

Interactive comment on “Change in global aerosol composition since preindustrial times” by K. Tsigaridis et al.

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We feel that the assumptions being made in this article with regards to the mechanisms of SOA formation merit discussion. The issues that we wish to address are encompassed in, yet not limited to, the following sentence from this work:

“However, we assumed that in the case of biogenic hydrocarbons the only oxidant leading to SOA formation is O_3 , while for the aromatic VOC both OH radicals and O_3 are initiating SOA production.”

It is unlikely that O_3 initiation of SOA production from aromatics is of much importance. The reaction of aromatic species with O_3 is very slow, relative to reaction with OH. While it should not substantially alter their calculation to include such an ineffec-

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tive mechanism, it seems potentially misleading and does not reflect accurately the chamber experiments from which the SOA yield parameters for the aromatics were extracted.

We also question the authors' assumption that the only oxidant initiating appreciable SOA formation from biogenics is O_3 . We consider the explanation for this given in Tsigaridis and Kanakidou (2003) – that the products formed from oxidation of monoterpenes by oxidants other than O_3 would follow the RO_2 pathways of isoprene, leading to products that are too volatile to form appreciable amounts of SOA. This is supported by the study of Hoffmann et al. (1997) and by data from Griffin et al. (1999), where α -pinene had higher SOA yields from ozonolysis (up to 30%) than photooxidation (up to 20%). However, also in Griffin et al. (1999), β -pinene had lower SOA yields from ozonolysis (5%) than photooxidation (up to 30%). Calculations attribute much of this photooxidation yield of β -pinene to reaction with OH (with the caveat that no O_3 was initially present for these experiments, though some is generated during the experiments). Additionally, the yields of NO_3 oxidation of β -pinene were even larger, up to 90%. Furthermore, while the reaction of α -pinene with O_3 has the highest SOA yields when no other oxidants are initially present in the chamber, this does not necessarily mean that oxidation of primary biogenics by OH and NO_3 is a negligible source of SOA in the atmosphere, where all three oxidants are likely present, similar to the photooxidation experiments. While we recognize that the current model takes into account NO_3 and OH concentrations via the formation of second generation products (equations 4-7 of Tsigaridis and Kanakidou (2003)), it has been shown (Ng et al., *ES&T*, 2006) that the limiting step for SOA formation from α -pinene and β -pinene is the initial VOC oxidation, for both ozonolysis and photooxidation experiments. Therefore, initiation of SOA production from oxidants other than O_3 is likely non-negligible.

Overall, it seems that the model implementation in this paper inaccurately represents SOA production by overlooking a few mechanisms shown to produce SOA and may also underestimate the influence of anthropogenic NO_x emissions on SOA concentra-

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tions by neglecting the formation of SOA from NO_3 oxidation of β -pinene.

Given the updates made to the SOA scheme since the referenced model paper (Tsigaridis and Kanakidou (2003)), we would appreciate inclusion in the present work a more detailed explanation and assessment of the current implementation. Hopefully, this would address the issues mentioned above and also clarify other points, such as

- When does the model use the NO_x -independent yield parameters (for α -pinene and xylene), and when does it switch to using the NO_x -dependent parameters? Or are these used coincidentally, and if so, how?
- When the model is using the NO_x -dependent yield parameters, what is the cutoff point for switching from the low- NO_x to the high- NO_x parameters (for α -pinene and xylene)?

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