Atmos. Chem. Phys. Discuss., 12, C10199–C10204, 2012
www.atmos-chem-phys-discuss.net/12/C10199/2012/

Atmospheric Chemistry and Physics Discussions

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

This paper describes a modeling study of organic aerosol levels in Paris measured during the MEGAPOLI study. It describes the development and application of an updated scheme to simulate secondary organic aerosol (SOA) formation from semivolatile and intermediate volatility organic compounds (SVOC and IVOC) based on surrogate compounds. The predictions of the updated model are compared to a previous version which used a more empirical approach to simulate SOA from SVOC and IVOC. The performance of both models is also evaluated against field data. Both models do a reasonable job reproducing the measurements.

Overall I liked the paper. Given the lack of speciation data for SVOC and IVOC

emissions, there is value to exploring different surrogate based approaches. I recommend that the paper be published after the authors have addressed the following comments.

The proposed approach is significantly more complicated than a purely empirical scheme such as Grieshop et al. (which appears to be the basis of the reference model). In the end, both approaches appear to predict similar amounts of SOA (e.g. Figure 2). Is this agreement simply an artifact of fitting the rate constants for the non-alkanes surrogates to match the results (page 23477 line 17)?

We tried first to use a rate constant of 2 x 10-11 molecules-1.cm3.s-1 for non-alkanes surrogates and it gave fairly close results to those presented here with 3 x 10-11 molecules-1.cm3.s-1 . The latter value was selected in order to fit the results of Grieshop et al. For the first hours.

If you are fitting key model parameters of the surrogate model, what is the value of what is the value of this additional complexity? I am not arguing for the Grieshop approach (which has its own problems) but as a community we need to struggle with and justify the addition of complexity to these models. The paper would benefit from a discussion of these issues. What is the essential complexity that the model needs?

A discussion has been added to explain why we developed “H2O-Mech”

"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

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taken into account in “H2O-Ref” whereas it could be 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."

Assigning surrogates - This paper used the speciation data from Schauer to assign the surrogates. However, Schauer only speciated a small fraction of the low-volatile (SVOC and IVOC) emissions. The paper should explicitly state the percentage of emissions that were speciated. The paper should also do a better job justifying the assignments. Implicit in the approach is that the composition of the unspeciated is the same as the speciated component. That is unlikely to be true. For example recent work by Goldstein group suggests that most of the unresolved complex mixture is branched alkanes (Isaacman et al. Analytical Chemistry 2012). How would that alter the model predictions? It may not if key parameters have simply been fit to experimental data. However, branched alkanes have lower yields than aromatics.

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)."

Model Evaluation – The paper only uses organic and elemental carbon measurements made using filters or an in situ filter based approach. These data (provide relatively little constraints for the model. Did MEGAPOLI collect AMS, thermode-

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nuder or other data that would help differentiate between the different modeling approaches. E.g. AMS data might help differentiate between models based on O/C ratio.

There are AMS measurements available for the PM1 fraction. However, comparing the measurements of OM in PM1 with the AMS with the measurements of OC with filters and the sunset in PM2.5 is difficult. Therefore, we chose to use only those measurements in the PM2.5 fraction because of different size fraction. The temporal profile of AMS data seems closer to the temporal profile of the measurements with the Sunset field instrument. An inspection of the AMS data suggests are typically lower than those of the Sunset field instrument (using OM/OC=1.6), which is consistent with the PM1 vs PM2.5 cutoffs.

Minor comments Fitting emissions with measured data (page 23483, line 23). A challenge with this approach is that it assumes the model has captures the effects of meteorology and concentrations. That should be pointed out. Given the uncertainty in meteorology it seems like the fitted profile is likely no better than the TPM approach.

We agree that fitting a temporal profile implies making some assumption on the meteorology being correct and that the profile should not be taken to estimate emissions on any other period and that is probably better to use the TPM profile. Fitting the profile was, however, interesting to evaluate whether differences between the model and measurements may be due to errors in the temporal profile of emissions.

Effects of temperature on gas-particle partitioning (page 23484 line 17) – The paper hypothesizes that problems with temperature predictions may explain some of the problems with model performance during the morning rush hour. Recent data suggest that the sensitivity of POA to temperature is on the order of a few percent mass loss per K (Ranjan et al. AST 2012), which comparable to data for SOA. How much would the model predictions of temperature need to be off for

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this to be a plausible explanation. It seems like problems with emissions and/or boundary layer height are more likely than temperature problems.

The boundary layer height cannot explain why the morning peak is present for the EC concentrations but not for OC. But it is also true that the effect of temperature would be only of a few percent and cannot alone explain the presence of the morning peak. The statement has softened as follows: "It is also possible that the gas-particle partitioning of primary SVOC is strongly affected by temperature and that an underestimation of temperature during the morning rush hours could lead to a significant overestimation of POA." has been replaced by "It is also possible that the gas-particle partitioning of primary SVOC is affected by temperature and that an underestimation of temperature during the morning rush hours could lead to a slight overestimation of POA."

Page 23480 line 40 – typo ?Sciare Corrected.

Page 23480 Last paragraph beginning with "During the this Megapoli" Were the dynamic blanks run with the denuder? If so, it seems like the denuder is not operating very efficiently?

Indeed the dynamic blanks were running with the Sunset VOC denuder. Carbon impregnated strips of the VOC denuder were changed just before the beginning of the campaign. Such blank issues with the sunset field instrument have been widely reported in literature and associated with a breakthrough of the VOC denuder (Bae et al., 2004; Arhami et al., 2006; Polidori et al., 2006; Offenberg et al., 2008; d'Argouges, 2009).

Arhami, M., Thomas Kuhn, Philip M. Fine, Ralph J. Delfino, and Constantinos Sioutas, Effects of Sampling Artifacts and Operating Parameters on the Performance of a Semi-continuous Particulate Elemental Carbon/Organic Carbon Monitor, Environ. Sci. Technol., 2006, 40 (3), pp 945–954, DOI: 10.1021/es0510313

Bae MinSuk, Schauer JJ, DeMinter JT, Turner JR, Smith D, Cary RA. Validation of a

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semicontinuous instrument for elemental carbon and organic carbon using a thermal–optical method. Atmos Environ 2004;38:2885–93

D'Argouges, O., Mise en place d'une mesure rapide de la composition chimique de l'aérosol en zone urbaineÂă: Etudes en mégapoles, Thèse, Univ. Paris VII, November 2009

Offenberg, J.H., Michael Lewandowski, Edward O. Edney, and Tadeusz E. Kleindienst, Investigation of a Systematic Offset in the Measurement of Organic Carbon with a Semicontinuous Analyzer, Journal of the Air Waste Management Association. Vol. 57, no. 5, pp. 596-599, 2007

Polidori A, Turpin BJ, LimHo-Jin, Cabada JC, Subramanian R, Pandis SN, Robinson AL. Local and regional secondary organic aerosol: insights from a year of semi-continuous carbon measurements at Pittsburgh. Aerosol Sci Technol 2006;40:861–72

Page 23485 line 23 –Phase mixing of SOA and POA. It seems strange to invoke another modeling study to "prove" that there is not phase mixing. The published experimental data on this subject are mixed. (Song et al. GRL 2007 versus Asa-Awuku et al. GRL 2009)

"These results confirm the results of the modeling study of Pun (2008) in which she found that POA and SOA do not mix well together." has been replaced by "Those results are confirmed by experimental studies: POA and SOA were shown not to mix (Song et al., 2007) or to mix but with interactions between compounds inïňĆuencing the partitioning of SVOC (Asa − Awuku et al., 2009)."

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