

Interactive comment on “ α -Pinene secondary organic aerosol yields increase at higher relative humidity and low NO_x conditions” by Lisa Stirnweis et al.

Anonymous Referee #1

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This work is laboratory and modeling study of SOA from alpha-pinene photooxidation under different RH conditions, and various NO_x/VOC ratios. The authors investigated the effects of various seed compositions, notably hydrophobic vs. hydrophilic seed, which in my opinion is a clever way to deduce that the RH effect is significantly based on liquid water and particle phase mixtures. The authors primarily used AMS, PTRMS, and SMPS to measure the compounds/particles of interest and performed wall loss corrections for particles under one RH condition. Vapor wall loss was not considered. Appropriate blanks were performed. The work demonstrates a liquid-water-based enhancement of SOA yields that may be due to a combination of many chemical and physical factors. The authors also attempted to give insight into phase partition by us-

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ing the AOIMFAC model and their own observational inputs. The paper is well-written and the method is thoroughly described. A more thorough discussion of the mechanisms involved, and additional clarity about the modeling, would be welcomed. I have some comments and suggestions before publication can be recommended.

General comments:

1. The authors stated that lack of corrections for vapor wall deposition do not “influence the comparison between the experiments.” The statement is hard to understand when the RH dependence of vapor wall loss has been documented. For example, please see Loza et al EST (2010) and Nguyen et al PCCP (2016), where hydroperoxide, hydroxypoxide, and organic acid wall losses were measured under different humidity conditions in chambers and differ substantially between different RH conditions. Nguyen et al PCCP (2016) even gave a parameterization for these compounds as a function of RH in a 24 cubic meter Teflon chamber (e.g., $k_{wall_HMHP} = -1.4 \times 10^{-5} \times RH \text{ min}^{-1}$, $k_{wall_H2O2} = -9.6 \times 10^{-6} \times RH \text{ min}^{-1}$, and $k_{wall_HCOOH} = -2.2 \times 10^{-6} \times RH \text{ min}^{-1}$). As the authors can see, not only is vapor wall loss different for each RH condition, it is different for each chemical compound. The papers listed to support the authors’ statement, namely Zhang et al PNAS (2014) and Nah et al ACP (2016), were only studied under dry (RH < 5%) conditions so are not applicable to the current case. I do not believe that retro-actively applying the vapor wall loss corrections is critical to this work, but request that the authors conservatively estimate the errors that ignoring such a correction in the alpha-pinene system (which is known to produce compounds readily lost to walls) would cause. This may actually increase the enhancement that the authors observed.

2. Adding to that subject, the authors are also suggested to monitor particulate wall losses at different RH conditions and for different composition in their future works in lieu of picking an average and going with it for all particles and all conditions. There is usually a noticeable difference in the rates of deposition depending on particle characteristics and wall wetness (related to RH). This is especially advisable since the authors

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are using so many different seeds that may respond to wall wetness in different ways (I would guess the CF seeds would not show the same increase in sticking as the hydrophilic seeds when water layers on the walls increase, with similar effect to their SOA-derived observations). Again, the suggestion here is to approximate and report uncertainty that may be caused by ignoring these dependencies in the revised version of the paper.

3. I have a general criticism of the way “NO_x” is used in this paper. It is too vague. When the authors say “44.4(0.8) ppbv of NO_x” does that mean 42 ppb of NO₂ and 2.4 ppb of NO or any of the other innumerable combinations...? Additionally, it’s not really “NO_x” that’s important here, but rather nitric oxide (NO) because it changes the course of the reaction with the RO₂ radical, while NO₂ doesn’t do very much unless the precursor is an aldehyde (which in this case it is not). Can the authors be more clear about how much NO there is, instead of “NO_x”?

4. The authors mentioned hydrophilicity and solubility several times in the article, yet it’s not clear how this is considered by the model, if at all? Also, despite the authors’ statement that the few products considered in the model are adequate, more support is needed to understand how these few products can be fully representative of such a complex chemical system.

Some detailed comments

Pg 13, In 12: It’s not clear why the authors conclude that the NO_x dependence is definitely due to low NO_x conditions forming less volatile compounds? Perhaps the low-NO_x conditions form more soluble compounds? Perhaps more well-mixed particles?

Pg 13, In 18: How much of the reaction is actually ozonolysis? The authors should give an indication of ozone mixing ratio in these reactions, and calculate the prevalence of side reaction given the O₃+α-pinene rates. If a significant fraction is ozonolysis, then RH will change the gas-phase product distribution as well.

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Pg 14, In 13: It would also be beneficial if the authors can talk about these products in terms of RO₂ reactions. Also, why cite a 2011 modeling study when talking about hydroperoxide and carbonyl products from RO₂+HO₂ and RO₂+NO chemistry, when the mechanisms were deduced much earlier by Atkinson and many others and are now textbook knowledge?

Pg. 16, In 17-20: The authors highlighted the importance of solubility in understanding the RH-dependent SOA yields, but the parameterizations only include volatility. The authors say later on that it’s assumed that the hydrophilicity is proportional to the volatility, but that would mean treating a chemical process just like a physical process. Given that the model does not consider aqueous reactions, and how important these reactions have been shown to be for SOA (i.e., works of McNeill, Ervens, Carlton, and others), it’s not clear to this reviewer that the augmented cases with fragmentation and lower volatility products (i.e., more volatility-driven solutions) give the right answers for the right reasons. How do the authors believe the modeling results would change if solubility and aqueous reactions were directly considered?

Table S4: Which chemical (i.e., NO, HO₂) regime do these compounds belong to? Can the authors list the abundances that they derived, for each “NO_x” regime? What were the hydrophilicity parameters that the authors assigned for these compounds?

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