Authors' response to Anonymous Referee #1

We thank the reviewer for their thorough reading and many insightful comments, which we have found very helpful in improving our manuscript. We hope that the changes we have made and outlined below answer the Reviewer's questions and that the paper can now go forward to publication.

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 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.

- We have removed the misleading parenthetical reference here to C*. We have also expanded the explanation of C* on page 18006, lines 6-9:

"The 9th and lowest volatility bin in the emissions ("SVOC1", centered on $C* = 1x10^{-2}$ $\mu g\ m^{-3}$, where C* is the effective saturation concentration) corresponds to n-alkane carbon chain lengths of 24-25 under the JRMY scheme but 32-33 for NAN."

P18002/L1: It is not generally true that C* = Coa 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.

- We have removed the erroneous explanation rather than elaborating it, as it is not necessary to the discussion at this point.

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.

- We have deleted this sentence rather than attempt to more accurately represent the wealth of model studies available, since such a review is not necessary to our discussion.

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.

- We agree and have replaced the misleading sentence with references to some measurement studies providing detailed characterisation of ambient organic aerosol:

"Indeed, recent advances in high resolution mass spectrometry analytical techniques have enabled characterization of many hundreds of individual OA constituents (e.g. Nizkorodov et al., 2011 and references therein; Chan et al., 2013; O'Brien et al, 2013; Kourtchev et al, 2014))."

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?

- We do not explicitly account for autoxidation processes in GECKO-A. However, we find that a significant proportion of the predicted a-pinene SOA already has even higher oxygen content than is suggested by Ehn et al. Autooxidation may enhance the initial forest case aerosol mass formation rate, however it is already pretty fast in our simulations.

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.

- This was an oversight. We have re-plotted Fig2a with a longer timescale on the x-axis.

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^3. It also seems that the JRMY 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 JRMY case, but don't really address the convergence issue. I suggest that some (brief) discussion is added.

- We agree. We have amended the text to better reflect the asymptoting of the particle mass in both cases:

"Downwind, the JRMY case aerosol increases its mass excess over the NAN case, growing by more than a factor of 3 in two days before reaching an asymptote at about 30 μg initial m^{-3} at the end of day 4, slightly sooner than in the NAN case."

- We have also briefly mentioned the convergence issue, immediately after our discussion of Pvap differences that explain the faster production and earlier slowdown in the JRMY case:

"One should not read too much into the slightly higher ending mass of the JRMY aerosol, since this run used lower outflow temperatures. The main result here is that the predicted multiday nature of OA mass production is not unique to one particular vapor pressure scheme."

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.

- We have discovered that the dilution rate applied in our forest DIL/3 case was actually 0.46 day^{-1}, not 0.3 as intended. Accordingly we have re-named case DIL/3 to SLOWDIL. The recalculated plume-integrated mass (M$_t$OA) in the forest SLOWDIL case lies between the values for the Reference and NODIL cases, which is much easier to explain:

"Slower dilution rates lead to higher aerosol mass concentrations, favoring condensation. In the forest scenario, dilution rate reductions (runs "SLOWDIL" and "NODIL") give incremental increases in plume-integrated particle mass, as expected."

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?
- We already say in our Discussion that heterogeneous oxidation could either increase or decrease the total SOA mass. We have added a couple more references and an explicit mention of the potential effect on O:C:

"Other possible conversion processes include in-particle accretion reactions (Barsanti and Pankow, 2004), heterogeneous oxidation (George and Abbatt, 2010a; Smith et al., 2009; Molina et al., 2004), photolysis (Nizkorodov et al., 2004), and multiphase chemistry (Pun and Seigneur, 2007; Ervens and Volkamer, 2010; Lim and Ziemann, 2009b). These processes which become increasingly important at longer timescales could either increase or decrease particle mass, affect particle hygroscopicity (e.g. George and Abbatt 2010b), and will also likely increase the SOA O:C ratio (e.g. Heald et al, 2010)."

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?

- We have now updated the Aiken results and included a reference to Canagaratna et al. We have also added a discussion of how our calculated O:C increases when the entire aerosol (including the background seed) is considered. These values are more directly comparable to the updated field data, which sampled bulk OA, irrespective of origin:

"O:C values are highly sensitive to the aerosol fraction considered. Our simulations use a pre-existing seed aerosol with a mass concentration of 2 (1) µg m^{-3} in the urban (forest) scenarios respectively. We assign this seed aerosol the same O:C ratio as seen at the end of our forest case (0.9), consistent with a regional background aerosol that is well oxidized and/or of largely biogenic origin (e.g. Hodzic et al. 2010). Including the seed aerosol raises calculated O:C to 0.35 (0.87) at the start of outflow in the urban (forest) cases. The seed aerosol contribution continues to influence the O:C ratio in the outflow, raising urban values to 0.55 after 24 hours and 0.71 after 2.2 days (rather than 7 days). These values are comparable to measurements in Mexico City (0.4-0.73, Aiken et al., 2008; corrected as per Canagaratna et al., 2014), although the strong sensitivity of the O:C ratio to the background aerosol means that model-measurement comparisons are of only limited utility if the background contribution is not known."

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.

- We have made this point more explicitly in our discussion:

"Our forest model-generated OA fraction shows higher O:C ratios throughout (Fig. 2b, lower), developing from 0.84 to 0.90. The differences between the urban and forest scenarios are consistent with the forest case particle phase being already well oxidized at the beginning of the outflow phase, with delayed chemistry in the urban case outflow resulting from [OH] suppression, and with different precursor assemblages giving differently-oxidised products (e.g. Chhabra et al., 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.

- We thank the reviewer for pointing this out and have revised the Figure so that the dashed lines are gas phase only, not gas+particle.

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.")

- We have removed this sentence. The "later discussion" already covers the point we wished to make.

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.

- Good idea. We have re-plotted the figure panel with a y-scale upper limit of 0.6.

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 hey 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.

- We have not yet developed GECKO-A to be able to deal with sesquiterpenes. We have added a paragraph to our section 2.2 discussing the implications of their omission:

"Our forest case precursor mixture omits sesquiterpenes because our model has not yet been validated for their complex chemistry. Sequiterpenes would likely increase the quantity of SOA formed, however we would not expect significant changes to the timing of downwind SOA formation. Like monoterpenes, sesquiterpenes have lifetimes of the order of an hour or less (Atkinson et al., 1990; Shu and Atkinson, 1995). Changing multi-day formation rates would thus require the lifetimes and SOA yields of second or higher -generation sesquiterpene products (Ng et al., 2006) to greatly exceed those for monoterpenes since sesquiterpene source fluxes are relatively low (of the order of 10% or less of monoterpene fluxes during the BEACHON campaign, Kaser et al., 2013a)."

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.

- This is a good point. We have re-worded:

"…suggesting that the first-generation reaction products of the evaporating primary species are of sufficiently low volatility to partition strongly back to the particle phase."

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

- As the reviewer noted earlier, heterogeneous process are among several different types of process that are outside the scope of this study. We have added a mention of longer timescales to the relevant paragraph in our discussion:

"These processes which become increasingly important at longer timescales could either increase or decrease particle mass… "

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

- We have simplified our wording:

"…since these fractions show comparatively minor losses."

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.

- The reviewer understood us correctly. We have re-worded to make our meaning clearer: "The production must therefore be largely due to ongoing incorporation of previously uncondensed material from the gas phase."

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

- We have re-worded this to read: "Figure 6 and Table 2 illustrate the temporal development of gas-particle partitioning for the urban case."

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.

- We agree that this sentence was incorrect, and have removed it. It does not affect our conclusions about the timing of the growth.

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 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?

- The two studies represent a range of different model conditions: the 2013 study uses the JRMY vapor pressure scheme and an effective 1.5km boundary layer, whereas the 2014 study uses the less-aggressive N08 vapor pressure scheme and a 3-D model whose US boundary layer is often shallower than observations. We agree that the later work should also be appropriately considered:
"Explicit chemistry simulations have dry deposition to be more important than wet deposition (Hodzic et al., 2014). It reduces anthropogenic –origin SOA by 15% -40% and biogenic-origin SOA by 40-60% over regionally-relevant timescales, and depending on model conditions and boundary layer depth (Hodzic et al., 2013, Hodzic et al, 2014)."

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.

- We agree and have re-worded:
"…the multiday particle mass production we predict from first principles represents a large but diluting secondary source which is not easily discerned in concentration data."

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.

- We have added the word 'background' in 3 places.

P18001/L1: "Related" is ambiguous.

- … and unnecessary. We have deleted the word.

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

- We will work with production staff to ensure the figures are reproduced satisfactorily.