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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Global modelling of secondary organic aerosol in the troposphere: A sensitivity analysis" *by* K.Tsigaridis and M. Kanakidou

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We would like to thank the reviewer for his/her suggestions that helped improving the paper and particularly the presentation of our results. Her/His comments have been taken into cosideration in the revised version of the manuscript as follows:

- Comparison with laboratory results. It is not the topic of the present paper to validate parameterizations derived from chamber experiments and already published in literature. It is even very difficult to have access to the full set of experimental data from chamber experiments with the time evolution of gaseous and particulate compounds that will allow to evaluate both the gas and particulate phase chemistry in the model. Most of the chamber experiments are not sufficiently documented for this purpose.

To address this point we have added at the end of section 2.2 the following discussion:

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"Note that the chemical lumping of VOC forming SOA precursors and their products is a source of large uncertainties (Pun et al., 2003) that requires systematic evaluation in the future on the basis of targeted experiments. Unfortunately, all requested information to evaluate the SOA formation parameterization in our model against chamber experiments is not available in the literature. Only the full set of experimental data from chamber experiments with time evolution of gaseous and particulate compounds can allow evaluation of both the gas and particulate chemistry in the model. The time evolution of the oxidant levels that deplete the VOC precursor molecules of the VOC levels and of the aerosol mass in the chamber is the minimum prerequisite for evaluation of the aerosol module."

- The importance of the secondary oxidation reactions. The following discussion has been added in the new section 3.4 addressing also the comments by Serena Chung: "This hypothesis is taken into account in case S1.3 and is not contradicted by the smog chamber experiments. Simple box model calculations considering the a- and b- pinene oxidation as described in section 2.2 have been performed using conditions close to Griffin et al. (1999a) experiments. They show that the calculated difference in the aerosol yield between S1 and S1.3 exceeds 2% after more than 10 hours. To our knowledge, most chamber experiments do not last long enough to detect these expected differences in the aerosol yield that are also within the uncertainty of the experimental data. However, this procedure might be important globally and in longer timescales and is therefore investigated here"

The global impact is discussed later on in the paper (text already in the ACPD published version) "Near the surface, taking into account the formation of the secondary condensable products, leads to higher SOA concentrations compared to the reference case. This happens because the second generation products are assumed to have higher partitioning coefficients, resulting in higher aerosol yield. On the contrary, in the upper troposphere a decrease of SOA concentration is calculated because of the condensation of the gas-phase condensable species at lower altitudes." (end of new section 5).

- Choice of scenarios for simulations. We do not provide any chemical explanation for the condensation of SOA that we assume that can occur also on the sulfuric and nitrate, ammonium particles. This is definitely a hypothesis that experimental data are needed to confirm or contradict. We consider that the ammonium and sulphate aerosol types are rather dissimilar from SOA and thus the Lamda value of 0.7 is used for calculating the activity coefficient on these particles. These simulations are described in section 3.1: "S1 considers only the condensation on carbonaceous aerosols, both organic and BC, while S3 assumes that condensation also occurs on sulphuric (sulphate and methanesulphonate) and ammonium aerosols, for instance by absorption. Note that BC consists both from graphitic carbon and organic material at percentages not precisely quantified. Therefore, in our study we include black carbon as an absorptive medium for SOA with decreased ability compared to the pre-existing SOA. This is parameterized using Lamda values of 0.7 (for hydrophobic BCins) to 0.8 (for hydrophilic BCsol) that is smaller than that of 1.0 adopted for SOA (Eq. 19; Table 2). For ammonium and sulphate aerosol types the Lamda value of 0.7 is used."

- The no-evaporation scenarios (S2 and S4) The no-evaporation label for the scenarios S2 and S4 is rather misleading. Thus in the revised version we use the "irreversible sticking onto aerosols". It is now clarified in section 2.3: "If the semi-volatile organics undergo chemical or physical processes on particles (e.g. chemical reactions to form non-volatile compounds and/or inhibition of evaporation by other non-volatile components on the particle), the evaporation of SOA is being suppressed. It is expected that some reactions or other irreversible sticking mechanism do occur on the particles but they do not necessarily transform the total amount of SOA to non-volatile. In that case by neglecting evaporation from the particles, an upper limit of the SOA production can be calculated and the equilibrium equation is applied only to the gas phase of the semi-volatile compounds."

S1 and S3 consider that the semi-volatile products can evaporate from the particles whereas in S2 and S4 irreversible sticking is assumed to occur on the particles. (sentence added in section 3.1)

- The SOA partitioning algorithm for these scenarios should be explained. In the present study, the iterative solution for Mo is calculated based on the bisectional method. The number of iterations depends on Mo and on the relative error allowed that is prescribed to be 1% and not larger than 10 ng m-3. (text added in section 2.3).

- The sensitivity to the primary organic aerosol emission should be tested. A new simulation S1.6 with double primary carbonaceous emissions has been added (Table 5 and Table 6), it is presented in section 3.1 and discussed in the budget calculations (section 4) and the comparison with measurements (new section 6).

- The importance of the treatment of the removal processes should be discussed a little more. Two more case studies (S1.7 and S1.8) have been added and discussed in sections 3.3, 4 and 6 to satisfy both ref#1 and ref#2 see reply to ref#1 comment on the importance of the hydrophobic to hydrophilic conversion of primary carbonaceous aerosol.

- Presentation of the sensitivity analysis results. The discussion is restructured as suggested also by ref #1 by focusing first on Table 6 results, ranking the uncertainty factors and then getting in more details- vertical distribution - comparison with observations.

- Several figures can be deleted to reduce the length of the paper The number of figures and panels in the individual figures has been reduced: We decided to keep figure 3 because the contribution of the biogenic relative to the anthropogenic SOA is clearly depicted there. The February distributions have been removed from Figure 4 (old figure 5) since comparison between Feb and Aug is shown in Figures 3 (horizontal distribution) and 5 (vertical distribution- old fig.4). Figure 6 has been kept in the revised version since it points to the effect of temperature on the vertical distribution of SOA that is also a major factor of uncertainty in the model calculations. Figure 7 has been removed. Figures 6 and 7 (old figure 8) depict only the August panels. Old figures

9 and 10 have been deleted. The old figure 12- now figure 9 has been modified as follows: Panel (a) shows the comparison of overall range of the model results for all studied cases outlined in Table 4 with the observations on OA. Panel (b) depicts the model results for the case S1.8 (no hydrophobic-to-hydrophilic conversion of POA) and compares them to the observations. Panel (c) is giving the range of calculated ratio of SOA to OA ratios for all the data shown in panel (a). These last two panels have been added to elucidate the discussion session.

- Table 6 and the discussion in the text are sufficient for the presentation of the results. We believe that information on how the vertical distribution of the OA is affected by the different factors of uncertainty is a rather interesting issue for climate studies and deserves to be highlighted as also mentioned by ref #1 and we kept in the manuscript the highlights of this information.

- Synthesis. The conclusion has been rephrased to provide synthesis of the results and recommendation for future research addressing also ref#1 comment.

- The authors could use the comparison with the observations here to say something more about the different scenarios despite the uncertainty of the primary OC emissions. Already in the ACPD version of the paper there was already a statement in the abstract that "Comparison of model results to observations, where available, shows a better agreement for the upper budget estimates than for the lower ones". We realise that this was not clearly stated in the discussion of the results. Discussion in section 6 has been modified as follows: "To analyse the differences between calculated and observed OA concentrations, the rural, marine (coastal) and open ocean data have been distinguished in Figure 9a with different colours. The areas where the model predicts too low OC concentrations are mainly remote marine areas, suggesting either that the model might have very high removal of organic aerosols or that condensation on sea-salt aerosol (not taken into account in our study) might be of importance for these areas or that an oceanic source of organic particles is missing. Indeed, neglecting the hydrophobic to hydrophilic conversion of primary organic particles the removal of the aerosols from the atmosphere is reduced and the corresponding comparison between calculated and observed organic aerosol data is improved (case S1.8, Figure 9b). For all simulations the least square correlation coefficient r2 ranges between 0.45 and 0.53 (n=40) with slopes from 0.69 to 0.96 (case S4 simulates best the measurements). Case S1.6 (with double primary carbonaceous aerosol emissions) overestimates the high rural data since the corresponding slope is 1.26" and further: "Figure 9c presents the SOA/OA ratio as a function of the OA observations and supports that indeed SOA can be more than 50% of the total organic aerosol in many cases and up to 90%. Thus, discrepancies between modelled and observed organic aerosols can be partially due either to high SOA removal by wet deposition or too low SOA chemical production, or both." Figure 9 has been modified to provide information on location of the measurements presented and compared to the model results (see above comment on the number of figures).

- Numerics. Information has been added in section 2.3 to satisfy also ref #1 relevant comment.

- BC data. We do agree with the reviewer, the corresponding discussion has been modified as follows: "All models seem to capture the order of magnitude of the BC data. Note that the scale in this figure is logarithmic and unfortunately no statistically significant correlation can be derived from this comparison."

- May be providing some statistics of the performance instead of a qualitative statement would help. Statistics on the performance of the model for the OA simulations are now given in section 6 (see point on comparison of OA model calculations to observations).

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 2879, 2003.

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