

Interactive comment on “Anthropogenic influence on biogenic secondary organic aerosol” by C. R. Hoyle et al.

C. R. Hoyle et al.

christopher.hoyle@env.ethz.ch

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We would like to thank the reviewer for taking the time to review our manuscript, and to suggest revisions. The manuscript was intended as a review of published results and not a presentation of new work, therefore we have taken the reviewers advice and made some changes to clarify this. Our changes made in response to the detailed comments are listed below:

p19522 Section 2.2.1 While the authors stress the importance of nighttime chemistry of BVOCs as the focus of future studies, I would like to add that nighttime chemistry of monoterpenes are especially important. It is worthy to note that monoterpene emissions are only weakly dependent on available sunlight (while temperature dependence is strong). This means that the reaction of monoterpenes with NO₃ could represent a

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larger source of oxidized hydrocarbons than other BVOCs.

Although original parameterisations of monoterpene emissions included no light dependence, recent studies have shown that monoterpene emissions from some plants do have a strong light dependence (Kesselmeier and Staudt, 1999; Kuhn et al., 2002; Otter et al., 2003; Greenberg et al., 2003; S.Moukhtar et al., 2005; Dindorf et al., 2006). Further, it has been shown during studies in the Amazon (Kuhn et al., 2002), in southern Africa (Greenberg et al., 2003) and in Europe (Dindorf et al., 2006), that the emissions of monoterpenes from many (vegetation) species may be modelled in the same way as isoprene emissions. However, it is still the case that more monoterpenes than isoprene are emitted at night and text has been inserted to indicate that monoterpenes and sesquiterpenes should be the focus of nitrate initiated SOA yields.

p19523 Section 2.2.2 The NO_x dependence of SOA yields is nicely summarized here. However, as Dr. Surratt pointed out in his short comment, there has been new understanding of the NO_x effect on SOA formation from isoprene, and possibly other conjugated dienes (such as myrcene, ocimene). The importance of PAN-type compounds as an SOA intermediate could imply that at high NO₂/NO ratios, SOA formation could be even more efficient than under pristine (low NO_x) conditions. This effect observed in chamber studies should be verified by field measurements, because this could represent an important enhancement on BSOA by anthropogenic NO₂. Future models should calculate the contribution of isoprene to SOA formation directly from MPAN, instead of parameterization using indirect proxies like NO₂/NO ratio.

The paragraph on p 19524 regarding isoprene/NO_x has been edited to include the work of Chan et al. and Surratt et al.: “Yields for low VOC:NO_x ratios reported by Chan et al. (2010) are higher than those reported by Kroll et al. (2006). The experiments of Chan et al. (2010) were carried out at atmospherically relevant NO₂/NO ratios (3-8), which favours the formation of a second generation product methacryloylperoxynitrate (MPAN), which in turn leads to aerosol formation upon further oxidation (Sur-

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ratt et al., 2010). NO₂ was also found to increase the SOA formation from acrolein and crotonaldehyde (Chan et al. 2010), and therefore similar effects may be seen for other VOC which have alpha, beta-unsaturated aldehydes as oxidation products. The low VOC:NO_x SOA yields measured by Chan et al. (2010) were also larger than those seen by Kroll et al. (2006) for high VOC:NO_x ratios. Since the NO₂/NO ratio tends to be higher in urban regions than rural regions, this suggests that SOA from isoprene and particular other VOC could actually be enhanced in urban areas. This is certainly an effect which warrants further investigation, particularly though field studies.”

Pg. 19524 Section 2.2.2 lines 7-14 Using initial VOC/NO_x ratio is only a proxy for the branching ratio between RO₂+NO and RO₂+HO₂ reactions, and can be misleading. In experiments by Dommen et al. (2006), no OH precursor was used and HO₂ is generated from alkoxy radical + O₂. In experiments by Kroll et al. (2006), OH+H₂O₂....

We added the following text to the isoprene paragraph: “However, it is important to note the differing oxidant conditions (HO₂ generated from RO + O₂ in Dommen et al. (2006); from OH + H₂O₂ in Kroll et al. (2006)) present in these two experiments, which may skew the RO₂ radical fate.”

*Pg. 19525 line 20-21 The reverse of the NO_x effect seen in sesquiterpenes is attributed to higher yield of sesquiterpene nitrates (as higher carbon number allow for more efficient isomerization) and lower yield of decomposition products, not just lower volatility of sesquiterpene nitrates. **There is no indication that nitrate yields approach unity for large carbon numbers. Zhang et al 2004 (Zhang, J, Dransfield, T. J. and Donahue N. M., J. Phys. Chem. A 2004, 108, 9082-9095) present a generalized model for nitrate formation and summarize the available literature data for carbon numbers up to C₇, all of which point to a maximum nitrate yield between 20 and 40%, depending on temperature and the specific RO₂ species. The remainder of the RO₂ + NO reaction appears to give radical products (RO + NO₂) under all conditions. Consequently, we do expect radical propagation (and thus an NO dependence on the primary products) to be important for sesquiterpenes***

and, indeed, any reaction between OH and an organic compound. Matsunaga and Ziemann (PNAS vol107, no15, 2010) find yields of beta-hydroxynitrates and dihydroxynitrates in the particle phase increased with at carbon number up to ca C15, however this was primarily due to enhanced gas to particle partitioning.

Can the authors discuss the role of amines in new particle formation? Amines are produced by agricultural activities, and have been shown to form aminium salts efficiently. This could also represent a significant anthropogenic perturbation to new particle formation.

We added the following paragraph: “Very recent computational studies with quantum-chemistry and first experiments in chambers and flow tubes resulted in strong evidence that amines could be important and explain the missing puzzle-piece in the particle formation process. Loukonen et al. (2010) studied the hydration of sulfuric acid- dimethylamine clusters and found dimethylamine enhances the addition of sulfuric acid to the clusters much more efficiently than ammonia when the number of water molecules in the cluster is either zero, or greater than two. More research is needed, however amines may play a major role in the nucleation process.”

Pg. 19537 line 25-27 I would consider, e.g., Weber et al. (2007) to be “quantitative evidence.” Also, the authors could mention Goldstein et al, PNAS 2009 in the field study review section, as it provides evidence of BSOA in populated regions from satellite observations.

We agree with the reviewer, therefore, this part of the sentence has been removed and now reads: “The results from these studies suggest that it is possible that the incorporation of biogenic species into organic aerosol is more efficient in polluted air.”

We have also included the Goldstein reference: “Remote sensing data was presented by Goldstein et al. (2009), showing an increase in summertime aerosol optical thickness (AOT) over southeastern USA. They demonstrate that the AOT increase is consistent with secondary aerosol formed from BVOC, and suggest that the formation

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of this SOA is modulated by anthropogenic emissions.”

Fig. 1 (SOA yields vs. VOC/NO_x) might be out of date. This figure has been updated to include Chan et al. (2010)

Fig 2 can include a more comprehensive review of radiocarbon measurements It is not within the scope of the present review to provide a detailed review of radiocarbon investigations. The intention of the figure is to give an overview of some of the available studies, to illustrate the differences between rural and urban environments, and we know that many more studies, especially on ¹⁴C in aerosols, could have been included.

Additional figures will be helpful. One can summarize the correlation between BSOA proxies and anthropogenic emissions, since this is the best field evidence supporting the concept of anthropogenically enhanced BSOA. Also, a workflow diagram of the proposed approach to isolate the anthropogenic component of BSOA might be helpful.

We added the second figure suggested here. We think that the second figure also provides a good deal of information on how the different proxies are associated with anthropogenic emissions, addressing some of the issues which would have been covered by the first figure proposed.

Interactive comment on Atmos. Chem. Phys. Discuss., 10, 19515, 2010.

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