

## ***Interactive comment on “Multiday production of condensing organic aerosol mass in urban and forest outflow” by J. Lee-Taylor et al.***

### **Anonymous Referee #1**

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Review of “Multiday production of condensing organic aerosol mass in urban and forest outflow” by J. Lee-Taylor

The authors present results on secondary organic aerosol production from box-model simulations using the GECKO-A chemical mechanism. They find that for an “urban” plume case (main precursors = aromatics and alkanes) that dilution-corrected production of SOA continues over many days downwind of the urban source region. This is because many of the compounds that ultimately form SOA are the result of multigenerational chemistry, which occurs on a multiday timescale given typical reaction rates. In contrast, for a “forest” plume case (main precursors = monoterpenes), they find only relatively small multiday production of dilution-corrected SOA. This reflects the relatively fast reaction rates of the monoterpenes and many of the SOA species being the

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result of first generation chemistry. This work represents a more detailed examination of results first reported by Lee-Taylor in 2011, and includes useful sensitivity studies to examine the generality of their results. This manuscript is suitable for publication in ACP once the questions/comments below have been addressed.

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P18001/L27: The “C\*” in parentheses is unnecessary and misleadingly used, as it is actually saturation concentration (defined in the next sentence), not volatility.

P18002/L1: It is not generally true that  $C^* = C_{oa}$  when species are equally partitioned. This is only correct in a single component system. In a multicomponent system, one must explicitly account for the Raoult’s Law vapor pressure depression, at least if one is using absorptive partitioning theory.

P18002/L20: The authors state that SOA in “tropical and/or remote SOA tends to be closer to observations or even overestimated (Lin et al., 2012).” Is this really a general result? What about the early study of Heald et al (2005)? Also, more broadly regarding this entire paragraph, lots of different models with very different formulations are being compared, making it difficult to understand whether results are general or not.

P18003/L15: The authors state “Another problem of scale is inherent in the sheer number of potential chemical reactions and products leading to SOA formation, as compared to the bulk aerosol properties accessible from environmental chamber studies.” This would lead one to believe that the only thing ever measured in chamber experiments are “bulk aerosol properties.” This is not true. There are many groups that characterize the diversity of individual compounds in SOA formed in chambers.

GECKO-A: Various recent experimental results have been pointing towards the importance of intramolecular isomerization (auto-oxidation) in the oxidation of organic compounds. Does GECKO-A account for this process? Especially in considering ozonolysis of alpha-pinene (see Ehn et al., Nature, 2014). If not, can the authors comment on

how consideration of such processes more explicitly might alter their results?

P18009/L25: It's not clear why, if the authors did the simulations, they wouldn't just increase their x-axis in Fig. 2a for the additional 3 days of simulation.

P18010/L10: SOA production in the NAN model does not "continue unabated." On the previous page the authors just stated that the base case urban model asymptotes at 30 ug per initial m<sup>3</sup>. It also seems that the JRM and NAN model results are converging, at least approximately, at long times. This is easy to understand. Earlier generation products get "trapped" in the particle phase at earlier times when their vapor pressures are predicted to be lower. When their vapor pressures are higher, they must be converted to lower vapor pressure species to condense, which takes time but doesn't strongly influence the total OA formed. (In the absence of fragmentation, these would be no different at long times.) The authors mention the reason for the faster production of SOA in the JRM case, but don't really address the convergence issue. I suggest that some (brief) discussion is added.

P18011/L5: I believe that the authors could clarify/elaborate further the particular reasons for the decrease in the dilution-adjusted SOA for the forest DIL/3 case. I do not find the discussion to be overly clear.

Heterogeneous oxidation: The authors do not include heterogeneous chemistry, which can lead to oxygenation of aerosols as well as particle mass loss on time scales of ~1 week (see work by Abbatt/Kroll/Wilson and others). How might the inclusion of heterogeneous oxidation pathways influence their conclusions regarding both total SOA mass and O/C?

O/C comparison: There has been a suggested update to O/C values determined from the Aerodyne AMS (see Canagaratna et al., ACPD, 2014) that increases O/C values over those previously reported. Are the authors using "old" or "new" O/C values in their comparisons?

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O/C between urban and forest: The differences are not only the result of "delayed chemistry in the urban case outflow resulting from [OH] suppression...and faster oxidation rates of the biogenic precursors." They are also related to the nature of the compounds being oxidized. The O/C from SOA depends on the precursor identity, which differs between the different cases. See, for example, Chhabra et al., ACP, 2011.

Figure 3: The dashed lines are not actually gas-phase. As drawn, the dashed lines overlap with the solid lines and can even slightly be seen on top of the solid lines at very low C\* values, where the partitioning will be nearly 100% in the condensed phase. I think that this is simply an issue of presentation that needs to be clarified.

P18013/L4: I do not see what about the urban case becomes "more complex" as time progresses. I find this statement to be overall vague, and the authors should either address in more detail here or move all mention to later (as in "see later discussion.")

Figure 4: I suggest for panel a to use a different y-axis scale than for panel c that better shows the model results. In other words, I suggest setting the upper limit to 1.

Forest Case: Sesquiterpenes are not included in the model simulations. Is this because they don't exist in that forested environment? Or because GECKO-A has not been developed for them. Even if they are in much lower abundance than 10 carbon monoterpenes, they have substantially larger SOA formation potential (yields) and thus should not be discounted unless there is an explicit reason to do so.

P18013/L10: Instead of "...suggesting that the evaporating species re-partition to the particle phase after one generation of chemistry," I suggest "...suggesting that the evaporating species react to form lower volatility products, and the first generation species are of sufficiently low volatility to partition back to the particle phase." I don't like the term "re-partition" because to me this indicates the same species is "re-partitioning." But this is not the same species, but a new species formed from chemical reactions.

P18013: The discussion of evaporation/reaction/condensation of initially semi-volatile

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species is correct as far as it goes, but since heterogeneous oxidation is not accounted for in this model might give a somewhat incorrect picture. Can the authors comment on how inclusion of heterogeneous chemistry might influence the results? It is true that heterogeneous reaction rates tend to be slower than gas-phase reaction rates, but heterogeneous chemistry is fast enough to be somewhat important on multi-day timescales.

P18014/L11: I find the bit starting "...since the concurrent declines..." to be a bit awkward.

P18014/L14: I find "fresh" to be ambiguous. What is "fresh" material? I believe that what the authors mean is SOA produced from gas-phase precursors that have not previously existed in the particle phase. Or, if they did at some point exist in the particle phase, where fragmentation has produced smaller carbon number species with larger O/C.

P18014/L15: I'm not sure "pathways" is really the right word here.

P18020/L25: In what context are light aromatics not normally considered to be significant contributors to SOA production? As just one example of where light aromatics are considered important, consider Ensberg et al., ACP, 2014. Certainly polycyclic aromatics have larger SOA yields, but this does not mean that light (single ring) aromatics are generally considered unimportant. If the authors disagree, I suggest that they provide a (comprehensive) reference to back this up. It seems to me that this statement just serves to emphasize the perceived importance of their finding that light aromatics do contribute to the SOA burden.

P18021/L13: Does "dry deposition" refer only to losses of particles, or gases too. A more recent paper by Hodzic et al. (GRL, 2014) than the 2013 paper cited indicates a very important role for dry deposition of vapors in determining the SOA budget. This seems to counter the statement that "dry deposition [is] a relatively minor factor." Perhaps the issue is simply that the 2014 study is for the US and the 2013 is for the Mexico

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City urban outflow? Or is there some more fundamental difference between these studies that would lead them to reach contrasting conclusions regarding the importance of dry deposition. Is it that the 2014 study also includes wet deposition?

P18021/L21: I am not certain that this is a "previously unrecognized global source" of SOA. Multiday "ageing" is, in part, what the "ageing" add-on to the 1-dimensional VBS attempts to account for. Certainly there remains much discussion about the fidelity of VBS implementations into global models that include "ageing" reactions, but I would contend that even such simplistic models (compared to GECKO-A) recognize multiday particle mass production as a global source of SOA.

P18022/L5: I find the discussion regarding NH ozone to be a bit misleading, in that it is not clearly stated that the authors are talking about background ozone levels.

P18001/L1: "Related" is ambiguous.

Figures: In general, I suggest that the authors provide higher resolution figures for publication. They are all quite grainy.

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 17999, 2014.

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