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Atmospheric
Chemistry
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Discussions

Interactive comment on "Combined effects of surface conditions, boundary layer dynamics and chemistry on diurnal SOA-evolution" *by* R. H. H. Janssen et al.

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We would like to thank Referee #2 for the constructive and helpful remarks on our manuscript. We will revise the MS according to these comments as described below:

General Comments: The manuscript presents a new model that combines land surface conditions, boundary layer dynamics and chemistry and the authors use it to describe the contributions of these factors to the diurnal evolution of organic aerosol. The authors evaluate the model for a case study in the boreal forest of Finland. This work shows the importance of entrainment in the budget of organic aerosol and

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suggests that to adequately interpret the diurnal evolution of organic aerosol the land surface, boundary layer dynamics, chemistry and free tropospheric conditions all need to be considered. It is unfortunate that there is not a more direct comparison between measurements and the model (owing to a lack of measurements) but the paper is clear, well written and is appropriate for publication in Atmospheric Chemistry and Physics once the authors have addressed the following comments below.

We agree with both referees that a comparison with a more complete data set would have been favorable. We looked for the most complete data set available in terms of above-canopy observations of dynamics, gas-phase chemistry and organic aerosol. Indeed, for that purpose the HUMPPA-Copec campaign would provide a good opportunity. However, when we set up this study the data from that campaign were not yet available. In a follow-up study, we plan to use data from HUMPPA and other recent campaigns.

Note, however, that although a lot of campaigns are already including more meteorological data, there is still information that is missing (also in the HUMPPA campaign). As our study suggests, the concentration jump at the interface of the BL and the FT are key to help the further evaluation of the gas phase species and aerosol-concentrations. Another key variable that is usually not measured continuously is boundary layer height.

The authors demonstrate the sensitivity of the model to land surface conditions and subsidence but I wonder about the sensitivity of their results to uncertainities in the chemistry of SOA formation from the terpenes. The reaction rates, yields and gas to particle partitioning of the subsequent products have large uncertainties - what affect do these factors have on the results, please comment?

Indeed, the uncertainties in the SOA formation from terpenes could affect the calculated SOA-formation.
For the case study entrainment dominates, and drives the strong decrease of Coa during the day which is also observed in the measurements. More/less production will not change this conclusion qualitatively, since the chemical term will always remain positive.
The sensitivity analyses basically show the competing effects of entrainment and chemistry on Coa-evolution. Also here an increase/decrease in SOA production may change exact numbers and the position of the limits of e.g. the entrainment- and chemistry driven regimes, but not qualitatively.
In addition, we already reported a weak sensitivity of Coa to varying OH-concentrations (see Sect. 3.1), which has a similar effect as changing the reaction rate of the TERP + OH reaction.

The authors refer to one of the oxygenated organic aerosol factors as OOA2. This terminology has now been superseded by the term SV-OOA (see Jimenez et al., 2009; Science, 326, 1525-1529) and the authors should reflect this in the paper. I would suggest adding text to page 9343, line 10 where the term is introduced something like "One of them (SV-OOA, formally OOA2)..."

We changed all occurrences of OOA2 into SV-OOA and included a text as suggested.

Table 1 shows the reaction rates for the included chemical reactions. What is the origin of this data, it is not clear. The source of the rates should be clearly stated. How were the loss rates of TERP determined, they are not well documented in the literature?

The reaction rates of TERP were taken as the reaction rates of alpha-pinene from

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Atkinson and Arey (2003) and the other reaction rates are from IUPAC. We added this reference and some explaing text on page 9336:

page 9336, line 3:
”It is based on and further extends the simplified reaction schemes used by Krol et al. (2000) and Vilà-Guerau de Arellano et al. (2011) with reaction rate coefficients from the International Union of Pure and Applied Chemistry (IUPAC) Subcommittee for Gas Kinetic Data Evaluation (http://www.iupac-kinetic.ch.cam.ac.uk/).”
page 9336, line 18:
”All terpenes in our model are assumed to behave as α-pinene with reaction rate coefficients from Atkinson and Arey (2003).”

The isoprene flux given in table 3 is similar to that for a-pinene, can its contribution really being ignored when the yield of SOA could contribute ∼5 % to organic aerosol mass?

As a test for the assumption that SOA from isoprene can be neglected, we performed a run for the case study including SOA from isoprene in the volatility basis set approach with aerosol yields from Tsimpidi et al. (2010). We found only an increase of 1% of Coa at the end of the day compared to the terpene-SOA only case, which confirms our assumption that SOA from isoprene can be ignored without changing our results qualitatively.
Note also that processes which make a contribution of only 5% are typically ignored in our modeling approach.

As the authors show with their model, the entrainment of free troposphere air dominates the budget of organic aerosol in the boundary layer and in urban areas this is *likely to be larger due to the lack of available soil moisture and thus a lower evaporation flux compared to forested regions. This could be important for explaining the high radiogenic carbon (14C) content of organic aerosols in urban areas if the dominant source is entrainment of organic aerosols that are predominantly biogenic in origin. This is potentially an important finding that perhaps the authors should consider alluding to in the manuscript.*

The importance of entrainment on urban SOA will depend on the balance between the surface energy budget, the conditions in the FT and the efficiency of SOA-formation from (anthropogenic) VOCs. This would certainly be an interesting follow-up study and our integrated approach could be extended to urban conditions.

Page 9341, Line 8 – 10 – it is not clear from the description what measurement error is affecting the NO2 data. If the instrument being used contains a molybdenum convertor to convert NO2 to NO, then it is likely that the data are biased high due to interferences from partial conversion of PAN and nitric acid to NO2, it would be good to clarify this. A recent paper (Steinbacher et al., 2007; Journal of Geophysical Research-Atmospheres 112, D11307. doi: 10.1029/2006JD007971) has looked into the bias issues of commercial NO2 instruments and discusses these issues and could be referenced if deemed appropriate.

We asked Petri Keronen from the Univ. of Helsinki who was in charge of these measurements and he gave the following possible explanations: "We didn't have an NO2-specific converter in use in the NO & NOx analyser in Aug. 2001 and because of this the observed NO2 concentration might be biased upwards. Then there might be also the possible effect of the 100 m long sampling line on the observed NO concentrations." We will clarify this in the text.

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All other technical corrections have been applied as proposed.

References

Atkinson, R. and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds, Chemical Reviews, 103, 4605–4638, doi: 10.1021/cr0206420 0009- 2665 doi: 10.1021/cr0206420, 2003.

Krol, M. C., Molemaker, M. J., and Vilà-Guerau de Arellano, J.: Effects of turbulence and heterogeneous emissions on photochemically active species in the convective boundary layer, J. Geophys. Res., 105, 6871–6884, 2000.

Tsimpidi, A. P., Karydis, V. A., Zavala, M., Lei, W., Molina, L., Ulbrich, I. M., Jimenez, J. L., and Pandis, S. N.: Evaluation of the volatility basis-set approach for the simulation of organic aerosol formation in the Mexico City metropolitan area, Atmos. Chem. Phys., 10, 525–546, aCP, 2010.

Vilà-Guerau de Arellano, J., Patton, E. G., Karl, T., van den Dries, K., Barth, M. C., and Orlando, J. J.: The role of boundary layer dynamics on the diurnal evolution of isoprene and the hydroxyl radical over tropical forests, J. Geophys. Res., 116, D07 304, 2011.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 9331, 2012.