

**Answers to referee comments: "Semi-empirical parameterization of size-dependent atmospheric nanoparticle growth in continental environments" by S.A.K. Häkkinen et al., 2013.**

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Answers to Anonymous Referee #2

*The manuscript describes work to explore the growth of nanoparticles in the atmosphere. Observations of nanoparticle growth from air ion number size distributions are used to evaluate different scenarios of particle growth. The study confirms a large contribution of secondary organics to nanoparticle growth and presents evidence for a yet unknown vapor that contributes to “background” particle growth rates. The paper will be of interest to both the particle formation and secondary organic aerosol communities. It is within scope of ACP and I suggest publication after the following minor comments have been dealt with.*

We thank you for your constructive comments that will help us improve the manuscript. Please find the point-by-point answers to the comments below.

#### *Minor Comments*

*One of the intriguing findings of this paper is the possible existence of an organic compound with little seasonal cycle in its contribution to particle growth rates. I think a little additional discussion (e.g. on P8512 or elsewhere) would be useful on 1) uncertainty in sulfuric acid concentrations and the relevance for this background organic; 2) Uncertainty in  $GR_{1.5-3}$ . You already mention that uncertainty in  $GR_{1.5-3}$  is likely greater than uncertainty in GR for larger particles. Is there also likely to be larger uncertainty in  $GR_{1.5-3}$  in winter (when there are fewer particle formation events to constrain GR) than in spring and summer?*

These are both very good points, and indeed deserve some further discussion in the paper.

1) Particle growth by sulfuric acid has uncertainties that arise from uncertainties in measurements and in the calculation of sulfuric acid growth itself. These uncertainties indeed affect our GR parameterization – particularly for the smallest particles and thus the conclusion about the presence

of the third condensing species. To explain the GRs with only sulfuric acid and  $\text{SORG}_{\text{MT}}$ , the sulfuric acid concentrations would have to be 10-20 higher than used in the parameterization. Besides the experimental uncertainty in the detection of gas-phase sulfuric acid (on which the sulfuric acid concentrations used in the calculations rely), this uncertainty could also be caused by e.g. significant clustering of the sulfuric acid and the participation of these clusters in the growth process – which might be significant specifically for the smallest particles. Sulfuric acid closure study by Boy et al. (2005) suggests, however, that the measured sulfuric acid concentrations can be reproduced with a chemical kinetics model – indicating that at least the order of magnitude of the sulfuric acid concentration (including the potential clusters) should be reasonable. In addition to possible uncertainties in the calculation of particle growth by sulfuric acid, there is also about a factor of 2 uncertainty in the observed particle growth rates. These issues are somewhat touched upon in the present manuscript, but we will discuss this matter further in the revised manuscript (Sect. 4).

2) As you pointed out based on statistics there is a greater uncertainty in  $\text{GR}_{1.5-3}$  (also in  $\text{GR}_{3-7}$  and  $\text{GR}_{7-20}$ ) during winter months since the number of particle formation events is clearly lower than during other seasons. We have added a mention about this to the revised manuscript (Sect. 3.2).

*P8494. What about isoprene? Maybe worth mentioning here. I know that you refer to isoprene later in the MS.*

We have mentioned the fact that we left isoprene out of the analysis already earlier in the revised manuscript (Sect. 2.1.1) as you suggested.

*P8496, L19. Is there sensitivity to your assumed particle diameters that represent each size class? It appears that you selected the mid-point in  $dp$  space of each size class. Since  $I_{\text{tot}}$  depends on  $dp^2$  how different would your calculations be if you selected the midpoint in  $dp^2$  space (e.g. 15 nm instead of 14 nm for the 7-20 nm size class)?*

We tested different ways of choosing the representative diameter of the different size ranges, and found that there is very little change in the parameters ( $k$ -values and  $C_{\text{SORG,bg}}$ ) when  $d_p^2$  space is used instead of  $d_p$  space (see Table 2.1) – as compared with the experimental uncertainties. Maximum difference between the parameter values obtained using diameters 2, 6 and 15 nm instead

of 2, 5 and 14 nm was around 8%, usually below 3%. We have summarized these results in the revised manuscript (Sect. 2.1.2).

*P8498, LI-8. Give the exact locations (lat/lon) of the sites.*

Hyytiälä: 61° 50' N, 24° 18' E, Melpitz: 51° 32' N, 12° 54' E, Hohenpeissenberg: 47° 48' N, 11° 00' E, Vaviihill: 56° 01' N, 13° 09' E, Finokalia: 35° 20' N, 25° 40' E, K-pusztá: 46° 58' N, 19° 35' E. We have added this information to the revised manuscript (Sect. 2.2.1).

*P8499, LI8. The treatment of monoterpenes in GLOMAP is described in Spracklen et al. (2006).*

This is correct and we apologize for the mistake. We have added the reference Spracklen et al. (2006) to the revised manuscript (Sec. 2.2.3).

*P8502. How do GLOMAP monoterpene concentrations compare to the monoterpene concentrations observed by the PTR-MS? This comparison would be useful since it is less influenced (compared to SORGMT) by ambient O<sub>3</sub> and OH concentrations or uncertainties in kinetics.*

Fig. 2.1 displays the monthly median concentrations of monoterpenes (MT) and SORG<sub>MT</sub> (for comparison). Three data sets were used: GLOMAP, PTR-MS and MT-parameterization by Lappalainen et al. (2009). It can be seen that the difference in the differently defined monoterpene concentrations is very similar to the difference in the concentrations of the oxidation products (also Fig. 2 in the manuscript), suggesting that the main source for the differences in the SORG<sub>MT</sub> concentrations are the monoterpene concentrations, not the O<sub>3</sub> and OH or the oxidation calculation. We have added a brief discussion about this to the revised manuscript (Sect. 3.1.1).

*P8509, LI-3. What about tropical forest environments?*

Most probably there are different growth mechanisms and condensing vapors (isoprene in more significant role) in the tropics and therefore our parameterization may not give reliable results in tropical forests. We have mentioned this in the revised manuscript (Sect. 4).

*Figure 2. I found it difficult to work out which of the lines refer to the different assumptions. If possible make this clearer in the text somewhere (e.g. on P8500). Some issues with referencing (e.g. P8493, L3: “X. Zhang et al.,”)*

We agree that Fig. 2 was probably a bit cumbersome to read. We have clarified the figure caption in the revised manuscript.

We have also carefully checked the referencing. The citation to the two papers published in 2012 by different authors with the same last name (X. Zhang and R. Zhang), however, was handled according to the recommendation of the ACP editorial office

Table 2.1 Comparison of parameters using different representative particle diameters – 2, 5 and 14 nm (diameters describing the size bins in  $d_p$  space) and 2, 6 and 15 nm (diameters describing the size bins in  $d_p^2$  space). The concentration of background organics ( $C_{\text{SORG,bg}}$ ,  $\text{cm}^{-3}$ ) and weighing factors ( $k_{\text{MT}}$  and  $k_{\text{bg}}$ ) from the mass flux fit using data from Hyytiälä (SORG<sub>MT</sub> from GLOMAP) and EUCAARI (SORG<sub>MT</sub> from GLOMAP) are presented. Fits were performed using monthly median data sets.

	Hyytiälä ( $D_p$ : 2, 5, 14 nm)	Hyytiälä ( $D_p$ : 2, 6, 15 nm)	EUCAARI ( $D_p$ : 2, 5, 14 nm)	EUCAARI ( $D_p$ : 2, 6, 15 nm)
$k_{\text{MT},1.5-3}$	0	0	0	0
$k_{\text{MT},3-7}$	0.25	0.27	0.73	0.77
$k_{\text{MT},7-20}$	1.00	1.00	1.00	1.00
$C_{\text{SORG,bg}}$	3.8e7	3.9e7	5.8e7	5.9e7
$k_{\text{bg},1.5-3}$	0.34	0.33	0.33	0.32
$k_{\text{bg},3-7}$	0.71	0.72	0.69	0.71
$k_{\text{bg},7-20}$	1.00	1.00	1.00	1.00

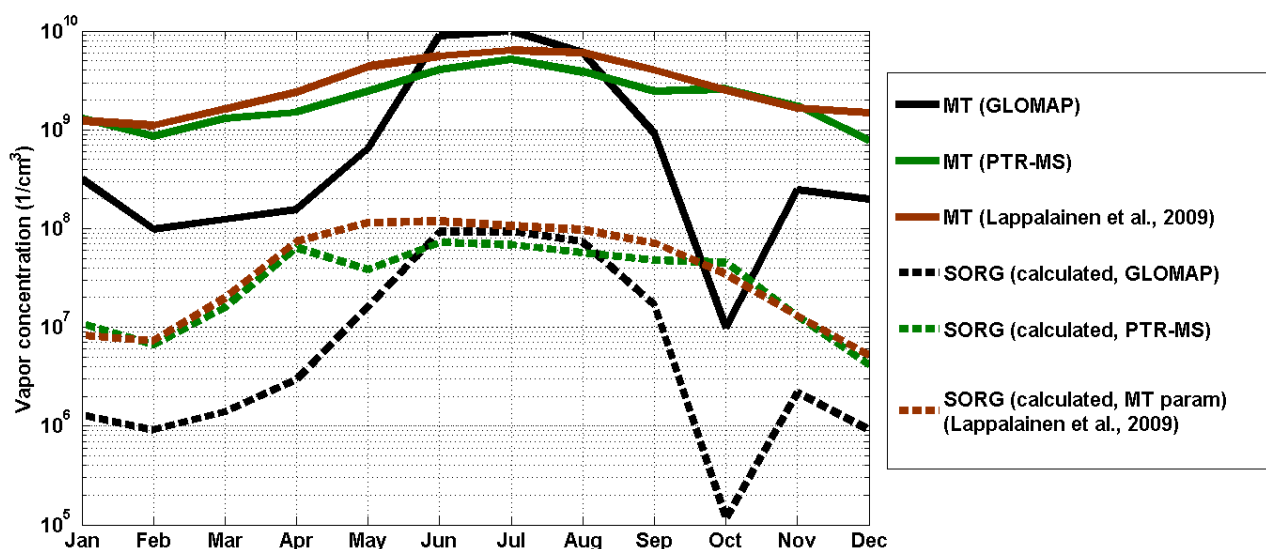


Fig. 2.1 Monthly median daytime concentrations of monoterpenes (MT) and  $\text{SORG}_{\text{MT}}$  in Hyytiälä, Finland, obtained three different ways – from GLOMAP, from PTR-MS and from MT parameterization by Lappalainen et al. (2009). The MT concentrations (solid lines) were taken directly as given in the data whereas the  $\text{SORG}_{\text{MT}}$  concentrations (dashed lines) were calculated from MT data using  $\text{O}_3$  and OH data. The correspondence between the measured MT concentrations (PTR-MS) and the concentrations obtained using the MT-parameterization is very good. MT concentrations from GLOMAP are estimated well during summer months. However, during winter the correspondence is poor – concentrations are approximately one order of magnitude lower using GLOMAP than the measured ones. Similar behavior was observed when comparing differently defined  $\text{SORG}_{\text{MT}}$  concentrations.

## References

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