Atmos. Chem. Phys. Discuss., 7, S5970–S5976, 2007
www.atmos-chem-phys-discuss.net/7/S5970/2007/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Secondary organic aerosol in the global aerosol – chemistry transport model Oslo CTM2" *by* C. R. Hoyle et al.

C. R. Hoyle et al.

Received and published: 13 October 2007

We would like to thank the reviewer for their suggestions for the improvement of this manuscript.

The model does appear to produce higher organic aerosol values in the upper troposphere than that of Tsigaridis2003 or Chung2002. We aim to carry out comparisons with aircraft measurements in the future, however we believe that this would be best included in a more specific publication. To make a meaningful comparison with aircraft measurements we need to obtain flight path information and use this to control model output during a simulation for the specific period of the measurement campaign, which is a large undertaking.

With regard to a comparison with SOA measurements, we are not aware of suitable non-urban studies which report SOA fractions of total organic aerosol. If the reviewer has particular data sets in mind, we would be interested in carrying out this comparison.

1) Page 9056, line 6: This paragraph now reads: "Some classes of compounds included in anthropogenic emissions are capable of forming SOA upon oxidation in the atmosphere. These include toluene, xylene and trimethylbenzenes. The contribution of these species to global SOA budgets has been evaluated by Tsigaridis2003 as well as Lack2004, and found to be a minor fraction (approximately 2-6%, and 5-8% respectively) of the contribution from naturally emitted precursors."

2)Page 9056, lines 13-18: The fact that VOC are being oxidised in these studies does not mean that semi-volatile compounds are being produced, however there is some evidence from chamber studies that this does occur. The following sentence has been added to the paragraph: "Chamber experiments also show that the oxidation of several monoterpene species by NO_3 can lead to SOA formation Griffin1999a,Bonn2002,Spittler2006."

3) We agree that deposition on land and water should be differentiated in the model and this is something that we aim to improve in the future. In the present study we do not believe that it will have a significant impact on the results however, as the vast majority of organic aerosol is present over the continents. Additionally, most of the organic aerosol is hydrophilic, and the aging of hydrophobic aerosol is fairly rapid. The deposition of gas phase species is calculated using a deposition velocity approach, and is dependent on the surface type. More general details of the model can be found in Flatlandsmo2004.

4)Page9063, line 26 The description of increased SOA from aromatics has now been shifted together with that from isoprene.

5)Page 9066 lines 21-22 The study by Tsigaridis2003 considered, among other things, irreversible condensation, and we assume that it is this to which the reviewer is referring. We have included the following text in the paper to clarify the difference between our experiment and that of Tsigaridis2003. “The effect of irreversible condensation of SOA was considered by Tsigaridis2003, who found it lead to a 516% increase in SOA production. However, even if the condensation of SOA is considered to be irreversible, this will not lead to a partitioning of the entire semi volatile mass into the aerosol phase, as described here (this is demonstrated by the increase in SOA production reported by Tsigaridis2003 when condensation onto sulphate and ammonia aerosols, as well as irreversible partitioning is considered.)”.

6) The reason we did not use a finer temporal resolution for the EMEP data was that the data are from 2002-2003, and the model run was performed for 2004. Differences in biomass burning emissions and meteorological factors could have a large influence on the data on short time scales. We have, however, now plotted seasonal means of the EMEP data against the same values from the model, for summer and winter, and found that the model may represent the EMEP data slightly better in the summer. We have also included a scatter plot of the IMPROVE data vs model data for all days on which measurements were made. With the increased time resolution, one sees that the model actually represents the measured data reasonably well on many days.

7) This is an uncertainty which to some degree is associated with all measurement sites, when one works with a global model. It is simply not possible to entirely represent terrain features and localised meteorological features with a model resolution of 2.8×2.8. As it is nevertheless necessary to carry out these comparisons, the only option is to point out to the reader that these effects may influence the comparison. We avoid quantitative comparisons with sites where it is clear that the model has no chance to reproduce the results (e.g those situated in isolated industrialised areas). We have kept two sites in the comparison (Ispra and Nanjing) which are located within

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

large areas with elevated anthropogenic emissions, as it is interesting to see how well the model represents the difference between these and rural sites.

8)The reviewer is correct, this may be an additional source of the underestimation. The sentence has been modified to “This indicates that the cause of the underestimation does not lie with the partitioning of SOA between gas and aerosol phase, rather that emissions of precursors or POA may be too low (including the possibility of SOA precursors which are yet to be identified), or that loss processes in the model may be too fast.”

9)We have actually removed this statement, as pointed out by one of the other reviewers, due to the uncertainty in the aging and the solubility of POA, the fact that the model represents sulphate aerosol well does not mean that the wet deposition works well for organic aerosol.

10) We agree with the reviewer that it would be best not to use the yield for β-pinene reaction with NO_3 for all species. We have performed an additional experiment with yields from Spittler2006, and find that the significance of NO_3 for SOA formation is reduced, however still significant (the global annual mean contribution of NO_3 reduces from 27% to about 21%). This experiment is described in section 4.2 of the manuscript. We find that in polluted regions, towards evening, the concentrations of NO_3 increase rapidly as the sun sets, and that if this increase begins before the emissions of monoterpenes cease, there is a short period of overlap where the oxidation of monoterpenes by NO_3 is by far the major source of condensible products. As the concentrations of monoterpenes and NO_3 change rapidly during this time, the amount of oxidation by NO_3 is sensitive to the exact timing of the increase in NO_3. This is also discussed in section 4.2.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

EGU

11) We think the model does a reasonable job of representing NO_3. We agree with the reviewer that one needs to take care comparing model grid box values with point measurements of NO_3, but unfortunately this is the only possibility for a comparison of NO_3 with measurements.

12) See point 10.

13) Added “or both” to the end of the sentence.

14) We have given each of the footnotes a separate line, however, as figure captions are to be above the tables, we leave it to the typesetter whether the notes should be above or below the tables.

15)A factor of 1.6 was used, the caption of table 2 has been edited accordingly.

16) We agree with the reviewer that using the same E/R values for all classes is not an ideal approach, however, as a starting point, leaving the general details of the SOA scheme as in Chung2002 enables us to examine the effect of differences such as the inclusion of more precursors, and the underlying model on the SOA values. With respect to the different temperature dependence of α-pinene and β-pinene oxidation by NO_3, when significant concentrations of NO_3 are reached, in the evening and at night, OH concentrations are low, and as the reaction with NO_3 is much faster than with O_3, some uncertainty in the rate will not make a significant difference to the relative amounts of terpene oxidised by O_3 or NO_3. We do however aim to improve our SOA scheme in the future. The following text has been included in the manuscript “ The use of the same E/R values for the calculation of reaction rates in all classes may introduce some uncertainty, as the temperature dependence of the reaction rates will vary for different species, however this approach simplifies the chemistry scheme in the model and allows us to compare our results better with those of Chung2002."

17)Table 4 We thank the reviewer for pointing out the bad phrasing in this caption. We did of course mean that in our model SOA from the isoprene + O_3 reaction is considered insignificant, however the oxidation of isoprene by O_3 is accounted for. The table caption has been changed.

18) We meant that the partitioning coefficient for isoprene was given for 295K, not 298K like the others. This caption has been reworded.
19) We have removed this station from the table.

References

[Berglen et al.(2004)Berglen, Berntsen, Isaksen, and Sundet] Berglen, T. F., Berntsen, T. K., Isaksen, I. S. A., and Sundet, J. K.: A global model of the coupled sulfur/oxidant chemistry in the troposphere: The sulfur cycle, J. Geophys. Res., 109, doi:10.1029/2003JD003948, 2004.

[Bonn and Moorgat(2002)] Bonn, B. and Moorgat, G. K.: New particle formation during a- and b-pinene oxidation by O_3, OH and NO_3, and the influence of water vapour: particle size distribution studies, Atmospheric Chemistry & Physics, 2, 183–196, 2002.

[Chung and Seinfeld(2002)] Chung, S. H. and Seinfeld, J. H.: Global distribution and climate forcing of carbonaceous aerosols, J. Geophys. Res.-Atmos., 107, doi:10.1029/2001JD001397, 2002.

[Griffin et al.(1999)Griffin, Flagan, and Seinfeld] Griffin, R. J., Flagan, R. C., and Seinfeld, J. H.: Organic aerosol formation from the oxidation of biogenic hydrocarbons, J. Geophys. Res., 104, 3555–3568, doi:10.1029/1998JD100049, 1999.

[Lack et al.(2004)Lack, Tie, Bofinger, Wiegand, and Madronich] Lack, D. A., Tie, X. X., Bofinger, N. D., Wiegand, A. N., and Madronich, S.: Seasonal variability of secondary organic aerosol: A global modeling study, Journal of Geophysical Research (Atmospheres), 109, doi:10.1029/2003JD003418, 2004.

[Spittler et al.(2006)Spittler, Barnes, Bejan, Brockmann, Benter, and Wirtz] Spittler, M., Barnes, I., Bejan, I., Brockmann, K. J., Benter, T., and Wirtz, K.: Reactions of NO_3 radicals with limonene and α-pinene: Product and SOA formation, Atmospheric Environment, pp. 116–127, 2006.

[Tsigaridis and Kanakidou(2003)] Tsigaridis, K. and Kanakidou, M.: Global modelling of secondary organic aerosol in the troposphere: A sensitivity analysis, Atmos. Chem. Phys., 3, 2879–2929, 2003.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 9053, 2007.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper