

Reply to Referee #3.

First of all, we would like to thank the anonymous referee #3 for the detailed comments and suggestions to allow us to improve the manuscript. We have considered these comments carefully and have done as much as we can to modify the manuscript. The reviewer comments are in italics followed by our responses starting with “Reply: ”.

*The paper “Global mechanistic model of SOA formation: effects of different chemical mechanisms” by Lin et al. explores the impacts recent developments in our understanding of SOA formation using a global model. Overall, I think this is a useful study, and the paper is generally clear and well written. I wish the authors would be a bit more careful with regards to how they describe model performance relative to the observations (no need to oversell, it’s OK if there is more work to be done). Also, I think they could make their manuscript more important by digging a bit deeper into the implications of when and where their model improved agreement with observations, so as to posit some conclusions regarding which mechanisms may or may not dominate in the atmosphere. The introduction includes a fairly broad description of recent history of SOA, which, although not entirely necessary, I think is nice to have. At the rate at which this field moves, the authors should check for more recent SOA modeling works that have been published since the time they submitted their manuscript. Overall, I recommend this work for publication after the following issues are addressed.*

*(p.s. So as not to be biased, I have written this without looking over other reviews that have been posted, so I apologize if there is overlap).*

Reply: Thank you for your encouragement. We will describe the performance of the model more carefully by getting rid of generalizations, and also try to examine where the ne\_oSOA and ne\_IEPOX parts of the model (which are new compared with the literature) has improved the agreement with observations.

#### *1 Comments*

*(format: page.line)*

- The title just doesn’t read very well, and I’m not sure it’s even grammatically correct. Can you refer to “a model”? or eliminate the colon and use the word mechanism only once? Colon’s in article titles can almost always be eliminated if the title is better crafted. Can the type of mechanisms being considered be mentioned? For example, “Modeling the impacts of aqueous aerosol production, organic nitrates and peroxides on global SOA distributions” would be much more informative.*

Reply: We will change the title to: Global modeling of SOA formation from dicarbonyls, epoxides, organic nitrates and peroxides and its sensitivity to HOx recycling

- 49: I think it is worth pointing out that recent modeling studies of urban SOA can even overestimate observed concentrations (Dzepina et al., ES&T. 2011; Hodzic et al., ACP, 10, 5491 – 5514, 2010), or at least come much closer (Li et al., ACP, 11, 3789 – 3809,*

2011). *Maybe that's a point to be brought up more on page 51, in which case you may want to refer to the studies in this paragraph as related to "traditional" SOA, or SOA from absorptive partitioning.*

Reply: We agree. We are going to clarify the studies in this paragraph as "traditional absorptive partitioning SOA models", and extend the description on page 51. Specifically, Dzepina et al., 2011 and Li et al., 2011 will be cited on line 19, page 51. One more sentence will be added on line 21 on page 51: "These studies show that adding this new SOA source can bring the model simulation much closer to the observations in Mexico City (Li et al., 2011), or even to over-predicate the observations in Mexico City (Dzepina et al., 2011; Hodzic et al., 2010)."

• *51.1 : Citation of Chung and Seinfeld here seems out of place, as that study predated inclusion of SOA from isoprene. Also, Henze 2008 addresses aromatics (Henze 2006 deals with isoprene).*

Reply: Chung and Seinfeld paper did show that SOA came from monoterpenes and sesquiterpenes but given that we were talking about isoprene here, we will delete this citation. Henze et al., (2008) includes both isoprene SOA and aromatics SOA and finds that isoprene SOA dominates. So we will keep this reference in this paper.

• *53: This model resolution seems very coarse given the sparsity of data with which to compare. Can you comment on whether or not this leads to underestimates of SOA, and if so, by how much?*

Reply: The resolution affects the SOA formation in two ways. First, local POA and VOC emissions (e.g., isoprene) cannot be represented very well in large grids and will be diluted. Decreased POA will reduce SOA formation by reducing the pre-existing OA that SVOC can condense on. Second, the local VOC (e.g., isoprene) emissions and NO<sub>x</sub> emissions are also artificially diluted at coarse resolutions. Noting that SVOC formation nonlinearly depends on the VOC level, NO<sub>x</sub> level, and VOC/NO<sub>x</sub> ratio, the SOA formation will be affected by the artificial dilution of VOC emissions and NO<sub>x</sub> emissions. Overall, the resolution has a very complex effect on SOA formation due to this non-linear chemistry. It is likely that the lower resolution also contributes to model under-prediction of urban SOA measurements in urban regions (e.g. urban sites in AMS network) or regions with high local biogenic emissions (e.g. Ispra in the EMEP network). We already have some discussion of the bias caused by the coarse resolution on line 21 on page 75, and we will extend the discussion based on description above. It is beyond the scope of this paper to quantify the underestimation of SOA due to the low spatial resolution, but we will refer to the paper by Stroud et al. (2011).

• *56: I think it's misleading to refer to the absorptive partitioning description of SOA as "non-evaporative". If you remove the surrogate secondary gas-phase species from such models, the SOA will evaporate.*

Reply: yes, this was misleading and our first reviewer did not understand this either.

ne\_oSOA is indeed formed from condensed semi-volatile organic compounds, which are partitioned into the aerosol phase through gas-particle partitioning. We will clarify this in the revised paper. Specifically, we will delete the explanation of ne\_oSOA starting on line 25 on page 56, i.e., “we call these SOA as ne\_oSOA hereafter in this paper (see Table 1). “Ne” stands for “non-evaporative”, and “oSOA” means “other oxidative SOA” to differentiate from SOA formed from the uptake of glyoxal, methylglyoxal and epoxide which will be described in Section 2.2.2 “, and move it to below the line 18 on page 62 to add one more paragraph of explanation as below:

“For convenience, we refer to the SOA formed through the mechanism above as ne\_oSOA hereafter in this paper (see Table 1). “Ne” stands for “non-evaporative”, and “oSOA” means “other oxidative SOA” to differentiate from SOA formed from the uptake of glyoxal, methylglyoxal and epoxide which will be described in Section 2.2.2 below. It should be noted that this “non-evaporative” SOA is formed from condensed semi-volatile organic compounds, which are partitioned into the aerosol phase through gas-particle partitioning.” The budgets of condensed semi-volatile organic compounds are not reported in the current manuscript. However, we will report them in the revised version.

• 57.18: *Wasn't this work of Song 2007 on very fresh particles, with a very unoxygenated organic substrate? Interesting, but how relevant as actual SOA substrate likely to much more aged?*

Reply: You are correct that the work of Song may not be that relevant to the global model. We will change this to “ though the inclusion of the hydrophobic un-oxidized POA may tend to overestimate the yield of SOA (Song et al., 2007).”

• 58.4: *This is not strictly correct. The two-product model assumes that the final yields in chamber data can be fit using surrogate species, which are placeholders for any number of oxidation steps in the gas-phase (Ng et al., 2006).*

Reply: We will modify this paragraph as follows.

“However, this simple approach cannot account for the full complexity and the dynamics of SOA production. First, SVOC formation strongly depends on ambient conditions, e.g. temperature, photolysis introduced by UV light, and most notably on the fate of RO<sub>2</sub>, which can react with NO<sub>x</sub>, HO<sub>2</sub>, and other RO<sub>2</sub>. This is usually described as a VOC: NO<sub>x</sub> dependence. This dependence was parameterized in a simple way for aromatics by Henze et al. (2008) based on two different SOA product yields in low NO<sub>x</sub> and high NO<sub>x</sub> conditions (specifically, a high yield in low-NO<sub>x</sub> conditions and a low yield in high NO<sub>x</sub> conditions). But SOA formation is more complex than such simple parameterizations. SOA formation from isoprene at high NO<sub>x</sub> is also reduced (Kroll et al., 2005b, 2006). While SOA formation is broadly similar at all NO<sub>x</sub> levels in the ozonolysis of limonene, (Zhang et al., 2006). Unlike aromatics and isoprene, SOA formation is increased at high NO<sub>x</sub> in the photo-oxidation of sesquiterpenes (Ng et al., 2007). In addition, the SVOC products may be formed from the first or higher generation products, and these products may undergo further reactions in the gas phase or aerosol phase (Ng et al., 2006; Camredon et al., 2007; Chan et al., 2007; Hallquist et al., 2009). As a consequence of

these complexities and dynamics, the use of simple SOA yields from laboratory data may not account for the actual SOA system without a significant increase in these data and the complexity of the parameterizations.”

- 58.10: *Also not strictly correct, as many of the more recent (post 2005) two product models are fit to yield data in NO<sub>x</sub> free conditions.*

Reply: True, more recent data have looked at NO<sub>x</sub> free conditions. We will modify this paragraph as in the previous reply.

- 58.17: *I think the justification for the choice of model could be made stronger. Just recognizing that it is explicit seems like a weaker argument than, say, mentioning how such explicit representation leads to analysis that would not otherwise be possible with more empirical models.*

Reply: Good point. We will rewrite the argument as follows: “Nevertheless, we follow this philosophy here because this type of mechanism

- is more explicit in its description of the oxidation products that lead to SOA formation,

- handles the VOC:NO<sub>x</sub> dependence in SVOC formation based on first principals as deduced in the explicit mechanism,

- is easily extended as more knowledge of VOC oxidation schemes becomes available, and

- predicts products that can be explicitly compared to observations.”

- 58.25: *Use a list format.*

Reply: done.

- 61: *The subject of reversible vs irreversible uptake usually compares Kroll (2005) to Liggio (2005). The former was a long enough experiment to assess an equilibrium state, while the latter had the experimental setup necessary to assess kinetics. So these works aren't at odds as much as they are measuring different things.*

Reply: Thank you, we will clarify this. We will modify line 28 and 29 on page 60 as below:

“The formation of oligomers in heterogeneous reactions within or on aerosols may be reversible or irreversible. Liggio et al. (2005a) had an experimental set up designed to look at kinetics and demonstrated that the reactions in the aerosol phase after uptake of glyoxal were irreversible on the 4 hour time scale of their experiments. The experimental setup for Kroll et al. (2005) was designed to look at equilibrium products. They examined the possible heterogeneous uptake...”

- 65.16: *Can references be provided for these sources?*

Reply: References for all these sources are already given somewhat later in the manuscript. But we will add a table with the magnitudes of sources and references and

refer here to the table. Specifically, the reference for organics from sea spray is on line 20 on page 65, for fossil fuel and biofuel on line 10 on page 66, and open biomass burning emissions on line 13 on page 66.

- 66: *It's not clear how evolution of the aerosol size distribution is being treated, if at all, or if the model only tracks aerosol partitioning.*

Reply: Thank you. We will put the description of the assumed pre-existing size distribution on page 53. In particular, we will add it to line 4 following “In this work”. “In this paper, we used the same microphysics module as Liu et al. (2005). We prescribed the SOA size distribution to be the same as that for biomass burning OM in Liu et al., (2005), but allowed it to interact with sulfate through condensation of sulfuric acid, through coagulation with pure sulfate aerosols, and through aqueous formation of sulfate.”

- 68.6: *It could be useful to briefly recap the simulation setups here.*

Reply: We will put a brief recap on line 7 on page 68 following “formed in this study” : “(i.e. Simulation A without HOx recycling, Simulation B with Peeters et al. (2009) HOx regeneration, and Simulation C with reduced HOx recycling rate)”

- *Should results from Fu 2008 be included in Table 5?*

Reply: We will include this, thank you.

- 73: *The statistical assessment could use some work. I think an additional useful metric would be a correlation coefficient or coefficient of regression. The NMBs, by themselves, don't reflect the fact that there is a lot of variability in the data that is not captured by the model. Also, it would probably be best to take the average of the IMPROVE data in grid boxes where there are multiple data points.*

Reply: Thank you. We have done the average of the IMPROVE data in grid boxes where there are multiple data points, and re-calculated the NMB and added correlation coefficients (R). So in the revised paper Table 7 will be:

| Simulation name | IMPROVE network |      | AMS measurements (Zhang et al., 2007) |      |                      |      |             |      |
|-----------------|-----------------|------|---------------------------------------|------|----------------------|------|-------------|------|
|                 |                 |      | Urban sites                           |      | Urban downwind sites |      | Rural sites |      |
|                 | NMB             | R    | NMB                                   | R    | NMB                  | R    | NMB         | R    |
| Simulation A    | -11.0%          | 0.31 | -21.4%                                | 0.47 | -2.2%                | 0.68 | 10.5%       | 0.50 |
| Simulation B    | -20.2%          | 0.34 | -38.4%                                | 0.42 | -25.4%               | 0.51 | -3.7%       | 0.49 |
| Simulation C    | -11.1%          | 0.35 | -30.3%                                | 0.46 | -10.5%               | 0.62 | 5.3%        | 0.48 |

Correspondingly, we are going to modify the description of the comparison with the IMPROVE network and AMS measurements (Zhang et al., 2007) in the paper.

- 73.15: *This seems out of place. Shouldn't this source of SOA be addressed earlier in the*

*work where the model's treatment of SOA formation are discussed?*

Reply: We don't understand what you referred to. Line 15 on page 73, we are describing the statistical assessment for the comparison. We are not discussing anything about the source of SOA here.

• 75.22: *Might they also just deposit, rather than evaporate?*

Reply: Thank you. We will change it to "concentrations that might later evaporate or deposit. "

• 75.27: *But does introduction of the mechanism make the urban comparison worse?*

Reply: Yes, in terms of NMB. We will make this clear by adding a statement at the end of this paragraph: "while it tends to under-estimate the urban observations even more."

• 77: *So overall, it seem that the model is getting large global burdens, but for the wrong reason?*

Reply: Based on only the comparison with these 3 sites, yes. We do not know if these sites are not actually representative of large grid average tropical values or if an improvement of the mechanism could produce better agreement.

• 79.6: *reiterate here how they compared.*

Reply: This paragraph is only a short summary of what we did in this paper. For how they compared to observations, we have conclusions and deep discussions in the paragraph starting on line 18 on page 80.

• 79.14: *yet most of the enhancement you are seeing from POA is from POA from biomass burning?*

Reply: Yes, globally POA from biomass burning dominates, but anthropogenic POA probably makes a great contribution in some regions (e.g. east Asia).

• 79.27: *The comments here about estimates of future SOA values seems out of place. Also, there are other modeling studies which show that owing to a balance of effects, the net impact on SOA is close to zero.*

Reply: We will delete this comment.

• 80.23: *I think the agreement is a long way from being "close". For example, the model has no predictive skill compared to the EMEP observations.*

Reply: We will revise the description as follows: "The low normalized mean biases against measurements from the IMPROVE network and AMS surface measurements

contrasts with the under-predictions of observations by other models (Chung and Seinfeld, 2002; Liao et al., 2007; Farina et al., 2010; Utembe et al., 2011; Yu, 2011). The low correlation coefficients  $R$  (varying from 0.3 to 0.5) between the simulations and observations, however, indicate that the model does not capture the spatial variability of the measurements very well. These may be compared to the correlation coefficients  $R$  of around 0.65 between simulations and observations from the IMPROVE network reported in other models (Park et al., 2003; Liao et al., 2007; Farina et al., 2010). The comparison with the EMEP measurements demonstrates that the model under-predicts surface OC concentrations in Europe, which may be the result of an underestimation of POA in the winter and of SOA in the summer.”

• 81: *Can the authors posit any broader conclusions here regarding mechanisms? In other words, what can we learn from the fact that the model overestimated in some places but underestimated in others? Does this help rule out / support any particular mechanism?*

Reply: Thank you. We will modify the last paragraph in the Section 5 as follows:

“Comparison with the IMPROVE network and with AMS surface observations in the Northern Hemisphere shows that the model can predict the surface organic aerosol concentrations reasonably well with low normalized mean biases ranging from -15% to 15% in rural regions. The low normalized mean biases against measurements from the IMPROVE network and AMS surface measurements contrasts with the under-predictions of these observations by other models (Chung and Seinfeld, 2002; Liao et al., 2007; Farina et al., 2010; Utembe et al., 2011; Yu, 2011). The low correlation coefficients  $R$  (varying from 0.3 to 0.5) between the simulations and observations, however, indicate that the model does not capture the spatial variability of measurements very well. These may be compared to the correlation coefficients  $R$  of around 0.65 between simulations and observations from the IMPROVE network reported in other models (Park et al., 2003; Liao et al., 2007; Farina et al., 2010). The comparison with the EMEP measurements demonstrates that the model under-predicts surface OC concentrations in Europe, which may be the result of an underestimation of POA in the winter and of SOA in the summer. In pristine tropical forest regions, the model over-estimates the OM burden by roughly a factor of three compared to three surface AMS measurements made in West Africa, Amazon and Malaysia, respectively. This overestimate is present both with and without the  $\text{HO}_x$  recycling mechanism in the isoprene oxidation scheme. Our overestimation in the Amazon basin differs significantly from predictions in the GEOS-Chem model which underestimated OM (Chen et al., 2009), but is consistent with the TM5 model over-prediction (Gilardoni et al., 2011a). Because  $\text{ne\_GLYX}$ ,  $\text{ne\_MGLY}$  and  $\text{ne\_IEPOX}$  components account for a major fraction of total OM predicted at these sites (Table 9), it is important to improve the formation of these compounds in the model. Trainic et al. (2011) conducted experiments to study the uptake of glyoxal on ammonium sulfate seed aerosols under hydrated conditions over a wide range of relative humidities, (RH from 35% to 90%) and found that the reactive uptake rate decreased with increasing RH. The ratio of the final organic aerosol mass to the seed mass at the 50% RH condition was similar to that found by Liggio et al. (2005a) (who conducted their studies at 49%

RH), but decreased by 57% when the RH increased from 50% to 90%. This trend was attributed to the slower glyoxal oligomerization rate caused by the dilution of the ammonium sulfate aerosol at the higher RH values (Liggio et al., 2005a; Trainic et al., 2011). Thus, the work of Trainic et al. (2011) may indicate that the uptake coefficient adopted here (which was based on Liggio et al. (2005a)) is too high in much of the tropics where typical RH values are around 90%. In addition, the simple treatment of irreversible surface controlled uptake might be misleading if there is a competition between reversible vs. irreversible uptake and of bulk reactions vs. surface processes (Ervens and Volkamer 2010). Furthermore, the same uptake coefficient for both cloud droplets and aqueous aerosols can not account for the differences in the chemistry of carbonyl compounds between cloud water and aerosol water (Lim et al., 2010; Ervens and Volkamer 2010). Therefore it may be that improvements to the processes responsible for uptake of glyoxal, methylglyoxal and epoxide would improve the model. Given the sparse amount of data, however, the conclusion that the model overestimates surface OM concentrations observed at 3 sites in the tropical forest regions may not necessarily lead to the conclusion that the model is in error. It would be valuable to have more measurements and model studies to examine the properties of organic aerosols in the tropics. In the free troposphere, the model reproduces the OC observed during the ITCT-2K4 aircraft campaign over the North America relatively well, but clearly underestimates OC observations during ACE-Asia campaign off the coast of Japan. However, the model simulates Asian pollution layers above 3 km during the INTEx-B campaign very well.”

## 2 Corrections

Reply: Thanks. We will correct these or add them up where necessary in the revised version.

- 50.13: *Slowik 2011, not 2010?*
- 51.1: *Chung. A few other places the same typo.*
- *Surratt 2010 listed twice.*
- 53: *I think it's more proper to cite Ito et al. than to name the mechanism as Ito mechanism.*
- 56: *Peeters and Mueller (2010) missing from Bibliography.*
- 57.6: *Change K to Ki. Also, C\_ needs a species index i.*
- 57.12: *Why say “assume”? Isn't this just a definition?*
- 58.9: *are built*
- 66.14: *Zhang 2000 not in Bibliography*
- 66.14: *Zhang 2000 not in Bibliography*
- 78.23: *the explicit . . . the 2-product → an explicit . . . a 2-product*

## References:

Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation under high-NO<sub>x</sub> conditions, *Geophys. Res. Lett.*, 32, L18808, doi:10.1029/2005GL023637, 2005b.



Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation, *Environ. Sci. Technol.*, 40, 1869–1877, 2006.

Zhang, J. Y., Huff Hartz, K. E., Pandis S. N., and Donahue, N. M.: Secondary organic aerosol formation from limonene ozonolysis: Homogeneous and heterogeneous influences as a function of NO<sub>x</sub>, *J. Phys. Chem. A*, 110, 11053–11063, 2006.

Ng, N. L., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Kroll, J. H., Kwan, A. J., McCabe, D. C., Wennberg, P. O., Sorooshian, A., Murphy, S. M., Dalleska, N. F., Flagan, R. C., and Seinfeld, J. H.: Effect of NO<sub>x</sub> level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes, *Atmos. Chem. Phys.*, 7, 5159–5174, 2007.

Stroud, C. A., Makar, P. A., Moran, M. D., Gong, W., Song, S., Zhang, J., Hayden, K., Mihele, C., Brook, J. R., Abbatt, J. P. D., and Slowik, J. G.: Impact of model grid spacing on regional- and urban- scale air quality predictions of organic aerosol, *Atmos. Chem. Phys.*, 11, 3107–3118, 2011.