

Review of Beardsley et al.

The authors use UNIPAR model to simulate isoprene SOA formation as a function of VOC/NO_x and inorganic seed compositions. The authors found that the isoprene SOA formation is most sensitive to [H⁺], but dynamically related to other parameters (LWC, VOC/NO_x, etc). While the research topic is interesting, the discussions are not clear and conclusions are not well justified. I recommend accepting manuscript after major revisions.

Major comments:

1. The role of LWC and [H⁺] on isoprene SOA formation

(1) The use of [H⁺] or fraction 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/m³ air or nmol/m³ 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, Y_{SOA} 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.

(2) 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.

(3) 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.

(4) 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.

2. Model setup

(1) 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).

(2) The photooxidation of VOC is predicted explicitly offline and then the concentrations are set at the peak HO₂/NO ratio. This treatment is problematic since the gas phase composition changes dramatically with time. In Figure S2, modelled O₃ and NO_x 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 γ in Eq. (7).

(3) In Eq. (6), do the authors consider the aerosol phase reaction between two species or species in two different bins?

(4) 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, OM_{AR} is much larger than OM_p (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 OM_{AR} and OM_p?

(5) More model vs measurements plots should be included in order to better evaluate the model performance. For example, the modeled [H⁺] and [SO₄²⁻]_{OS} should be compared to the measurements (by C-RUV) in the format of time series or scatter plot.

(6) 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?

3. SOA yield vs NO_x/VOC ratio.

(1) The authors found that with increasing NO_x 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 6-8 and p33137 line 7-9, the authors claim that “the presence of any significant amounts of NO_x will lead to SOA at lower yields than photooxidation under low NO_x 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/NO_x ratio and the isoprene SOA yield is higher under intermediate NO_x level. With that said, the conclusion in this manuscript is not novel and the conclusion is consistent with previous laboratory studies.

(2) 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/NO_x, Y_{SOA} increases in all cases”. However, p33137 line 22: “Therefore, increases in VOC/NO_x within the

simulation condition of this study leads to increases Y_{SOA} .” 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).

(3) p33137 line 10-11. The authors claim that very little investigation has been performed in the low NO_x regime (VOC/NO_x > 5.5). The authors need to justify why this regime is interesting.

Minor comments:

1. 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.
2. 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)?
3. p33131, line 3. Why do the authors use the prime over $C_{mix,i}$?
4. p33137, line 22. What's C510OOH? It seems to represent a peroxide instead of peroxy nitrate.
5. 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.
6. p33139, line 4, subscript “i” after MF.
7. p33143, line 25. It should be 10^6 instead of 10^{-6} .

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