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Interactive comment on "Comprehensive analysis of particle growth rates from nucleation mode to cloud condensation nuclei in Boreal forest" *by* Pauli Paasonen et al.

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We thank the referee for very valuable comments and suggestions.

Questions/Request for clarification:

Question 1: Page 5, line 5 I think it would be helpful for the reader if you quantify the typical number of n, i.e. PSD measurements per day, or at least the time-resolution of the DMPS system. This would help the reader to identify how many PSDs usually fall in the range for a GR determination, or how strong the smoothing by the five-time-step-median filter actually is.

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[Discussion paper]

This is correct, in the revised manuscript we express the time resolution of the DMPS measurements (10 min) in Sect. 2.1 (page 3, line 25) and add "(i.e. PSDn with $1 < n < 7$)" in the sentence denoted by the reviewer: "If the first peak is determined in PSD0, the timewise closest peak in PSDn>0 is added to the same group, if it takes place within an hour from PSD0 (i.e. PSDn with $1 < n < 7$) and is close enough in size (maximum allowed difference is 10 nm for peaks with 5 dP < 50 nm and 50 nm for peaks with dP > 150 nm).")

Question 2. In my opinion, the current manuscript does not really discuss, how well the new method actually works and what limitations it has. Is it for example catching most growth periods which were analyzed classically as they follow NPF?

This is true. We decided to make a small comparison to manually analyzed growth rates after NPF events. We received GRs and their start and end times in size range 3-25 nm in Hyytiälä during 2003-2013 (Nieminen et al., 2014) from Dr. Tuomo Nieminen and compared our results with those. In the data we received there were 153 manually determined GRs, for which the start and end times were available. Out of these 153 manually determined GRs, our method captured 73 % (111 growth periods). The GRs determined with the automatic method also correlated well with the manual GRs (R = 0,81). The comparison of the growth rates is presented in Fig. R1 below. We find this accuracy to be reasonably good, since our method was not developed for determining growth rates especially in the nucleation mode, but in Aitken and accumulation modes. In the manual determination, the selection of peaks in particle size distribution data (white circles in Fig. 1) from which the GR is determined, is made visually and human eye can naturally connect more information for verifying the reliability of the determined GR than our automatic method. It should be also noticed that, since the manual method relies on visual inspection of the data, exactly similar results would not be expected from different persons using the exactly similar manual method.

We added the following sentences to the Methods Sect. 2.2 of the manuscript: "We made a comparison between GRs determined with our automatic method and man-

ually determined GRs for nucleation mode particles (Nieminen et al., 2014). For the comparison, we received start and end times of 153 growth periods during years 2003-2013. It is notable that the manual growth rates were determined only for the time until the mode reaches 25 nm in diameter, because the initial purpose for their determination had been calculating the new particle formation rates, whereas the compared automatic GRs were for growth periods, which had initial diameters below 25 nm. In order to prevent the possibility of comparing different growth parts of a growth period during which the growth rate would have drastically changed, we chose for comparison only the growth periods for which the automatic and manual growth periods overlapped for at least two hours. Another note to be made on the manual GR data is that these 153 events represent only a small fraction of the manual GR values for the years 2003-2013, but for the rest of the manual GRs only the dates (without start and end times) were readily available."

To the Results (Sect. 3.1) we added the following sentences: "The comparison of nucleation mode GRs with manually determined GRs from Nieminen et al. (2014) showed a strong correlation (R = 0.81) between automatic and manual GRs. Out of the 153 manually determined growth periods our method found 111, equaling to 73 %. In 93 % of the growth periods detected with both methods, the automatic GR was within a factor of two, and in 76 % within a factor of 1.5 from the manually determined GR. We find this accuracy to be reasonably good, since our method was not developed for determining growth rates especially in the nucleation mode, but in Aitken and accumulation modes. In the manual determination, the selection of peaks in particle size distributions (white circles in Fig. 1) from which the GR is determined, is made visually and human eye can naturally connect more information for verifying the reliability of the determined GR than our automatic method. It should be also noticed that, since the manual method relies on visual inspection of the data, exactly similar results would not be expected from different persons using the exactly similar manual method."

Question 3: Additionally, I think the authors should clarify that the method only infers

apparent growth rates, which might cause problems if it is applied to heavier polluted environments. For example coagulation within the growing population might mimic condensational growth and this is not captured by this method. Kuang et al. 2012 (ACP) and Pichelstorfer et al. 2018 (ACP) developed methods which take such effects into account, however they did not yet demonstrate to work with this kind of DMPS data sets.

This is also true. We added to the Sect. 2.2 the following: "It should be noted that our method simply searches for monotonic increases of particle mode diameters, it does not differentiate the condensational growth from growth due to coagulation or possible other phenomena that may cause apparent growth of a particle mode. Such phenomena, e.g. the faster coagulation scavenging of the smallest particles within a mode in comparison to the largest particles within the same mode, are typically considered more significant for particle growth in diameter ranges below 10 nm and in more polluted environments. Thus, we assume that the results in this article are not significantly impacted by them. "

Question 4: Section 2.3 and especially Table 1. I very much appreciate the simplicity of the model, but it seems to me that it was tuned a bit to fit the results. In Table 1, the molecular volume V does not correspond to M/rho, why? The surface tension of 0.08 is by more than a factor of 2 higher than values usually assumed for organics (see e.g. Tröstl et al. 2016, (Nature)) and bigger than to one of water. This leads to a significantly increased Kelvin-diameter of roughly 12 nm. As a consequence the range when the effects of SVOC dimerization start to be important is set to larger diameters. It would be good if you could specifiy why the values were chosen that way. Also, e.g. Kdim lacks any explanation.

This notification by the referee is very valuable. We had applied, mistakenly, some parameter values from an old "back of an envelope" calculation and forgotten to double-check them. We have updated Table 1 and replotted Figure 11 with surface tension 0.023 N/m, density 1.4 g/cm3 (values from Tröstl et al. 2016) and molecular weight

equaling to M/rho (2.15*10-4 m3/mol). The value for Kdim is taken from Apsokardu and Johnston (2018), who based their value on a study by Ervens and Volkamer (2010). We added all relevant references and explanations to the Table 1. The "tuning" of the figures occurs through choosing ELVOC and SVOC concentrations with which the model results end up in a reasonable magnitude. Promisingly, such ELVOC and SVOC concentration levels are also reasonable for atmospheric conditions.

Question 5: Fig. 4 and Section 3.2. Whenever the authors correlate the GR with a particle size they use the initial size of the growth. Growth rates are inferred from a minimum size to a maximum size, and as GR and the observed growth period varies as the authors point out in Sec. 2.2 I would assume that the mean size of the growth rate measurement gives a more representative value for the diameter where the GR is actually observed.

We also considered this issue but realized through trying that choosing mean size of the observed growing mode causes artificial bias to the results (see Fig R2 below). This occurs, because, while limiting the minimum duration of the growth periods, the higher growth rates automatically lead to larger mean (and end) diameters for the modes that started at the same initial diameter. By choosing mean or end diameter of the growing modes we would overestimate the impact of diameter on GR.

We added to the manuscript (Sect 3.2) the following clarification: "We chose the initial diameter of the growing mode, instead of e.g. the mean diameter, for describing the impact of particle diameter on GR, because applying the mean diameter of the growing mode would cause an artificial bias to the results (if two growth periods with similar duration and different GRs started at same diameter, the one with higher GR would have larger mean diameter than the one with lower GR; this would result in positive correlation between GR and mean diameter, even though the diameters were the same in the beginning and thus the reason for different growth rates should not be the diameter.)"

Technical corrections:

1) Please consider to cleanup your Figures. Generally I recommend using bigger axis ticks to make the axis better readable. Additionally, while, e.g. Figure 10 has very well readable axis labels, this is not the case for Figures 1-4 and 6.

We have generally improved the figures, softened the colors and increased the fonts.

2) Please check carefully the usage of definite articles, e.g. p.2 l.8 "by condensation growth", p.2 l.11 "the importance of growth", p2. l.13 "fraction of CCN originating from growth of smaller particles", p.8 l.15 "that we inspected was temperature", p.10 l.27 "50 to 60 nm with temperature, monoterpene concentration", etc.

Corrected

3) Page 3, lines 6-8. I would point towards Tröstl et al., 2016 (Nature), because they directly describe the Kelvin effect for organics and its influence on growth.

Done

4) Fig.5, Fig.7 and Fig. 9 I am just wondering, if a reduction of used bins would make the Figures far easier to read and understand, without losing the main conclusions.

Since the studied variables - temperature, particle size range, and condensation sink - all correlate on some level, as shown in our manuscript, we find it is necessary to limit one of the factors to narrow enough bin in order to study the impact of the others. Thus, we prefer not to reduce the number of bins by making them wider. On the other hand, we also oppose showing e.g. only every second bin, because by showing them all, we demonstrate the consistent behavior of GR as a function of these variables.

5) Page 9, l. 6-15. This paragraphs lacks a conclusion. Monoterpene concentrations are expected to have a weaker correlation than temperature, as temperature not only controls the emissions but also the reaction rates. Given the negative correlation found with the CS and discussed in Sec. 3.2.2. it seems to be logical that the correlation with monoterpene oxidation rate is the strongest. This could be pointed out.

We are slightly confused with this comment since it seems to point to a paragraph where the commented issues are not discussed. Thus, we break this comment down to pieces and respond to them separately.

The lack of conclusion of the pointed paragraph. We think there was a conclusion but agree that the explanation was not clear enough for making it easy to understand. We rearranged the last sentences of the paragraph (page 10, lines 22-27) for clarifying the conclusion. Impact of temperature on monoterpene concentrations via temperature dependency of the reaction rates. We estimate that the temperature dependency of the reaction rates is negligible in comparison to the temperature dependency of the emissions. Where the increase of temperature from 270 K to 300 K increases the reaction rate between MT and O3 by a factor of 1.2 (kOH+MT = a *exp(-580/T), from Atkinson et al., 2006), the emission rate increases by a factor of 27 (E = a*exp(0.10*(T-303.15)), Tarvainen et al., 2005).

Correlation between CS and GR. We agree that due to the positive correlation (probably misspelled by the referee as negative correlation) between CS and GR it is logical that monoterpene oxidation rate correlates better with GR than calculated oxidation product concentration. However, since we inspect separately the relation between CS and GR only in the next Section, we prefer not to discuss it here in order not to confuse the reader.

6) Page 12, l. 13 and Fig. 11 a. While in the text Ke is set to 1 the Figure legend says Ke=0.

The figure legend is corrected to Ke = 1.

References

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organic species, Atmos. Chem. Phys., 6, 3625–4055, doi:10.5194/acp-6-3625-2006, 2006.

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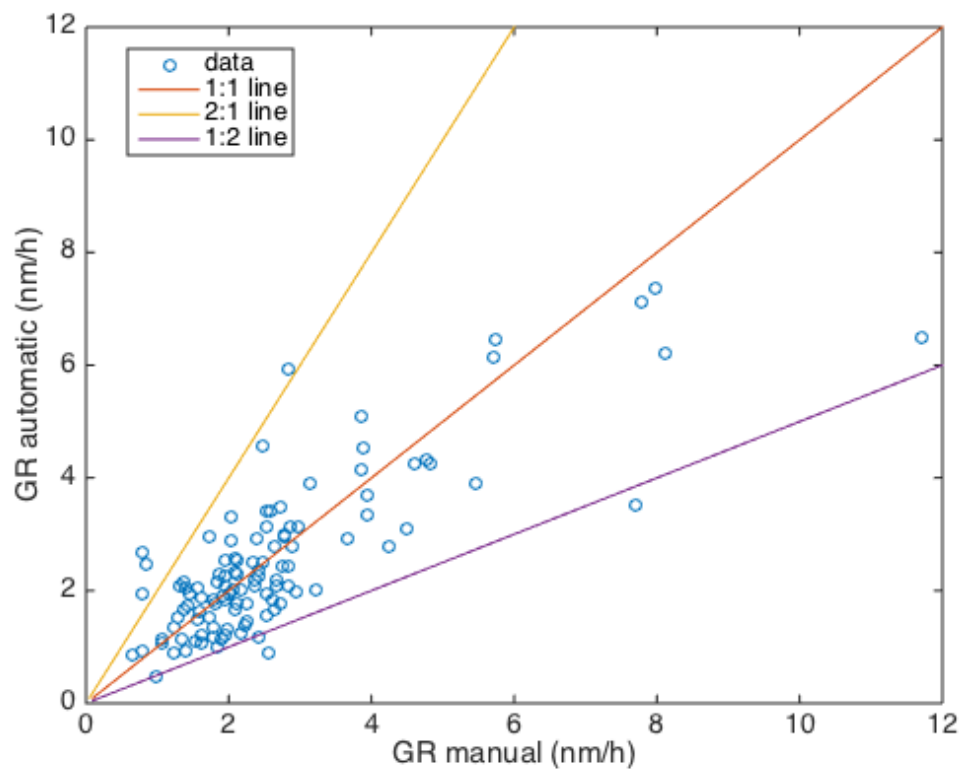
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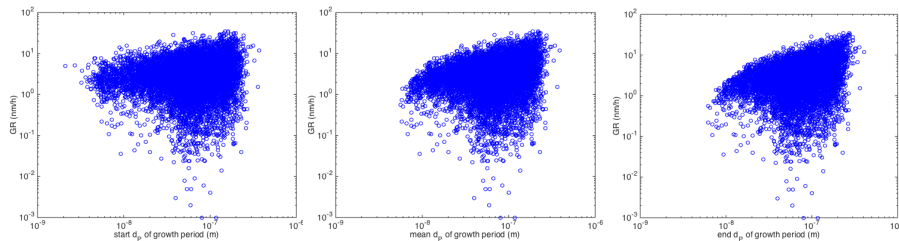Printer-friendly version

Discussion paper

Fig. 1. Figure R1, not added to the manuscript. Comparison of automatically and manually determined growth rates for growth periods overlapping for at least 2 hours. More details in text.

Fig. 2. Figure R2, not added to the manuscript. Observed particle growth rate as a function of initial (left), mean (middle) and end diameter (right) of the growing mode during April-September.