

***Interactive comment on “Parameterising secondary organic aerosol from  $\alpha$ -pinene using a detailed oxidation and aerosol formation model” by K. Ceulemans et al.***

**K. Ceulemans et al.**

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We would like to thank all reviewers for their insightful remarks and questions. We trust that the adaptations made in response to their input have led to substantial improvements in the quality of our article.

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**1 Reviewer 1**

Reviewer 1: *“Initial concerns are that comparisons with just SOA max from different chamber studies are presented as opposed to showing how their simulations fit the entire SOA time concentration profile as SOA is being generated in the different chamber studies. It would also help the reader if similar simulations of SOA profiles from different chamber studies with the full-blown BOREAM model could also be shown, since it’s what the parameterised model in this study is supposed to be simulating.”*

Reply: We have included a more extensive comparison with the time evolution of SOA in the low- and high-NO<sub>x</sub> experiment of Ng et al. (2007), for which additional data were given in Valorso et al. (2011), see Fig. 2 and Section S2 in the Supplement. Time evolution data were not available for each experiment for which the SOA yields are listed in Table 1, however. In Capouet et al. (2008) we have also shown BOREAM model comparisons with time series of Nozière et al. (1999). We agree however that further model validation would be desirable, preferentially against SOA experiments including long-term photo-chemical ageing.

Reviewer 1: *“Further comments 1. The biggest concern is the issue of prompt production of SOA products if such a parameterised model is implemented in a global model. For example, much of the higher yields obtained in the low-NO<sub>x</sub> scenario is due to several days of ageing. However, implementation of a parameterised model developed here (that implicitly assumes yield from ageing) will lead to prompt SOA production for each timestep, leading to overestimation of SOA at shorter time-scales.”*

Reply: This concern is indeed justified, and has prompted an important revision to our method. The parameter model presented in the ACPD version of this article was

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able to reproduce SOA concentrations calculated by the full model at SOA equilibrium. However, further model calculations showed that the parameter model did not represent well the time-evolution during the SOA build-up phase. However, contrary to the Reviewer's expectations, the parameter model seriously underestimated the SOA concentrations during the build-up phase. It took longer for an SOA equilibrium to be established in the parameter model. It should first be noted that the SOA yields of the parameterisation are found to be increasing functions of  $M_O$ . Therefore, in the build-up phase, i.e. at low  $M_O$ , the SOA yields are also lower.

More importantly, the difference in time evolution between parameter model and the full model was due to a conceptual error in the method for estimating the yield of condensable products. It was assumed that, once SOA is at equilibrium, this equilibrium is maintained due to a balance between the additional production of aged organic material and the organic aerosol lost due to deposition. As we have seen, this evaluation of the yields leads to the correct SOA concentrations at equilibrium, but it underestimates SOA during SOA build-up. Moreover, when calculating the (time-dependent) yield as  $Y = (\Delta[OA] + \Delta[OA]_{\text{dep.}})/\Delta[\alpha\text{-pinene}]$ , where  $\Delta[OA]$  is the actual organic aerosol concentration increase during one day, and  $\Delta[OA]_{\text{dep.}}$  the amount deposited during this day, this yield is found to be highest during the first days of the simulations, and to gradually decrease afterwards. This is contrary to the expectation based on the partitioning theory (Pankow, 1994) that yields should increase with increasing mass loadings.

The reason for these failings is the existence of a second loss mechanism for SOA at SOA equilibrium, besides deposition. This second loss is the net effect of photochemical processes. These processes include both decomposition and functionalisation reactions. On average, these structural changes lead to an increase in volatility, and by consequence to a decrease in SOA. We have conducted sensitivity tests to estimate how much SOA material is lost in this way (see Figs. 3 and 4). This was achieved by turning off further  $\alpha$ -pinene oxidation and further product deposition on day 13 of

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the simulation. In this way the further changes in SOA concentrations are only due to photo-chemical reactions acting on these condensable species, among which reactions with OH and photolysis are the most significant ones. It is found that these tests result in a significant decrease of SOA loadings. This might seem contrary to the notion that photo-chemical reactions are responsible for oxygenation of SOA material, and therefore to increases in SOA loadings. However, here SOA is already at an equilibrium and has undergone significant ageing. For this aged material further photolysis reactions can lead to decomposition of the condensable molecules and repartitioning towards the gas phase. Separate tests show that if only OH reactions were to take place, without any photolysis, the SOA concentrations would still increase further due to increased functionalisation. The combined effect of photolysis and OH reactions still invariably leads to a decrease of SOA.

Therefore in the updated method we estimate the net amount of SOA lost during one day due to photochemical processes, which we call the photochemical OA loss,  $[OA]_{\text{pl}}$ . The correct SOA yield is then  $(\Delta[OA]_{\text{dep.}} + \Delta[OA]_{\text{pl}})/\Delta[\alpha\text{-pinene}]$ . Using the above formula for calculating the SOA yield, the additional production must be balanced in the parameterisation by an additional sink besides deposition. We therefore introduce a pseudo-photolysis reaction of the condensable products in the parameter model, with a photo-rate  $J_{\text{pl}}$  fitted based on the photochemically lost material estimated from full BOREAM model runs. For each scenario, the same photolysis rate is applied to both condensable compounds of the two-product model, in the gaseous and in the particulate phases. The procedure for estimating  $[OA]_{\text{pl}}$  and the temperature-dependent fitting of the photo-rates for each oxidation scenario will be described in more detail in the Supplement, Section S3. Since our model scenarios used maximum photolysis rates calculated assuming a 20° solar zenith angle, extrapolation of the SOA photolysis rate to any radiative condition is made by scaling the retrieved maximum photo-rate with the photolysis rate of higher aldehydes:

$$J_{\text{pl}} = f_{\text{pl,max}} \cdot J_{\text{ald}}$$

with  $f_{\text{pl,max}} = J_{\text{pl,max}}/J_{\text{ald,max}}$

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where  $J_{\text{pl,max}}$  and  $J_{\text{ald,max}}$  are the maximum photolysis rate of SOA and of higher aldehydes, respectively, in our model scenarios. For each of the 5 oxidation scenarios considered, we then derive a temperature-dependent fit for the functions  $f_{\text{pl,max}}$  (see Table S9 in the Supplement).

We have updated all simulations conducted with this new version of the parameter model. Comparison between the full model and the parameter model shows that although agreement near SOA equilibrium has not improved in the new method, the time-evolution during SOA build-up agrees much better now with the full model. Still, it was not possible to match this time evolution in all cases. Sometimes during the first days significant underestimation persists, especially at low  $M_O$  concentrations (below  $0.5 \mu\text{gm}^{-3}$ ) and high temperatures (298 K-303 K). The best possible agreement was aimed for in the range of atmospherically relevant  $M_O$  values ( $0.5 - 20 \mu\text{gm}^{-3}$ ). We have conducted an extensive comparison of the full and parameter model yields, and find that in the majority of cases agreement is satisfactory. We have included a number of comparisons of the full and parameter model using meteorological and chemical conditions obtained with a global CTM, the IMAGESv2 model (Stavrakou et al., 2012). Averaged over all scenarios and locations the deviation is about 25%, with only a small number of deviations of more than a factor 2, occurring only at low SOA concentrations. The above model update and verification is now described in Sections 3.2-3.4 of the new manuscript.

Reviewer 1: *"In addition the paper could be dramatically strengthened if comparisons with the VBS modelling approach could be shown for, again the same chamber data." "In that context, the VBS method with ageing allows representation of SOA formation at different time-scales and might turn out to be more accurate temporally. One interesting approach to be considered to address this concern is to introduce SOA parameterisation based on ageing. The implementation of such a technique in a global model can be implemented by tracking the age of the reacted alpha-pinene mass."*

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*"3. Have the authors considered a condensed kinetic lumped product technique instead of the 2-product model approach? This again can help the accurate kinetic representation of the process of ageing, currently a big uncertainty for global models"*

We agree that an approach using a volatility basis set ('VBS') might be promising too. However as such a transition towards a fitting of a VBS would imply a significant deviation from the approach which we originally undertook, we have opted to retain the original aspect of fitting two products per scenario in this study. Stanier et al. (2008) showed that it is possible to fit the temperature-dependence of SOA yields using a 1-dimensional VBS for one oxidation scenario. A remaining problem was however that the values for the enthalpies of vapourisation were also fitted against that particular scenario. It has not been shown yet whether it is possible to fit accurately multiple temperature-dependent scenarios using one VBS with products for which properties such as enthalpies of vapourisation are all fixed. This deserves further investigation, given the obvious advantage of the VBS method that the VBS products for  $\alpha$ -pinene could be reused for the parametrisations of SOA due to other precursors.

It is not clear how the age of reacted  $\alpha$ -pinene mass could be tracked in a framework based on our parameter model. A more complex formulation would be needed in order to account for the changes in SOA properties due to ageing. One such approach can be found in Xia et al. (2011), where a fitted VBS with a high level of accuracy in reproducing the full model SOA evolution was obtained. One drawback was however that the fitting took place at a fixed temperature of 298 K.

The parameters in our model were adjusted based on the concentrations of aged SOA at equilibrium. We have verified however that the SOA build-up is also well rendered (see above), and found that the agreement with the full model under atmospheric conditions is generally reasonable (see Sections 3.3 and 3.4).

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Reviewer 1: "2. 10-product model is a misleading term. The box-model essentially is used to get parameters for a 2-product model, albeit for 5 different starting conditions. This is equivalent to performing 5 sets of smog chamber experiments and fitting a 2-product model for each set. I would suggest not using the term 10-product model as it can be misleading to the readers."

Reply: We agree with the referee, and will therefore only use the term 'parameter model' to refer to the fitted small-size model. The model still contains 10 condensable products however, besides 4 peroxy-radicals. There are now 25 photo-chemical equations (of which 10 new photolysis reactions) in the parameter model.

Reviewer 1: 4. "This approach might be harder for aromatics and isoprene, where the explicit chemistry is not fully developed, particularly particle-phase reactions. Also, the effects of types of seed and lower concentrations of seed is harder to quantify in a parameterised model."

Reply: We have not verified this approach yet for aromatics and isoprene, exactly for the reason suggested by the reviewer.

## 2 Reviewer 2

Reviewer 2: "The authors interchanged the use of terms such as 'full model', 'fitted model', 'parameterised model', 'box model', 'parameterised BOREAM model', 'BOREAM full model' etc. throughout the manuscript. It is confusing at times as to which model the authors are referring to. This makes it difficult to interpret some of their results and follow the discussions. The authors should be consistent in their description and use of different terms, both in the text as well as the figure labels."

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"3. Page 23434, last paragraph of Section 2.5: a. Line 3. 'Modelled and experimental SOA mass yields. . .'. I assume the authors are referring to the 'full model'? The authors should be consistent and clear with their use of different terms such as 'full model', 'fitted model', 'parameterised model', 'BOREAM model', 'BOREAM full model' etc."

Reply:

We have only conducted simulations of smog chamber data using the full BOREAM model. The parameter model in this study has been adjusted in order to reproduce aged SOA, and therefore would not be necessarily appropriate to simulate shorter duration smog chamber experiments. To avoid any confusion, the revised manuscript mentions whether the 'full' or 'parameter' model is meant.

Reviewer 2: "2. Section 2.3: The authors wrote 'The present model version includes aerosol phase photolysis, with identical J values and product distributions as in the gas phase, in view of lack of more reliable data'. Does this mean that the authors consider only the photolysis of those species that are present in both particle- and gas-phases? Can this potentially underestimate the effect of photolysis by excluding the photolysis of compounds that are only present in the particle-phase? (formed through particlephase reactions etc). "

Reply:

All condensable products considered in the full model partition between the aerosol and the gas-phase. The current BOREAM model does not take particulate phase chemistry into account (except photolysis). Reliable rate constants for other types of

particle phase reactions are still very scarce, and therefore particle phase chemistry is generally not included in SOA formation models for monoterpenes, such as Valorso et al. (2011), Xia et al. (2008) and other studies.

Reviewer 2: " *b. Line 4. The authors noted that the factor of 2 of overestimation may arise from uncertainties in yields of products such as pinic acid formed in ozonolysis reactions. However, as  $\alpha$ -pinene ozonolysis and photooxidation form very similar products, such products are also formed in  $\alpha$ -pinene photooxidation. How does this uncertainty affect the results of their photooxidation simulations? "*

Reply: The experiments of Takekawa et al. (2003) are photo-oxidation experiments, in which a considerable fraction of  $\alpha$ -pinene undergoes ozonolysis. Pinic acid represents about 8% of the SOA in the experiments of Takekawa et al. (2003) at 303 K, for which SOA mass yields were overestimated by around a factor 2. Even if pinic acid production would be suppressed under high- $\text{NO}_x$  conditions, this difference alone could only partly explain the model overestimate of the SOA yield. Besides pinic acid, most species in the SOA in these experiments bear a peroxy acetyl nitrate group. Uncertainties for the formation and decomposition of such species could therefore explain part of the model overestimates for Takekawa et al. (2003). For other experiments, such as Ng et al. (2007), pinic acid production is negligible as most  $\alpha$ -pinene reacts with OH there.

We have adapted the discussion of these experiments in the text:

'In some experiments, such as Takekawa et al. (2003) and Hoffmann et al. (1997), there is a considerable ozone production, so that part of the  $\alpha$ -pinene undergoes ozonolysis. A small part of the large overestimations (more than a factor 2) found for three experiments of Takekawa et al. (2003) might be related to uncertainties regarding the yield of carboxylic acids, such as pinic and hydroxy pinonic acid, which are formed in  $\alpha$ -pinene ozonolysis, but for which the formation mechanism is not well understood

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(Ceulemans et al., 2010). Their production yield is held fixed in the model, although it is very probably dependent on photochemical conditions, e.g. the  $\text{NO}_x$  abundance. Pinic acid is found to represent about 8% of the SOA in the experiments of Takekawa et al. (2003) at 303 K. Therefore errors in pinic acid production alone cannot explain much of the model overestimates. Most species in the SOA in these experiments bear a peroxy acetyl nitrate group. Uncertainties regarding the formation and decomposition of such species could therefore be responsible for part of the model overestimates.'

Reviewer 2: " *4. Page 23436. According to the authors, the full model is conducted under 5 scenarios in which  $\alpha$ -pinene is limited to one oxidant under high or low  $\text{NO}_x$  conditions. But in the ' $\alpha$ -pinene +  $\text{O}_3$ , high  $\text{NO}_x$ ', is the  $\alpha$ -pinene truly only reacting with ozone? With the presence of  $\text{NO}_x$ , some OH will be formed (I think this is how 'traditionally' photooxidation experiments have been carried out in the past, for example, Odum et al, Griffin et al., before the use of  $\text{H}_2\text{O}_2$  and HONO). I will expect some  $\alpha$ -pinene will react with OH. Hence it's not truly 'limited to one oxidant'. Please clarify."*

Reply: In these full model simulations we limited the  $\alpha$ -pinene oxidation to one oxidant by setting the reaction rates with the other two oxidants to zero in the model. Oxidation products were allowed to react with all oxidants present however. In the simulations under ambient conditions generated with the CTM IMAGESv2,  $\alpha$ -pinene was allowed to react with all oxidants.

Reviewer 2: " *5. Page 23438. Comparison of full model and parameterised model, Figure 1. Why does the  $M_O$  start at higher values with decreasing temperature? The parameterised model seems to level off at higher  $M_O$  values but not the full model, why? "*

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Reply: In the updated version of the article the figure referred to has become Fig.6.a. For the fitting of the parameter model, 14-day full model simulations of 5 oxidation scenarios were performed at 7 different temperatures and at 28 different  $\alpha$ -pinene concentration levels, in order to cover SOA formation over a range of  $M_O$ . We used the same 28  $\alpha$ -pinene concentrations at all temperatures. Therefore at lower temperatures the minimum values of  $M_O$  increased. We agree that at the higher  $M_O$  concentrations (above  $50 \mu\text{gm}^{-3}$ ) the agreement of the fitted parameter model with the original full model is often bad. This is due to our choice to seek the best possible agreement in the atmospherically most relevant range of about  $0.5\text{--}20 \mu\text{gm}^{-3}$ .

Reviewer 2: "6. Page 23439. Regarding the intermediate  $\text{NO}_x$  experiment, the authors wrote 'In the full model, however, a reaction with  $\text{HO}_2$  can be followed by a reaction with  $\text{NO}$ , leading the formation of a much volatile product.' Why is that such reaction (a reaction with  $\text{HO}_2$  can be followed by a reaction with  $\text{NO}$ ) only occurs in the full model but not the parameterised model? Shouldn't the branching of  $\text{RO}_2 + \text{HO}_2$  vs  $\text{RO}_2 + \text{NO}$  be taken into account in the parameterised model too and hence the  $\text{RO}_2$  in the parameterised model can also react with  $\text{NO}$ ? (since the authors have obtained different parameters for low  $\text{NO}_x$  and high  $\text{NO}_x$  conditions, I would expect the parameterised model should also be able to handle the intermediate  $\text{NO}_x$  condition)."

Reply:

The parameters for low- $\text{NO}_x$  and high- $\text{NO}_x$  conditions were obtained from simulations in very high or very low  $\text{NO}_x$ , i.e. in conditions such that there is no competition between the  $\text{NO}$ - and  $\text{HO}_2$  reactions of peroxy radicals. In the BOREAM model, the low-volatility compounds which make up SOA are polyfunctional compounds resulting from a succession of oxidation steps involving therefore several peroxy radicals. In absence of  $\text{NO}_x$ , each of the several successive peroxy radical reactions adds a hydroperoxide group, thereby lowering the vapour pressure by several orders of

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magnitude. At intermediate  $\text{NO}_x$ , in the full model, the yield of these polyfunctional hydroperoxides is proportional to  $(f_h)^n$ , where  $f_h$  is the fraction of each peroxy radical reacting with  $\text{HO}_2$ , and  $n$  is the number of peroxy radical steps required to form the low-volatility compounds. In a parameter model including only one generation of peroxy radical, the yield of low- $\text{NO}_x$  compounds is proportional to  $f_h$ . Since  $n$  is higher than one, it is easily seen that the yield of very low-volatility compounds typical of low- $\text{NO}_x$  conditions decreases more rapidly with  $[\text{NO}]$  in the full model than in the simple parameter model. It was hence found necessary to modify the scheme and introduce second generation peroxy radicals, in order to more closely match the  $\text{NO}_x$  dependence of SOA yields of the full model.

Reviewer 2: "7. Page 23440. Sensitivity of photolysis as well as  $\text{OH}$  and  $\text{HO}_2$  concentrations. In Figure 5 the authors present the results on the effect of  $\text{NO}_2$  levels on BOTH the full model and the parameterised model. However, in Figure 6, they only present the results on the effect of photolysis/ $\text{OH}/\text{HO}_2$  on the 'BOREAM model' (as noted in the C12308 axis label). Is this (Figure 6) the full model or the parameterised model? If it is the full BOREAM model, then what are the effects of photolysis/ $\text{OH}/\text{HO}_2$  on the parameterised model? Is that similar to the full BOREAM model?"

Reply:

This section indeed lacked a proper discussion of the effects of variations in photolysis/ $\text{OH}/\text{HO}_2$  on the parameter model. We have now included graphs and a discussion of sensitivity tests to photolysis/ $\text{OH}/\text{HO}_2$  with the parameter model in Section 3.4.2 and 3.4.3. As the impact of these factors had not been explicitly fitted into the parameter model, there are some discrepancies between full model and parameter model when the levels of radiation,  $\text{OH}$  and  $\text{HO}_2$  have values differing from the ones used in the parameter fitting simulations. In particular, the parameter model is not sensitive to changes in  $\text{OH}$  and  $\text{HO}_2$  at the very low  $\text{NO}_x$  level. By contrast, the

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increase when radiation is lowered by changing the zenith angle to 45° is larger in the parameter model than in the full model, again resulting into an extra deviation between parameter and full model.

Reviewer 2: "8. Page 23441, line 4. 'Small but significant uncertainty?' - what does this mean? Small, or significant?"

Reply: The error introduced by choosing one fixed concentration profile for OH and HO<sub>2</sub> amounts to 10-15% in the discussed test. We have changed this sentence to: 'In conclusion, the use of a fixed diurnal profile for OH and HO<sub>2</sub> in the model calculations introduces an uncertainty in the parameterised SOA formation rate, estimated to be typically of the order of 10-15%.'

Reviewer 2: "9. Page 23441. Section 3.5: a. The title of this section is 'Comparison with parameterised models based on experimental yields'. I am very confused whether they are comparing the results from their full BOREAM model or parameterised model to other models. In their discussions, it seems like they are referring to the parameterised model. However, in the figure, the results are referred to as 'BOREAM' and they look different from those parameterised models results in Figure 3 (for example, in Figure 3, the SOA yield at  $M_O=30 \mu\text{g}/\text{m}^3$  for OH, low  $\text{NO}_x$  is  $< 0.5$ , but in Figure 5, the SOA yield at  $M_O=30 \mu\text{g}/\text{m}^3$  for OH, low  $\text{NO}_x$  is  $> 0.5$ ). This section needs to be clarified as to which model they are actually discussing about."

Reply: There was indeed an inconsistency in the graphs presented, where in some cases only the full model yield curve, and in some cases only the parameter model yield curve was given, as indicated by the reviewer. We have resolved this problem by giving both in Figs. 7 to 9 (revised article numbering). In Fig. 12 the curves are the parameter model curves, which however do not deviate very strongly from the full

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model ones.

Reviewer 2: "b. Figure 1 and Figure 6 both compare the results from this study to other studies. The manuscript will be more well-organised if the descriptions of these two figures were combined and discussed in a more-coherent way. If possible, the authors should also put other data points (instead of just Ng 2007) on Figure 6. Note: Two data points (black \*) in Figure 6 are labeled as Ng 2007 high- $\text{NO}_x$ . One of those experiments should be an intermediate  $\text{NO}_x$  experiment instead of high- $\text{NO}_x$  (I think probably that is why the authors excluded that in Table 2). This needs to be corrected.."

Reply: We wanted to first discuss performance of the full BOREAM model against experiments before introducing the parameter model based on this full model. Therefore we prefer to keep the organisation of these sections in the revised version. We now show only the low- and high- $\text{NO}_x$  experiments (experiments 1 and 4 of Ng et al. (2007) for which additional data and modelling was given in Valorso et al. (2011)) in Fig. 12 of the revised article. The other experiments were more problematic, as was discussed in the text. For the intermediate- $\text{NO}_x$  experiment in Valorso et al. (2011), which was wrongly indicated as low- $\text{NO}_x$  in Fig. 12) it was found impossible to reproduce both the  $\alpha$ -pinene decay and ozone-production. These difficulties were also found to some extent by Valorso et al. (2011). As we felt that the uncertainty introduced to the SOA production by such errors in the gas phase chemistry is large, we chose not to include this experiment in the modelling results. We acknowledge that this modelling problem deserves further investigation. However other tests show that for most other experiments the BOREAM model is reproducing ozone and NO profiles well (see Section S2 in the Supplement).

Reviewer 2: "c. The authors noted that one of the reasons for the large difference in the simulated yields and measured yields could arise from the shorter duration of

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*the experiments (several hours) as opposed to the multi-day ageing in their models. However, as the authors pointed out, Presto et al. (2005) high-NO<sub>x</sub> experiments agreed well with their high-NO<sub>x</sub> simulations. The experiments in Presto et al. (2005) were performed in a 10m<sup>3</sup> chamber under moderate oxidation conditions; I do not think multi-day ageing was achieved in those experiments either. If the authors' argument is correct, how would that explain the good agreement between the Presto et al. (2005) results and their results?"*

*"9.d. The authors noted that under low-NO<sub>x</sub> conditions, ageing increases their simulated SOA yields through further reactions with OH and HO<sub>2</sub>, while under high-NO<sub>x</sub> conditions, aging decreases their simulated SOA yields through decomposition of the products. However, in the high-NO<sub>x</sub> experiments, shouldn't the prolonged exposure to OH also increase functionalisation of some products and lead to a higher SOA yield? Please clarify."*

First of all our original appraisal that the Presto et al. (2005) high-NO<sub>x</sub> yields agree well with our high-NO<sub>x</sub> yields was not correct; the Presto et al. (2005) yields were actually lower. It should be noted that for a large range of  $M_O$  values there were no data available for the high-NO<sub>x</sub> fitting in Presto et al. (2005), probably adding to the uncertainty of this fitting.

We find that some ageing at first increases the SOA yields at high-NO<sub>x</sub>. Evidence for this is provided by ozonolysis experiments in the presence of an OH scavenger (see for example Presto et al. (2005)), which generally show lower SOA yields under high-NO<sub>x</sub> than experiments where ageing is possible.

However if ageing is continued over a long time scale until equilibrium is reached, further ageing generally leads to an increase in volatility, such as shown in the simulations in Fig. 4, presumably because the impact of product decompositions overtakes the importance of functionalisation. Ageing might therefore indeed increase the SOA yields

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over a short time-scale (several hours), whereas long-term ageing might decrease the yields. Such an effect was also observed during ageing experiments in the recent study of Lambe et al. (2011).

We have updated the discussion in Section 3.5 of high-NO<sub>x</sub> yields in the parametrisations. The updated discussion includes the following:

'By contrast, for the high-NO<sub>x</sub> parameterisation based on BOREAM, SOA yields are lower than in most parameterisations from other studies based on high-NO<sub>x</sub> photo-oxidation experiments. In the BOREAM simulations of photo-oxidation at high-NO<sub>x</sub>, the reaction with NO yields mostly alkoxy radicals, and some nitrates or peroxy acyl nitrates (PANs) as side products. The alkoxy radicals can in some cases decompose, which leads to smaller carbon chains or to a loss of oxygenated functional groups, increasing volatility. This explains the large difference found between high and low-NO<sub>x</sub> yields, and also why ageing over a long time period of two weeks under high-NO<sub>x</sub> conditions might lead to lower SOA yields than seen in high-NO<sub>x</sub> photo-oxidation experiments of shorter duration (several hours). As an illustration, the high-NO<sub>x</sub> experimental yield of Ng et al. (2007) experiment 4 is shown in Fig. 12. This yield is higher than in the BOREAM scenario for photooxidation at high-NO<sub>x</sub>. It should be noted that in the simulation of this experiment, the full BOREAM model calculated SOA yields comparable to the experimental SOA yields (see Fig. 1, Fig. 2. b and Fig. S6 in the Supplement).

One exception is the high-NO<sub>x</sub> case of Presto et al. (2005) in which even lower yields were found. This last experiment was a dark ozonolysis experiment with an OH scavenger, resulting in only first generation products, which are generally less condensable than more aged products.'

Reviewer 2: "10. Has the effects of aqueous-phase chemistry (e.g. Ervens et al., 2011) been considered in all these simulations?"

C16179

Aqueous-phase chemistry has not yet been considered in the BOREAM model. Its possible impact especially at high RH deserves further investigation.

### 3 Reviewer 3

Reviewer 3: *"The authors note that there is a very large uncertainty in the generic chemistry part of their model, because the choices of rate constants for further-generation oxidation products are made for a large number of reactions with no differentiation between them. It is unclear whether the uncertainty stemming from the choice of rate constants will lead to a large uncertainty in their eventual results; perhaps this uncertainty could be explicitly addressed in a subsection of Section 3 (by analogy to the other sections where changes in the parameters are explored). In the conclusion, the authors restate the large uncertainty due to the chemistry of further generation products; for this reason, it would be good to see them attempt to estimate the magnitude of this uncertainty."*

Reply:

In order to address uncertainties due to the generic chemistry mechanism, we conducted several sensitivity tests on smog chamber simulations, and added the following paragraph to the main article, Section 2.5.

' Fig. 2 shows the sensitivity of calculated SOA to changes in the values of key parameters in the generic chemistry scheme of the BOREAM model, such as the assumed value for ' $k_{LX}$ ', the reactivity towards OH (see Table S1.2.1 in the Supplement), and the J-value ' $j_{LXALD}$ ' of the generic part of the generic species (see Table S1.2.2 in the Supplement). The tests show that their impact on simulated SOA mass yields is limited for both the low- and high- $\text{NO}_x$  experiments 1 and 4 of Ng et al. (2007). Tests

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in which the branching ratios of alkoxy radicals towards decomposition and H-shift isomerisation are varied, show that these have a larger impact on predicted SOA in the high- $\text{NO}_x$  case. A test in which 100% of alkoxy radicals undergo H-shift isomerisation leads to a large increase of predicted SOA yields. However this assumption is most likely not realistic, and even an assumed branching ratio of 50% of H-shift might be on the high side. In that case there is still a significant increasing effect on SOA yields. Addressing this uncertainty of the generic chemistry scheme would require characterising more explicitly the species corresponding to the different generic species classes, for example with the help of a self-generating mechanism approach such as used in Valorso et al. (2011). Structure activity relationships for alkoxy radicals such as those in Vereecken and Peeters (2009) and Vereecken and Peeters (2010) can then be used to obtain a more thorough estimate of the alkoxy radical branching for generic species.'

Reviewer 3: *"On page 16-17, I would ask the authors to include a statement about how the reference molecular weight ( $MW_{\text{ref}}$ ) of molecules in the SOA was estimated or determined."*

Reply:

The following clarification was added to Section 3.2:

'The values for  $MW_{\text{ref}}$  are chosen per oxidation scenario, at a temperature of 298 K and for an  $\alpha$ -pinene concentration leading to an equilibrium SOA concentration around  $2.5 \mu\text{g m}^{-3}$ . In simulations with the full model at other temperatures and  $\alpha$ -pinene concentrations,  $MW$  varies by not more than roughly 5% from this reference value. In the full model the average  $MW$  of SOA is calculated based on the molecular masses of the explicit species and on estimates for the generic species classes.'

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