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Interactive comment on “Potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol in the Mexico City region” by A. Hodzic et al.

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Overall, I find the content of this manuscript quite interesting. It builds upon the very thorough study conducted previously by the same authors (Hodzic et al., 2009). However, I agree with Anonymous Referee #1 that the paper “suffers from a number of serious shortcomings” and requires “major revisions and subsequent re-review.” My reasons are complementary to those of Anonymous Referee #1 and R. Ahmadov, as described below.

Before going further, I should come clean and acknowledge that I haven’t paid enough attention to Mexico City modeling studies in the past because

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1. I assumed the emissions inventory to be highly uncertain and to have very different characteristics than the inventories of more developed countries.

2. I did not expect the findings from intensive field campaigns in Mexico City to be generally transferable when modeling other less-polluted regions of the world.

However, the surging number of organic aerosol (OA) modeling studies in Mexico City published in just the past year (e.g., Dzepina et al., 2009; Fast et al., 2009; Hodzic et al., 2009; Tsimpidi et al., 2009; Hodzic et al., 2010) has led me to question these pre-judgements. Given my relative ignorance of the Mexico City pollution studies, my comments here are restricted to the Abstract, Introduction, and Modeling Methods.

Relaxed use of terminology

In general, newcomers to any field of research are likely to be influenced by the most recent papers on the subject. Given the large number of recent studies on Mexico City coupled with the growing popularity of the VBS approach for modeling OA, the present study could potentially have a large influence on the future of OA modeling. For example, I expect that many scientists will soon begin translating the findings from these Mexico City studies into model applications over other domains (e.g., TexAQS2, CALNEX). To avoid the propagation of some erroneous concepts, I urge Hodzic et al. to exercise more caution and restraint when describing their findings as suggested in the following examples.

1. The authors state in their Abstract (P658 L5-7), “CHIMERE is applied to quantify the contribution to SOA formation of recently identified S/IVOC”

There are several problems with this statement. First, SVOC have been known to exist for several decades and have even been quantitatively measured for more than a decade (e.g., Fraser et al., 1998) so they are by no means “recently identified.” Second, most of the published information on IVOC has been deduced from anecdotal evidence and, to my knowledge, none of the IVOC have been chemically identified. Third, the emissions of S/IVOC from Mexico City are extremely uncertain (Tsimpidi et al., 2010) and their contribution to SOA are totally unknown, so it is very misleading to state that

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the S/IVOC contribution to SOA has been *quantified* in this study. Replacement of the word “quantify” with “obtain a rough estimate” would be more accurate.

I find the authors’ wording selection later in the Abstract (P658 L11-12) to be more appropriate: “This study highlights the important *potential role* of S/IVOC chemistry in the SOA budget”

Likewise in the Introduction (P663 L4-5), the authors appropriately state that “The overall objective of the present study is to assess the *potential importance* of SI-SOA in the highly polluted environment of Mexico City.” I urge the authors to be even more conservative with this wording (e.g., change “assess” to “estimate”).

Similarly on P663 L8, I would change “assessed by” to “attempted by”

On P666 L11, the authors ought to change “determine” to “roughly approximate” or some other word that better conveys the enormous uncertainty in estimating S/IVOC emissions from Mexico City.

2. In the Abstract (P658 L26-28), the authors also state that “The predicted production from anthropogenic and biomass burning S/IVOC represents 40–60% of the total SOA at the surface during the day and is somewhat larger than that from aromatics”

A reader might easily interpret this statement as a presumption that the S/IVOC from anthropogenic emissions and biomass burning are *non-aromatic* compounds, but I suspect this was not the authors’ intent.

3. In the Introduction (P660 L1-2), the authors state “many studies have reported that observed levels of SOA in polluted regions at both local and regional scales cannot be explained by current modeling assumptions”

Statements such as this cast the false impression that SOA can be directly observed and that model output can be evaluated against such observations in some straightforward manner. A similarly misleading phrase is found on P664 L17. In both of these cases, the authors should be clear about the quantities being compared (e.g., observed OOA vs. modeled SOA).

4. On P663 L18, the authors make reference to “surrogate SOA concentrations.” This

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seems to validate my concern about the earlier phrase “observed levels of SOA” but it is still unclear to new readers what is meant by the word “surrogate” in this sentence. Are the authors referring to OOA? If so, that should be stated explicitly.

5. Also in the Introduction (P664 L7-8), the authors make reference to “The fair agreement between modeled and observed POA concentrations (Fast et al., 2009)”

As in the case of SOA, this leaves readers with the false impression that POA can be directly observed and that model output can be evaluated against such observations in some straightforward manner. As the authors are well aware, there is no direct measure of ambient POA. Fast et al. (2009) are quite explicit in their Abstract, stating that modeled POA was compared with “primary anthropogenic” components derived from PMF. I urge the authors of this paper to sharpen their language in a similar manner.

Another example of a misleading statement about observed POA is found on P663 L25.

Methodology for estimating emissions

Emissions of S/IVOC are among the largest uncertainties in this study, so the procedure for estimating them must be described clearly and thoroughly.

1. The authors state (P666 L11-13) that the S/IVOC co-emitted with the modeled particulate POA is determined by “assigning a volatility distribution of POA concentrations.” They go on to state (P666 L22-23) that “evaporated mass was added to the model in order to achieve equilibrium with the emitted POA.” In lieu of these vague statements and the loosely-related equation that follows at the bottom of P666, the authors should articulate exactly how they derive S/IVOC from the inventoried POA values. In my opinion, the recent publication by Tsimpidi et al. (2010) does a fine job of this and may serve the authors as an example to emulate.

2. After arguing that only one third of the POA emissions reside in the particle phase at ambient conditions, the authors proceed to state (P667 L9-10) that “total SVOC emissions were determined by multiplying the POA emission fluxes by a factor of 3.”

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As written, this implies that the authors have supplemented each ton of inventoried POA emissions with an *extra* 3 tons of SVOC. If so, that would result in only one fourth of the total emissions residing in the particle phase.

3. In the next sentence (P667 L11), the authors state that “additional mass has been added to IVOC₇, IVOC₈, and IVOC₉.” Did the original inventory contain some emissions of these 3 species? If so, where did those emissions come from? If not, the sentence ought to be clarified accordingly (i.e., remove the words “additional” and “added”).

4. In the next sentence (P667 L12-13), the authors state that the additional IVOC mass was “assumed to be 1.5 times the mass reported in POA emissions.” This too is unclear. Is the 1.5 factor applied before or after the POA emissions were tripled?

5. The authors then argue that the factor of 1.5 is a conservative estimate, stating (P667 L13-14) that the “ratio of total IVOC to POA was experimentally determined, and it ranges from 1.5 to 3.0.” As in my preceding comment, it is unclear whether or not the POA referred to in this ratio is inclusive of the SVOC that the authors have added. Moreover, a careful search of the *f* values in Table 1 reveals no factor of 1.5 (aside from text in the caption). Summation of *f* values in the 3 IVOC bins (based on the definition provided on P666 L15) yields 170% or a factor of 1.7.

6. On P667 L16-19, the authors provide some ambient concentrations as an illustrative example of their calculations and refer to a previously published table (SI-3 by Dzepina et al., 2009). But even the example is misstated and adds confusion. The aforementioned table provides a gas/particle ratio of 6.7 for conditions in which the *total* particle-phase organic concentration (c_{OA}) is $10 \mu\text{g m}^{-3}$. It is not referring to POA in isolation. However by this point, it is unclear what exactly the authors mean by the term “POA.” I can only guess that POA is intended to mean the portion of SVOC that was initially emitted in the particle phase (i.e., one third or one fourth? of the material regarded as SVOC at the point of emission).

To complete this example, it would be helpful if the authors added a pair of parenthesis-

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ical notes after each instance of the word “material” on L19 in which rough estimates of the extra material concentration (e.g., $\sim 70 \mu\text{g m}^{-3}$) and total material concentration can be provided.

7. On P667 L23-26, we learn that certain minor sources of POA “were not considered as semi-volatile in this study.” This seems like a rather cryptic way of stating that those emissions are treated as non-volatile, unless I’ve misinterpreted this altogether. Are these emissions scaled up by a factor of 3 like the other sources? The authors rationalize this special treatment by stating that “their volatility distribution was not available.” This phrase will give readers the false impression that the volatility distributions of all other organic aerosol sources have been measured. The rationale requires revision. At the end of this paragraph (P668 L1), I believe the words “from the Tula complex” should be inserted before “were occasionally”

Given the critical importance of S/IVOC emissions to the conclusions of this study, the authors need to be crystal clear with their terminology and emissions treatment in the revised manuscript.

Miscellaneous technical comments

1. Some findings reported in the Abstract (P658) appear to be inconsistent with each other. On L17-19, the authors state that the addition of S/IVOCs enhances the modeled SOA concentrations by a factor of 3-6. Then on L26-28, they state that anthropogenic and biomass burning S/IVOCs represent only 40-60% of the total SOA. Can this apparent contradiction be resolved in the revised abstract?

2. In the Introduction (P660 L13-14), the authors state “Although activity coefficients are included in this formulation, they are typically set to 1 due to lack of constraints on their values.”

A casual reader may interpret this as a shortcoming of traditional OA models, but the authors make this same assumption in their study (see P666 L17). Perhaps this entire sentence should be omitted from the Introduction, since it does not add valuable

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content to the paragraph.

3. **Grieshop parameterization.** When describing this parameterization (P668 L21), the authors state that “No biomass burning emissions of IVOC are considered.” This is contradictory to Table 1 ($f_7 = 10\%$) according to the definition of IVOC provided by the authors (P666 L15). The authors also imply (P669 L1-2) that revised OH reaction rate constants are provided in Table 1, but they are not.

4. On P669 L6, the authors indicate that V-SOA forms from biomass burning. Which volatile organic compound(s) is this formation attributed to? Why isn't V-SOA formed from biomass burning in the traditional simulation (as implied from the lack of mention on P669 L11-13)?

5. **Computational requirements.** In a supplemental table, it would be very helpful of the authors to tabulate the full set of OA species that were added to CHIMERE for the present investigation. I gather from Hodzic et al. (2009) that 8 hydrophobic and 2 hydrophilic organic aerosol species were needed to simulate V-SOA in the REF simulation of the present study (presumably all 10 of these species were added in the gas phase as well as to each of the 8 particle size sections, yielding a total of 90 extra model species). How many more species were required to simulate the volatility distribution and O/C ratio of the modeled organic aerosol in this study? What was the computational expense of adding all these species?

References

Full citations for all papers referenced in this comment are provided by Hodzic et al. (*ACPD*, 2010).

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 657, 2010.

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