

## **Author response to referee comments for Westervelt et al. (2013): Analysis of feedbacks between nucleation rate, survival probability, and cloud condensation nuclei formation**

*Referee comments in italics*, responses in normal typeface

### **Anonymous referee 1**

*The results from earlier global simulations are given in introduction (p. 32180) with only one range (5-60% sensitivity of CCN to nucleation). These are explained in some more detail in Westervelt et al. (2013). However, would it be possible to build a table from the existing results (nucleation scheme and coefficients, sensitivity of CCN, etc.)? I think this would benefit the reader to get a clear picture of current understanding and to put the presented results into context. I think for this paper, citing 2-3 percentage numbers from earlier literature might be too vague. Also, Makkonen et al. 2012 studied the sensitivity of global CCN concentrations to 5 different nucleation mechanisms, and could be included in the reference list.*

The table is a good idea and has been added to the revised manuscript. We also agree that Makkonen et al. (2012) should be referenced in this paper. It is now included in the new Table (Table 1) and the reference list.

*The survival of nucleated particles is dependent on further growth and surrounding particle sink. In the global scale, it is therefore important if nucleation is occurring rather in locations of high sink or of high growth. The manuscript includes simulations with ion-mediated, binary homogeneous, activation-type and ternary nucleation. These mechanisms have a somewhat distinct spatial pattern (seen e.g. in Fig. 2), and the spatial variability in nucleation is discussed in p. 32195. However, it would be useful to have additional simulation with organic-influenced nucleation. Depending on selected parameterization, this could provide an additional spatial pattern of nucleated particles. In a rather extreme case, nucleation only by organic vapours would lead to a situation where nucleated particles are co-located with growing vapours, enhancing their survival probabilities.*

We chose not to simulate an organic-based nucleation mechanism for a few reasons. To the best of our knowledge, there is currently no “standard” organic-based nucleation mechanism that has been evaluated rigorously in global models. There are some empirically based first and second order correlations, but these are still areas of ongoing research and are based on data from very few ambient studies. Even using the activation-kinetic based organic nucleation correlations, some questions remain. For example, which organic vapor should be used as the precursor species (i.e. the sulfuric acid analogue)? Recent work by Schobesberger et al. (2013) suggests that monoterpene oxidation products (highly oxygenated organic acids) are most likely playing a role in initial stages of organic-based new particle formation. Metzger et al. (2010) used 1,3,5-trimethylbenzene (TMB) in a laboratory study and acknowledged that although they cannot deduce the identity of the nucleating species from their data, it was more likely to

be a monoterpene or sesquiterpene. Other issues include determination of the functional form of the nucleation rate equation. Some dependencies have been reported on organic precursor alone, whereas others have involved both organic vapors and sulfuric acid. Finally, the role of organics may also be more complementary to sulfuric acid formation, in which organic presence stabilizes developing clusters (Zhang et al., 2004).

*Related to above comment: why is ION experiment not included in e.g. Fig. 2-3?*

This was mostly due to those figures already being overcrowded with so many panels of the different nucleation mechanisms. Note that we also did not include the TER3 and ACT1 nucleation scenarios. Also, the global statistics are presented for all simulations in Table 2 and Fig. 4, including those not shown in Fig. 2 and 3. The ION results are quite similar to the other simulations. We present the ION simulation plot for CCN(0.2%) and total number but leave it out of the revised manuscript and refer the reader to the summary Fig. 4 and the tables.

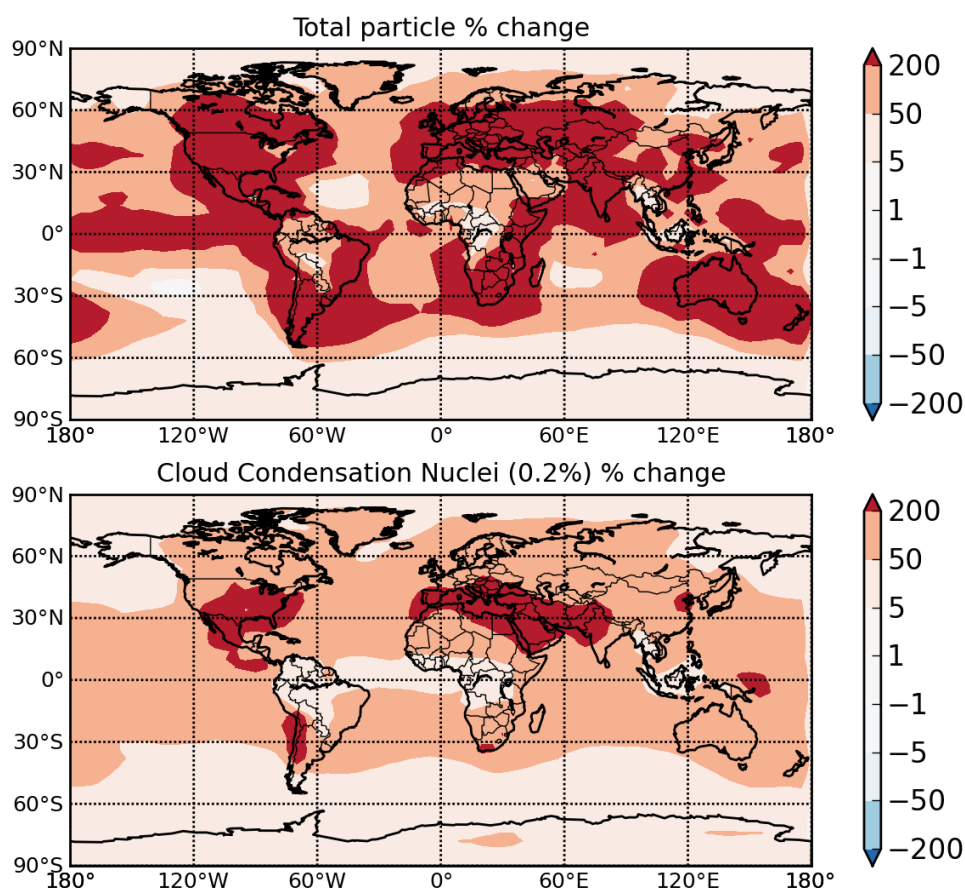


Figure 1: Total particle and CCN(0.2%) percent change (sensitivity) for ION nucleation.

*p. 32195, l. 23: Fix sentence: "It is also appears that mechanisms"*

Done, fixed in the revised manuscript.

*Section 2.2.1: Is one-month spin-up enough for the upper troposphere and lower stratosphere?*

One month of spinup is probably a little short for the lower stratosphere. However, we focus mostly on boundary layer nucleation in this work. Additionally, zonal CCN difference plots are presented in Figs. 2 and 3. If there were any major issues with the short spinup time, they would likely be visible there.

*Section 2.2.1: Why such a small perturbation to the activation nucleation coefficient? Usually, the coefficient is varied from  $10^{-5}$  to  $10^{-7}$  (see e.g. Spracklen et al., 2010)*

Indeed, previous studies have varied the coefficient in order of magnitude increments (e.g.  $2 \times 10^{-6}$ ,  $2 \times 10^{-7}$ ) (Spracklen et al., 2008, 2010). We expect that our smaller perturbation will have essentially a negligible effect on CCN, and according to Fig. 4, it does. The factor of 2 change in nucleation rate complements our orders-of-magnitude changes in the series of ternary nucleation simulations. Also note that for CCN(0.2%) in Fig 4a, the slope of the activation line is essentially the same as the slope of the ternary line. Although they are different mechanisms, orders of magnitude increases in coefficients do not seem to be very important.

We have added a line to the manuscript to elucidate this idea:

“The factor-of-two change in the A value is smaller than order-of-magnitude changes evaluated in previous studies (Spracklen et al., 2008, 2010). We use this smaller perturbation in nucleation rates to determine how much CCN will increase due to a relatively smaller enhancement in nucleation rates compared to our ternary simulations (TER, TER3, TER5).”

*Section 3.1: "especially over the oceans where increases from nucleation may not be expected". Why would it not be expected, and why would activation-type nucleation be too active above oceans? Due to too low simulated sink?*

For ternary nucleation, the ternary species (ammonia), often acts as the limiting factor for nucleation to occur over the oceans, since our model predicts low amounts of ammonia in these regions. This is also consistent with observations which have found aerosol to be acidic in the marine environment (Covert, 1988) However, with activation nucleation, this limit is not present. This is why it is too active over oceans and why we would not expect it.

The manuscript now reads:

“One major characteristic of the ACT2 simulation is that the activation mechanism predicts a large enhancement of N10 in the boundary layer, especially over the oceans where increases from nucleation may not be expected. This is partially due to the activation simulation lacking a third nucleating species that helps regulate whether or not nucleation occurs in certain environments. For example, in TER simulations, low amounts of ammonia over the oceans prevent nucleation from occurring.”

*Section 3.2.1: Hyytiälä is selected for closer comparison. As seen in Fig. 2, ternary nucleation is relatively inefficient in Hyytiälä. I would suggest to add a location where ternary nucleation has a relatively stronger effect, e.g. from North America. Indicate why only ternary nucleation is presented in Hyytiälä analysis.*

As seen in Table 3, mean nucleation rates ( $J_3$ ) at Hyytiälä are 2.3, 7.4, and 15.1  $\text{cm}^{-3} \text{s}^{-1}$  for TER5, TER3, and TER. Median values are also given. This is quite high actually compared to ternary nucleation rates at Pittsburgh and Atlanta, polluted North American sites (Westervelt et al., 2013). The annual average nucleation rate at Pittsburgh is 1.5  $\text{cm}^{-3} \text{s}^{-1}$ . Arguably, ternary nucleation should have a strong effect at Hyytiälä, too. We also refer the reader to Westervelt et al. (2013) in which 5 sites including Hyytiälä were analyzed.

*p. 32205, l.13: "We also find that CCN1.0 are" → "We also find that CCN(1.0%) concentrations are"*

Done.

*Section 4. The global results are rather clear in terms of global CCN. However, it should be mentioned that the spatial pattern of nucleation-CCN enhancement is rather important for the actual climate effect: which of the CCN changes e.g. in Fig.3 are modifying actual clouds and radiative fluxes. It could be that your global CCN results are indicative of modifications in cloud forcing, but this can not be simulated with the current model setup.*

Yes, this is true. We have added the following to the manuscript:  
"Additionally, although aerosol indirect forcing cannot be estimated with the current model setup, nucleation impacts on aerosol forcing are likely larger in certain regions. Future work should seek to explore the sensitivity of forcing to nucleation."

*Figures, general: Make font types and sizes consistent in figures. Include boxes around each panel (7b, 10a-d). Check notations carefully.*

Done, added to revised manuscript.

*Fig. 4: Mention that these are global average values (since later figures have also single station-values). Include meaning of colors (red, green, blue) in figure caption. Maybe combine panels with careful choice of colors/symbols? As the manuscript claims that CCN is rather insensitive to nucleation rate, it would be useful to easily compare the effect of particle growth (100 Tg additional SOA).*

Done. We will provide the combined figure here in the response, but prefer to leave the figure in the manuscript as is. For more on the effect of SOA and condensational growth on CCN formation, see D'Andrea et al. (2013).

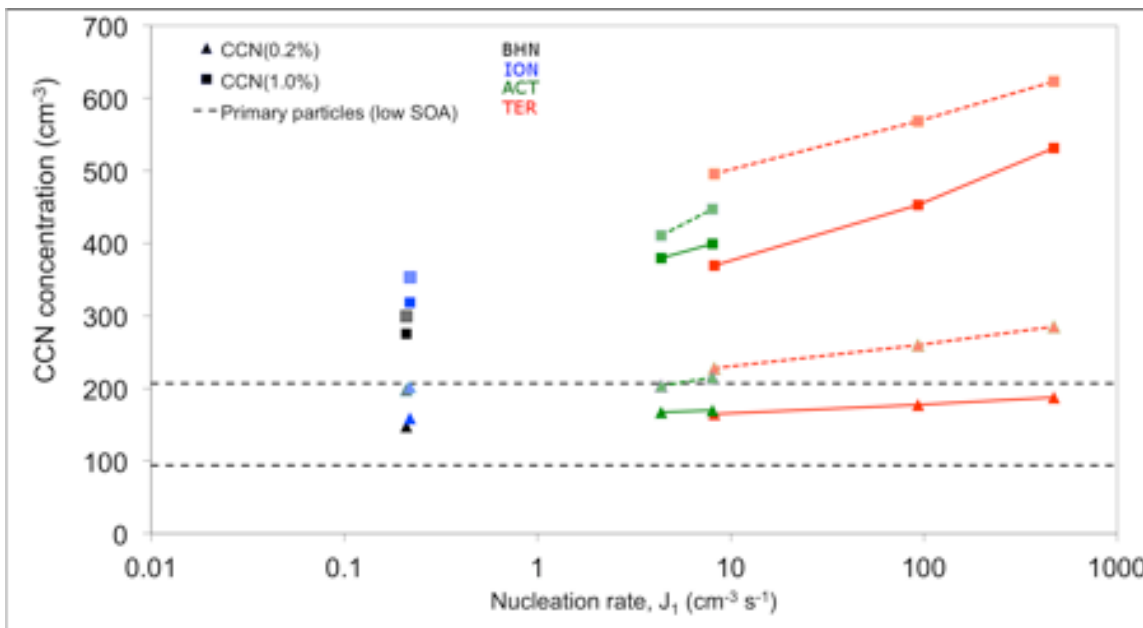


Figure 2: Global CCN concentration versus nucleation rate. The dashed/lighter colors represent the higher SOA simulations whereas the solid colors are the base cases. The two dashed lines are the primary particle levels for the base case (low SOA) simulations for CCN(0.2%) (higher line) and CCN(1.0%) (lower line). Triangles are CCN(0.2%), squares are CCN(1.0%). Red = ternary, green = activation, blue = ion, black = binary.

Fig. 9a,c (and a few other places): Since "SP" is not extremely common nomenclature, help the reader by including "SP3-50" and SP3-100 in x-axis label (also missing from some other figures, e.g. 6).

Done.

Fig. 10d: include fit-formula as in 10c. Perhaps write as  $SP = \exp(-a \cdot CS^2)$  ?

We have updated the figure to be written as recommended. The fit formula is the same in panel C and D. This is part of the point: that the same functional form based on simple scaling arguments explains both sets of data at Hyytiälä to first order. We have added a couple of phrases to make this clearer in the caption and the main text.

Write CCN(0.2%) instead of CCN0.2 and CCN(1.0%) instead of CCN1.0.

Done.

Correct references to "Vehkamäki" to "Vehkamäki"

Done.

## Anonymous referee 2

Please review the terminology related to 'area', 'Fuchs area', 'sink' in the entire manuscript and use it consistently. It is correctly acknowledged by the authors that

*condensation rate is indeed proportional to surface area in the kinetic and to diameter in the continuum regime, but still the term 'surface area' is used loosely in some instances in which 'sink' or 'Fuchs area' would be more appropriate.*

We did a search of the following words through the entire document: “area”, “Fuchs”, and “condensation sink”. We have corrected 5-6 instances in the manuscript where “Fuchs” surface area is probably more correct than just “surface area”

*2. On page 32181, line 20: it is mentioned that nucleation mode particles have a larger Fuchs surface area than geometric surface area. Is this really a significant difference?*

After looking into the definitions of Fuchs surface area a little more carefully and thinking about how it is calculated, we have decided to delete this line of reasoning from the manuscript. Basically, we are now convinced that the Fuchs area in the kinetic regime should exactly equal the geometric surface area. This is because the beta correction factor should be unity in the kinetic regime. We are confident that the other reasons provided about nucleation enhancing surface area are strong enough.

*3. On page 32189, arriving towards eq. 7, it is mentioned that GR and CS are linearly anti-correlated. I understand how this comes from a steady state analysis for vapour concentration - but, isn't it possible that same sources that contribute to vapour concentration contribute also to CS (indicating a possible reason for 'some positiveness' in the correlation between GR and CS)?*

Yes, this is possible. The production rate of vapors should be correlated with condensation sink, as well. We have added a caveat for steady state analysis as well as the following commentary:

“It is also possible that the same sources that add to the vapor production rate also may contribute to condensation sink, adding another source of uncertainty in the simple model. However, to the extent that this simple formulation captures the actual changes in survival probability predicted by the full model (where vapor production does contribute to condensation sink), we can conclude that this effect is small.”

*4. Comparison of figures 6 and 7: Why is there such a big difference in GR (compared with the difference in CS)?*

This is a good point. The ratio between GR\_TER5 and GR\_TER should be roughly equal to the ratio between CS\_TER and CS\_TER5. In Fig. 8, which shows the entire year of nucleation events, this seems to be the case. The issue with the example day in Figs. 6 and 7 it has to do with the time averaging of the growth rate (from 3-25 nm) and condensation sink. In Fig. 7, the CS is shown for the entire day, but the event duration begins at about 0600 and ends at 1600. For that same time period (Fig. 6), the nucleating mode reaches 25 nm much faster than 10 hrs. Hence, the growth rate is averaged over a much shorter time period. If we were to time-average the growth rate over the full 10 hours, the growth rate values decrease quite a bit and the ratios match better.

*5. How coupled are GR and J for the Hyytiälä simulations? Based on the several papers published by Kulmala and coworkers, it seems that sulphuric acid (+ maybe amines or ammonia) are responsible for nucleation, but organics dominate growth – so that GR and J are not necessarily very strongly coupled. Would your analysis also be valid in a different type of environment - in which the same vapour(s) are responsible for both nucleation and growth?*

.The analysis should still be valid, since the condensation sink calculation is the same no matter the potential condensable vapors (sulfuric acid and organics). With the exception of a few heavily polluted industrial regions (the Pittsburgh, PA / Ohio Valley USA region comes to mind), organics seem to dominate growth whereas sulfuric acid is universally needed for the initial steps nucleation. So there are not likely many environments where this would apply.

*6. Figure 10d and related text on page 32201: It is mentioned that the TER5 model fit "applies to" the TER case also. This is quite a strong statement and the reader may understand the fit to be universally valid. How would 10d look with a logarithmic y-axis?*

Good point. We have softened the language, which now reads:

This is also consistent with our claim that CCN concentrations do not change much with changes in nucleation theory or nucleation rate, since the same fit applies, in this specific example at least to first order, to two nucleation schemes with vastly different nucleation rates (see Fig. 8).

The quality of the fit is independent of the scale of the y-axis. The points that lie along the x-axis are REALLY at zero survival probability. These are likely events that did not grow to 50 nm.

*7. Having the analysis repeated for some other site (with very different conditions, in addition to Hyytiälä), would make the paper stronger. This is, however, no requirement from my point of view - the work is very nice already as such.*

We have decided not to add another site, as discussed above.

## **References:**

Covert, D. S.: North Pacific marine background aerosol: Average ammonium to sulfate molar ratio equals 1, *J. Geophys. Res.*, 93(D7), 8455, doi:10.1029/JD093iD07p08455, 1988.

D'Andrea, S. D., Häkkinen, S. a. K., Westervelt, D. M., Kuang, C., Levin, E. J. T., Leaitch, W. R., Spracklen, D. V., Riipinen, I. and Pierce, J. R.: Understanding and constraining global secondary organic aerosol amount and size-resolved condensational behavior, *Atmos. Chem. Phys. Discuss.*, 13(7), 18969–19007, doi:10.5194/acpd-13-18969-2013, 2013.

Metzger, A., Verheggen, B., Dommen, J., Duplissy, J., Prevot, A. S. H., Weingartner, E., Riipinen, I., Kulmala, M., Spracklen, D. V., Carslaw, K. S. and Baltensperger, U.: Evidence for the role of organics in aerosol particle formation under atmospheric conditions., *Proc. Natl. Acad. Sci. U. S. A.*, 107(15), 6646–51, doi:10.1073/pnas.0911330107, 2010.

Schobesberger, S., Junninen, H., Bianchi, F., Lönn, G., Ehn, M., Lehtipalo, K., Dommen, J., Ehrhart, S., Ortega, I. K., Franchin, A., Nieminen, T., Riccobono, F., Hutterli, M., Duplissy, J., Almeida, J., Amorim, A., Breitenlechner, M., Downard, A. J., Dunne, E. M., Flagan, R. C., Kajos, M., Keskinen, H., Kirkby, J., Kupc, A., Kürten, A., Kurtén, T., Laaksonen, A., Mathot, S., Onnela, A., Praplan, A. P., Rondo, L., Santos, F. D., Schallhart, S., Schnitzhofer, R., Sipilä, M., Tomé, A., Tsagkogeorgas, G., Vehkamäki, H., Wimmer, D., Baltensperger, U., Carslaw, K. S., Curtius, J., Hansel, A., Petäjä, T., Kulmala, M., Donahue, N. M. and Worsnop, D. R.: Molecular understanding of atmospheric particle formation from sulfuric acid and large oxidized organic molecules., *Proc. Natl. Acad. Sci. U. S. A.*, 110(43), 17223–8, doi:10.1073/pnas.1306973110, 2013.

Spracklen, D. V., Carslaw, K. S., Kulmala, M., Kerminen, V.-M., Sihto, S.-L., Riipinen, I., Merikanto, J., Mann, G. W., Chipperfield, M. P., Wiedensohler, A., Birmili, W. and Lihavainen, H.: Contribution of particle formation to global cloud condensation nuclei concentrations, *Geophys. Res. Lett.*, 35, 5 PP., doi:200810.1029/2007GL033038, 2008.

Spracklen, D. V., Carslaw, K. S., Merikanto, J., Mann, G. W., Reddington, C. L., Pickering, S., Ogren, J. A., Andrews, E., Baltensperger, U., Weingartner, E., Boy, M., Kulmala, M., Laakso, L., Lihavainen, H., Kivekäs, N., Komppula, M., Mihalopoulos, N., Kouvarakis, G., Jennings, S. G., O'Dowd, C., Birmili, W., Wiedensohler, A., Weller, R., Gras, J., Laj, P., Sellegri, K., Bonn, B., Krejci, R., Laaksonen, A., Hamed, A., Minikin, A., Harrison, R. M., Talbot, R. and Sun, J.: Explaining global surface aerosol number concentrations in terms of primary emissions and particle formation, *Atmos. Chem. Phys.*, 10(10), 4775–4793 [online] Available from: <http://www.atmos-chem-phys.net/10/4775/2010/> (Accessed 7 April 2011), 2010.

Westervelt, D. M., Pierce, J. R., Riipinen, I., Trivitayanurak, W., Hamed, a., Kulmala, M., Laaksonen, a., Decesari, S. and Adams, P. J.: Formation and growth of nucleated particles into cloud condensation nuclei: model–measurement comparison, *Atmos. Chem. Phys.*, 13(15), 7645–7663, doi:10.5194/acp-13-7645-2013, 2013.

Zhang, R., Suh, I., Zhao, J., Zhang, D., Fortner, E. C., Tie, X., Molina, L. T. and Molina, M. J.: Atmospheric new particle formation enhanced by organic acids., *Science*, 304(5676), 1487–90, doi:10.1126/science.1095139, 2004.