

Interactive comment on “Development of a secondary organic aerosol formation mechanism: comparison with smog chamber experiments and atmospheric measurements” by L. E. Olcese et al.

L. E. Olcese et al.

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- Page 8363, line 6. POA is typically not used to describe primary carbonaceous aerosol that includes organic and black/elemental carbon. Rather, POA should be used to describe only the organic part. // The referee is right. Remove: They may stick to the surface of primary carbonaceous particles (POA) particles, which are mainly composed of black carbon (BC) and other nonvolatile organic compounds (OC). Add: They may stick to the surface of organic aerosol particles (OA) particles, which are mainly composed of primary organic aerosols (POA) and other preexisting SOA.

- Page 8363, line 20. Generally, the modeling methods described do not use a sticking coefficient for semi-volatile organic species. Rather, the chamber parameters used are

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overall equilibrium descriptors and implicitly include this parameter. // The sticking coefficient refers probability for a collision of a gas phase molecule to stick to the surface of an aerosol, we had inadvertently picked up language from some recent publications which were not very precise. We changed the word "sticking" by "partitioning".

- Page 8363, line 22. Catalysis by what? // Acid catalysis. Remove: ...the aerosol phase due to catalysis... Add: ...the aerosol phase due to acid catalysis...

- Page 8363, line 23. References are needed at the end of the sentence describing uncertainties in SOA models. // Add at the end of the phrase at page 8363, line 23: (Volkamer et al., 2006 and Tsigaridis and Kanakidou, 2003)

- Page 8363, line 28. The Griffin 2002 approach is not one that uses alpha and K derived from chambers. // The referee is right, the Griffin work does not use this approach, the reference was related to the ability to reproduce atmospheric measurements. Remove: ...often can reproduce SOA concentrations obtained from measurements in smog chamber experiments or in atmospheric measurements (e.g. Griffin et al., 2002), but, as explained below... Add: ...often can reproduce SOA concentrations obtained from measurements in smog chamber experiments or in atmospheric measurements, but, as explained below...

- Page 8364, line 8. This is not true. Reaction rate coefficients are not derived from chamber experiments. Rather overall average partitioning coefficients of the products are derived. Generally, the reaction rate coefficients of the primary hydrocarbons are known from separate experiments. // We agree, the reaction rate values are not obtained from the same smog chamber experiments and can also be determined in flow reactors. Remove: ...Typically, $k_{i,j}$ and the stoichiometric coefficients $a_{i,j,k}$ are determined by fits to smog chamber experiments... Add: ...Typically, the stoichiometric coefficients $a_{i,j,k}$ are fit to smog chamber experiments results...

- Page 8364, line 14. The statement regarding particle-phase reactions not being included is not exactly true. In reality, because the parameters derived from chamber

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experiments tend to be from the end of the experiments, the effect of any particle phase reactions are implicitly included in the partitioning coefficients. // The values of the experimental partition coefficients includes all the processes, but the smog chamber experiments cannot separate the individual contributions of different gases. In the long term, it is necessary to know the aerosol composition to predict its stability. We will mention your point, though.

- Page 8364, line 21. The authors claim to calculate partitioning coefficients differently than other methods. How? Other models are also based on the theory of Pankow. Also, how are hydrophobic versus hydrophilic aerosols treated in the model of the authors? What inorganic aerosol model is used? Is one? // The method used to calculate the partition coefficient is not original, and the references are on Page 8369, line 3. The phrase "based on a different chemical mechanism, differ in the method used to estimate the partition coefficients, in the SOA precursor selection, and in the treatment of hydrophilic and hydrophobic aerosols." is not related to a completely new approach to the SOA modeling, but to general differences between this and other models. The SOA precursor selection method is not original, nor is the method used to estimate the partition coefficients, and the methods used are properly referenced. The original work here was to develop a model using different components (partition scheme, species selection method, etc.), together with a chemical mechanism that has been used in a global chemistry model for treating ozone. This has been clarified in the new version. Most experimental studies of SOA have shown that these aerosols are only slightly hygroscopic (Russell et al., JGR, 2005; Meng et al., JGR, 1998; Pun et al., EST, 2002). Therefore, we have not included a model for the amount of water associated with our SOA. Add, in Page 8364, line 22: ... we use only the aerosols treatment by Pankow et al. (1994a).

- Page 8364, line 28. The authors state that other calculations have been unsatisfactory. How? Why? // We agree with the referee, the phrase is changed: Remove: Previous attempts to explain these measurements through calculations have been un-

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satisfactory. As described below, calculations using the mechanism described here show improved agreement in comparison with measurements. Add: Previous attempts to explain some of these measurements through calculations have identified significant discrepancies between measurements and theory (Johnson et al., 2006a and 2006b). The details in defense of this statement are presented later in the manuscript (Page 8372, line 27), as follows: "These results can be compared directly to the trajectory calculation reported by Johnson et al. (2006a and b) on which it is based. Johnson et al. (2006a) found that they were able to match the experimental results only if they assumed that gas-aerosol partition coefficients were higher than theoretical values by a factor of 500. Here, results show reasonable agreement with observations without any adjustment to the partition coefficients derived from theory. The possible cause of this difference is the inclusion in this work of different species in the partitioning scheme, mainly derivatives from biogenic precursors. Johnson et al. (2006b) reports that the average contribution of species derived from anthropogenic emissions to the simulated mass of SOA is 60%, but our calculations showed that this contribution is only 40%."

- Page 8365, line 10. Generally, black carbon is not thought to be an absorptive medium for SOA. Is this included in their calculations for K? If so, what properties are used? // No, BC is not included as an absorptive medium for SOA. This is clarified in the new version.

- Page 8365, line 15. It should only be the organic compounds that contribute to the average molecular weight for the partitioning coefficient calculation presented here. This should be specified. // The referee is right. Remove: ...the average molecular weight of the compounds in the aerosol phase... Add: ...the average molecular weight of the organic compounds in the aerosol phase...

- Page 8367, line 3. The authors say that Kroll specifies only small yields but that the Henze paper shows significant SOA globally from isoprene. However, the Henze model is based on the laboratory results of Kroll. This seems to be contradictory. // Although that the SOA yield from isoprene is small, the large amount of global isoprene

emissions (about 500 Tg C y⁻¹) makes the formation of SOA from isoprene derivatives relevant, from a global point of view. We will clarify this.

- Page 8367, line 15. The authors cite the Iinuma paper that shows a 40% effect of acidity. The model presented in this paper is closer to observations without including this effect. How is this possible? Does this not imply that the authors model overestimates SOA from the mechanisms presented here? It is known that aerosols tend to be acidic in at least one of the regions discussed (New England). // Perhaps the reviewer is right, but if the mechanism is acid catalyzed in the organic phase, we would expect our use of the non-evaporating model to account for this in a crude way. Our large SOA production is associated with the large partition coefficients that we calculate for some of the (especially biogenic) compounds. Smaller coefficients would allow a larger role to be played through the effect of acidity. This is something we hope to explore with our 3-D model.

- Page 8368. For this discussion, it must be specified that the partitioning theory presented is only looking at partitioning between gas and a condensed organic phase, not total aerosol. // The referee is right. Remove: ...is its partitioning coefficient between the aerosol and gas phases... Add: ...is its partitioning coefficient between the organic aerosol and gas phases...

- Page 8369, line 3. Other authors have used the Myrdal and Yalkowsky approach and yet still see underpredicted SOA values. What is the big difference then between this work and that presented previously? Is it all due to differences in the gas-phase mechanism? This needs to be explored in much greater depth as this appears to be the significant improvement of this model over others of the same type (MADRID, MCM, etc.). // The differences are not only related to the gas-phase mechanism, but to the species selection. The other models have not used the Myrdal and Yalkowsky approach for vapor pressure estimation together with the Griffin approach for SOA partitioning species selection. Note that on Page 8373 we speculate that our simulation of TORCH differs from that of Johnson et al. because of the inclusion of different species

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in the partitioning scheme, mainly derivatives from biogenic precursors. Johnson et al. reports that the average contribution of species derived from anthropogenic emissions to the simulated mass of SOA is 60%, but our calculations showed that this contribution is only 40%.

- Page 8369, line 10. The Pankow and Kamens paper state that activity coefficients of unity are appropriate for chamber experiments. Is this really true in the ambient atmosphere, particularly in urban areas with POA that is vastly different than SOA or in areas with high aerosol LWC? This assumption needs to be better justified. If the method of Bowman and Karamalegos is implemented, how different are the results? // Most of the literature consulted uses either a constant value of one, even for atmospheric simulations or for smog chamber experiments. There are several papers that use the Bowman and Karamalegos method or a similar one. We ran the ambient tests using the same initial conditions under the two different schemes for activity coefficient representation, and the final SOA concentrations were within 1%. The reason for the low sensitivity is the high partition coefficient that we derive for isoprene. This is now reported in the paper.

- Page 8369, line 28. Why only selected species? Should it not be all? // The wall removal process is only for the species that have their loss rate measured or calculated, many species do not suffer wall losses. We have clarified this.

- Page 8371, line 3. The isoprene comparisons should be more quantitative. The experiments of Kroll et al. used ammonium sulfate, which is not acidic. Also, these are definitely not the only isoprene experiments described in the literature. // The referee is right, we added a comparison of SOA formation from isoprene, from the work by Dommen et. al (GRL, 2006). The results of the comparison is similar to the a-pinene, toluene and xylene results.

- Page 8371, line 20. I would not call a 20K difference small. It implies that there could be issues with the authors' calculations of vapor pressures. In addition,

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it is very easy for the authors to blame the experimental results. Is there some other temperature driven process going on then? In addition, the differences in parameters cited should be quantified. // Comparing the cases PIN-102 and 103 with 301 and 302 (Table 2 in Page 8365), there is also a 20K difference, but these cases also have 4 times more initial α -pinene and 3 times more initial NO / NO₂. However, the final SOA concentration of the four experiments ranges from 36 to 95 mg m⁻³. By contrast, the cases PIN-101 and PIN-303 only differ in the temperature and the final SOA has a difference of 4.5 times. Nevertheless, you may be correct in that the partition coefficient for PINT (α -pinene oxidation product) may be too high. This is explained now in the text.

- Figure 1 should show the ratio of observed to simulated versus observed, rather than just simulated versus observed. In addition, in the results shown in Figure 1, how does the SOA behave as a function of time? Is it appropriate compared to chamber results? Instead of just showing final results, it is important to determine how the SOA model behaves over the entire course of a set of experiments since the final results are not always what are appropriate for the ambient atmosphere. // The reported studies just show final values, not the time evolution. We can add a plot with the simulated time evolution, but this would only be the results of the simulation. We believe the scatter plot represents the results more appropriately than a ratio plot.

- Page 8374, line 4. Why no POA emissions? // The ambient simulations do not intend to predict the total organic aerosol concentrations found in urban-influenced or rural sites, but only to have a rough estimation of SOA production under those conditions. Hence there was no need for POA emissions, and, typically measured SOA are much larger than POA. If we increase the initial POA by 100%, the final SOA will change less than 1%.

- Page 8374, line 5. 5000m seems high for average mixing height, especially since they are considering one that is constant. This is half the troposphere! // The referee is right, we reported incorrectly the mixing height, the right value is 1500 m. Page 8374,

line 5, remove: The calculations assume a constant mixing height of 5000 m Add: The calculations assume a constant mixing height of 1500 m

- Page 8374, line 8. If the evaporating model is more realistic (at least based on the theory upon which their model is established), it is the one that should be used. The non-evaporating model is essentially a vapor pressure correction (albeit smaller than that needed by other authors). It should not be used simply because it gives better results. // The molecules, once in the aerosol phase, can undergo dimerization and oligomerization reactions, thus lowering their vapor pressure. The non-evaporative model essentially assumes that these reactions occur and cause the organic molecules to have a lower vapor pressure. Nevertheless because the partition coefficient for the major SOA components are large, there is at most a 25% difference between the predictions of the evaporative and non-evaporative models. This has been clarified in the text.

- Page 8374, line 17. Five species contribute all of the SOA mass. Does this not seem unrealistically simple compared to the complexity of the real atmosphere, especially since the authors are using a first principles approach. Does this mean that the lumping in the gas-phase mechanism is inappropriate? // The lumped or surrogate-species representation of organics certainly means that fewer species are represented than in, for example, the Master Chemical Mechanism, which includes thousands of species. As discussed in the paper (p. 8364) we did a comparison between the lumped mechanism and a full calculation with the MCM and found little difference. Specifically, the runs simulating the smog chamber results using toluene as an SOA precursor, showed a 7% average difference between the runs using our chemical mechanism and the MCM. As stated on p. 8365, the mechanism includes 194 species and certainly does not lack for detail in comparison with other global model representations of gas-phase chemistry. As described on p. 8367, we identified 22 secondary semi-volatile oxygenated species that were capable of partitioning to the aerosol phase, and found that 6 of these partition in significant quantities. The mechanism did not include a detailed rep-

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resentation of high-carbon-number species, which include many more species capable of partitioning to the aerosol phase but which are present in much smaller quantities. Again, the reviewer is correct that the chemical representation would be improved if a detailed representation of high-carbon number species were added (greatly increasing the number of species which partition to the aerosol phase), but the actual representation is not at all simplified. Our purpose in these simulations was to test whether, in fact, we are able to use this mechanism.

- Page 8374, line 29. These results are in contrast to those from chamber experiments (Song, Presto) that show decreases in SOA with higher NO_x. As a result, the authors need to do zero-dimensional runs and compare to these experimental results to ensure that their model behaves appropriately with changes in NO_x before applying to three dimensions and making these claims. // The results presented are obtained from a zero-dimensional model. As the reviewer said, the work by Song et al. (Environ. Sci. Technol., 2005), states that experiments using m-xylene in a smog chamber, produces more SOA if the NO_x concentration is lower. Also, the work by Presto et al. (Environ. Sci. Technol., 2005) presents smog chamber experiments of SOA formation using a-pinene as precursor, and they report that for VOC/NO_x ratios below 15, the SOA yield decreases dramatically. Chen et al. (2006) find results that are in keeping with those from the smog chambers. We made a mistake in one reaction in the chemical mechanism and some results have changed, being one of them the NO_x sensitivity studies. Now, for the urban-influenced simulation, an increase of 40% in the VOC emissions produces 46% more SOA after three days, and an increase of 40% in the NO_x emissions decreases the final SOA concentration by 5.3%. For the rural site, the same increase in VOC emissions produces a decrease of 6.9% in the final SOA concentration, and the increase in NO_x emissions raises the SOA concentration in 44%. A discussion of these comparisons has been added to the paper.

- Page 8375, line 27. The authors should also consider the results from a Tsigaridis 2007 paper that states higher SOA from biogenic precursors results from increased

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O₃ and OH near urban areas. // Add at the end of line 29, page 8375: ... Recent simulations performed by Tsigaridis and Kanakidou (2007) showed that SOA formed from biogenic precursor dominates (about 90% of the total SOA), and also that higher SOA is formed from biogenic precursors near polluted land masses due to increased O₃ and OH fields. Add reference: Tsigaridis, K. and Kanakidou, M.: Secondary organic aerosol importance in the future atmosphere, *Atmos. Environ.*, 41, 4682-4692, 2007.

- Page 8376. It would also be appropriate to compare to the results of Chen et al. (2006) who performed three dimensional SOA calculations in the eastern United States and found dominance of terpenes in SOA formation. // The referee is right, comparison added.

- Page 8377, line 4. The authors claim that their model is advantageous because it does not rely on smog chamber parameters. They are not the first to take this approach (MCM, MADRID, among others) and this should be cited. // We had previously explained that our approach is similar to that of MADRID model, which is cited in page 8364, line 19. The MCM is a chemistry only model, though aerosols were added by Johnson et al. in the TORCH simulations.

- Page 8377, line 15. The authors say that some anthropogenic pathways may be missing from their model by discussing the modeling of Heald et al. and Volkamer et al. I suggest the authors also do some simulations (similar to what was done for comparison to deGouw) of these scenarios. These results would certainly help strengthen their arguments. // Although this is a good idea, we don't have enough data on the initial conditions to do such simulations. Moreover, a 1-d model would be needed to examine the SOA in the free troposphere as was studied by Heald. This is beyond the scope of this paper.

- Page 8377, line 25 (and following). Again, the recent results of Tsigaridis need to be discussed here. // Add in page 8377, at the beginning of line 25: The results of a model based on the two-products approach by Tsigaridis and Kanakidou (2007) show that

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the SOA from isoprene oxidation contributes about 30% of the total SOA over ocean, although the concentrations are low. Over tropical forests, isoprene also contributes significantly to the total SOA, but the SOA products from terpene oxidation dominate.

- Page 8378. The extrapolation to global values is completely inappropriate. If the authors want to estimate global SOA from certain compounds, then the SOA model should be implemented into the GCM that has been used by co-author Penner numerous times over the past years. If this is not done, the global portion of this paper needs to be removed. // We agree that a GCM model is needed for a realistic value of global SOA production, the values presented are only an estimate (Page 8378, line 23). A GCM model that includes SOA formation is under development, as stated in page 8379, line 6. Again, the mistake in the chemical mechanism and partitioning species led to a high global SOA estimation, now the results are still higher than other estimations but lower than our previous estimation.

- Page 8393. Include observations on Figure 4. // There are no observations in the de Gouw work of OC concentration at different photochemical ages.

- Abstract - Should not use "0" but rather "zero"-dimensional. Also in the abstract, x should be in subscripts. These should be applied throughout the document. GCM need not be defined in the abstract since it is not used again until the main body of the paper. // The referee is right.

- Page 8363, line 8. The paragraph contains only one sentence, which is inappropriate grammatically. // The referee is right.

- Page 8364, line 27 (and throughout). De Gouw should be de Gouw. // The referee is right.

- Page 8376, line 4. Need a space between influenced and conditions. // The referee is right.

- Page 8376, line 25. Should be of not os. // The referee is right.

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 8361, 2007.

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