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

silja.hakkinen@helsinki.fi

Answers to Anonymous Referee #1

The manuscript presents a semi-empirical parameterization for growth rates of particles smaller than 20 nm. The manuscript is well written and it is within the scope of Atmospheric Chemistry and Physics. However, my main concern about the manuscript is how useful such a parameterization is for global scale models.

We thank you for your valuable comments which we think have improved the manuscript. Please find below our point-by-point responses to your concerns. We believe these responses demonstrate the applicability of the approach we present – in particular for models where computational requirements limit the detail that aerosol dynamics can be described with.

On page 8493, it is said that in large-scale models, the SOA is assumed to be either non-volatile and assumed to condense kinetically or have range of volatilities but to be in thermodynamical equilibrium. There is also a possibility to calculate the condensation kinetically assuming SOA to have a range of volatilities and still calculate condensation kinetically. This method has been used by e.g. Pierce et al. (2011). What would be the benefit of the parameterization given in the current manuscript over the method used by Pierce et al. (2011)? The correlation between the observed and parameterized growth rates do not seem overly good.

While it is naturally true that the condensation of SOA components could be treated by combining knowledge on their volatility (given that their equilibrium vapor pressures are known) with kinetic condensation equations, this is often not computationally feasible in large scale models. Furthermore, while Pierce et al. (2011) used such an approach to calculate condensation of SOA components to nucleation mode particles, they did not deploy a global or regional-scale model. In the study by Pierce et al. a 0-dimensional box model, which does not have the computational requirements of a 3D-model, was used. We have added a mention about this to the revised manuscript.

The parameterization presented here is targeted towards models that aim to treat the dynamics of atmospheric aerosol number size distributions but keep the computational costs relatively low (such as e.g. climate models that resolve both the aerosol as well as the atmospheric transport dynamics). The strength of this approach is that it is already directly applicable in many large-scale atmospheric models that currently approximate the SOA as non-volatile condensing species (e.g. Geos-Chem and GLOMAP) – making it particularly suitable for studies that target capturing atmospheric number concentrations with relatively low computational cost.

The obtained correlations between GR_{obs} and GR_{fit} are statistically significant (p-values < 10^{-5}) and the correlation coefficients are above 0.45 which we think are reasonably high values, taken that we have combined data from different environments (Table 4 in the manuscript). In addition, there is always uncertainty in the GR values determined from the measured particle number size distributions – the uncertainty being the highest for the smallest particles (Yli-Juuti et al., 2011). Yli-Juuti et al. (2011) quoted a factor of two as a conservative estimate for this uncertainty. Given this uncertainty in the GR estimation method, we would deem the agreement between the parameterized and observed growth rate to be very satisfactory for the first parameterization of its kind. We therefore tend to disagree with the reviewer on the performance of the parameterization. Given the considerable simplicity of the approach (which on the other hand is needed for addressing the needs of large-scale models) we think that it is doing a relatively good job in reproducing the magnitude and seasonality of nanoparticle growth. That being said, further work for testing and improving the parameterization (in particular independent data sets to test the parameterization with) is definitely desirably in the future.

The k parameter values given on page 8508 differ significantly between those fitted to Hyytiälä and EUCAARI stations. Did you compare how the values differ for individual EUCAARI stations and if so, how did they compare? It would be vital to see how fitted and observed growth rates differ for individual stations in e.g. Fig 7 before the parameterization could be recommended to be used in global models. In addition, the parameterization should be compared against observations in different types of locations.

Indeed, the k-values obtained for Hyytiälä and EUCAARI stations are somewhat different. The difference is the largest for particles 3-7 nm in diameter, being $k_{MT,3\text{-}7}$ = 0.2-0.4 for Hyytiälä and $k_{MT,3\text{-}7}$ = 0.7 for all EUCAARI sites. This is expected since the ambient conditions vary from station

to station. However, the general behavior – k_{MT} being zero for 1.5-3 nm particles and approaching 1 for 7-20 nm particles – is similar using both data sets.

We agree that determining the *k*-values and $C_{SORG,bg}$ for all stations individually would be ideal. It would also potentially provide important insights into the mechanisms driving nanoparticle growth in different environments. Unfortunately, the amount of data on size-resolved growth rates from each of the EUCAARI stations was not enough to produce statistically significant fits with Eq. 1. Commenting on the performance of the parameterization based on the individual stations is thus very difficult. This is why we chose to use the whole EUCAARI data set instead of the individual stations. This highlights the need for collecting more long-term observations of size-resolved growth rates, and we hope that more and more such data from different environments will be available in the future, allowing also for improved growth rate parameterizations where needed. If we nevertheless look at the performance of the parameterization on a station-to-station basis (see Fig. 1.1, also Fig. A1 in Appendix A of the revised manuscript), the results suggest that the particle GRs were generally captured within a factor of two, with the exception of some months in Hyytiälä, Vavihill, Finokalia and Hohenpeissenberg. GRs were somewhat overestimated for Hyytiälä and Vavihill whereas for K-Puzsta, Melpitz and Hohenpeissenberg the correspondence was generally good. The growth of the smallest particles (1.5-3 nm) was reproduced well in Finokalia but the growth of larger particles was not. For environments similar to Hyytiälä e.g. to (boreal forest, background site) we suggest using the parameters obtained from Hyytiälä analysis (manuscript, Table 3) rather than the ones from EUCAARI analysis.

We have added a brief discussion on this to the revised manuscript (Sect. 3.2).

Minor comments:
Although it may obvious for most readers, it would be informative to say that the sizes are in diameter.

We agree, and have clarified this in the revised manuscript.

Page 8511, lines 8: What do you mean by "the scale at which many global models operate"?

To answer the questions that atmospheric 3D models are usually used to address (such as the feedbacks between emissions, aerosol loadings and climate patterns), it is not necessary to reproduce the details of the aerosol distribution evolution on a given day, but rather reproduce the seasonal and diurnal trends along with the overall aerosol loadings correctly. This is what we meant with the quoted statement. We have clarified the text accordingly.

Page 8512, lines 13-15: What do you mean by "This result is reasonable in the light of the thermodynamics of evaporation.."

The Kelvin effect on the equilibrium vapor pressures of organics causes their evaporative mass flux density from the particles to increase with decreasing particle size. This causes the net condensational flux to decrease with particle size:

$$I \propto p_v(1-\mathrm{K}(D_\mathrm{p})\cdot\mathrm{R}), \qquad (1.1)$$

where p_v is the vapor pressure far from the particle, K describes Kelvin effect that is a strong function of particle diameter (D_p) and R describes Raoult's law. This behavior is, instead of the full thermodynamic treatment of the vapors, now taken into account with the *k* factors in Eq. 1 (in the manuscript). We have clarified this in the revised manuscript.

Pages 8531-8535, Figures 3-7: The 1/1 line would be easier to visualize if x and y axis were the same.

We agree and will make the x and y axis of Figs 3-7 the same in the revised manuscript.

Some global models that include SOA use two-product or volatility basis set approach. Could this parameterization be implemented in such models? How would you take into account the loss of gaseous SOA precursors of different volatilities during growth of sub 20nm particles?

As discussed in e.g. Riipinen et al. (2011, 2012); Pierce et al. (2011) and the present manuscript, there are currently essentially two different approaches applied in atmospheric large-scale models to represent SOA condensation: calculating the thermodynamic equilibrium of SOA (e.g. with the VBS, the two-product approach or other saturation vapor pressure prediction methods) or assuming

the SOA to be non-volatile and calculating its condensation kinetically. Currently, these two approaches give somewhat different results, the former being able to capture the aging and evaporation of aerosol mass better, while the latter does better in capturing nucleation mode growth (and thus aerosol number size distributions, accounting for the impact of new particle formation).

The parameterization presented here has been designed for models applying the latter approach. In the future, as the mechanistic understanding of the SOA condensation processes improves, also approaches that reproduce the SOA contribution to both aerosol mass as well and number will become available. Until then, however, the choice of the appropriate approach depends on what scientific questions (e.g. aerosol mass vs. aerosol numbers, direct vs. indirect climate effects etc.) are targeted.

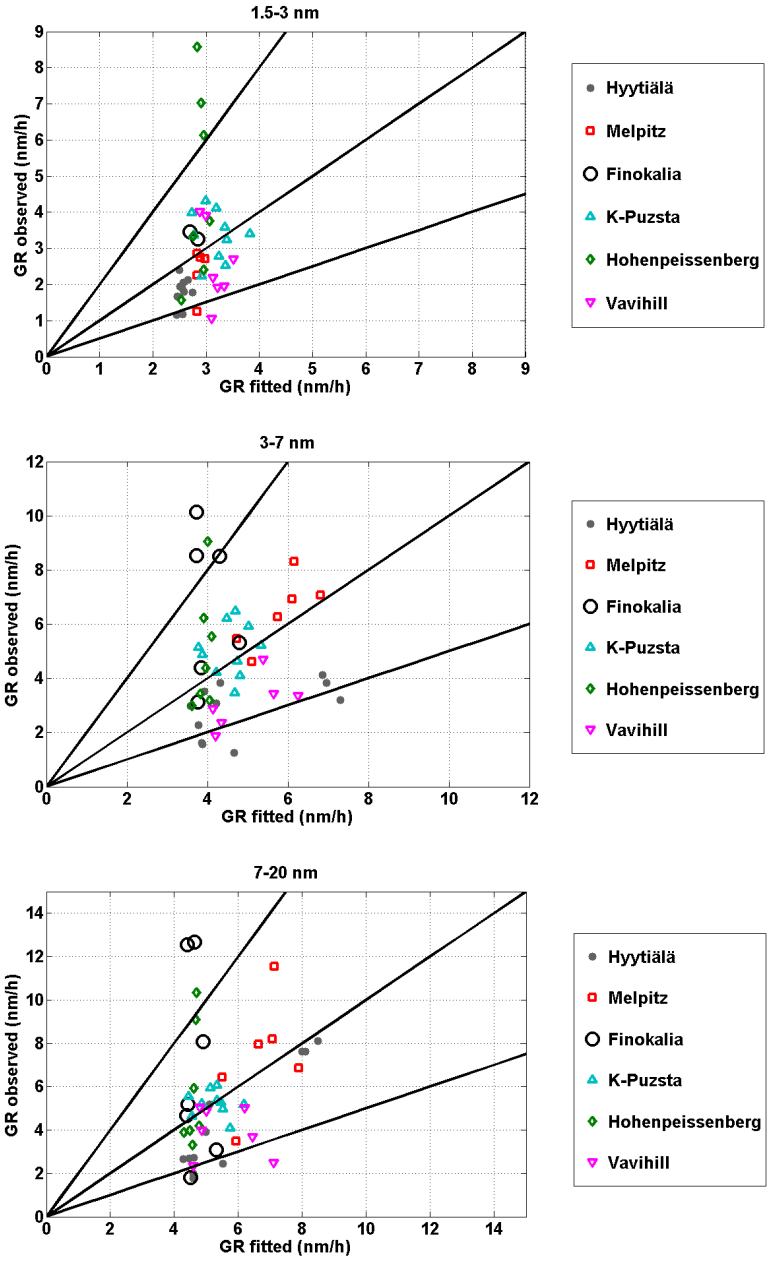

Fig. 1.1 Comparison of monthly median growth rates from field observations and from EUCAARI parameterization (see Table 4 in the manuscript for the parameters) for three particle size bins, 1.5-3 nm, 3-7 nm and 7-20 nm. The presented parameterization reproduces particle growth on a monthly scale well at different environments. For K-Puzsta, Melpitz and Hohenpeissenberg (excluding few exceptions) the correspondence between the observed and parameterized growth rates is the best, for Hyytiälä and Vavihill the growth rates are slightly overestimated when using the parameterization, whereas for Finokalia growth rates are more often underestimated (however, note the small amount of data points).

References

Pierce, J. R., Riipinen, I., Kulmala, M., Ehn, M., Petäjä, T., Junninen, H., Worsnop, D. R., and Donahue, N. M.: Quantification of the volatility of secondary organic compounds in ultrafine particles during nucleation events, Atmos. Chem. Phys., 11, 9019–9036, doi:10.5194/acp-11-9019-2011, 2011.

Riipinen, I., Pierce, J. R., Yli-Juuti, T., Nieminen, T., Häkkinen, S., Ehn, M., Junninen, H., Lehtipalo, K., Petäjä, T., Slowik, J., Chang, R., Shantz, N. C., Abbatt, J., Leaitch, W. R., Kerminen, V.-M., Worsnop, D. R., Pandis, S. N., Donahue, N. M., and Kulmala, M.: Organic condensation: a vital link connecting aerosol formation to cloud condensation nuclei (CCN) concentrations, Atmos. Chem. Phys., 11, 3865–3878, doi:10.5194/acp-11-3865-2011, 2011.

Riipinen, I., Yli-Juuti, T., Pierce, J. R., Petäjä, T., Worsnop, D. R., Kulmala, M., and Donahue, N. M.: The contribution of organics to atmospheric nanoparticle growth, Nature Geosci., 5, 453–458, doi:10.1038/ngeo1499, 2012.

Yli-Juuti, T., Nieminen, T., Hirsikko, A., Aalto, P. P., Asmi, E., Hõrrak, U., Manninen, H. E., Patokoski, J., Dal Maso, M., Petäjä, T., Rinne, J., Kulmala, M., and Riipinen, I.: Growth rates of nucleation mode particles in Hyytiälä during 2003−2009: variation with particle size, season, data analysis method and ambient conditions, Atmos. Chem. Phys., 11, 12865–12886, doi:10.5194/acp-11-12865-2011, 2011.