**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Evaluation of the volatility basis-set approach for the simulation of organic aerosol formation in the Mexico City metropolitan area" *by* A. P. Tsimpidi et al.

Anonymous Referee #3

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This work is aimed at incorporating several relatively new developments in the chemistry of organic aerosol into an existing model, with application to the Mexico City Metropolitan Area. This is an important study, as it shows that such changes bring modeled aerosol loadings (both primary and secondary) more in line with measurements than models typically do. At the same time, the authors are careful not to overinterpret the results. This paper is certainly worthy of publication in ACP. Prior to publication I recommend a few substantial changes, listed below. Most involve expanding the explanation of the model or the discussion of the results, which are glossed over in several places.

P. 13699, line 27 (and elsewhere): I find the term "non-traditional SOA" to be confusing and not terribly helpful. The SOA itself is completely "traditional"; it conforms perfectly to the earliest definition of SOA that I can find (which is by one of the authors of this paper!): particles "formed in the atmosphere by the condensation of low vapor pressure products of the oxidation of organic gases" (Pandis et al., 1992). But the term also apparently doesn't mean "SOA formed from precursors not traditionally included in models", because the authors consider SOA from isoprene (which wasn't regularly included in models until 2006-2007) to be "traditional". Instead "non-traditional SOA" apparently means "SOA from precursors of volatilities not traditionally considered in models, not counting those originally emitted as primary OA." Why not simply classify the SOA by the volatility of the precursor? This gives "V-SOA" (SOA from VOCs), "I-SOA" (SOA from IVOCs), and "S-SOA" (SOA from semivolatiles). These aren't ideal labels, but they are less confusing and arbitrary than "Traditional SOA", "Non-Traditional SOA", and "OPOA".

Section 2.1: It is unclear to what extent the different aerosol types are lumped within the volatility bins. One of the oft-cited benefits of the volatility basis set is that it enables lumping among different aerosol types, keeping the number of tracked species relatively manageable. Were bins from different SOA precursors lumped? (If so, what was done about the differing molecular weights?) Were they lumped with POA?

P. 13706: More details are required about how the background OA is treated. I assume it is treated as nonvolatile and unreactive? If so, it would seem to be somewhat problematic to include biomass burning OA in with this, given that it's semivolatile and subject to further atmospheric oxidation (Grieshop et al., 2008).

Section 4: a major difference between this model treatment and previous ones is that "aging" of the organics is included. Therefore the effect of this aging needs to be discussed. How much additional oxidation (in terms of average number of reactions with OH) do the SOA and POA components undergo? This is important not just for understanding the role of aging, but also for model-measurement comparisons. For

example, if the OPOA is formed from only one OH+SVOC reaction, the O/C ratio of the resulting aerosol is probably not high enough to be considered "OOA" (Presto et al., 2009).

P. 13707, lines 24-28: why exactly is calculated ("traditional") SOA so much higher in this case? Is this from the NOx dependence? The aging of the aerosol? The use of four model semivolatiles (volatility basis set) rather than just two (Odum model)? Or is it simply from the new aromatic yield parameters from recent chamber studies?

Section 6: In this section (as well as in the previous paragraph) the uncertainties in the modeled OA, and caveats with comparing model and AMS data, are laid out very nicely. However, the discussion in this section is focused entirely on model inputs, and there is little consideration of uncertainties in the model itself. A particularly large unknown is how organic aerosol changes upon further oxidation ("aging"). Here it is assumed that each oxidation step lowers the vapor pressure by a factor of 10 (and increases mass slightly). This is about the same as saying each oxidation step involves addition of one carbonyl group to the carbon skeleton. That is a reasonable first guess, but given that we know that gas-phase oxidation can lead to larger decreases in volatility (addition of multiple/different functional groups) or even increases in volatility (by fragmentation reactions), such an assumption introduces a large amount of uncertainty to any treatment of aging. (The relationship between aging product distribution and NOx – which may be different from the NOx-dependence of SOA from small organics – increases this uncertainty further.) Simulations aimed at understanding how the choice of aging parameters affect predicted OA loading would be extremely useful here (and would increase the impact of this study).

Other points:

Section 2.1: a simple schematic figure illustrating the different aerosol types and chemical processes modeled may be helpful for laying out the general modeling scheme (and the unique aspects of the present work).

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P. 13696, lines 14-15: this (important) sentence seems out of place, given this is a general introduction to the topic.

P 13702, lines 2-4: the possibility of a complex NOx dependence is alluded to here, but is never followed up on in sections 4-5. To what degree was SOA formed under low-NOx conditions?

P. 13704 (and throughout): IVOCs are repeatedly referred to as "missing", which is an unusual term. "Unmeasured" is probably a better descriptor.

P. 13704, lines 18-21: I'm unclear as to what this means. Do derived vapor pressures agree to within a factor of 10? If so, what are the exact values of c*?

Table 2: the second line (starting with "VOC") should also be part of the header of the table rather than part of the table body.

Table 3: differing volatilities of IVOCs are likely caused by differences in molecular weight; however in this work all are assumed to the same molecular weight (roughly that of a C18 alkane, which is relatively volatile). Differences in molecular weight would change the oxidation rates (which are dependent on moles rather than mass); does this affect results?

Figure 5 (and accompanying discussion, p. 13707): it should be made clear that these fractions do not include background OA.

Figures 5-6: the color scales differ in each panel; they should be the same for easy comparison.

References cited: 1. Grieshop, A.P., Logue, J.M., Donahue, N.M., Robinson, A.L., 2008. Laboratory investigations of photochemical oxidation of organic aerosol from wood fires - Part 1: Measurement and simulation of organic aerosol evolution. Atmospheric Chemistry and Physics Discussions 8, 15699-15737.

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