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Comment on acp-2021-571

Arto Heitto et al.

Author comment on "Effects of oligomerization and decomposition on the nanoparticle growth: a model study" by Arto Heitto et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-571-AC1>, 2021

Reply to the reviewers' comments on the manuscript "Effects of oligomerization and decomposition on the nanoparticle growth, a model study" by Heitto et al.

Comments by the reviewers are written below on **bold**, our reply in normal text and modifications for manuscript in *italic*.

RC 1

The Manuscript provides good insights about the role of oligomerization and decomposition. It is well written and deserves to be published. I have the following comments for clarification of the methodology:

We thank the Reviewer 1 for the supportive comments. We have now carefully considered the comments and revised the manuscript accordingly. Please find below our detailed reply for each comment.

- **Page 2: Please provide specific examples of decomposition reactions in particle phase and their expected rates. Currently examples are provided for oligomerization, but decomposition just seems to come from fitting.**

It is true, that our examples come only from fitting. The reason for this is, that at the moment, the reaction rates and identities of decomposing compounds are largely unknown and uncertain, and therefore we also lack good examples of measured reactions and reaction rates.

- **Please clarify if oligomerization is only considered for molecules in particle phase or does it include both gas and particle phase molecules in a given volatility bin. It seems the authors only consider particle phase oligomerization/decomposition, but some discussions later on make this confusing. See my comments later.**

We indeed consider oligomerization and decomposition only in the particle phase. In order

to clarify this, we have added "*particle-phase*" in the text in last paragraph of the Introduction where we state our study focus (line 60, in the marked up revised manuscript version).

- **Line 240: If oligomerization is just in particle phase, why does reducing gas-phase concentrations from compounds oligomerizing in same bin hinder growth? If particle phase oligomerization reduces why will it reduce gas-phase concentrations? I would think it will be the opposite. Due to decrease in oligomerization, more reacting compounds will be available to establish equilibrium with gas-phase in a given bin, so gas-phase concentrations will be higher. This is confusing and needs explanation.**

It seems that our explanation has been unclear and has caused a misunderstanding. Oligomerization reaction does not reduce gas-phase concentrations in our simulations. In our simulations the gas phase concentrations are given as input and assumed constant and therefore gas-particle equilibrium will not be achieved by using up the gas phase compounds by condensation. Instead, the effect mentioned here is related to the amount of reacting compound, i.e. the driving force of the condensation and reactions. In case of compound reacting with itself (same VBS bin) there is only 1/3 of that one bin available as reacting compound and the growth is hindered compared to the case where compounds from two separate bins react with each other (1/3 of each bin). This is because of our assumption that same fraction (1/3) of the gas-phase concentration of each bin is assigned as reactive compound, i.e. allowed to go through the oligomerization reaction, and therefore the total reacting concentration is smaller in case where only one bin is reacting instead of two different bins reacting with each other. However, also in this case oligomerization does still enhance the growth compared to the case where no particle-phase reaction is taking place. In order to clarify this, we have revised the text and it now reads (line 258) as:

*"In Fig. 2 e-f the case when $C^*_{o,2}$ is $10 \mu\text{g m}^{-3}$, i.e. when both reacting compounds have same volatility, is diverging from the general trend of how volatility of reacting compound affects the growth. The reason for this is, that since we have assumed only one third of a bin are compounds that can go through reaction in the particle-phase, the total gas-phase concentration of reacting compounds is lower (one-third of one bin) than in the case of compounds of different bins reacting with each other (one-third of each bin)."*

Note also that in the revised manuscript we have added in Fig. 2 e-f a simulation where 2/3 of the bin with $C^* = 10 \mu\text{g m}^{-3}$ can react, in order to demonstrate the pure effect of volatility of the reacting compounds and avoid the effect of reduced total concentrations of reacting compounds when reaction is between the compounds of same bin. Please see our response for Reviewer 2.

- **Line 220: Why is there an enhancement in condensation (from gas-phase?) due to oligomerization?**

Condensation of the reacting compounds is enhanced as oligomerization reactions use the condensed reactive compound and therefore decreases its particle phase molar fraction and further its equilibrium vapor concentration. As the oligomerization product is assumed only to form in the particle phase, its gas phase concentration is zero and it will evaporate to some extent. The net effect of oligomerization on particle growth rate is the sum of these two effects. In order to clarify this in the manuscript, we have added in the text (on line 234) following:

"Also in this case, oligomerization reactions decrease the molar fractions of the condensing compounds in the particle phase therefor decreasing their equilibrium vapor concentration and enhancing their condensation."

▪ **Line 260: How does difference in volatility between oligomerizing and product compounds affect growth of sub-5 nm particles?**

The net effect of oligomerization on particle growth rate is combination of enhanced condensation of the reacting compound and evaporation of the formed oligomer. The former depends on C^* of reacting compound and the latter on C^* of the product, and therefore the net effect depends on the difference in these volatilities. If the difference in volatilities of the reacting and product compound is large enough, the growth is enhanced also for sub 5nm particles. To clarify this, we have changed the word "affect" to "enhances" in line 287 and added text (on line 288):

"If k_{olig} is high, even the small equilibrium particle phase concentration of the SVOCs, which is decreased further for small particles due to surface curvature, may lead to significant oligomer production, and if the product is enough low volatile, the increase in equilibrium vapour concentration due to the surface curvature will not drive it to evaporate quickly even from the smallest particles and, thus, particle growth is enhanced."

▪ **Line 305: What are relative timescales for oligomerization and evaporation of higher volatility compounds?**

As noted by Reviewer 2, the original sentence was not exact. We have modified text here, following the suggestion by Reviewer 2, and do not refer to time scale of evaporation at this point anymore. The text now reads (on line 333):

"Even for simulations where the most volatile compounds in our setup (bin 1 and 2) oligomerize, growth does not increase much with these low k_{olig} , since the rate of production of the less volatile oligomers is low due to the small equilibrium particle phase concentrations of the reacting compounds and the low reaction rate coefficient. With larger k_{olig} however, these higher volatility molecules will oligomerize significantly despite their small equilibrium particle-phase concentrations."

▪ **I understand the authors did not consider diffusion limitations. But it would be good to say what particle sizes would diffusion limitations be important? For example, I would think larger particles will have larger diffusion limitations, and there, if diffusion limitations prevent evaporation of higher volatility molecules that oligomerize, would the growth rate be higher?**

The size at which particle phase diffusion limitations become important depends on the viscosity of the particles and there are uncertainties related to viscosity of secondary organic aerosol. For SOA particles formed in oxidation of α -pinene, laboratory measurements at atmospherically relevant RH have indicated viscosities of up to 10^9 Pa s (e.g. Renbaum-Wolf et al., 2013; Zhang et al., 2015; Yli-Juuti et al., 2017). Characteristic time of bulk diffusion corresponding to this viscosity would be less than an hour for particles of 10 nm in diameter and over a day for 100 nm particles (Shiraiwa et al., 2011). Considering that the growth of nanoparticles takes place over hours, this suggests that particle phase diffusion limitations would become important between 10 nm and 100 nm.

Particle phase diffusion limitations, arising from the viscosity of the particles, slow the mixing of molecules inside the particle. This may have various effects of particle dynamics in the atmosphere, where gas phase concentrations may change. If gas phase concentrations around the particles would decrease, for instance due to weakening of photo-oxidation, to the point that evaporation of the condensed semi-volatile molecules would be thermodynamically favorable, the evaporation of semi-volatile compounds could slow down due to particle phase diffusivity limitations. If the semi-volatile compounds go through oligomerization reactions, this slowing of evaporation would allow them more time to convert to less volatile compounds. However, in situation similar to our simulations, i.e. with constant gas phase concentrations, particle growth could be slowed down due to particle phase diffusion limitations as condensing semi-volatile molecules would not mix instantaneously within the whole particle. The non-instantaneous mixing could increase their equilibrium vapor concentration (due to the Raoult's effect) and their oligomerization reactions could also slow down. On the other hand, if condensed lower volatility molecules decompose and form more volatile molecules, the evaporation of the products could be slowed down due to the particle phase diffusion limitations and in this case particle growth could be faster than in case on liquid-like particles. Effect of viscosity is a topic of future studies and out of the scope of this manuscript. Due to the complexity of viscosity effects, we prefer not to add discussion of its possible effects on growth rate. We have included following text at the end of Sect 2.1 (line 139):

"For example, viscosity of 10^9 Pa s, corresponding to upper limit estimates of α -pinene SOA particles at atmospherically relevant RH (Renbaum-Wolf et al., 2013; Zhang et al., 2015; Yli-Juuti et al., 2017), would indicate characteristic time of bulk diffusion of less than an hour for 10 nm particles and over a day for 100 nm particles (Shiraiwa et al., 2011). Considering that the growth of nanoparticles takes place over hours, with such high viscosity, particle phase diffusion limitations could become important in the size range between 10 nm and 100 nm. The lower the viscosity, the larger the size where particle phase diffusivity becomes important (Shiraiwa et al., 2011)"

RC2

In the study at hand, Heitto et al. investigate the effect of condensed-phase oligomerization and decomposition reactions on the growth of atmospheric nanoparticles. The study consists of two parts. In the first part, an explorative sensitivity study is performed to determine model parameters that affect particle size/growth rate as primary model output. In the second part, atmospheric observations of particle growth rates are compared to model simulations using best guesses of these parameters. Using literature data of gas phase concentrations of organic molecules, the authors show that agreement between previously measured and modeled particle growth rates can only be achieved by including oligomerization. The authors also admit that this result depends on which parametrization for the saturation vapor pressure C^* of the product bins is used, so a definite answer is not possible at this stage.

The presented model seems quite well behaved and all parameters seem to affect the model result in certain sensitive ranges. The authors derive the parameter ranges for which oligomerization rate, oligomer decomposition rate, monomer volatility, and oligomer volatility are sensitive from the systematic sensitivity study. This is very technical work and no major conclusions can be

drawn given the uncertainty in many input parameters. However, this study might prove helpful as a compass for future investigations. The manuscript fits overall well within the scope of ACP. The manuscript is well-written from a technical perspective and easy to understand, though, it will benefit from copy editing to improve grammar and punctuation and increase overall readability. I can thus recommend publication after a few comments are addressed as detailed below.

We thank the reviewer 2 for the thorough review and comments that helped us to improve the manuscript. We have carefully considered all the comments and made the required revisions. Please find our point-by-point response below.

General Comments

I. 130, "The particle is assumed to be liquid like and have no particle phase diffusional limitations." – But particle-phase diffusivities are defined (Table 1) and evaluated (I. 256)? How is diffusion treated here?

Thank you for pointing out this typo. In our original manuscript, we had an unfortunate typo in the tables. The variable D in the tables is gas-phase diffusion coefficient, not particle-phase diffusion coefficient. In our simulations, mixing within particle-phase is assumed to be instantaneous and no particle phase diffusivity is included in the model. We have corrected the typo in Tables 1 and 2.

I. 152, please indicate where the ranges for upper and lower limits of oligomerization rate coefficients stem from, same for decomposition rates in I. 159.

The ranges of the oligomerization and decomposition rate coefficients overlap approximately those presented in previous studies (Kolesar et al., 2015; Roldin et al., 2014; Vesterinen et al., 2006). However, the exact ranges for our simulations are defined by our sensitivity tests, which showed that there were no significant changes in the results if reaction rates were outside this range compared to the upper/lower limits of this range. We have clarified this by adding text: "*We chose these limits based on sensitivity tests, which showed...*" in line 161 and text "*We chose these limits based on sensitivity tests, which showed that with higher or lower decomposition rate coefficients there were not any significant changes in the results compared to these upper and lower limits, respectively.*" in line 170

I. 176. "In addition, we have 280 product compounds (group IV)" – This comes surprising as groups I-III were already defined further above. What is this and what is it for? What diffusivity is mentioned here (I. 177), gas-phase diffusivity?

Group IV is the 'product compound' group, which include all possible products formed in oligomerization or decomposition reaction. Not all the 280 products are included simultaneously, but these are the possible compounds which may form depending on what kind of reaction is set for the simulation. Each simulation with oligomerization reaction have in addition to compounds of groups I-III one compound from group IV and simulations with decomposition reaction have two compounds from group IV. Group IV is introduced at the beginning of Sect. 2.1. (line 87) Now we have also added a mentioning of this group in section 2.2. where reactions of compounds from other groups are discussed in lines 155 and 165. Also we have clarified this by replacing the sentence

Reviewer mentions by (line 189):

"For group IV compounds, which are the oligomerization and decomposition products (280 compounds), the properties were defined based on the reacted compounds and volatility of the product"

Diffusivity mentioned is indeed gas-phase diffusivity, we have now added term "gas-phase" to clarify it in line 191. We believe the confusion comes from the typo in Tables 1 and 2, where we in reality define gas-phase diffusion coefficient instead of particle-phase diffusion coefficient as erroneously stated in our original manuscript.

I. 216-221 "In some simulations the growth rate is decreased also by oligomerization" - This result is interesting; can you comment on whether you think it is relevant for the atmosphere?

The reviewer raises a good point and with this particular results it is worth noting about the atmospheric relevance. Considering the expected dependence of C^* on molecular composition (Li et al., 2016), combining two LVOC is likely to produce an oligomer with C^* more than one order of magnitude lower than the initial compounds. We have now added included a note about this in line 233: *"For the sake of completeness these simulations were included in our simulation set, even though they may be unlikely in real atmospheric conditions, based on the dependence of C^* on molecular composition (Li et al., 2016). Also in this case, oligomerization reactions decrease the molar fractions of the condensing compounds in the particle phase therefor decreasing their equilibrium vapor concentration and enhancing their condensation."*

Figure 2 - It is an interesting result in panel e/f that the 3rd highest (1 $\mu\text{g}/\text{m}^3$) and highest volatility (100 $\mu\text{g}/\text{m}^3$) bin have the largest potential for enhancing growth. This was seen previously for particles in the accumulation mode, even for higher volatility bins of more than $10^4 \mu\text{g}/\text{m}^3$, and was needed to explain the slow growth of SOA in an environmental chamber after an initial rapid growth phase (Berkemeier et al. 2020). Overall, the authors seem to have missed this recent study in which the effects of oligomerization and viscosity on the growth and evaporation of SOA was investigated in a similar process model. How would higher volatility bins > 100 $\mu\text{g}/\text{m}^3$ behave here, are they relevant for Hyytiälä?

The reviewer arises an interesting question. In our study we have concentrated on compounds that are traditionally considered in relation to nanoparticle growth, i.e. those that could have an effect to the growth even without oligomerization. However, as reviewer points out, the higher volatility compounds could also have an impact if they go through particle phase reactions. We have now demonstrated this in the manuscript by adding new figure (Fig. 6) where we present simulations with a more volatile reacting compound. We have also added a paragraph on line 366:

"In the main body of our study, we have concentrated on compounds that may contribute to the particle growth of an atmospheric particle even without going through particle-phase reactions. However, via oligomerization even higher volatility compounds can contribute to the growth (Berkemeier et al., 2020). To demonstrate this effect, we conducted few additional simulations, where we increased the volatility (to $10^4 \mu\text{g m}^{-3}$) and gas-phase concentration (up to five-fold) of our highest volatility bin (originally $C^ = 10^2 \mu\text{g m}^{-3}$) and allowed this compound to react with itself forming less volatile oligomers. These simulations are presented in Figure 6 along with reference simulations where C^* of reacting compound was $10^2 \mu\text{g m}^{-3}$. The results suggest that even compounds with C^* of $10^4 \mu\text{g m}^{-3}$ could affect the particle growth via oligomerization if their gas-phase*

concentration and oligomerization rate is high enough. In Fig. 6 a-b, the simulations presented k_{olig} was set to $10^{-12} \text{ cm}^3 \text{ s}^{-1}$, i.e. fastest oligomerization rate constant in our simulations. These simulations show that with similar gas phase concentrations, setting the C^* of the most volatile compound to $10^4 \mu\text{g m}^{-3}$ instead of $10^2 \mu\text{g m}^{-3}$ decreases growth rate. However, already with doubling of gas phase concentrations for the compounds with C^* of $10^4 \mu\text{g m}^{-3}$ results in a faster growth due to the oligomerization compared to the initial case with highest volatility bin of C^* of $10^2 \mu\text{g m}^{-3}$. Assumption of higher volatility compounds having higher gas-phase concentrations compared to less volatile compounds is reasonable based on atmospheric observations (Hunter et al., 2017). Figure 6 c-d demonstrates the sensitivity of the contribution of the compounds with C^* of $10^4 \mu\text{g m}^{-3}$ on k_{olig} for the emphasized case with five-fold concentration compared to the initial highest volatility bin of $10^2 \mu\text{g m}^{-3}$. Unlike with the $10^2 \mu\text{g m}^{-3}$ compounds, enhancement of growth by oligomerization of $10^4 \mu\text{g m}^{-3}$ compounds differs between the three highest tested k_{olig} values (10^{-12} - $10^{-14} \text{ cm}^3 \text{ s}^{-1}$) and is insignificant for $k_{olig} < 10^{-15} \text{ cm}^3 \text{ s}^{-1}$.

The observation that oligomerization is not so efficient when the 2nd highest (10 $\mu\text{g}/\text{m}^3$) volatility bin is chosen was curious to me at first, but after reading I. 240, I understand that the calculations are set up such that only half of the total mass can oligomerize if $C^*_{O1} = C^*_{O2}$. I genuinely wonder if something can be changed in the model setup to avoid this curiosity, e.g. allowing 2/3 of the bin to react instead of 1/3 in that specific case. Otherwise, it would be helpful to put another disclaimer somewhere so reader does not spend too much time trying to understand Fig. 2f when looking at figures first.

In our simulations we have assumed, that 1/3 of total concentration of a VBS bin compounds can go through oligomerization reaction and this is the case also for simulations where a compound from a VBS bin reacts with a compound from the same bin. We agree that this may arise curiosity and have tried to better explain reasons for this by rephrasing our manuscript on line 258, please see our response to Reviewer 1. We have also now added to the Fig. 2 e-f a simulation, where we have 2/3 of bin reacting instead of 1/3, as Reviewer suggested. We have added to the line 264:

*"As a comparison, the simulation where $C^*_{o,1}$ and $C^*_{o,2}$ are both $10 \mu\text{g m}^{-3}$ and where 2/3 of a bin is allowed to react is also presented in the Fig. 2 e-f (dotted cyan line). This simulation follows the similar trend as simulations where two compounds with different C^* are reacting and gives a very slightly faster growth than the simulation where $C^*_{o,1}$ is $1 \mu\text{g m}^{-3}$ and $C^*_{o,2}$ is $10 \mu\text{g m}^{-3}$."*

and at the end of the caption to Fig 2:

"Fig. 2 e-f also present simulation, where both oligomerizing compounds are from same volatility bin ($C^ = 10^1 \mu\text{g m}^{-3}$) and 2/3 of compounds in that volatility bin can go through oligomerization reaction. In other simulations 1/3 of a bin can go through a reaction."*

I. 257 "particle phase concentrations, which are very low in the small particles" – Is this because you initialize the calculations with pure sulfuric acid particles?

This sentence refers to the experimental work by Wang et al. (2010) where they observed that oligomerization was nearly inhibited for smallest particles. The reason for this was the increase in equilibrium vapor pressures of organic compounds in small particles, caused by the surface curvature, as stated by Wang et al. (2010). We have clarified this by adding: "due to increase in equilibrium vapor concentrations caused by the surface

curvature (Kelvin effect).” in line 283. To clarify, we also rephrased the next sentence with refers to our simulations. In some of our simulations we see the similar effect where surface curvature increases equilibrium vapor concentration, thus preventing other than rather low-volatile compounds to have substantial particle phase concentration. Our initial assumption of pure sulfuric acid particles also affects the simulation and particle composition at the beginning of the simulation. In order to minimize the effect of the initialization assumption, we start our analysis only after particle size reaches 3 nm. This is stated in the manuscript on line 295.

Fig. 5 – I would suggest to use the same color scaling as in Fig. 4, or use a color-scaling that is not as incremental as the one used here. Otherwise Fig. 5 might give the impression that k_{dec} is more sensitive than it really is.

Since the potential effect of decomposition to the particle growth is much smaller than the potential effect of oligomerization, it is not possible to use same color scaling as in Fig. 4, for the difference of different simulations would be very hard to see. We have now changed the color scaling in Fig. 5 entirely and made the color scale in Fig. 5 a bit wider still to emphasize the difference. Also, to point out, that the scale in Fig. 5 is not very wide, we have added to line 364 the text:

“ Note that the color scale in Fig. 4 extends much wider range of GR than in Fig. 5, since the simulated effect of decomposition to the particle growth is much smaller than that of oligomerization.”

Figure 7 – I wonder if plotting a line of a single particle size versus time through an image plot depicting particle number density and the evolution of many particles at the same time is a fair comparison. The reader’s eye follows the upper and lower contours of the “banana” in the image plot and assumes that the line for a single particle size must follow the same trend and slope. Can the authors expand more on this process and what potential pitfalls might be? Would it be possible to create a similar image plot by running a full particle size distribution through the model? Would this model result also show the spots of darker red color that seem to appear at ~13-14 h?

Since our aim was to focus on particle-phase reactions, we haven’t included size distribution or coagulation in the model. In Hyytiälä conditions, with rather low particle concentrations, the growth is mainly driven by condensation and coagulation has only a minor effect. As inputs in our simulations, we have used mean values of measured gas phase concentrations and ambient conditions over the NPF event, and therefore changing the starting time of the simulation (or repeating the simulation with multiple starting times) would not change the simulation result but would only shift the simulated particle diameter in time. In terms of particle growth rate, the outer lines of ‘banana’ can give a misleading information. Instead, the change of the mode mean diameter of the nucleation mode is a better reference. Therefore, we have now added geometric mean diameters of the nucleation mode as a function of time in the fig. 7a and 7b. The geometric mean diameters were found by fitting multi log-normal distribution function with the measured particle size distribution. We also shifted the simulated particle growth curves in time in such a way that the base case simulation matches with mode geometric mean diameter at the beginning. More precisely, we selected to match the simulation with the third fitted mode mean diameter as from that point onwards the fitted mode diameters exhibited clear growth. This will help readers to compare the measured and simulated particle growth. To explain this in the text we added in line 438: *“2014 and geometric mean*

diameter of nucleation mode are presented in Figure 8. The geometric mean diameters of nucleation mode were determined by fitting multi log-normal distribution function to the measured particle size distribution (Hussein et al., 2005)..” and in line 445: “In the figure, the starting point of the simulations is set so that the base case simulation matches with the third fitted geometric mean diameter.” and in to the caption of Fig 8. :”... , geometric mean diameters of nucleation mode ...”.

I. 449 “For instance, survival probability of particles from 3 nm to 20 nm calculated for the 450 NPF event presented in Fig. 7 were 15 %, 25 % and 44 %, respectively” – Were these calculations performed for this paper? How is this calculated? This is not described in the methods section.

We agree with the reviewer’s remark that this requires more clarification. These estimates were done using the method presented in Lehtinen et al. (2007, equations 6-7) which utilizes the measured time evolution of the number concentration distribution. As the survival rates are not the main focus of this manuscript, we do not repeat the equations here, but instead add the reference (Lehtinen et al., 2007) where the method is presented and changed the text to (line 511): “the survival probability of particles from 3 nm to 20 nm calculated by applying the method by Lehtinen et al. (2007) for the measured size distribution evolution of the NPF event presented in Fig. 8 were 15 %, 25 % and 44 %, respectively, when using the GR from the slowest growing, base case and fastest growing simulation among the ones where one-third of a bin could react.”

Technical Comments

In many places “gas phase” needs to be replaced with “gas-phase” (l. 16, l. 37, l. 40, l. 43, l. 45 ...)

We have now replaced these throughout the manuscript.

The mentions of what the model can theoretically do (l.125, l. 136) are irrelevant for this work and confuse the reader more than help the presentation of this study.

We have removed these mentions and moved the reference to MABNAG model, for which MODNAG model used in this study is based on, to the beginning of model description section to line 72.

I.171, it would probably help the understanding when the cases were named / introduced earlier, e.g. line 64.

The Cases are now introduced at the end of Introduction on line 63 where we have added text “...we carried out two sets of simulations. In Case 1, ..” and on line 66 the text “In Case 2...”

Figure 2: C*_O2 was somewhat confusing at first as it suggests to mean molecular oxygen. It would have been clearer what the “2” stands for if C*_O1 and C*_O2 would have been introduced around l. 233.

We have changed the C^*_{O1} and C^*_{O2} as well as C^*_{p1} and C^*_{p2} (that are decomposition product compounds) to $C^*_{O,1}$, $C^*_{O,2}$, $C^*_{p,1}$ and $C^*_{p,2}$ respectively. $C^*_{p,1}$, $C^*_{O,1}$ and $C^*_{O,2}$ are now introduced in lines 248, 251 and 249, where we have added subscripts $p, o, 1$ and

$C_{o,2}^*$ to the C^* values. Also for decomposition simulations, we have introduced $C_{D,1}^*$, $C_{p,1}^*$ and $C_{p,2}^*$ in lines 298, 301 and 299 and changed 'C*=' to " C_{p1}^* and C_{p2}^* both equal to" in line 301.

Fig. 4 - Should the subplot x and y axes be labelled C^*_{O1} and C^*_{O2} ?

Thank you for pointing out this typo. We have corrected the labels as $C^*_{O,1}$ and $C^*_{O,2}$

I. 305 "oligomerization happens so fast that even these higher volatility molecules will oligomerize before evaporation" – This sounds like these molecules were placed in the particle phase at the beginning of the simulation. Should this be "... these higher volatility molecules will oligomerize significantly despite their small equilibrium particle-phase concentrations"?

We thank the reviewer for the suggestion. We have revised the text accordingly (in line 337)

I. 336 "ELVOC" – was not yet introduced.

We have added the definitions of ELVOC, LVOC and SVOC in Model description in Section 2.1 where we also introduce the abbreviations. The added text in line 79 :

"The bin with C^ of $10^{-4} \mu\text{g m}^{-3}$ is defined as extremely low volatile organic compound (ELVOC), bins from $10^{-3} \mu\text{g m}^{-3}$ to $10^{-1} \mu\text{g m}^{-3}$ as low volatile organic compounds (LVOC) and bins from $10^0 \mu\text{g m}^{-3}$ to $10^2 \mu\text{g m}^{-3}$ as semi volatile organic compounds (SVOC) based on Donahue et al. (2013)."*

I. 374 "Ehn et al. (2007) observations behind a thermodenuder determined size distributions showed that the growth rate was one-third of the GR measured with a normal DMPS-system." – I think the meaning of this sentence would be very difficult to understand if the original paper is not known.

We have rephrased the sentence to (line 431): "*Ehn et al. (2007) compared ambient particle size distributions and those measured after heating to 280°C in a thermodenuder for new particle formation events. They found that the growth rate of the non-volatile fraction of particles, observed as the size distribution behind a thermodenuder, was one-fourth of the GR measured with a normal DMPS-system.*"