

***Interactive comment on* “Formation of secondary organic aerosol from isoprene oxidation over Europe” by M. Karl et al.**

Anonymous Referee #1

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This paper is a very useful contribution to the literature on SOA formation, and from isoprene in particular. The methodology follows the same pattern as the earlier Tsigaridis and Kanakidou paper, with systematic sensitivity tests of a number of possible configurations of isoprene-SOA formation. The paper is well written for the most part. My only major reservation concerns the physical plausibility of some of the sensitivity tests, but after attention to this and the other issues discussed I think the paper can be well worth publishing in ACP.

My main concerns are with two tests that originate in the earlier Tsigaridis and Kanakidou (2003) paper. These tests are not physically plausible in my opinion, and the fact that they have been published earlier does not make the methodology correct.

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- In one of the sensitivity tests, ammonium sulfate is treated as part of the organic mass (part of C_{OM}) for partitioning. Although ammonium sulfate is important in smog-chamber experiments, it should not be treated as just-another component of C_{OM} in this way. The partitioning theory the authors are using applies to very specific assumptions concerning absorption - and is not easily applied to mixtures of organic and inorganic components. Lots of nasty factors come into play if sulfate is to be included in this system. (e.g activity coefficients! See Clegg et al.'s papers in ACP, 2008)
- The second test attempts to simulate irreversible sticking of vapour onto the particle. Such a one-way transport from gas to particle is indeed interesting to test, but the K values derived from an assumed equilibrium cannot be used at all in such a methodology. If I have understood T&K (2003) correctly, the authors are using normal K values at each model time-step to assign an aerosol yield, but then not allowing the aerosol to lose mass. How are K values relevant at all if there is no equilibrium? Surely the correct method is just to calculate the loss rate of the vapour to a particle?

I would suggest that the authors find a better method of dealing with the above problems, or just omit these tests from the paper.

1. In general, the literature cited seems a little old. In SOA terms old can mean 2-3 years old, but there have been some important new ideas that are not even mentioned in this paper. For example, the well cited paper of Robinson et al. (Science, 2007) raises important issues. A nice review of some of this can be found in Donahue et al. (AE, 2009), Kroll and Seinfeld (AE, 2008) or Hallquist et al. (ACPD, 2009).
2. p2858. Some more recent literature on in-cloud processes involving isoprene should be given, since the original Ervens et al. (2004) mechanism has had

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- important revisions since then. e.g Ervens et al. (GRL, 2008).
3. p2858. The 12-70 Tg/yr estimate has been undergoing significant upward revision in recent years. Goldstein and Galbally (2007) found 140-910 Tg C/yr. These figures have been revised further by Hallquist et al. (ACPD discussions) who estimate recent range of 0-180 TgC/yr from biogenic VOCs, with best estimate 88.
 4. p2862. Again, the 12-70 Tg/yr estimate...
 5. p2862. Line 7. A reference to the published paper of Guenther et al. (1995) would be appropriate here.
 6. p2862. Line 13. A reference to the published paper of Steinbrecher et al. (2009) would be appropriate here.
 7. p2862. The assumptions that ORVOC can be split as 50% α -pinene, 50% β -pinene assumes that these compounds are terpene-like. Do you have literature to support this? One ORVOC from plants for example would be ethene, and terpenes seem a bad substitute for this compound.
 8. p2863. The Guenther et al equations are not needed here – they are so well documented in other papers.
 9. On the other hand, it would have been useful to give the OC partitioning equations as background for the discussion.
 10. p2867, lines 10-15. Why the special treatment for BCAR2p?
 11. p2869, section 3.2. I found the discussion of the VOC/NO_x dependency confusing. it would have helped to show an equation here. Also, the text mentions

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- that reaction with of RO₂ with NO leads to more aldehydes, ketones and organic-nitrates, but none of these are included in the two-product model used here I think.
12. It should also be pointed out that VOC/NO_x is a crude approximation to deal with these matters. Wouldn't it have been both better and easier to use the HO₂/NO ratio from the model for deciding the yield?
 13. p2871. Wet deposition may be the most efficient removal mechanism for aerosols, but for SOA a large fraction of the compound is in the gas-phase. Halquist et al have suggested that dry deposition of the vapours may be a very significant loss process for the compound as a whole.
 14. p2880, line 15. the 6% yield is higher than that found in smog-chambers and this is explained as a consequence of the higher OA calculations over Europe. It isn't clear the model does have higher OA though. Fig. 3 shows SOA of max 6 ug/m³, which is within the range of the smog-chamber studies.
 15. p2881. The authors discuss a budget for SOA in the same terms as for an inert pollutant such as BC. But concentration of SOA is not necessarily interesting - it represents an instantaneous partitioning of an equilibrium system. This is a tricky area and I am not sure what the best approach is, but the discussion needs some qualifications if it is to be kept.
 16. p2883. The term POM is used for particulate organic matter, but this is confusing. POM is most often taken to mean primary, e.g. as in Fuzzi et al (ACP, 2006).
 17. p2883, lines 15... In discussing model performance for OA, it would be good to know how well TM5 performs for other secondary compounds, e.g. sulfate, nitrate.

18. p2884, lines 17... In discussing the summertime SOA, the discrepancy is attributed only to temperature-dependence or emissions. The mechanism itself can play a large role of course, as demonstrated by e.g. Pun et al. (EST, 2003) and the fact that the EMEP model does perform very well for these Nordic sites in summertime (Simpson et al., JGR, 2007).
19. p2885, lines 27-28. Again the results of Simpson et al. are very relevant here - the wood-burning discrepancy was addressed in some detail there.
20. p2888, lines 7-8. The inventory of Kupiainen & Klimont (AE, 2007) is relevant here, since it addresses European emissions in more detail than Bond et al.
21. p2888, lines 20-21. The positive artefact of OC is mentioned as a possible reason for model underestimation. What about the negative artefacts?

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