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Atmospheric
Chemistry
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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.

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We thank the reviewer for their helpful comments and suggestions. Each point is addressed below.

Pg 9055 ln 29: Removed Tsigaridis2003 from the publications listed in this sentence.

The subsequent paragraph has also been edited and now reads as follows:
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, and found to be a minor fraction (approximately 2-6%)

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of the contribution from naturally emitted precursors. Tsigaridis2005 evaluated the natural variability of the chemical production of SOA over a decade and found this to be equal to the formation of SOA from oxidation of anthropogenic VOC (8%).

Pg 9056 ln24-25 Although much of the work presented here has been addressed in previous studies, it is a useful to repeat these experiments with a different model. The fact that the production and burden are rather different from that of Chung2002, despite the use of a similar SOA scheme shows that the results depend to a large degree on the underlying global model, and processes such as transport, chemistry and deposition. Secondary organic aerosol formation is influenced by the existing organic aerosol mass and through this feedback, sensitivity to differences in temperature, transport, chemistry and deposition is enhanced. The effect of smaller yields of NO_3 oxidation of monoterpenes has also been investigated.

The statement about reducing the uncertainty has been changed to reflect the above discussion.

Pg 9058 The studies which we have cited, referring to the light dependent emission of monoterpenes, include in addition to beech and several other European species, species found in the Amazonian forest. As this region, together with southern Africa (where there is also evidence for a significant light control of monoterpene emissions Otter2003,Greenberg2003), accounts for the greatest portion of emissions, we chose to limit the monoterpene emissions to the day time. This should be an accurate representation for broad leaf species. Coniferous species have storage ducts for monoterpenes, enabling some emissions after dark, when monoterpenes are no longer produced, and emissions from these ducts underlie a temperature control. However, emissions of monoterpenes from many of these species have also been observed to respond to changes in light Kesselmeier1999 and it is beyond the scope of the present study to construct an emissions scaling scheme where the distribution and relative abundance of plant species are taken into account. The effects of such a scheme on the SOA burden in different areas would be an interesting topic for subsequent research though.

The section now reads:
"The emissions of monoterpenes have been previously modelled by an equation which does not take into account a light dependence Guenther1995. Recently a number of studies have shown that monoterpene emissions from many species do in fact exhibit a strong dependence on light, with negligible emissions taking place during the hours of darkness Kesselmeier1999,Kuhn2002,Otter2003,Greenberg2003,Moukhtar2005,Dindorf2006. Further, it has been shown during studies in the Amazon Kuhn2002, southern Africa Greenberg2003 and in Europe Dindorf2006, that the emissions of monoterpenes from many species may be modelled in the same way as isoprene emissions.

Here we apply the equation given by Guenther1995 to represent the temperature dependence of isoprene emissions, to scale both isoprene and monoterpene emissions, Eq.(1). Although this will not be correct for all species of plants, we believe that the majority of global emissions will be accurately represented in this way, and this represents a first step towards a better temporal integration of biogenic VOC emissions from inventories in the OsloCTM."

Pg 9059: Light sensitivity is not treated as a function of solar elevation angle, the solar elevation angle is simply used as an on off switch. As there are many factors which may affect the amount of light reaching plants (clouds, shadows from topography etc), it would be difficult to represent this in a global model, therefore we have decided, for simplicity's sake, not to take light variations during the day into account. This is justifiable given the model grid resolution, and the 1 hour time steps used for

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emissions, and the overall uncertainty in the actual emissions and their distribution. We believe that the temperature scaling used to distribute the emissions during the day time is a good first approximation.

Pg 9059 ln 18-19: SOA formation from gasoline vapour was discussed by Odum1997, who showed that the oxidation products of trimethylbenzene and several other aromatic species will also form SOA. We use the “other aromatic species” emissions to represent possible SOA precursors the emissions of which are too low to justify explicit representation in the model. This sentence in the manuscript now reads:“In Oslo CTM2, emissions of trimethylbenzene are added to the m-xylene tracer, as these species have similar aerosol forming properties Odum1997. Emissions of "other aromatic species” are added to the toluene tracer. This latter lumping is necessary to reduce the number of species which the model needs to transport and react. Considering the lack of species specific data for emissions, oxidation and partitioning, as well as the low total mass represented by the “other aromatic species” category, this lumping is justifiable, and will not significantly affect the results”.

Section 2.4: A scaling factor of 1.6 was used to convert OC fossil fuel and biofuel combustion OC to organic matter (OM) Turpin2001,Yttri2007. This information has been added to the manuscript.

Section 2.5 : We use mass based stoichiometric coefficients, and are only interested in the mass concentration of the products, therefore the choice of molecular masses does not influence the results.

Table 4: The reaction rates for toluene and xylene are from Atkinson1994, as was used by Tsigaridis2003 and that for isoprene and OH is from Atkinson1990. This

information has now been added to the table caption. Also the misleading sentence "reaction with O_3 or NO_3 was ignored" has been altered to "in this model, reaction products from reaction with O_3 or NO_3 do not contribute to SOA."

Table 5 and 6: Citations added to manuscript. The coefficients for Class I-V species are from Chung2002, while those for Toluene and Xylene are from Tsigaridis2003, and the coefficients for Isoprene are from Henze2006.

Table 7: Citations added to manuscript. The Henrys law coefficients for all the biogenic species are fromChung2002, those for the other species are from Tsigaridis2003.

Section 3: The following text has been added to the manuscript: "A similar study was carried out by Tsigaridis2003, where the effect of SOA adsorption into sulphuric and ammonium aerosols was investigated. They found that the total SOA production increased from 7.47Tgyr^{-1} to 14Tgyr^{-1},an increase of around 87%, if reversible uptake is assumed, as it is here. This is substantially larger than the 25% increase between R_1 and R_{sulf}. Adsorption into sulphuric and ammonium aerosols caused the fraction of the total production due to anthropogenic SOA precursors to increase from about 3.8% to 5.3% in Tsigaridis2003".

Section 3.1: We have performed the suggested sensitivity experiment with a 1.15 day aging time for hydrophobic POA, and found that the effect on SOA production and burden is minor. A new section has been added to the manuscript describing the differences in the zonal mean, annual mean fields of POA and SOA. We find that the burden of POA in Chung2002 is rather higher than in our work, due to the greater emissions in the dataset of Liousse1996 which was used by Chung2002 (approximately 80 Tg/yr vs 35 Tg/yr). The area weighted, annual, global mean SOA

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burden at the surface, is about 12% greater in our work than in that of Chung2002 due to the additional precursors and higher contribution of NO_3 to precursor oxidation (which leads to higher SOA yields). This difference in SOA concentration increases to about a factor of 2 with increasing altitude. This is likely due to a more rapid convective transport of condensible products to the colder regions of the upper troposphere, in the OsloCTM2, and contributes to the higher SOA production values. Horizontal diffusion of SOA and the gas phase precursors (especially towards the high northern latitudes) is more limited in the OsloCTM, which helps to push more SOA into the condensed phase, especially near the surface.

Section 3.1: The experiment where all SOA partitioned to the aerosol phase was actually performed by setting the partitioning coefficients to 1×10^{15}, not, as stated in our original text, by increasing the POA, although the effect is the same (see equation 5). The total burden increased to 2.1 Tg and the production was 178 Tg/yr.

pg. 9065, ln 4-5, We believe the reviewer is correct, the greater enhancement of anthropogenic SOA over natural SOA is indeed a result of the co-location of the ammonium sulphate aerosol source and the sources of the anthropogenic SOA precursors. This text has been added to the manuscript.

pg. 9065, ln 22 The following explanation has been added to the manuscript:
As allowing SOA to partition to ammonium sulphate aerosols changes the distribution of the SOA burden, the increase in SOA lifetime between R_1 and R_{sulf} may be explained by an increase in the SOA burden in mid latitude (industrialized) areas where the wet deposition is not as active as in the tropics.

pg.9066 ln 13 This sentence has now been changed:

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“ The modelled values were interpolated to the latitude and longitude of the station and a mean was calculated over the same days as for the measurements, using data from the model level with an altitude closest to the altitude of the measurements.”

p.g.9067: The following text has been added:
"All the sites except Ispra and Nanjing are rural or background sites, and the latter two sites are included here as they are located in large industrialized agglomerations, where the modelled aerosol levels should be elevated.”
We have also added this information to the figure caption.
Additionally, the following text has been inserted:”The modelled OA at the Ispra site is only the sixth highest value for the set of European stations, whereas it is clearly the highest among the measured data, obviously the model grid is too coarse to resolve this area of high emissions.”
And:” It is interesting to note the increase in modelled SOA between the background stations of Gosan and Fukue, and the Nanjing station is less than a factor of two, this indicates that despite the widespread sources in the region, suburban SOA levels remain higher than the model can predict.”

We have removed the comparison with measurements from Lahore, they are probably not representative of background values.

The IMPROVE measurements are all from stations in national parks or the like.
The EMEP stations are all “rural background” or “natural background” stations, apart from Ispra which is described as "near city background” Yttri2007

Gosan and Fukue island should be representative of background conditions:
"Gosan is [a] representative background site in Korea”Han2005
There are no large industrial areas on Fukue island, and during the study from which

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the data from Fukue island are taken, the wind was mostly from the north west Takami2005, i.e. air reaching the sampling site was not crossing the island, therefore this can also be considered a background site.
The data for Nanjing was collected at Purple Mountain Observatory, which is indeed a suburban site, however, as it is located in a huge industrial agglomeration, it is interesting to see how well the model represents this point.
Aboa is a remote site.

Pg.9068 ln 7. We believe that missing SOA formation mechanisms can be ruled out, since even the values for R_{max}, where all semi-volatiles condense, are too low. The main loss of the precursors is oxidation to condensible semi-volatiles, so in the R_{max} run, it is really not possible to form any more SOA from the emitted precursors. An underestimation of condensible oxidation product yields from chamber studies would also contribute to the low modelled SOA values.

Pg 9068 ln 10-11:
Due to different hydroscopicity of OA and sulphate aerosol, this was not a good comparison. The text about the validation of wet deposition with ammonium sulphate aerosol has been removed and replaced with “ or loss processes in the model, such as wet deposition may be too fast.”.
The following text has been added to the conclusion:
“These results suggest that there may be unaccounted for sources of POA, or SOA precursors, although a too-rapid removal of OA from the model atmosphere as well as uncertainty in the SOA yields from the oxidation of precursors may also contribute.”

Section 4. The discussion of oxidation by NO_3 has been extended. The large contribution of NO_3 comes from the period of the evening where NO_3 concentrations are rapidly increasing, especially in relatively polluted air masses, and monoterpene emissions have not yet ceased. We have performed an additional model experiment

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with lower yields for NO_3 oxidation of alpha pinene (0.16), and limonene (0.4) Spittler2006, and find that the effect of NO_3 is far lower, but still significant. The timing of the decrease in monoterpene emissions and the increase in NO_3 concentrations is important in determining the oxidation contribution of NO_3, as the gradient of the concentration of both species is very steep near sunset.

Pg 9070, ln 22. Replaced “Despite this improvement” with "Despite the improved agreement”.

References

[Atkinson(1990)] Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds: a review , Atmospheric Environment Part A-General Topics, 24, 1–41, 1990.

[Atkinson(1994)] Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds, J. Phys. Chem. Ref. Data, Monogr. 2, 1–216, 1994.

[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.

[Dindorf et al.(2006)Dindorf, Kuhn, Ganzeveld, Schebeske, Ciccioli, Holzke, Köble, Seufert, and Kesselmeier] Dindorf, T., Kuhn, U., Ganzeveld, L., Schebeske, G., Ciccioli, P., Holzke, C., Köble, R., Seufert, G., and Kesselmeier, J.: Significant light and temperature dependent monoterpene emissions from European beech (Fagus sylvatica L.) and their potential impact on the European volatile organic compound budget, J. Geophys. Res.-Atmos., 111, doi:10.1029/2005JD006751, 2006.

[Greenberg et al.(2003)Greenberg, Guenther, Harley, Otter, Veenendaal, Hewitt, James, and Owen] Greenberg, J. P., Guenther, A., Harley, P., Otter, L., Veenendaal, E. M., Hewitt, C. N., James, A. E., and Owen, S. M.: Eddy flux and leaf-level measurements of biogenic VOC emissions from mopane woodland of Botswana, Journal of Geophysical Research (Atmospheres), 108, 2–1, doi:10.1029/2002JD002317, 2003.

[Guenther et al.(1995)Guenther, Hewitt, Erickson, Fall, Geron, Graedel, Harley, Klinger, Lerdau, McKay, Pierce, Scholes, Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873–8892, doi:10.1029/94JD02950, 1995.

[Han et al.(2005)Han, Moon, Kong, Lee, Kim, and Kim] Han, J. S., Moon, K. J., Kong, B. J., Lee, S. J., Kim, J. E., and Kim, Y. J.: Seasonal variation of chemical composition in fine particles at Gosan, Korea, Environ. Monit. Assess., 107, 221–237, 2005.

[Henze and Seinfeld(2006)] Henze, D. K. and Seinfeld, J. H.: Global secondary organic aerosol from isoprene oxidation, Geophys. Res. Lett., 33, doi:10.1029/2006GL025976, 2006.

[Kesselmeier and Staudt(1999)] Kesselmeier, J. and Staudt, M.: Biogenic Volatile Organic Compounds (VOC): An Overview on Emission, Physiology and Ecology, J. Atmos. Chem., 33, 23–88, 1999.

[Kuhn et al.(2002)Kuhn, Rottenberger, Biesenthal, Wolf, Schebeske, Ciccioli, Brancaleoni, Frattoni, Tavares, and Kesselm Kuhn, U., Rottenberger, S., Biesenthal, T., Wolf, A., Schebeske, G., Ciccioli, P., Brancaleoni, E., Frattoni, M., Tavares, T. M., and Kesselmeier, J.: Isoprene and monoterpene emissions of Amazônian tree species during the wet season: Direct

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and indirect investigations on controlling environmental functions, J. Geophys. Res.-Atmos., 107, doi:10.1029/2000JD000303, 2002.

[Liousse et al.(1996)Liousse, Penner, Chuang, Walton, Eddleman, and Cachier] Liousse, C., Penner, J. E., Chuang, C., Walton, J. J., Eddleman, H., and Cachier, H.: A global three-dimensional model study of carbonaceous aerosols, J. Geophys. Res., 101, 19 411–19 432, doi:10.1029/95JD03426, 1996.

[Odum et al.(1997)Odum, Jungkamp, Griffin, Flagan, and Seinfeld] Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Flagan, R. C., and Seinfeld, J. H.: The Atmospheric Aerosol-Forming Potential of Whole Gasoline Vapor, Science, 276, 96–99, 1997.

[Otter et al.(2003)Otter, Guenther, Wiedinmyer, Fleming, Harley, and Greenberg] Otter, L., Guenther, A., Wiedinmyer, C., Fleming, G., Harley, P., and Greenberg, J.: Spatial and temporal variations in biogenic volatile organic compound emissions for Africa south of the equator, Journal of Geophysical Research (Atmospheres), 108, 41–1, doi:10.1029/2002JD002609, 2003.

[S.Moukhtar et al.(2005)S.Moukhtar, Bessagnet, Rouil, and Simon] S.Moukhtar, Bessagnet, B., Rouil, L., and Simon, V.: Monoterpene emissions from Beech (Fagus sylvatica) in a French forest and impact on secondary pollutants formation at regional scale, Atmos. Environ., 39, 3535–3547, 2005.

[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.

[Takami et al.(1995)Takami, Miyoshi, Shimono, and Hatakeyama] Takami, A., Miyoshi, T., Shimono, A., and Hatakeyama, S.: Chemical composition of fine aerosol measured by AMS at Fukue Island, Japan during APEX period, Atmos. Environ., 39, 4913–4924, 1995.

[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.

[Tsigaridis et al.(2005)Tsigaridis, Lathière, Kanakidou, and Hauglustaine] Tsigaridis, K., Lathière, J., Kanakidou, M., and Hauglustaine, D. A.: Naturally driven variability in the global secondary organic aerosol over a decade, Atmos. Chem. Phys., 5, 1891–1904, 2005.

[Turpin and Lim(2001)] Turpin, B. J. and Lim, H.-J.: Species contributions to PM2.5 mass concentrations: revisiting common assumptions for estimating organic mass, Aerosol Science and Technology, 35, 602–610, doi:10.1080/02786820119445, 2001.

[Yttri et al.(2007)Yttri, Aas, Bjerke, Ceburnis, Dye, Emblico, Facchini, Forster, Hanssen, Hansson, Jennings, Maenhaut, Pu
Yttri, K. E., Aas, W., Bjerke, A., Ceburnis, D., Dye, C., Emblico, L., Facchini, M. C., Forster, C., Hanssen, J. E., Hansson, H. C., Jennings, S. G., Maenhaut, W., Putaud, J. P., , and Tørseth, K.: Elemental and organic carbon in PM_{10}: a one year measurement campaign within the European Monitoring and Evaluation Programme EMEP, Atmos. Chem. Phys. Discussions, 7, 3859–3899, 2007.

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