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**Title:** Simulating the SOA formation of isoprene from partitioning and aerosol phase reactions in the presence of inorganics

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## **Anonymous Referee #1**

### **General comments:**

#### **1. Referee's Comment:**

“It is not clear in the introduction section what the authors are trying to accomplish in this paper. There are in fact many models that already exist which model the formation of isoprene SOA including aqueous reactions and OS formation etc...(McNeill et al., 2012; Pye et al., Gaston et al., 2014, and likely others.). In this case, what is the issue which the authors are trying to address? Is there a clear deficiency in these other models that their model can improve upon? Is there missing chemistry for isoprene in other models? Although there are some places in the paper that hint at what the point of this paper is, it is far from clear and would benefit from stating these facts up front rather than buried somewhere in the paper.”

#### **Response:**

There have been some recent model studies that employ uptake coefficients predicted as a function of inorganic aerosol composition to simulate the aqueous phase reactions of isoprene photooxidation products, such as the study by McNeill et al. (2012) in which the photochemical box model GAMMA was used to predict aqueous phase SOA production in the presence of deliquesced ammonium sulfate, and Pye et al. (2013) in which the aqueous phase, heterogeneous uptake of IEPOX and methacrylic acid epoxide (MAE) were added to CMAQ. These approaches focus on a few chemical species utilizing empirically determined uptake coefficients or effective Henry's constants (when available), and set branching ratios to estimate OS formation. They require parameters for each compound, which is why they focus on compounds such as IEPOX and glyoxal whose individual SOA formation have been experimentally investigated due to contributing a significant amount to ambient and chamber generated SOA and being used as tracers for aqueous phase SOA formation. While, the aqueous phase SOA formation of these compounds contribute significantly to the overall SOA mass production of isoprene, they do not account for the majority of the mass production. Although most isoprene photooxidation products are highly volatile, they are also highly reactive allowing for the formation of oligomers through aqueous phase reactions, but also through organic-organic oligomerization reactions and partitioning of later generation products. Surratt et al. (2006) measured the composition of isoprene SOA under

varying NO<sub>x</sub> conditions with and without effloresced inorganic seed and in the presence of deliquesced, acidified ammonium sulfate seeds, and found oligomers contributed a large fraction of the total SOA mass in all cases. A number of other studies have also observed organic-organic oligomerization in isoprene SOA, including Nguyen et al. (2010) who measured oligomers after an hour of isoprene ozonolysis without inorganic seed with ‘the absolute majority’ of detected peaks corresponding to highly oxidized oligomers. The formation of a wide range of high MW products from isoprene oxidation in the absence of an inorganic aqueous phase demonstrates the importance of organic-organic oligomerization reactions. Furthermore, these studies show that a large number of compounds are contributing to SOA mass even if their individual contributions are small. For example, Nguyen et al. (2010) assigned 1000 peaks with only a small fraction corresponding to known products. This is also the case in the presence of inorganic acids. In Surratt et al. (2006), the presence of acidified ammonium sulfate seeds led to 3.6 times more SOA mass, but 2-methyltetrols and C<sub>5</sub> alkene triols, which are proposed to be major products of aqueous phase reactions, contribute only 0.46% and 0.06% to the total SOA mass. Additionally, a matrix-assisted laser desorption ionization mass spectrometer was employed to determine the range of *m/z* of the SOA products, and the product distributions were similar for low NO<sub>x</sub> isoprene SOA in the presence of dry ammonium sulfate seed and liquid acidified ammonium sulfate seed. Similarly, in Edney et al. (2005) 2-methylglyceric acid and 2-methyltetrols only made up 6% of the SOA in the presence of acidic inorganic seed with a majority of the SOA mass being unidentified. Therefore, while the aerosol phase products of IEPOX and glyoxal are viable tracer species due to their high concentrations and distinct fragmentation signatures, the aqueous phase SOA formation of these products is not fully representative of the total mass from isoprene SOA formation. The photooxidation of isoprene produces a wide range of highly reactive products (epoxides, carbonyls) that can form SOA products through a number of aerosol phase reactions.

UNIPAR utilizes the near-explicit Master Chemical Mechanism (MCM) to estimate the SOA formation of all of the known isoprene photooxidation products through partitioning, inorganic aqueous phase reactions (hydration, acid-catalyzed, OS formation), and organic-organic oligomerization reactions. The lumping structure of SVOC utilized by UNIPAR was developed to be representative of the thermodynamic properties and particle phase chemistry of organic compounds. All of known products of isoprene photooxidation products from MCM are lumped as a function of VOC/NO<sub>x</sub> using the individual chemical structures from the Master Chemical Mechanism, which allows for estimation of vapor pressure and chemical reactivity in aerosol phase accretion reactions. In previous work, the aerosol phase reactivity of various model carbonyls with acidic inorganic seed was measured in a flow reactor and the aerosol growth was used to establish a predictive model for the aerosol phase rate constant,  $k_{AR,i}$ , of each

species (*i*). In the absence of inorganic seeds or in the organic layer of a liquid-liquid phase separated (LLPS) aerosol, the same predictive model is used to estimate  $k_{AR,i}$ , but the terms associated with inorganic aerosol approach zero and it is just a function of the reactivity of *i*. This allows UNIPAR to simply predict the SOA formation of isoprene and other VOCs for varying aerosol composition (organic only, mixed inorganic-organic, LLPS in-or). In this way, UNIPAR exploits the individual product structures provided by the explicit gas model, but does not require the explicit model to be run online. The gas phase concentrations are scaled to VOC/NO<sub>x</sub> and the SOA formation is determined as a function of the properties of the partitioning species and the size and composition of the aerosol phase.

The distribution of isoprene's lumped stoichiometric mass coefficients ( $\alpha$ ) in UNIPAR highlights the potential SOA mass contribution of other reactive isoprene products. Table 1 shows the combined  $\alpha$  of IEPOX, glyoxal, and methylglyoxal along with the summed  $\alpha$  of all other isoprene products with one or more aldehyde and/or epoxide for a range of initial VOC/NO<sub>x</sub>. It is clear that while the individual contribution of other products may not be as large as that of IEPOX or glyoxal, the total contribution of other reactive species can be as great or greater than the contribution from those few species.

VOC/NO <sub>x</sub>	100	62.5	50	33	25	16	12.5	8
IEPOX+GLY+MGLY	0.02	0.03	0.04	0.06	0.08	0.10	0.11	0.11
OTHER M, F, VF	0.28	0.31	0.32	0.34	0.34	0.34	0.34	0.31

Table 1. Summed stoichiometric mass coefficients from UNIPAR of IEPOX, glyoxal and methylglyoxal, and all other reactive species (one or more carbonyl/epoxide) as a function of VOC/NO<sub>x</sub> ratio (ppbC/ppb). The reaction begin with sunrise and the reaction time is determined based on the model protocol (near 1PM).

In order to clarify the purpose of this work and how it relates to previous model studies of isoprene SOA formation from aerosol phase reactions, the introduction has been modified and reads now (changes marked in red),

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Volatile organic compounds (VOCs) are emitted into the atmosphere from both biogenic and anthropogenic sources. Once emitted, these compounds react with atmospheric oxidants and radicals to form semi-volatile products that may self-nucleate or partition onto pre-existing particulate matter to form secondary organic aerosol (SOA). Isoprene (2-methyl-1,3-butadiene) is a biogenic VOC with the largest emission of all non-methane hydrocarbons (Guenther et al., 2006), and yet it was initially thought to form insignificant amounts of SOA due to the volatility of its principal oxidation products. This conclusion was supported by early chamber investigations that found isoprene only forms SOA at concentrations much higher than ambient conditions (Pandis et al., 1991; R. M.

Kamens et al., 1982). However, recent chamber (Edney et al., 2005; Kroll et al., 2005, 2006; Limbeck et al., 2003) and field studies (Claeys et al., 2004; Edney et al., 2005) found that the large emission rate of isoprene makes the contribution to global SOA formation significant even at low yields, and it is estimated that isoprene is the largest single source of global organic aerosol (Henze and Seinfeld, 2006). The proposal of new SOA formation mechanisms, primarily the classical equilibrium partitioning theory by Pankow (1994) and the discovery of aerosol phase oligomerization reactions in the presence of inorganic acids (Jang et al., 2002a, 2003), led to the re-examination of the SOA formation potential of isoprene. More recent studies have found the SOA yield of isoprene and its oxidation products to be highly sensitive to aerosol acidity ( $[H^+]$ , mol/L aerosol) (Jang et al., 2002a; Kuwata et al., 2015; Limbeck et al., 2003; Surratt et al., 2010) and aerosol liquid water content (LWC), **but oligomers have been shown to comprise the majority of isoprene SOA mass even in the absence of aqueous inorganic seeds** (Nguyen et al., 2010; Surratt et al., 2006).

The tendency of isoprene photooxidation products to engage in oligomerization reactions in the aerosol phase is primarily due to the reactivity of its secondary products. The presence of two double bonds makes isoprene highly reactive and allows for rapid OH initiated oxidation in the atmosphere. The speciation of isoprene photooxidation products and the resultant SOA yields are dependent on  $NO_x$  concentrations and atmospheric aging. When  $NO_x$  concentrations are low,  $RO_2$  radicals react with  $HO_2$  radicals to form hydroperoxides (ROOH) at high yield. Then, ROOH further react with OH radicals to form dihydroxyepoxides (IEPOX) (Paulot et al., 2009). IEPOX has been found to undergo rapid reactive uptake onto wet ammonium sulfate (AS) inorganic aerosol and acidic inorganic seeds at all RH leading to the formation of tetrols, organosulfates (OS) and other lowly volatile oligomers. In the presence of high  $NO_x$ , SOA formation will depend on the ratio of  $NO_2$  to NO with isoprene SOA yields being higher at large  $NO_2/NO$  (Surratt et al., 2010).

In order to quantify and understand the impact of SOA on climate and human health, the prediction of SOA formation of isoprene is essential. SOA models have been developed and utilized to predict the SOA formation of various VOC systems. The two-product model was developed based on classical partitioning theory (Pankow, 1994) and represents SOA formation through use of two or more representative secondary products of varying vapor pressure (Odum et al., 1996). By fitting the stoichiometric and partitioning coefficients of each representative semi-volatile organic compound (SVOC) to experimental data, the SOA yield of a VOC is predicted as a function of the absorbing organic mass (OM) concentration without considering the numerous gas phase products. The simple and efficient handling of SOA mass formation from partitioning by the two-product model led to its widespread use in regional and global models. Nevertheless, the two-product model and its predecessors are limited in their ability to predict SOA formation from aerosol phase reactions in the presence of

inorganic aerosol due to the loss of individual product structures, which determine reactivity in the aerosol phase, and the need to fit new parameters for variations in atmospheric conditions. Many regional models have already incorporated different sets of parameters for each VOC under high and low NO<sub>x</sub> regimes, but cannot handle the variations seen in ambient aerosol LWC and [H<sup>+</sup>] that enhance SOA formation via aerosol phase reactions (Carlton et al., 2009).

More recent model studies have modeled the aqueous phase SOA production using empirically determined uptake coefficients or effective Henry's constants (when available) to estimate reactive uptake of major isoprene products, such as IEPOX and glyoxal, in the inorganic aqueous phase (Marais et al., 2016; McNeill et al., 2012; Pye et al., 2013; Woo and McNeill, 2015). For example, McNeill et al. (2012) developed the box model GAMMA to predict the aqueous SOA production of isoprene in the presence of deliquesced ammonium sulfate. Pye et al. (2013) modified the regional Community Multi-scale Air Quality model to include the heterogeneous uptake of IEPOX and methacrylic acid epoxide. While the addition of the aqueous phase reactions of known products improve the predictions of isoprene SOA formation over classical partitioning models, highly oxidized oligomers comprise the majority of isoprene SOA even in the absence of an aqueous inorganic phase with the majority products being unidentified, which can be attributed to organic-organic oligomerization reactions (Edney et al., 2005; Nguyen et al., 2010; Surratt et al., 2006). For example, Edney et al. (2005) measured the composition of isoprene SOA in the presence of acidic inorganic seed, and methylglyceric acid and 2-methyltetrols, which are tracer species for aqueous phase reactions, made up only 6% of the total SOA mass with the majority of the products being unidentified. The photooxidation of isoprene produces a large number of highly reactive products (epoxides, carbonyls), and the large fraction of high molecular weight (MW) species in the absence of an inorganic aqueous phase and the lack of mass closure in isoprene composition studies demonstrates the SOA mass contribution of species other than those that are tracers for aqueous phase reactions.

In this study, the Unified Partitioning-Aerosol Phase Reaction (UNIPAR) model, which was previously developed and applied to aromatic VOCs (Im et al., 2014), was updated and expanded to model the SOA formation of isoprene in the presence of low VOC/NO<sub>x</sub> (due to the high sensitivity to [H<sup>+</sup>] in the low NO<sub>x</sub> regime) and aerosol acidity under ambient temperature (T) and relative humidity (RH). UNIPAR predicts SOA formation from partitioning, organic-organic oligomerization reactions, and aqueous phase reactions using a lumping structure that was developed to be representative of aerosol phase reactivity. The model was validated using outdoor chamber data from isoprene photooxidation experiments with and without acidic inorganic seeds. The results and conclusions are discussed.

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2. **Referee's Comment:** 'The paper is also generally overly complex and disorganized. A number of equations can be in the supplemental information rather than in the main paper, and the same can be said for the explanation of these equations. It is not quite clear why the authors would use so many different parameters to describe acidity of the aerosol, and then try to investigate the effect of these parameters on SOA yield. At the end of the day it may be the particle pH that is important for aqueous reactions, but all the other parameters used will also affect the particle pH. For example, LWC affects the acidity, as does the "free sulfate". Because of this, it is not possible to understand what is actually controlling what process. I would suggest that the authors use one term that describes acidity and in particular the particle pH. The paper would be made much clearer if it was organized in such a way as to separately describe the effects of pH, LWC and sulfate (because SO<sub>4</sub> is responsible for OS and also effects the pH) on the SOA yield, rather than the manner which it is done currently.'

**Response:**

The model description has been modified and the full derivation of model equations has been moved to the supplemental information with only necessary equations being shown in the manuscript. The modifications span multiple sections (Sect 3.3 and 3.3.1) and are too long to copy here so please refer to the updated manuscript.

Referee #2 asked a similar question regarding the discussion of particle acidity and separating the discussion of each effect. Please refer to the response to Referee #2's Major Comments 1a-1d (one response for 4 comments).

3. **Referee's Comment:** Some experiments were conducted with acidic particles. It is unclear how relevant these particles are to the ambient atmosphere. The authors need to compare their aerosol acidities with what might be expected in the atmosphere. The same can be said for the range of VOC/NO<sub>x</sub> used in these experiments.

**Response:**

In the acidic seeded experiments of this study, H<sub>2</sub>SO<sub>4</sub> solution was nebulized into the chamber to generate inorganic seed. Although, pure H<sub>2</sub>SO<sub>4</sub> seeds are initially more acidic than typical ambient inorganic aerosol, NH<sub>4</sub><sup>+</sup> generated from the chamber walls and the formation of OS quickly begin to neutralize the H<sub>2</sub>SO<sub>4</sub>. Furthermore, since the isoprene SVOC and inorganic aerosol form a single homogeneously mixed aerosol phase, the growth of SOA mass will dilute [H<sup>+</sup>] (mol/L aerosol). In order to determine if the acidity of these experiments is relevant to ambient particles, the pH of our experimental aerosol can be compared to that of the S.E. U.S as was measured by Guo et al. (2015). The measured mean pH in the S.E. US, which is known to have highly acidic aerosol, was 0.94 with a minimum and maximum of -0.94 and a 2.23, respectively. In experiment SA1 of this study, the pH starts at -0.70 and steadily increases throughout the experiment to finally reach 1.35. Therefore, the acidity of the aerosol in this study are representative of regions of the ambient environment with acidic aerosol.

The range of high VOC/NO<sub>x</sub> (ppbC/ppb) used in these experiments, or low NO<sub>x</sub> or 'NO<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> decays more rapidly than VOCs meaning that NO<sub>x</sub> limited conditions will dominate this area, which is infamous for isoprene derived SOA. Low NO<sub>x</sub> 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<sub>x</sub>).

The relevance of our experiments to ambient aerosol has been reflected in the updated manuscript (Sect. 4.2 and 4.4)

### Specific comments:

1. **Referee's Comment:** Pg 33135, line 23-24: If it is acidity of some sort which is required for aqueous reactions to occur how does one explain the OM\_AR being the dominant contributor (65%) to experiments without any SA seed particles? For that matter, how is an experiment without any seed particles relevant to the ambient atmosphere? The authors are relying upon nucleation of isoprene products to make particles, which only occurs here because they are using ppm levels of isoprene in their chamber. This will not occur in the real atmosphere, and so the authors must explain the utility of such experiments without any pre-existing seed particles.

#### **Response:**

The purpose of the isoprene-NO<sub>x</sub> photooxidation experiments in the absence of inorganic seed is to test the model prediction of organic-organic oligomerization reactions. As was discussed in our response to Comment #1, oligomers have been detected in SOA from the oxidation of isoprene and many other volatile organic compounds (VOC) in the absence of an inorganic seeded aqueous phase. The volatility of isoprene photooxidation products means that partitioning cannot account for the SOA mass resulting in the absence of inorganic seed or the in the presence of effloresced (dry) inorganic seed, but the reactivity of these species due to the presence of carbonyls and epoxides allows for organic-organic oligomerization reactions to occur. In the absence of a aqueous inorganic phase, UNIPAR estimates the aerosol phase reaction rate of each compound using the same parameterization (Eq 7 in the manuscript), but the inorganic associated terms (LWC, [H<sup>+</sup>]) approach zero and the reaction rate is predicted as a function of the reactivity of the partitioning species.

Although isoprene concentrations will not be high enough in the ambient atmosphere for self-nucleation to occur, there may be areas in which sub-micron aerosol are dominated by organics or more typically where the inorganic and organic layers of the aerosol are liquid-liquid phase separated (LLPS). In either

case, there would be an aerosol liquid phase with highly concentrated organics that can interact and engage in organic only aerosol phase reactions. In our experiments, there are low levels ( $\sim 1 \mu\text{g}/\text{m}^3$ ) of preexisting seed ( $M_o$ ) even after pre-cleaning that allow for the initial absorption of isoprene SOA products. Theoretically, we could introduce an organic seed but there is no reason to believe that a single component organic seed would be any more representative of actual atmospheric processes. Performing isoprene photooxidation experiments in the absence of inorganic seed provides a simple means of evaluating our model for these organic-organic reactions.

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<sub>x</sub> was determined through comparison of the simulated OM<sub>T</sub> and experimental OM formation (OM<sub>exp</sub>). All OM<sub>exp</sub> 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<sub>x</sub> of  $\sim 17$  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<sub>T</sub> falls within the range of error of OM<sub>exp</sub> once the rate of SOA formation stabilizes and reaches a maximum. **OM<sub>AR</sub> makes up the majority of OM<sub>T</sub> (>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 the approximately 70% of the OM<sub>T</sub> is from lumping group 3OS<sub>p</sub>-M, of which more than 93% of the mass contribution is organic peroxides (MCM products C510OOH (~40%), C57OOH (~27%), C58OOH (~15%) and HMACROOH(11%), structures shown in Figure S7 of the SI). This agrees with the measurements of Surratt et al. (2006), in which 61% of the total mass in the absence of seeds is from organic peroxides.**

2. **Referee’s Comment:** Pg 33134, lines 1-4: It has already been shown (minerath et al., 2008, barsanti et al...) that functional groups such as alcohols and aldehydes are likely to react too slow under realistic atmospheric conditions to make much OS. Including them

here may be inducing more OS than is realistic. The authors need to justify including them here.

**Response:**

Minerath et al. (2008) investigated the bulk phase formation of OS from simple alcohols and stated that ‘it appears that these reactions are kinetically infeasible for low temperature upper tropospheric SOA’ and for lower tropospheric SOA ‘it appears that the aerosol acidity is rarely high enough such that these reactions are likely to be responsible’ for OS in SOA. However, bulk phase investigations may not be representative of actual aerosol processes, and many studies have measured the OS formation of alcohols and aldehydes in the aerosol phase (Eddingsaas et al., 2012; Liggio et al., 2005; Li et al., 2015; Zhang et al., 2012). E.g., Eddingsaas et al. (2012) measured OS formation from alcohols in SOA from particle-phase sulfate esterification of multi-functional alcohols, and concluded that esterification is likely faster for the complex alcohols typical of VOC photooxidation than for the simple alcohols investigated in Minerath et al. (2008). Therefore, we still predict the OS formation of all three functional groups within UNIPAR since they have all been found to form OS in studies of particle phase processes. The increased tendency of epoxides to form OS is accounted for in our model since epoxides have 2 potential reaction sites instead of one for alcohols and aldehydes.

3. **Referee’s Comment:** Pg 33124, lines 5-8: a mechanistic reason(s) for these facts should be included here if possible. Pg 33124, lines 4: “lowly” is poor grammar. This is also written throughout the paper and should be changed accordingly.

**Response:** The reasons for higher sensitivity at low VOC/NO<sub>x</sub> conditions have been added to the manuscript and the modified sentence is copied below. The use of ‘lowly’ has been removed throughout.

“In the presence of high NO<sub>x</sub>, SOA formation will depend on the ratio of NO<sub>2</sub> to NO with isoprene SOA yields being be lower at low NO<sub>2</sub>/NO due to RO<sub>2</sub> reacting with NO to produce volatile products (Kroll et al., 2006; Surratt et al., 2010).”

4. **Referee’s Comment:** Pg 33125, lines 3-4: poor grammar in this last line. Make it two sentences.

**Response:** Changed as shown below.

“The model was validated using outdoor chamber data from isoprene photooxidation experiments with and without acidic inorganic seeds. The results and conclusions are discussed.

5. **Referee's Comment:** Pg 33126, first paragraph: there is no mention of the issue of semi-volatile gas-phase wall losses. This is a recent area of concern for chamber studies and should at least be mentioned.

**Response:** SVOC wall loss was mentioned previously in Sect. 4.4 (Model sensitivity, uncertainty, and limitations). A few additional lines have also been added to the end of the paragraph beginning on page 33141 and ending on page 33142 in order to expand the discussion and potential implications. The sentences are copied below.

“A number of recent studies have found that the loss of gas phase vapors to chamber walls can compete with gas to particle partitioning (Matsunaga and Ziemann, 2010; Zhang et al., 2014, 2015). Vapor wall loss was not accounted for in this study and thus the experimental SOA mass may be low biased. However, based on the conclusions of Zhang et al. (2015), the large volume to surface area of our chamber and the high volatility of isoprene products likely results in gas to particle partitioning dominating the wall loss of organic vapors generated from isoprene SOA.”

6. **Referee's Comment:** Pg 33127, line 2: insert “the” after “on” Pg 33127, lines 23-27: Some justification or reasoning for selecting these reactivity bins, and how compounds were assigned to these bins would be very useful here.

**Response:** The typo was corrected. The following sentences have been added to this section of the revised manuscript to further describe how the reactivity bins were developed.

“The reactivity bins were developed based on previous work in which the measured equilibrium partitioning coefficients ( $K_p$ ) of toluene and  $\alpha$ -pinene SOA products were found to deviate from the theoretical value, and the degree of deviation was found to depend on the functionalization of the SOA product (Jang et al., 2002b; Jang and Kamens, 2001). The experimental  $\log K_p$  of ketones (S) were found to be only slightly higher than the theoretical value, while the experimental  $\log K_p$  of conjugated aldehydes (M) and the products associated with F and VF were found to be 10-40 times higher and 2 to 3 orders higher, respectively.”

7. **Referee's Comment:** Pg 33128, lines 8-10: choosing the concentrations of each group based on the maximum HO<sub>2</sub>/NO ratio seems arbitrary. The composition will be dependent upon a number of factors such as this ratio, and time etc... its not clear why this particular value was selected and what effect this would ultimately have on the final model results.

**Response:**

UNIPAR was developed to be a self-contained module which requires no additional inputs other than those commonly available within current regional and

global models. We cannot utilize the near-explicit Master Chemical Mechanism online since it not feasible to do so in a regional model. Since we cannot run an explicit gas phase model online within the current framework, we need to lump the individual products at a set time in order to determine the stoichiometric mass coefficients of each lumping group. In the previous application of UNIPAR to aromatic hydrocarbons, the concentrations of each of the SOA products were lumped when half of the VOC had reacted at each VOC/NO<sub>x</sub> (Im et al., 2014). In this version, we wanted to use a more dynamic method of determining the time of lumping based on different oxidative conditions of each run. The maximum HO<sub>2</sub>/NO was chosen as this represents the shift in RO<sub>2</sub> chemistry (and overall gas phase chemistry) where the more oxidized products that contribute to SOA are formed (i.e. IEPOX). Furthermore, the maximum HO<sub>2</sub>/NO also typically corresponds with the period in which the majority of SOA formation occurs. The early generation products of isoprene photooxidation (when HO<sub>2</sub>/NO is low) are highly volatile and unlikely to form SOA. While, this lumping approach with fixed concentration for each initial VOC/NO<sub>x</sub> is not as representative of the actual gas phase composition as the use of a fully explicit model would be, it is representative of the gas phase at the time in which most of the SOA are formed and provides a simple solution that fits within the framework of our self-contained model. Overall, we agree with the reviewer in that online explicit gas phase mechanisms could be incorporated within UNIPAR to allow for better prediction of dynamic compositions over atmospheric photooxidation of hydrocarbons, and we plan to test this for chamber simulations in the future. However, the current structure is most suitable for application in large scale models. Although the lumping structure would not be necessary within an online frame in the future, the gas-particle partitioning and reaction rate constants based on the organic molecular structures are still suitable for an explicit SOA model.

8. **Referee's Comment:** Pg 33129, lines 4-10: how similar are the compounds chosen in Bertram et al, to the products of isoprene? Is it valid to use these parameterizations? Also, how well does the UNIPAR model predict the O:C ratio?

**Response:**

Although the parameterizations in Bertram et al.(Bertram et al., 2011) were developed for model compounds with ammonium sulfate seed, the authors tested them for both isoprene SOA and ambient aerosol. These tests show that the parameterizations perform well for isoprene SOA and also for ambient aerosol comprised mainly of oxygenated organics, ammonium, and sulfate and not nitrate or other anions, which is true of the aerosol of this study. O:C was not measured for our experimentally generated SOA, but we compared our model prediction to published isoprene O:C from literature and found that it matched up reasonably well. However O:C will vary between different NO<sub>x</sub> and inorganic seed conditions. As is reported in Sect. 4.1 of the manuscript, the literature values of isoprene SOA range from 0.69 to 0.88, while the model predicted O:C range from

0.69-0.98. However, in UNIPAR we do not account for the reduction in O:C that would result from oligomerization, but our predicted O:C are still near literature values.

These parameterizations were applied within UNIPAR because they provide a computationally simple means of predicting the RH of LLPS, ERH and DRH of mixed oxygenated organic/inorganic SOA systems. As with predictions of most SOA parameters, predicting the RH of these important phase transitions is difficult due to the complexity and unknown nature of many products in mixed systems. Attempts have been made at developing a thermodynamic model for mixed inorganic-organic SOA systems (i.e. AIOMFAC), but these systems have huge uncertainty, are constrained using limited bulk phase liquid data for simple systems, and have large computational requirements (Zuend and Seinfeld, 2012). On the other hand, the Bertram parameterizations were developed empirically using SOA systems, and tested for the SOA similar to those of this study making them the most representative of the systems we are modeling and the most appropriate for our model. If a better approach is developed in the future that meets our requirements, we will revisit our handling of ERH, DRH, and RH of LLPS in UNIPAR.

9. **Referee's Comment:** Pg33131, equation: This equation and many of the following ones are misnumbered.

**Response:** The numbering of all equations has been updated.

10. **Referee's Comment:** Pg 33133, eq 11: it is not clear how this equation was derived. There are too many equations in this section and the text is rather complex and confusing. I suggest simplifying this page and putting it in the supporting info.

**Response:** This section of the model description has been modified. Many of the equations were removed and the full derivation was added to the supporting information. Please refer to Section 3.3 of the updated manuscript.

11. **Referee's Comment:** Figure 1: It would be useful to have a gas-phase flow chart associated with this one for the aerosol phase....or at least an additional schematic box attached above it.

**Response:** The figure has been modified and updated in the manuscript.

12. **Referee's Comment:** Figure 2: the compound acronyms in the legend need to be described in the caption.

**Response:** The full names of each of the reactivity bins has been added to the figure caption.

13. **Referee's Comment:** Figure 3: this figure is nearly impossible to read. It must be made bigger and clarified.

**Response:** The figure was small due to the vertical stacking of the 3 plots. The figures have been reconfigured and made bigger.

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