Jathar et al. present an important extension of the typical volatility basis set (VBS) modeling framework, effectively merging "traditional" SOA yield approaches with an multi-generational approach in a new "Hybrid" approach. In this manner, SOA formation from "traditional" (T) precursors and "non-traditional" (NT) precursors can be treated within a similar framework, which is very important if we are to quantitatively understand the contributions of these different SOA precursors to the total SOA burden through the use of models. They test this framework through consideration of photooxidation experiments that use aircraft exhaust. Through their analysis they find that oxidation of NT precursors can essentially be represented through the "traditional" (yield based) framework, with only a small need to account for additional oxidation reactions (multi-generational ageing). This finding, however, is strongly tied to the particulars of their model formulation and ageing timescale.

The development of this "Hybrid" method represents a useful advance over the previous method(s). However, I find that all of the discussion surrounding the particular details of the various experiment types/fuel types distracts from the main point of the paper. I believe that revision to provide a stronger focus on the main paper motivation (development of the Hybrid model) would be beneficial. Further, I find that some key aspects of the model formulation are not clear in terms of the actual implementation (as opposed to conceptual picture, which is clear), making it somewhat difficult to understand the final results. Also, it is not entirely clear whether the authors are developing the Hybrid approach as a more physically-based representation of SOA formation from NT precursors (and T-precursors, as well) or whether the primary motivation is simply better fitting of data. If the former, I have concerns about the particular details of their model formulation and interpretation of their results in terms of physical mechanisms, which are elaborated upon below. If the latter, the authors have succeeded reasonably well.

Although I believe that the Hybrid approach represents an important advance in the field, I believe that some key aspects must be clarified before this manuscript is publishable.

Primary concerns:

Eqn. 4: It seems inconsistent to me to allow the 2nd and later generation T-SOA and NT-SOA products to only undergo a 1 order of magnitude reduction in volatility while the production of 1st generation products occurs as a distribution. If the first generation of oxidation can produce products with distributions of volatility, why can't the nth-generation of oxidation do the same? Is this distinction made simply to allow for computational efficiency and to keep the number of required parameters smaller than it might otherwise be?

Eqn. 6: If I am reading the matrix shown in Eqn. 6 correctly, this indicates that the 4 products that are produced as first generation products span 4 orders of magnitude (which makes sense based on addition of ketones, alcohols and carboxylic acids, which span 4 orders of magnitude of volatility). However, it appears that the highest volatility species in this array of products has a volatility that is reduced by 3 orders of magnitude from the parent species. This means that the actual reduction in volatility, relative to the parent species, ranges from 3-6 orders of magnitude, which seems too large to

me. A range of 1-4 orders of magnitude seems more reasonable to me, based on addition of ketones, alcohols and carboxylic acids (see Pankow and Asher, 2008). As such, whereas the Robinson et al. (2007) formulation might underestimate the decrease in volatility per reaction, it seems as if the Hybrid method is over-estimating. This said, I am open to the idea that I am completely misinterpreting how the Hybrid method is actually being implemented because I am having some difficulty reconciling what is shown in Table 3 with Eqn. 6 (see comment below regarding Table 3).

The combination of (1) allowing reactions of the initial precursors to form a distribution of species (over 4 orders of magnitude in volatility) while reactions of later generation species only reduce volatility by 1 order of magnitude and (2) the excessively large reduction in volatility (3-6 orders of magnitude) for products of initial precursors will inevitably make it such that the model is biased towards SOA formation from 1st generation products. Thus, it is not surprising that the authors find that the 1st-generation NT-SOA dominates the SOA mass (see Figure 6). Although this model formulation may fit the observed SOA formation with reasonable fidelity, interpretations (such as those in Section 4.3.2 and Section 5) in terms of physical meaning based on the model results are questionable.

Table 3: (1) This table should be mentioned in Section 4.3.2, not just in the conclusions. (2) I have a very difficult time understanding this table, and this lack of understanding arises due to some confusion on my part regarding how exactly the Hybrid method is being implemented. The authors' state that in order to reduce the number of parameters in their model from 40 to 4 they will assume that upon reaction there is "the same product distribution arising from each POC precursor, but shifted in volatility space by one order of magnitude" (P9955). I interpret this to mean that there is but one set $[a_1,b_1,c_1,d_1]$ that is adjusted to fit the Hybrid model to the observations for a given experiment, and not a different parameter set for each precursor (i.e. bin of the VBS). Further, based on Eqn. 6 I interpret this to mean that these parameter sets will correspond to different C* product ranges with the range dependent upon the volatility of the parent species. Table 3 makes it appear as if reactions of all POC species, no matter their C*, lead to production of species with C* values ranging from 10^0 to 10^3 ug m^{-3}. This seems highly inconsistent with what is shown in Eqn. 6. Further, in Table 3 POC species with varying C* values are listed as having different parameter sets. Shouldn't there be one $[a_1,b_1,c_1,d_1]$ set for each experiment (engine/fuel combination) and not for each POC C* value? Perhaps I am misunderstanding, but I find the manuscript to not be clear on these points.

Other Concerns/Questions

General: Most of the experiments took place at OH exposures < 1 x 10^7 molecules-hr cm^{-3}. For a C_{15} (for example) hydrocarbon, this corresponds to < 1 oxidation lifetime. (Of course, the specific relationship between exposure and oxidation lifetimes really depends on specific distribution of precursor compounds. However, I think that the idea expressed here is generally applicable.) In fact, one oxidation lifetime is not reached until the OH exposure is ~ 1.5 x 10^7 molecules-hr cm^{-3}. Only a few experiments go beyond this level of exposure. Given this, it is not surprising that the authors find that the SOA is

dominated by 1st-generation products. It is not clear to me that the experiments the authors compare/fit their Hybrid model with are really the best choice for the development of the model.

P9947/L14 (and throughout): I find the terminology POC a bit odd in the context of IVOC's and SVOC's. I have typically interpreted "primary" to indicate "particles that are directly emitted" from sources. Although this may be the ultimate source of IVOC's and SVOC's, it then seems strange to refer to "POC vapors," since the "vapor" aspect indicates that the species is no-longer "primary". Yes, this is purely semantics, but I feel that more precise terminology would be helpful to the community. Along these same lines, eventually the distinction between "traditional" and "non-traditional" SOA will need to be dropped, as what is currently "non-traditional" will become part of the "traditional" hierarchy. Perhaps now is the time to introduce new, exquisitely precise terminology?

P9947/L26: Certainly some of the emitted species are not branched or cyclic?

P9948/L18: Was the Robinson (2007) method really "fit" to measured SOA formation? I know that the volatility distribution of the POA was fit to observations, but was the method that involves allowing the gas-phase species to react actually explicitly fit to data? My reading of the Robinson et al. (2007) paper (including the SOM) gives no indication that the method was "fit" to measured SOA formation, although in a later paper Shrivastava et al. (2008) compare the Robinson et al. (2007) method to chamber data and demonstrate reasonable agreement (although the Shrivastava et al. comparison does not appear to have been truly a "fit" either). Perhaps this is just some confusion on my part as to what the authors specifically mean by "method"? I am interpreting "method" as the ageing scheme, per the first sentence of their previous paragraph. Further, it seems to me that the Pye and Seinfeld (2010) method is just as constrained as the Robinson et al. (2007) method; that is, neither is explicitly constrained through "fitting". Although it may not have been the authors intention, as written it sounds as if the authors are criticizing Pye and Seinfeld for this lack of laboratory constraints even though I would argue that the exact same criticisms apply to the Robinson et al. method. I suggest re-phrasing.

P9948/L26: It is not clear to me what the authors are getting at by pointing out that IVOC emissions are inferred from "other source test". Some elaboration on this point would be appreciated.

P9949/L6: The authors state that a limitation of smog chamber experiments is that they only capture the evolution of "the first few generations of oxidation", which only captures "5-10% of the time spent by precursors and their products in the atmosphere". Although this may be true, it seems a bit misleading to me in that after "a few" (which I will take to mean 3 or more) generations, the precursor will have decayed to exp(-3) = 5% of its initial concentration. This is then more like 95% of the "time spent" by the precursors in the atmosphere. True, the products may be around a bit longer, but they will also decay within "a few" lifetimes.

P9949/L8: If the authors are truly only focusing on "the first generation" of oxidation, then I do not understand the motivation for the development of the "hybrid" method. Shouldn't application of the "traditional" approach work if there is truly only one generation? Some clarification would be appreciated.

P9952/Section 2.1: A terminology question. The T-SOA (= traditional SOA) method typically assumes that the products are unreactive. In the hybrid model, products are reactive to OH. Are the products of these reactions then classified as NT-SOA, even if the original precursor was a "T" precursor? Or are they still T-SOA? Also (and more importantly) doesn't allowing the gas-phase products to continue to react preclude the use of the original T-SOA formalism, since the yields were derived under the assumption that the products were unreactive even though they may have actually been reactive? In other words, don't T-SOA yields in some crude way include reaction of products (although perhaps not in an accurate manner), which means that allowing gas-phase species in the T-SOA framework could be double counting? I say "could be" because I think that this will depend on how the yields were measured. If yields were measured after allowing the precursor to react over many lifetimes of oxidation, then oxidation of products is important. But if yields were measured after <1 lifetime, then oxidation of products is not as important and the measured yield may not include further oxidation of products. Could it be that the studies with higher yields tend to be those that have gone through more lifetimes of oxidation?

P9957/L1: I suggest that for the papers that are not published the authors indicate them as, e.g., Drozd et al. (in preparation) instead of Drozd et al. (2012).

Figure S1: I recommend moving this figure to the main text.

Table 2: It could be useful if the authors were to indicate the C* values for the VOC's, so that the initial volatility of species can be understood in the context of the volatilities of the POC species. For example, undecane has a C* ~10^7 ug m^{-3}, giving it a volatility close to the highest volatility bin of the POC. This, in some ways, raises the broader question of what is a "traditional" precursor and what is a "non-traditional" precursor in the context of the VBS (which ultimately defines compounds according to their volatility, not their identity). If these species overlap in volatility (i.e. end up in the same bin), are they distinguishable?

Section 3.4: It is not clear whether the authors used, in their modeling, an average [OH] or a time varying OH. If [OH] varies significantly throughout the experiment, this could have a dramatic influence on the model performance. This, I believe, to be very important and requires clarification.

P9960/L5: I missed the fractional error values in Figure 4 at first due to the large density of gridlines. I suggest using just major gridlines.

P9960/L19: The authors should justify the change in rate coefficient for the higher vs. lower volatility species. Presumably they are accounting for differences in the size of the molecules (which makes sense), but then why not use a k_{OH} that varies with log C*? Why a step function and what are the implications of using a step function?

P9961/L9: The authors state that NT-SOA yields increase with increasing C_{OA}. However, this appears to be the case only for some of the aerosol types, not all. Can the authors comment? Perhaps this statement should be revised to say that NT-SOA yields increase for some, but not all species?

P9962/L14: The authors need to clarify how they can have fractional values of q (which defines the number of volatility bins that a product decreases from the parent species). Presumably, they distribute mass into the different VBS bins based on a weighting scheme, but this is not clear. Or, perhaps I am misunderstanding the phrase "a range of 1 to 2" and the authors mean "either 1 or 2" with fractional values not allowed?

P9962/L14: It is not clear why the authors constrain the q values over the range 1-2. Why not allow larger values? Would this allow the NT-SOA model to perform better?

P9962, Line 19: It is not clear what the authors mean by "reproduce the SOA data." Consideration of Figure 4b appears to indicate that, in many cases, the SOA data are not "reproduced" by the model; the NT-SOA model simply does a better job than the T-SOA model alone.

P9963/L21: The high O:C is not straight-forwardly the result of precursors having to go through multiple generations to attain low enough volatility. It is a combination of the authors q values and the f_{oxy} values. If they have sufficiently small f_{oxy}, little oxygen will be added regardless of how many generations the products go through. Similarly, if they have large q and large f_{oxy}, lots of oxygen can be added after only a few generations. The point isn't that multiple generations are not important, only that the importance of the f_{oxy} and q terms appears to be somewhat understated here.

P9964/L5: It is not clear where the upper and lower experimental bounds derive from.

P9964/L9: It is certainly interesting that the first generation products of POC dominate the NT-SOA. However, this should not be surprising given the model formulation which assumes that all POC products decrease their volatility by 3-6 orders of magnitude. As stated earlier, this seems like too large of a decrease to me (given that even carboxylic acid addition will lead to volatility decreases of only ~4 orders of magnitude), which leads to a larger attribution of the NT-SOA to 1st generation products than may actually be occurring. However, if the aim of the hybrid method is to simply better reproduce the time-evolution of the SOA formed, perhaps this is reasonable.

Figure 8/P9964: It is not clear to me how the authors keep track of the SOA formed from each discrete precursor in the model. In the hybrid model, the products from the different precursors rapidly overlap given that each precursor gives rise to species that span 4 VBS bins. How do the authors keep track of which precursor formed what? Is this related to the assumption of "the same product distribution arising from each POC precursor, but shifted in volatility space by one order of magnitude" (P9955)?

P9965: I find this discussion relating to yields from the various precursors to be weak. Perhaps this is because I have some difficulty understanding how the yields are determined (see above comment), but also because the conclusions here are intimately tied to the particulars of the model formulation. Again, I come back to the point that the authors use a scheme in the hybrid method that assumes decreases of 3-6 orders of magnitude in volatility for the reaction of the parent compound (but only 1 order of magnitude for reaction of subsequent products). This choice will determine which species appear to contribute most to the SOA and will determine the yields from particular VBS bins. If the authors used a scheme that decreased volatilities by 1-4 orders of magnitude, I imagine that their conclusions would be

altered. Thus, it seems a bit of a stretch to, at this point, firmly conclude that yields in the 10^3-10^4 bins are lower but yields in the 10^5-10^7 bins are higher than equivalent n-alkanes and to subsequently use this to identify (in a general sense) the chemical nature of the precursors.

P9964/L18: Figure 8a shows precursors with C* = 10^3 and 10^4 ug m^{-3}, not C* = 10^2 and 10^3 ug m^{-3} (at least according to the labels in the figure). Panel b is similarly mislabeled.

P9951/L5: It is interesting that the authors note the potential for fragmentation reactions to *increase* volatility, but their proposed scheme does not explicitly include any sort of accounting of this effect. Perhaps this comes out in the [a, b, c, d] array? However, it would be good if the authors would comment on how their model does/does not capture the effects of these fragmentation reactions.

Fig. 6: For experiments where POA is substantial, the model indicates constant POA with time. Doesn't the POA evaporate in response to depletion of the gas-phase reservoir (see Miracolo et al., 2010)? Or is the volatility of the POA so low that this is not a concern?

Fig. 6: After looking over the comments of Reviewer #1, I must agree that some of the observed behavior shown in Fig. 6 for some of the experiments is quite odd and should be commented upon.

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