

Interactive comment on “Modeling secondary organic aerosol in an urban area: application to Paris, France” by F. Couvidat et al.

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Received and published: 5 December 2012

General Comments In this manuscript the authors used two related models to simulate SOA formation in Paris, for comparison with results of field measurements of OC and EC. SOA is simulated using the H2O (Hydrophilic/Hydrophobic Organic) model, which employs surrogate compounds to represent different classes of SOA species and accounts for the differences in partitioning of organic compounds to aqueous and organic phases. Simulations were conducted with the standard H2O model (H2O-Ref) and also with a modified version (H2O-Mech) that used a more molecular based approach to simulate aging of primary and aged SVOC. In general the model results agree well with the measurements. The paper is clearly written and the results are discussed in sufficient detail, with

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the authors providing reasonable possible explanations for situations when the results and measurements do not agree. The paper presents a useful evaluation of an approach to SOA modeling that is worthy of publication. The paper will be suitable for ACP once the following comments have been addressed.

Specific Comments 1. Table 1. Please explain why PAHs make up 30% of the primary SVOC emissions. This sounds incredibly high. It seems that this value is based on data from Schauer et al. (1999). Is this 30% value relative to the total mass of SVOC that was identified in their study or the total SVOC mass? Usually 80-90% of the total mass is present in an unresolved complex mixture that is dominated by branched and cyclic alkanes.

The speciation is based on the identified fraction of SVOC (14% of SVOC) and there is indeed a significant fraction of the unresolved complex mixture that is constituted of branched, cyclic alkanes and oxygenated aliphatics. However, according to the recent results of Isaacman et al. (Analytical Chemistry, 2012), there is also a significant fraction that is constituted of aromatics (27%) which correspond to the 30% of PAH in SVOC emissions.

The text has been modified to compare to the results of Isaacman et al. (2012):

"The speciation is based on the data of Schauer et al. (1999) on the identified fraction of SVOC from medium-duty diesel trucks (14% of SVOC). Molecules with similar properties (high, medium or low volatility) and type (acids, alkanes, polycyclic aromatic hydrocarbons (PAH)) are lumped into a single surrogate species. Isaacman et al. (2012) found that about 73% of SVOC above 15 carbons are aliphatic and 27% are aromatic. With the speciation used in this study, 70% of SVOC above 15 carbons are aliphatic and 30% are aromatic. The SVOC speciation used here is, therefore, consistent with the results of Isaacman et al. (2012)."

2. Page 23477, lines 12-13: The yields of products from reactions of aromatics with OH are generally dominated by ring-opened products containing aldehyde

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groups that should oligomerize, with intact aromatic products being a relatively small fraction. In addition, these ring-opened products are unsaturated and so react with OH radicals much faster than aromatic compounds and thus lead to rapid aging. Both of these factors are likely to lead to much more SOA than would be simulated with the H2O-Mech model.

The main goal of H2O-Mech was to estimate activity coefficients of primary SVOC and their oxidation products. A paragraph is added to clarify this point:

"The second type of mechanism called "H2O-Mech" uses a detailed treatment of primary and aged SVOC where a speciation of primary SVOC is used to attribute molecular structures to primary compounds and to estimate the formation of secondary organic aerosol by aging. The main goal of this mechanism is to attribute molecular structure to primary SVOC and their oxidation products to estimate their activity coefficients in the atmosphere with the UNiversal Functional group Activity Coefficient (UNIFAC) thermodynamic model (Fredenslund et al., 1975). The impact of activity coefficients on the partitioning of primary SVOC and their oxidation products are not taken into account in "H2O-Ref" whereas it is possible that POA and SOA have low affinities which each other (Pun, 2008; Song et al., 2007). With "H2O-Mech", the structure of primary SVOC and their oxidation products are known and it is, therefore, possible to estimate the impact of activity coefficients on their partitioning."

We agree that the aging mechanism could be improved but the goal of this mechanism is to attribute molecular structures to compute activity coefficients, and we try to keep the mechanism as simple as possible. The yields are probably wrong, because we also assumed that there is only one oxidation step (and therefore no further aging) and that there is no fractionation of SVOC (and therefore no ring opening for aromatics) to only lead to less volatile compounds. Moreover, taking into account oligomerization in the model would be difficult due to the lack of information.

The following paragraph has been added in the text:

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"This mechanism could be improved because it only takes into account one oxidation step, assumes that oxidation only leads to less volatile compounds and because aromatics oxidation products are mainly unsaturated ring-opened products containing aldehyde groups that should oligomerize and react rapidly leading to further aging. Nevertheless, the effect of a single-step aging on activity coefficients and on the interactions between POA and SOA can be estimated with this mechanism."

3. Page 23481lines 15-18: A little discussion of the criteria of performance quoted here would be helpful. What is the basis for these? Are they widely accepted?

Those criteria are widely used in the air quality modeling literature. The criteria of performance for ozone are used in most of ozone simulations. There are several criteria used for model performance for PM concentrations but the criteria of Boylan and Russell (2006) are among the most used criteria (Yu et al., Atmos. Sci. Lett., 2006).

4. The results regarding the sources of SOA in Figure 13 seem surprising. Recent results from the CalNex study in the Los Angeles area indicate that SOA is dominated by aromatic sources (Bahreini et al., Geophys. Res. Lett., 2010).

There are several reasons that can explain the low contribution of aromatics in Paris. One of the main reason could be that the French car fleet is dominated by diesel cars whereas the U.S. car fleet is dominated by gasoline car. As the emissions of aromatic compounds from diesel car are much lower than those from gasoline cars, it is not surprising that the concentrations of SOA from aromatics are significantly lower in France. Moreover, the meteorology of Los Angeles is very different from Paris. In the Los Angeles basin, episodes of high pollution tend to be associated with land-sea breeze conditions that lead to the accumulation of pollutants resulting from local emissions over several days. In Paris, the lack of natural geographic barriers leads to a greater contribution of long-range transports and, hence, a greater influence of biogenic emissions.

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Furthermore, I am not aware of other studies that have suggested that sesquiterpenes could be such a large source of SOA, especially in an urban area. Is there some reason why things should be so different in Paris?

According to Hodzic et al. (ACP, 2009), 30% of the organic aerosol over Mexico City was of biogenic origin and the regional contribution is 60% biogenic. In the case of Paris, the contribution of local emissions to SOA formation is weak (about 30%) and most of the organic aerosol is regional and therefore biogenic compounds have a strong contribution of SOA.

5. As a non-modeler I am always amazed at how good the agreement tends to be between models and ambient measurements, such as shown in Figures 4, 5, and 8. The modeling I have seen of chamber reactions involving a single compound and oxidant and very well controlled conditions rarely does as well. So this leads me to a question: To what extent were the many parameters and assumptions used in this modeling study adjusted to improve agreement with the ambient data, or was the modeling done completely “blind” and then compared with no further adjustments? This is not clear to me from the manuscript.

We used the same parameters as those used by Couvidat et al. (JGR 2012) for this modeling of PM over Europe. The parameters for the formation of SOA from the various precursors were fitted to reproduce the results of environmental chamber experiments were not changed during the subsequent air quality model simulations to improve agreement with measurements.

6. Some discussion regarding the likely sensitivities of the modeling results to the assumptions and parameters chosen for the study would be helpful.

The choice of the parameter used in this study for the H₂O-Mech mechanism are probably a minor source of uncertainties compared to the emissions, the meteorology and other parameters. There are already discussions on the mixing of SOA and POA and their interactions, which was the main point of using H₂O-Mech. For the influence of

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some other parameters, which were defined earlier during the original model development, discussions are already provided in Couvidat et al. (JGR 2012).

Technical Comments Page 23478, line 12: I think NO₃ is meant to be NO₂. No, it is NO₃ which can react with radicals under high-NO_x conditions.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 23471, 2012.

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