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Interactive comment on "A chamber study of the influence of boreal BVOC emissions and sulphuric acid on nanoparticle formation rates at ambient concentrations" *by* M. Dal Maso et al.

Anonymous Referee #2

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This study investigates the contribution of BVOC and sulphuric acid on the particle formation rate and growth. The BVOCs are produced using the emissions of plants in a plant chamber and a flow tube reaction chamber. The results are also compared to pure alpha-pinene and zero experiments. They find a contribution of BVOC oxidation products to the particle nucleation rate and growth rate. The contribution of BVOC to nucleation and growth is higher compared to alpha-pinene, indicating that a mixture of biogenic emissions is more efficient than pure alpha-pinene. The observed nucleation rates agree with field measurements when using a parametrization based on emission rates.

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Major comments: The paper is generally well written but lacks on certain parts consistency and clarity. It leaves the impression, that it provides a fundamental new approach, although it is more or less just a mathematical reformulation of other work. The fact that parametrizations used by others do not work here is due to limitations of their measurement and not that those parameterizations are not valid. There are also some serious concerns regarding the application of their method to determine nucleation rates (see below). To improve these to reach an acceptable level is difficult based on the presented data. Their application of the results to atmospheric conditions in a boreal forest is not justified. Although the authors point out that the condensation sink is completely different in the chamber (page 31342 line 9) and OH concentrations need to be taken into account (page 31342 line 20) they do not in their calculation and claim that this calculated J-value agrees with ambient observations. Regarding the OH concentration it is not only the influence on the fraction of NucOX formation but also their production rate which seems to be much higher in this chamber. For these For these reasons I cannot really recommend this paper for ACP.

The reaction chamber has a rather small volume and thus the dilution and wall losses are expected to be high. In this study as well as in most other studies wall and dilution losses are dominant. The calculation of J was made over a very broad diameter range (only 3 size rages 1.6 – 7 nm, 7-15 nm and >15 nm) and needs corrections which include size dependent terms (coagulation and wall losses). The J rate is also determined at a relatively late stage of the experiment in most cases when bigger particles are present in the flow tube yielding higher coagulation losses. Despite that the authors claim that this method is independent on the growth rate which is the limit of many other methods, I do not believe that these assumptions are valid using these broad size ranges. Especially in the very first bin 1.6 -7 nm the growth rate is expected to change dramatically (Nieminen et al., 2010). Only using 3 channels could bias these correction terms and could yield a dramatic over- or underestimation. It is also not clear, how these corrections are applied. Which values were used and how were they derived for the 3 size bins? These correction terms are not quantified in the

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paper. I would expect rather high correction terms with high uncertainties as the losses depend on the unknown size distribution of the particles within these bins. Similarly, the wall losses of 1.6 nm particles and 7 nm particles are very different. Here a wall loss rate of 5x10-4 s-1 (Page 31329 line 24) is given for the smallest measured size range. How did the authors derive this number and what are the uncertainties? The wall loss rates for NucOx are in the order of 10-2 s-1 (page 31339 line 9). Comparing the wall loss rates for NucOx and the smallest size range, I would expect big corrections on the J rate also yielding large uncertainties. A state-of-the-art uncertainty analysis should be given for this simplified data treatment and plotted in Figure 4.

With respect to equation 6 it is stated that these experiments do not show this correlation (page 31332 line 21). Instead they find a correlation using equation 7, which includes the source strength of BVOC. Equation 7 is rationalized with a simplified mechanism (R1-R5) which was also used in other works (Paasonen et al. 2010; Metzger et al., 2010; Riccobono et al. 2014). Equation 7 (or 11) is basically equivalent to equation 6 (based on their assumptions equation (8) reduces to a direct proportionality between BVOC and source strength). Therefore, both parametrizations should yield the same good/bad correlation, which is not seen in Table 2. That this is not the case is because their measurements of BVOC and oxidants in the reaction chamber are not good enough (page 31338 line 10). This is not made very clear in the paper as the conclusions say again, that there is no correlation with equation 6 (Page 31343 line 10).

Looking at Figure 5 it seems that also the experiments with zero ozone were included to fit the nucleation rate with the BVOC injection rate. This would mean that BVOC without oxidation would help nucleation as stated on Page 31339 line 1. However, From Figure 2 a decrease of BVOC is seen which indicates an oxidation process contrary to the statement given here. It seems quite unclear what is happening in this experiment and doubtful if it can be included into this correlation analysis. Excluding this would lead to a different J-dependence.

As seen from Figure 2 monoterpene concentrations in the plant chamber and the reaction chamber are quite different for lights off. If ozonolysis is small this should not be the case except dilution is large. It looks like a large but varying fraction of the BVOCs are already reacted away only by ozonolysis, when being injected into the chamber. The source strength of a-pinene was derived from its concentration in the reaction chamber. How reliable is this approach?

It is stated that particle growth correlates best with ozonolysis rates. The authors also state that the PSM sees a nucleation for UV off periods. But why should the particles not grow, when it is explicitly stated that the particle growth correlates with monoterpenes x O3? It also appears puzzling that OH actually is important for the nucleation but not for the growth. For nucleation low volatility compounds need to be formed which are expected to contribute to growth, too. MT and OH concentrations may vary rapidly in the beginning of the experiments, when growth rates are determined. How well can these be determined? As mentioned in the paper (P31326 line 24) OH depends on ozone concentration. Thus, why do [MT] x [O3] and [MT] x [OH] not correlate and yield different dependencies with growth rates (Figure 6 c and d). In the case of J-measurements it is admitted that BVOC and oxidants cannot be measured reliably. Can it really be done in this case? Which are the a-pinene experiments in Figure 6?

In this work a dependence of J from sulfuric acid and BVOC to their first power was found similar to Metzger et al. 2010. In a recent paper by some of the co-authors (Riccobono et al. 2014) a different relationship was found for biogenic oxidation products. This is not discussed in this paper.

Minor Comments: Page 31321 line 15 ff.: The authors state that "the roles of plant volatiles and sulphuric acid in the initial formation process remains open." Riccobono et al. 2014 (some authors of this study are even co-authors) has clearly shown the contribution of oxidized biogenic organics to aerosol nucleation.

Page 31323 line 1: Were these lamps also used or just the Philips UV lamps?

Page 31328 Equation (1): The growth term is wrong: Δdp is missing. Lehtinen et al., 2007: $Jm=Cm*Nm/\Delta dp$

Page 31330 line 6: The growth rate determination is not so clear. Is the rise time of the PSM compared to the rise time of the CPC or were the rise times of the channels used. Please clarify.

Page 31331: In this section the authors state that the sulphuric acid concentration increases as time progresses. What is the reason for this? Why should it increase? There is no explanation or proposed mechanism for this behavior. It makes the impression that it was not possible to keep the conditions stable in the reaction chamber. It is also stated that the changes in particle concentration, size distribution and BVOC were slow. Looking at Figure 2, this is not always the case. For the last four experiments, the J calculation was done very much in the beginning when still large changes in all the above mentioned parameters occurred.

Page 31335 line 9: A participation of organic in nucleation was shown by Zhang et al., 2009 and Riccobono et al., 2014.

Page 31355: Improve Figure 3. More tics/tic marks are needed on x- and y- axes. A legend would help understanding the figure.

Page 31356 Figure 4: Error bars/uncertainties are missing. This has to be included. Also the markers are difficult to distinguish. Also here a legend would be helpful. Figure 4 also shows that the chamber suffers from quite some contamination. The nucleation rate of the no-BVOC case is comparable to the a-pinene case. The color scale of log(H2SO4) also seems to be wrong, as then a sulfuric acid concentration of up to 10E14 cm-3 would have been measured.

Page 31357 Figure 5: Again a legend would be appreciated. It is not clear, which points were included in the fit and which not.

Page 31358 Figure 6: The different experiments are not indicated.

References:

Lehtinen, Kari EJ, et al. "Estimating nucleation rates from apparent particle formation rates and vice versa: Revised formulation of the Kerminen–Kulmala equation." Journal of Aerosol Science 38.9 (2007): 988-994.

Nieminen, T., Lehtinen, K. E. J., and Kulmala, M.: Sub-10 nm particle growth by vapor condensation – effects of vapor molecule size and particle thermal speed, Atmos. Chem. Phys., 10, 9773-9779, doi:10.5194/acp-10-9773-2010, 2010.

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