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

M. Karl et al.

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Reply to Referee 1

General comments

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.

In one of the sensitivity tests, ammonium sulfate is treated as part of the organic mass (part of COM) for partitioning. Although ammonium sulfate is important in smog-chamber experiments, it should not be treated as just-another component of COM in this way. The partitioning theory the authors are using applies to very specific as-

sumptions 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.8217;s papers in ACP, 2008)

The referee claims that sulfate is treated as a component of COM in our approach. This is actually not the case. The implementation of the gas-particle partitioning in TM5 takes into account the change of the activity coefficients of the absorbing particulate matter with change of composition. The activity coefficient ζi of the individual compound i of the absorbing particulate matter is allowed to change with time as a function of the chemical composition of the particulate phase. This effect is taken into account by applying the multicomponent Wilson equation (Prausnitz, 1969; Bowman and Karamalegos, 2002):

$$ln\zeta_i = 1 - ln\left(\sum_j x_j\Lambda_{ij}\right) - \sum_k \frac{x_k\Lambda_{ik}}{\sum_j x_j\Lambda_{jk}}$$

Where xi is the mole fraction of the compound i, Λ ij, Λ ik, and Λ jk are parameters representing the interactions between the compounds i and j, i and k, j and k, respectively. The Λ values for different compounds present in the carbonaceous aerosol have been selected based on their expected chemical similarity and lie within 0.2-1 (Kanakidou and Tsigaridis, 2003). The Λ values for sulphuric and ammonium aerosol, to which SOA can partition in the applied test, vary from 0.7 to 1.0, expected to be representative for atmospheric conditions (Bowman and Karamalegos, 2002).

The intention of the applied scenario is to tentatively simulate the impact of acid-catalysed enhancement of SOA formation from isoprene oxidation and the particle-phase reactions that lead to organosulfates. Both processes would increase the SOA yield over areas with higher sulfate particle loads, thus this effect can be simulated by inclusion of ammonium sulfate to the absorbing mass.

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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 TK (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 vapor to a particle?

Though at first sight it may seem that the equilibrium is not fulfilled in the no-evaporation case, the equilibrium situation is actually established between the gas-phase SOAg and the condensed particle-phase SOAa at every time step. However, one can assume that there is a process of physical trapping and/or chemical transformation involved which leads to the irreversible conversion of SOAa to a non-volatile compound between the current and the next time step. Stepwise, SOAg is being absorbed and equilibrated with SOAa at the first time-step; then SOAa is allowed to be converted to a non-volatile species (thus participating to the non-volatile OA, similarly to the pre-existing carbonaceous aerosol in the model); third, at the next time-step, the cycle closes with a new equilibrium between the SOAg and the newly formed SOAa. The time span between the time steps defines the time scale on which the trapping/conversion processes occur. The exact nature of the physical trapping or chemical transformation does not need to be known in this simplified implementation. In reality, not all condensed SOAa also is expected to be converted to a non-volatile compound, but only a certain fraction of it. Thus the no-evaporation case should serve as the upper limit of SOA formation, the evaporation case represents the lower limit, and the real situation lies between the two.

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

The above mentioned methods are physically correct, as explained in detail in our answers above. We assume that the explanations in the text were too short and we will

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improve their description in the revised manuscript.

Specific comments

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).

The mentioned papers will be included in the introduction of the revised manuscript.

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 important revisions since then. e.g Ervens et al. (GRL, 2008).

Ervens et al. (GRL, 2008) and other more recent literature on the in-cloud formation of SOA from isoprene will be included in the introduction of the revised manuscript.

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.

These higher estimates arise from a broader definition of secondary organic aerosol. The focus of the presented manuscript is limited to the formation of the so-called 8220;traditional8221; SOA originating from the photo-oxidation of VOC like isoprene, terpenes, and aromatics. Thus the Kanakidou et al. (2005) range of 12-70 Tg/yr reflects the commonly accepted bottom-up estimate for the total biogenic SOA flux which is directly comparable with our study. The higher estimate given in Hallquist et al. (2009) is derived from a top-down estimate by Goldstein and Galbally (2007). First, this estimate includes non-BVOC sources of SOA. These include low-volatile vapours produced during biomass burning which may be further oxidized and then condensed to particles (Robinson et al., 2007). These precursor VOCs are not included in the present study. This discussion will be included in the revised manuscript in the introduction and in section 2.3 in order to set the given biogenic SOA estimate in context with both perspectives.

4. p2862. Again, the 12-70 Tg/yr estimate...

See 3.

5. p2862. Line 7. A reference to the published paper of Guenther et al. (1995) would be appropriate here.

A reference to Guenther et al. (1995) will be added in the revised manuscript.

6. p2862. Line 13. A reference to the published paper of Steinbrecher et al. (2009) would be appropriate here.

A reference to Steinbrecher et al. (2009) will be added in the revised manuscript.

7. p2862. The assumptions that ORVOC can be split as 50% a-pinene, 50% bpinene 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.

Griffin et al. (1999b) have determined the contribution of individual chemical compounds to the emissions of ORVOC on a global scale based on the emissions from predominant plant species. 32% of the total ORVOC emissions contribute to the formation of SOA. Since 5% of the ORVOC emissions are supposed to be particle-forming sesquiterpenes, 27% of the ORVOC emissions remain to be explained by a-pinene and b-pinene. Among the remaining ORVOC constituents that contribute to the formation of SOA, 48% have a terpenoid molecule structure, while 52% have an aliphatic (C7-C9 n-carbonyls, higher olefines) or aromatic structure. Since b-pinene has significantly lower SOA yields in the ozonolysis than a-pinene (Griffin et al., 1999a), b-pinene is intended to represent the less effective aliphatic and aromatic fraction while a-pinene

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represents the more efficient terpenoids.

8. p2863. The Guenther et al equations are not needed here 8211; they are so well documented in other papers.

The equation will be removed from the revised manuscript.

9. On the other hand, it would have been useful to give the OC partitioning equations as background for the discussion.

The equation of gas-particle partitioning will be added in section 2.5, also in view of the discussion on activity coefficients and equilibrium partitioning.

10. p2867, lines 10-15. Why the special treatment for BCAR2p?

In contrast to the ozonolysis of a-pinene which produces only first-generation products, the ozonolysis of b-caryophyllene and other sesquiterpenes leads to a substantial growth of OM, even after the complete consumption of the parent hydrocarbon, indicating that the formation of second-generation products are important in the overall aerosol yield (Ng et al., 2006). The possibility to form the second-generation products seems to be related to the oxidation of the second carbon double bond of the sesquiterpene molecule. Special treatment of BCAR2p does account for this additional rate limiting step of SOA formation from b-caryophyllene. This statement will be added to section 2.5 of the revised paper.

11. p2869, section 3.2. I found the discussion of the VOC/NOx dependency confusing. it would have helped to show an equation here. Also, the text mentions 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.

Gas-phase products from the oxidation of the parent VOC largely depend on the fate of their corresponding organic RO2 radicals. The observed dependence of the SOA yield on the NOx levels is a consequence of the competing RO2 radical reaction pathways. At high NOx, RO2 is efficiently converted into RO via reaction with NO. The further

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fate of the RO radical depends on the structure of the parent VOC, leading mainly to aldehydes, ketones, hydroxycarbonyls, and different PAN-like compounds that all have high volatility. An alternative terminating channel of the reaction of RO2 with NO is the production of organic nitrates, which may be relatively volatile (Presto et al., 2005b). At low NOx levels, reactions of RO2 with HO2 and the self- and cross-reactions of RO2 become competitive and are the dominant reactions for NOx-free conditions. The RO2 reaction with HO2 in general leads to the formation of low-volatile hydroperoxides. In the photooxidation of isoprene under low NOx conditions, major SOA products are 2-methyltetrols, C5-alkene triols and organic peroxide oligomers (Böge et al., 2006; Surratt et al., 2006). For high NOx, major SOA products are acidic oligoesters with 2-methylglyceric acid as key monomer (Surratt et al., 2006).

In the current implementation a fixed VOC/NOx ratio of 8 is used as a threshold to divide between high and low VOC/NOx conditions, as proposed by Presto et al. (2005b) for a-pinene. The linear combination of the virtual compounds produced from the two product model represents the sum of the above stated products. At high NOx conditions the production of the more volatile product is favored; while at low NOx conditions the production of the less volatile product increases. In the two-product approach for isoprene, the yields from Henze and Seinfeld (2006) apply for high VOC/NOx (i.e. low NOx level). These yields were scaled with the NOx-dependence of a-pinene, as described by Tsigaridis and Kanakidou (2007).

The discussion of the VOC/NOx dependence of the yields will be changed accordingly in the revised manuscript.

12. It should also be pointed out that VOC/NOx 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?

Indeed the implemented VOC/NOx dependence is a simplification of the actual NOx

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dependence of the yields. First, because a fixed threshold between low and high VOC/NOx is used instead of gradually changing yields; second, because the VOC/NOx dependence for a-pinene was used for isoprene.

Under NOx-free or low NOx conditions, RO2 radicals can also undergo self- and cross-reactions. Using the NO/HO2 ratio thus would neglect the reaction of RO2 with other RO2 (either from the same or from other VOC) radicals. The RO2 self- and cross-reactions tend to be more important in chamber studies with elevated concentrations of the parent VOC than they are in the real atmosphere. Under atmospheric conditions - where HO2 is the major or only reaction partner under low NOx conditions - it is often the ratio of NO/HO2 that determines the fate of secondary gas-phase products and which is more important than absolute NOx concentrations for extrapolating results from environmental chamber conditions to atmospheric conditions (see e.g. Henze et al., ACP 2008). These considerations will be added to the revised manuscript.

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. Hallquist et al have suggested that dry deposition of the vapours may be a very significant loss process for the compound as a whole.

The high estimate of Hallquist et al. (2009) for the dry deposition of vapours of 800 TgC/yr refers to the global budget of organic non-methane carbon (VOC + SOA + primary OC). This estimated dry deposition flux likely includes a large primary component (emission of low-volatility vapours), precursor VOC, and other gaseous VOC. It is also stated that dry deposition of vapours is the flux with the highest uncertainty in the global non-methane carbon budget. In terms of traditional SOA, dry deposition of vapours is expected to be a minor removal pathway for the total SOA (not exceeding 10-20%). In our calculations the contribution of dry deposition of vapours to the removal of SOA is less than 15%.

14. p2880, line 15. the 6consequence 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 μg/m3, which is within the range of the smog-chamber studies.*

Elevated primary carbonaceous aerosol loads (BC+POC) are the reason for increased SOA yields. A figure of BC+POC will be included in the Supplement.

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 8211; 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.

The purpose of presenting the European budget for SOA during summer is to compare the relative contribution of major aerosol fluxes to the concentration of SOA. Within the budget, each scenario represents a different equilibrium state of the gas phase/particle partitioning of SOA. Thus the presented budget already contains the additional dimension of different possible equilibrium states. The budget holds for the summer period and will be different in winter, as the equilibrium shifts with temperature and available pre-existing absorbing particulate matter. Where necessary, the gas-phase compound fluxes were included in the text, e.g. for the transport of gaseous SOA compounds to higher altitudes, see section 4.1.4. This comment will be included in the revised manuscript.

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).

We initially used POM as used in AEROCOM (e.g. Textor et al., 2006; Dentener et al., 2006; Schulz et al., 2006, Kinne et al., 2006), which stands for particulate organic matter. Nevertheless, we decided to use OM instead of POM in the revised paper as the current usage may be confusing.

17. p2883, lines 15... In discussing model performance for OA, it would be good to

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know how well TM5 performs for other secondary compounds, e.g. sulfate, nitrate.

TM5 performs well in the prediction of the inorganic aerosol, e.g. sulfate, nitrate, and ammonium, over Europe (De Meij et al., ACP 2006). Observed surface concentrations of sulfate are matched well when using both the EMEP and the AERONET emission inventory; ammonium and nitrate surface concentrations are in better agreement when applying the EMEP emission inventory. This will be included in the text of the revised manuscript.

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).

Representation of SOA, mechanistic vs. empirical SOA-forming reactions, gas phase/particle partitioning parameters (Pun 2003), or different K values (Simpson et al., 2007) can result in large differences in predicted SOA concentrations. The latter example is already discussed in the text on p. 2887. These aspects will be added to the discussion in the revised manuscript.

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.

Simpson et al. mainly found wood burning as a missing OM source in Southeastern Europe. The presented manuscript can demonstrate that wood burning is also a candidate for missing OM in winter in other places in Europe. Some more details of the Simpson et al. paper on wood burning will be included in the revised manuscript.

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.

The inventory of Kupiainen and Klimont on primary carbonaceous particles is indeed more detailed for wood burning over Europe. It will be included in the discussion of the revised manuscript.

21. p2888, lines 20-21. The positive artefact of OC is mentioned as a possible reason for model underestimation. What about the negative artefacts?

Negative artefacts result from the evaporation of gaseous organic material from the particles on the filter. It is generally assumed that the positive artefacts prevail in collection with quartz fibre filters (Turpin et al., 2000).

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