

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

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We would like to thank Boris Bonn for his review of our manuscript and the recommendations for improvements. Our changes are listed below. We have made it clearer that this was intended more as a review than a presentation of new results. The effects of changes in land use etc on SOA are now mentioned and it is pointed out that the main focus of our paper lies elsewhere, with the short term effects of anthropogenic emissions. The title has not been changed as suggested, since the effects we discuss are not limited to the gas phase.

Missing analysis of anthropogenic effects on BVOC emissions:

We have edited the abstract to say that we examine the atmospheric effects of anthro-

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pogenic emissions on BSOA formation. The effect of atmospheric changes on BVOC emissions is now mentioned in section 3, and we suggest that, although highly uncertain, this may be quantified with combined vegetation/atmospheric modelling. Some discussion of the effects is included in section 4.2, and again in section 5.

p. 19518: The different types of OA are named. Please note that definitions and results mainly depend on the technique applied, i.e. if the aerosol is collected on a filter with continuous exposure to air etc. Thus, any improvement of measurement methods usually results in a newly defined sub-OA definition. Since not all organics can be detected and analysed by the different methods the current estimates are still not final and will be revised in the near future.

We have added the following statement: 'It should be noted that these definitions and the measured masses depend on the measurement techniques applied, and that as measurement techniques are changed or improved, new sub categories of OA are often defined. Not all organic species can be detected or analysed by the various techniques available.'

p. 19518: It's being stated that POA have somewhat higher volatility than SOA (Huffmann et al., 2009; Robinson et al., 2007). I think that is caused by the mixture of primary mass and volatile material ad- or absorbed on the surfaces. Because of the large size of primary particles the surface is sufficiently large and the partitioning notably enhanced. Heating up of SOA might result partially in polymerization etc which is not the case for POA compounds. However this does not necessarily mean that the originating compounds are less volatile.

Primary organic aerosol mass is if anything found on smaller particles, whereas SOA (OOA) mass is predominantly on the accumulation mode (see for example McFiggans et al Faraday Discussions 2005). However, the principal effects on partitioning are a combination of the surface area to volume and also the Knudsen number, which tends to slow evaporation from larger particles as diffusion

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in the gas-phase boundary layer becomes limiting in the transition from kinetic to bulk flow regimes ($Kn = 1$ at around 100 nm). As a consequence, there IS a concern that POA may seem somewhat more volatile than SOA of equivalent vapor pressures, but this is because it is on smaller particles, not larger particles. Furthermore, the Kelvin term becomes an issue, but the scale diameter is about 6 nm – Kelvin effects have little influence over the great bulk of the mass distribution of organics. The size dependence of evaporation and equilibration in thermodenuders is discussed in Riipinen et al, *Atmos. Environ.* 44, 597–607 [Equilibration time scales of organic aerosol inside thermodenuders: Evaporation kinetics versus thermodynamics. *Atmos. Environ.* 44, 597–607 (I. Riipinen, J. R. Pierce, N. M. Donahue, and S. N. Pandis) 2010]. Put simply, smaller particles will evaporate (equilibrate) more quickly in almost any setting because of their larger surface area to volume, and one does need to be careful about simply relating mass fraction remaining to volatility. However, authors such as Cappa and Jimenez (ACP, 2010) have gone through the exercise of modeling the thermal behavior of AMS / thermodenuder measurements using the volatility basis set and they reach the same conclusion – HOA (POA) is generally the most volatile constituent observed by the AMS in ambient air.

p. 19518: I guess the separation into biogenic and anthropogenic SOA is mainly for mitigation purposes.

We also think that the main practical use of an ASOA/BSOA/eBSOA separation is to simplify air quality improvement measures. This is mentioned in the introduction.

p. 19519: (2.1 Partitioning) The lower saturation vapour pressure compounds may also form in multiple oxidation steps or by ageing. Here providing ASOA will allow enhanced partitioning and subsequent ageing folwed by a higher total flux towards the condensed phase due to a change in the particle-phase concentration of species. Is this considered in here too?

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We agree with Dr. Bonn about the role of ASOA. This is now stated explicitly in the text.

“Any process that increases organic aerosol mass loading (e.g. anthropogenic SOA or POA) should then, in principle, result in increased BVOC yields.”

p. 19520: Problems of the miscibility might depend on the primary organic aerosol structure. This also applies for different mixtures in the atmosphere. So far we treat several species separately in the context of aerosols such as sulphuric acid, nitric acid, ammonia etc but several thousands with a enormous variety of properties as a single class, i.e. organics. This causes problems and maybe these would popp up as well when summing up all inorganics. Second, we need to be carefull about POA. This is essentially a mixture at least in the atmosphere of elemental carbon, oxidized carbon and unburned fuels, which are notably in contribution. This mixture certainly provides multiple ways of restructuration (density change), ageing, revolatilisation etc that EC does not.

This is a good point. We explicitly added the idea that particle phase plays a role and that composition and phase can change with ageing processes.

p. 19521: Surely the initial stage products of alpha-pinene oxidation are modest in hygroscopicity (Prisle et al., 2010) because of their oxidation degree increasing with time. This applies to all secondary products. Higher oxidation products such as pinic acid are thought to be formed mainly after multiple oxidation steps partially in the aerosol phase (Kanawati et al., 2007).

The hygroscopicity of alpha-pinene-derived aerosol has been studied in great depth, including changes in hygroscopicity with increases in chemical age (e.g. George and Abatt, 2010, Massolli et al., 2010). Overall these studies suggest little change in SOA hygroscopicity due to heterogeneous oxidation for realistic oxidant exposure although it is clear that chemical composition of the gas-phase and aerosol is changing with time. No change in wording of the text has been

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made.

p. 19522: The role of NO_x is written excellent. Probably the parameter delta VOC/NO_x is even better for parameterisation .

We decided to stick with VOC/NO_x

p. 19524: A further explanation concerning the drop in SOA yields at high NO_x not mentioned in here could be: The photooxidation experiments are commonly a mixture of OH and ozone oxidation with the latter leading to less volatile products. Thus increasing NO_x to higher values causes ozone to drop more efficient than OH. This causes the oxidation products to be more volatile and the SOA yield increases, i.e. background atmospheric chemistry.

It is not obvious that ozonolysis SOA products are less volatile than OH products. If anything the evidence points in the other direction. For example, linuma et al (Faraday Discuss 2005) report significantly higher SOA yields in experiments with excess α -pinene but no OH scavenger vs. identical experiments with OH scavengers. Under those conditions the OH radicals produced from the ozonolysis reaction almost exclusively react with α -pinene. Those authors attribute the difference to OH reaction products that more easily form oligomers.

p. 19525: Sesquiterpenes: Wait! Interpretation might be difficult. The contribution of the ozone-reaction dominates always in contrast to monoterpene oxidation. Thus increasing NO does not affect the primary yield of products. Since those oxidation products are larger NO is expected to be incorporated in the RO₂-reaction products without fragmentation. The larger the product and the higher the number of functional groups the lower the vapour pressure and thus the larger the SOA yield. It seems that for monoterpenes NO simply blocks the ozone contribution.

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.

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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.

p. 19526: As mentioned by the authors I would tend to be very careful in giving exact numbers of anthropogenic contributions to SOA in the Amazon region. The effects are due to a) the tremendous change in the Amazon region during the last years (not considered here) and b) the direct and indirect effects with the latter less obvious. Maybe state ca. 80% in line 20.

We now say ca. 80% and point out that a high degree of uncertainty is associated with the number.

p. 19527: (upper paragraph) The emission of Amazonian monoterpenes and NO depends strongly on the conditions of rain, forest fires (natural and anthropogenic ones) dry and humid season and is hard to be state in general with the coarse global models.

That is true. We added the following sentence: "Because of the dependence of Amazonian emissions of BVOC and NO_x on factors like season, rain, forest or biomass fires, it will be challenging to estimate the possible anthropogenic effects using large scale models."

p. 19527: New particle formation, organics and CCN - Since we clearly lack in mechanisms and exact products leading to SOA and number concentrations as well as the

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detailed ageing of several 1000 compounds the difference is apparent. Fortunately it seems that at least currently nature is balancing out some of these problems but not necessarily in a future condition. In the subsection it appears that NO would tend to negatively affect the nucleation intensity or occurrence. But this is very difficult to say since it can appear vice versa because of aerosol dynamics and radical chemistry playing a crucial and non-linear role. In some conditions number is expected to rise.

In section 2.3, we say that SOA production is generally presumed to be larger in low NOx environments, but that this dependence differs between the various VOC, and that in some cases, higher NOx leads to lower SOA amounts.

p. 19528: Lack of new particle formation in the Amazon region - The old argument. It might also happen that a nucleation starting compound requiring activation is limiting because of the multitude of reaction partners otherwise suppressing. The activation might occur extremely rapid because of the high VOC loading. Thus a new particle quickly rises to larger sizes 10-20 nm without stabilising inorganic compounds to remove the excess energy produced.

We added the following text: "There are also other possible explanations for these observations, for example that particle formation took place in the boundary layer or free troposphere and that the particles which reached the instruments in the canopy had grown since nucleation. Additionally, in this environment the high VOC emissions (Rasmussen and Khalil, 1988; Keller et al., 2009) in connection with sustained atmospheric oxidant capacity (Lelieveld et al. 2008) could lead to a high production rate of condensable vapors, thus causing the particles to rapidly grow out of the nucleation mode sizes via multi-component condensation."

p. 19530: BVOCs: The regional land use changes are very important on the global scale with respect to future climate projections and mitigation strategies. Since this paper might be used for such purposes this point should be mentioned quite briefly to indicate further important non-negligible effects. Land use changes are already

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briefly mentioned in this section, however the effect of climate on vegetation was not. The following text has been added to the end of section 3: "On long time scales, the distribution of different vegetation types, their emissions of BVOCs and therefore the formation of BSOA, will be influenced by atmospheric changes such as increasing temperatures, shifting rainfall patterns, changes in ozone and carbon dioxide concentrations. These changes can undoubtedly be classified as an anthropogenic modification. The net effects of the combination of such factors on SOA burdens is highly uncertain. Due to the long timescales involved, the resulting changes in SOA may be best quantified by modelling both the vegetation and atmospheric systems, for example Heald et al. (2008), Chen et al. (2009)."

The following text was added: "Pyrogenic carbon particles sampled in the Amazon, thought to be emitted by biomass or fossil fuel combustion, were examined by Pöschl et al. (2010) and found to have a partial organic coating. Chen et al. (2009) found that the organic loading in the Amazon basin increased by 50%, during periods with substantial influence of out-of-Basin-air masses, although it is difficult to quantify what fraction of this organic aerosol was formed locally. Both of these observations qualitatively support an anthropogenic enhancement effect."

p. 19535: The fraction of ASOA is slightly higher than expected by earlier studies but agrees with the normal assumption of about 10% contribution. However this might be an order of magnitude estimate so far (see comment for p. 19539). OK. The values from different studies do vary a lot.

p. 19538: Problems with results from bulk or filter analysis - It is always apparent that partitioning compounds are partially lost by filter sampling in a changing environment. Only the primary fraction remains unmodified. The same is known for mass spectrometry with hundreds of products partially very fragile and partially below the detection limit. However all might add up to a notable mass.

We added the sentence: "It should be noted that the partitioning of semivolatiles on

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filter samples may differ from the atmosphere or change during sampling, resulting in positive or negative biases for these compounds”.

p. Please note that the value of 10.3 Tg(C)/yr of SOA is among the lowest simulated ones! The higher the number of details and the more detailed the chemistry schemes the higher the simulated mass production. Detailed simulations as of Derwent et al. (2003) and others simulated around 60 Tg(C)/yr, hence about six times the value than cited and this is only for monoterpenes. The simplification to the two product schemes seems to fail in getting the number in the same height. With this in mind the increase by a factor of three to about 30 Tg(C)/yr is excellent and worth to postulate but might be in a different intensity with a more complex scheme.

That sentence actually referred to POA. SOA increased by 59%, as listed in table 3. (No changes made)

*And what about considering the aerosol dynamics and size distribution including Kelvin and Raoult effects? Otherwise this is very plausible. **In the two product model, such effects are implicitly accounted for, as the result is simply a mass yield. None of the models here include a description of the size distribution of the aerosol, as this would be too computationally expensive. (No changes made).***

In general it would be nice to make a short overview plot or figure of the individual effects and the ones considered in this study .

We think that the different sections provide a good overview of the different effects. We did add a new figure for the source apportionment of the different fractions of an OA sample though.

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