4^+] measured by the PILS-IC, and the particle pH. Once SOA formation starts, OS quickly forms and *[SO_4^{2-}]$_{OS}$* reasonably well predicted by the model with the predicted value being within the range of error once SOA mass stabilizes. pH increases throughout the experiment due to titration by NH_3 produced from the chamber walls, the consumption of SO_4^{2-} by OS formation, and the dilution of [H^+] by SOA mass."

7. **Referee's Comment:** 'OS formation. What's [SO4]? Does it represent the initial SO4 concentration? The calculation of [SO42-]free is confusing. For example, if the seed is NH4HSO4, then all the sulfate should be treated as [SO42-]free and [SO42-]free = 1. However, [SO42-]free is only 0.5 using the algorithm in the manuscript (p33133 line 14). This also applies to the FSS calculation. Also, have the authors compared the OS formation rates in this study to literature values?'

    Response: [SO_4^{2-}] is the total concentration of sulfate in $\mu mol/m^3$ at the given time step as is measured by PILS-IC. In the case of the H_2SO_4 experiments, this is the initial [SO_4^{2-}], but in the experiment which began with SO_2(g), [SO_4^{2-}] increases as the SO2 is oxidized in the gas phase to add additional H_2SO_4 (g). In the model we assume that only the SO_4 which is not associated with NH_4 can form OS, which is why we calculate *[SO_4^{2-}]$_{free}$*. Ranges from 0.0 for $(NH_4)_2SO_4$ to 1.0 for H_2SO_4. Our estimation of OS formation is not kinetically determined, but is calculated as a function of the available SO_4, the number of functional groups

that can engage in OS formation (alcohols, aldehydes, and epoxides with epoxides counting twice as much as the other groups), and a weighting parameter that was empirically determined in Im et al. (2014) by fitting the model predicted $[SO_4^{2-}]_{OS}$ to measured value for toluene SOA. The same parameter was applied to predict the $[SO_4^{2-}]_{OS}$ of isoprene SOA and performed well as can be seen in Fig. 1 above.

8. SOA yield vs. VOC/NO$_x$ ratio

Referee's Comment 8a: 'The authors found that with increasing NOx within the simulation conditions, isoprene SOA yield increases, which seems to be novel and contradicts with previous studies. However, this conclusion is based on the wrong interpretation of previous studies. For example, p33124 line 68 and p33137 line 7-9, the authors claim that "the presence of any significant amounts of NOx will lead to SOA at lower yields than photooxidation under low NOx conditions". This statement is wrong. Both Kroll et al. (2006) (figure 7) and Xu et al. (2014) (figure 6) have shown that isoprene SOA yield has a non-linear relationship with the VOC/NOx ratio and the isoprene SOA yield is higher under intermediate NOx level. With that said, the conclusion in this manuscript is not novel and the conclusion is consistent with previous laboratory studies'

> **Response 8a:** The sentence "the presence of any significant amounts of NOx will lead to SOA at lower yields than photooxidation under low NOx conditions was indeed too simplified and incorrect, and has been changed (copied below this response). However, while the non-linear relationship of isoprene SOA yields with VOC/NOx has been shown, there has not been any detailed investigation of the SOA yield in range of VOC/NOx of this study. As is stated in the manuscript, previous studies, including Kroll et al. (2006) and Xu et al. (2014), have primarily investigated isoprene SOA formation in the presence of high NO$_x$ or no NO$_x$, as is shown in the table below.

	Kroll et al. (2006)						Xu et al. 2014				
Isoprene (ppb)	46.7	43.5	42.7	49.1	42.7	42	97.7	91.4	114.6	105	100
NO$_x$ (ppb)	266	526	129	78	405	745	68.1	114.8	338.2	466.2	738.1
VOC/NO$_x$ (ppbC/ppb)	0.878	0.413	1.655	3.147	0.527	0.282	7.173	3.981	1.694	1.126	0.677

This table shows the VOC/NOx ratio of each of the experiments in those studies performed with NO$_x$, so the no NO$_x$ OH-initiated experiments are not included. It can be seen that with the exception of 1 experiment from Xu et al. (2014), that all of the runs were high NO$_x$. Therefore, the majority of the investigation of low NOx isoprene photooxidation was performed in the absence of NO$_x$, and while the conclusion that the relationship between isoprene and VOC/NO$_x$ ratio is non-linear may not be novel, the detailed investigation of the SOA yield and composition of the SOA for the low NO$_x$ range and in particular,

the varying impact of acidity on SOA yield within this range has not presented before to the best of our knowledge.

The manuscript has been updated to reflect this and more clearly represent what is new about this study. The changes are copied below.

"Recent studies have investigated the effect of NO_x on the SOA formation of isoprene for the high NO_x regime (VOC/NO_x < 5.5) and in the absence of NO_x (Chan et al., 2010a; Kroll et al., 2006; Xu et al., 2014), and found that in the Y_{SOA} of is non-linearly related to VOC/NO_x with Y_{SOA} being highest at intermediate NO_x conditions. However, very little investigation has been performed on isoprene SOA formation within the low NO_x regime (VOC/NO_x > 5.5 and NO_x > 0 ppb) of this study, which is typical of rural areas downwind of urban centers (Finlayson-Pitts and Pitts, Jr., 1993). To investigate the influence of the NO_x level on Y_{SOA} in this range, simulations were performed in which the VOC/NO_x ratio was increased incrementally from 10 to 100 with SA seeded SOA without titration and isoprene only SOA. The Y_{SOA} of each simulation are plotted in Fig 5. Overall, increasing NO_x within this range (decreasing VOC/NO_x) increases Y_{SOA} both with and without acidic seeds, which agrees with the general trend of Kroll et al. (2006) where intermediate NO_x conditions (VOC/NOx ~ 3) had higher Y_{SOA} than no-NO_x conditions. However, the degree of the increase in Y_{SOA} with increasing NO_x is different for the isoprene only SOA and the SOA formed in the presence of SA seeds, which has not previously been demonstrated to the best of our knowledge.

Y_{SOA} increases much more rapidly with increasing NO_x in the presence of SA seeds, which is due to an increase in the relative contribution of reactive species. RO radicals produced from the reaction of RO_2 radical and NO can lead to carbonyls via reaction with oxygen, or glyoxal and methylglyoxal through fragmentation, which are highly reactive in the aerosol phase. Furthermore, some late generation RO_2 radicals react with NO to form low volatility organic peroxides with carbonyl functional groups (C510OOH, C57OOH, C58OOH, HMACROOH in MCM, Sect S7). Therefore, increases in NO_x within the simulation condition (VOC/NO_x 10~100) of this study leads to increases Y_{SOA} with higher sensitivity to VOC/NO_x in the presence of inorganic seed. Figure S5 shows the stoichiometric mass coefficients ($\alpha_{m,n}$) of important products as a function of VOC/NO_x.

Referee's Comment 8b: 'The discussion in section 4.2 is really confusing, which may be caused by the typos in the manuscript. For example, p33137 line 14-15: "Overall, with decreasing VOC/NOx, Y_{SOA} increases in all cases". However, p33137 line 22: "Therefore, increases in VOC/NOx within the simulation condition of this study leads to increases YSOA." There are many typos in the manuscript, which make the discussions very confusing. Most of the equations are mislabeled. For example, it should be Eq. (11) in p33133 line 16, instead of Eq. (10).'

Response 8b: We apologize for this typos and they have been corrected.

Referee's Comment 8c: 'p33137 line 10-11. The authors claim that very little investigation has been performed in the low NOx regime (VOC/NOx > 5.5). The authors need to justify why this regime is interesting'

Response 8c:

The other referee asked us to discuss how relevant the range of VOC/NOx of this study is to the ambient atmosphere, and so we have copied it here.

"The range of high VOC/NO_x (ppbC/ppb) used in these experiments, or low NO_x or 'NO_x limited' conditions, are typical of rural or areas down wind of urban centers (Finlayson-Pitts and Pitts, Jr., 1993). Pun et al. (2003) measured the 24-hr average VOC/NO_x ratio within Atlanta and found it to always be greater than 5.5 and range from 5.6-8.4. As the plume moves downwind from the city, this ratio will increase as NO_x decays more rapidly than VOCs meaning that NO_x limited conditions will dominate this area, which is infamous for isoprene derived SOA. Low NO_x conditions are especially relevant for isoprene SOA as isoprene is a biogenic VOC whose emission will be highest in rural areas and highly forested areas, such as the S.E. U.S. (similar to conditions of this study) and the Amazon (very low NO_x)."

Minor Comments:

1. **Referee's Comment:** 'p33126, line 9-11. Briefly describe the C-RUV technique. Can you compare the measured [H+] with model simulation? Later (p33136 line 8), the authors also mention that using C-RUV to measure sulfate, which should be discussed in the method part as well.'
   Response:
   The colorimetry integrated with a reflectance UV-Visible spectrometer (C-RUV) technique (Li and Jang, 2012) is used to directly measure aerosol acidity without the use of solvents or high temperature extraction techniques, which are known to decompose OS. Particles are sampled onto Teflon-coated glass fiber filters that have been dyed with metanil yellow (MY) as an indicator for proton concentration. The presence of protons causes the filter color to shift from yellow to pink, which is measured with high sensitivity using the UV-Visible spectrometer, and used to estimate [H^+] (mol/L of aerosol) using a calibration curve based on the measured absorbance and the volume of aerosol sampled. In order to estimate the sulfate which formed OS, the actual aerosol [H^+] measured by C-RUV is compared to the [H^+] predicted by a thermodynamic model using the inorganic composition measured by the PILS-IC (Li et al., 2015). The PILS-IC uses high temperature steam to allow for the impaction of aerosol and subsequent measurement of composition by an IC. The high temperatures of the PILS leads to the decomposition of OS, and thus the [SO_4^{2-}] measured by the

PILS-IC is the total concentration ($[SO_4^{2-}] + [SO_4^{2-}]_{OS}$). The difference between the measured [H+] and the predicted [H+] using the inorganic composition from PILS-IC is attributable to the formation of OS. Thus, $[SO_4^{2-}]_{OS}$ is determined by reducing the measured $[SO_4^{2-}]$ until the measured and predicted [H+] are the same. Figure 1 above was added to compare the $[SO_4^{2-}]_{OS}$ predicted by the model and determined using the C-RUV technique. A brief discussion of the use of the C-RUV technique to measure OS was added to experimental methods and copied below.

"The C-RUV technique (Jang et al., 2008; Li et al., 2015; Li and Jang, 2012) was used to measure $[H^+]$ (mol L^{-1} aerosol) in experiment SA2. This method utilizes a dyed filter as an indicator for particle acidity and the change in color is measured using a UV-Visible spectrometer in absorbance mode. The shift in color (absorbance) allows for determination of $[H^+]$ using a calibration curve. Then the amount of $[SO_4^{2-}]$ which formed organosulfates (OS) ($[SO_4^{2-}]_{OS}$) can be estimated by comparing the actual particle $[H^+]$ measured by the C-RUV technique to the $[H^+]$ predicted using the inorganic thermodynamic model, E-AIM II (Clegg et al., 1998) with the inorganic composition from PILS-IC. OS are reversible in the high temperatures of the PILS and so the measured $[SO_4^{2-}]$ is the total sulfate including that which formed OS. Therefore, by reducing the $[SO_4^{2-}]$ input into E-AIM II until the predicted $[H^+]$ matches the actual value measured by C-RUV, the amount of $[SO_4^{2-}]_{OS}$ can be estimated. A more detailed explanation of the use of the C-RUV technique to estimate OS can be found in Li et al. (2015) and a more complete description of the experimental design and chamber operation can be found in Im et al. (2014)."

2. **Referee's Comment:** 'p33128, line 1. Have the authors considered the salting-in and salting-out effects of glyoxal and methylglyoxal (Waxman et al., 2015; Kampf et al., 2013)?'

   Response: While we are aware of the recent work regarding the salting-in and salting-out effects of glyoxal and methylglyoxal, these effects have not been directly input into our model. As with any model development, we must decide what to include and what not to include into our model based on the current overall progress of research in our field. While these effects are really interesting and important for the understanding of atmospheric SOA formation, the research into these effects is not complete and the effects are not yet fully understood. Waxman et al. (2015) state that "additional measurements need to be made for other water-soluble organic molecules such as IEPOX and methyl tetrol, and further work on mixed salt solutions should be performed to confirm whether (the parameterization provided) presents a good approximation over a wider parameter space of mixed salt solutions." Based on this, we have waited to add these effects to UNIPAR, but we will revisit the implementation of salting effects once they

have been more comprehensively investigated. A line has been added to Sect. 4.4 (Model sensitivity, uncertainty, and limitations) to document that the model does not account for this (copied below).

'Another new development in the SOA formation is the discovery of the salting-in and salting-out of glyoxal and methylglyoxal (Waxman et al., 2015). While these effects are very interesting and likely influence the SOA formation of these species, they are not yet included within UNIPAR. The topic will be reconsidered for application within our model once these effects have been more comprehensively investigated for a wider range of relevant water-soluble organic molecules and inorganic aerosol compositions.'

3. **Referee's Comment:** 'p33131, line 3. Why do the authors use the prime over Cmix,i?'
   Response: $C_{mix,i}$ is the concentration in µg/m3, while $C'_{mix,i'}$ is the concentration in mol/L of aerosol. This has been clarified in the manuscript.

4. **Referee's Comment:** 'p33137, line 22. What's C510OOH? It seems to represent a peroxide instead of peroxynitrate.'

   Response: The structure of C510OOH and the other compounds of high concentration in lumping group $3OS_p$-M are shown below and have been added to the supplemental information. This has be clarified in the manuscript as can be

C510OOH   C57OOH   C58OOH   HMACROOH
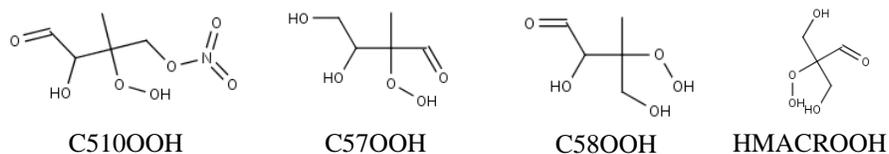
   seen in response to comment 5.

5. **Referee's Comment:** 'p33138, line 1-5. Would the effect of LWC on SOA formation change once you take into account the salting-in and salting-out of glyoxal and methylglyoxal? For example, increasing RH not only provides more absorbing medium, but also change the aqueous phase concentrations and hence affect the partitioning.'
   Response: If the salting-on of glyoxal and salting-out of methylglyoxal were added to the model, the effect of LWC may change slightly since decreasing the LWC may increase the partitioning of glyoxal, but would also decrease the concentration of methylglyoxal (and the rest of the water soluble organics). Therefore, depending on the relative contribution of glyoxal compared to the other isoprene photooxidation products, the relationship between LWC and SOA formation could be slightly different, but as was mentioned in the response to minor comment 2 above, we will not be adding these effects to UNIPAR until the understanding is more comprehensive and constrained.

6. **Referee's Comment:** 'p33139, line 4, subscript "i" after MF.'
   Response: This was corrected.
7. **Referee's Comment:** 'It should be 10^6 instead of 10^{-6}.'
   Response: This was corrected.