Response to reviewer's comments on "A chamber study of the influence of boreal BVOC emissions and sulphuric acid on nanoparticle formation rates at ambient concentrations" by Dal Maso et al.

The key to reading this response:

- **Reviewer comments in bold**
- Author comments in normal typeface

Reviewer 1

General Comments: The paper presents the results of new particle formation from real plant emissions and sulfuric acid in the chamber. Three representative tree species in the boreal forest were used. By adjusting the UV intensity and temperature in their chamber facility, they were able to vary the concentrations of BVOC and sulfuric acid. The newly formed particles were counted by three particles counters with three differ- ent size cutoffs, from which the particle formation and growth rates are reported. The major conclusion is the nanoparticle formation rate can be represented as the BVOC flux and sulfuric acid with the aid of a simplified mechanism. The relevance of the conclusion to the atmospheric application is also reported. Generally the paper is interesting and well written. I have a major comment on the application of the conclusion in the atmosphere. To solve my comment, I suggest authors to rephrase Qinflow to ΔQinflow,, which represents the reacted BVOC. More elucidation is presented in the major comments. I also have some other minor comments. They are not serious and just need to be clarified. In my opinion, the paper should be published in ACP.

We thank the reviewer for the efforts in reading our manuscript and for providing insightful comments to improve the manuscript. In the following, we will respond to the issues highlighted by the reviewer in a point-by-point manner.

Major Comments:

I have a little concern with the application of one finding in the paper to the atmospheric environment. In this study the authors attempt to quantity the aerosol formation rate with the BVOC flux and sulfuric acid. The BVOC flux here is

denoted by q, which is the flowrate at outlet of plant chamber. A simplified mechanism is also developed:

Qinflow→BVOC (R1)
BVOC+OX→i*OxVOC+n*NucOX (R2)
BVOC+(X)→dilution +losses (R3)
NucOX+H2SO4→nanoCN (R4)
NucOX+(X)→dilution +losses (R5)

from which, the nucleation rate is expressed as: J=K*q*[H2SO4], where K= n*kj/i*Y,NucOx (11)

The conclusion holds in their chamber study where all the BVOC are consumed. How- ever, the mechanism fails to take into account the unreacted BVOC, which can lead to a change in the mechanism:

Qinflow→BVOC (R1)
BVOC+OX→i*OxVOC+n*NucOX (R2)
BVOC+(X)→dilution +losses (R3)
BVOC→BVOCunreacted (R3.1)
NucOX+H2SO4→nanoCN (R4)
NucOX+(X)→dilution +losses (R5)

from which we seek a solution for q:q=n*kox*[OX]*[BVOC]+ i*kox*[OX]*[BVOC]+YBVOC+ [BVOC]unreacted (8) Eq.(8) doesn't lead to Eq. (11).

This is the most cases that the BVOC residuals (unreacted) are present from tree emissions. The direct application of the results appears to be problematic.

The reviewer raises an important point regarding chamber studies, namely that the situation is different to 'natural' conditions because processes are occurring in a closed volume. It is true that in our experiments, almost all of the BVOC entering the chamber were consumed by some processes, and that this will usually not occur in the natural atmosphere. However, our mechanism presented in R1-5 is able to handle this; unreacted BVOC are still remaining as BVOC, and we can actually solve for them (and have done so in getting Eq. (11)). It is correct that in the atmosphere, the assumption of $\gamma_{BVOC} << i*k_{OX}[OX]$ may not hold, which will affect applicability to atmospheric conditions (the simplification of Eq (10) to Eq (11) will be different). This is addressed in the revised version of our manuscript, both in the derivation of Eq 11 and in the section discussing atmospheric relevance.

Specific comments:

p31231, L27-28, Sulfuric acid levels are varying in ambient. The sites (e.g. Hyytiala, Finland) with which is compared should be mentioned in Sect. Experiment or Results and proper references should also be referred to.

We have added references to the observation sites used for the comparison data to our revision.

Sect. 2.1 I recommend the operation of reaction chamber to be described in more detail. The section can indicate clearly the operation of chamber in a flow mode. What are the inlet and outlet flowrates and from which the dilution ratio can be estimated? All the information can be inferred partly in the later manuscript but is worth to be described here already.

We will improve the description in our revision to give a clearer overview. The chamber was operated in the same manner as in other published work, e.g. Mentel et al. 2009, and Kiendler-Scharr et al., 2009. The flow rates were measured during the operation, and measured values were used in the dilution rate estimations where needed. On average, the flow rates were 30 l/min, which leads to a dilution e-folding time of ca. 50 min.

p31323, L15-17, does the VOC flux remain similar without such a treatment?

Environmental factors can influence trees' VOC emissions, and it is known that past conditioning can affect VOC fluxes. The method described here was chosen to minimize such effects.

Sect. 2.2 The instruments utilized in the study should be provided with their models and manufacturer.

We will add this information to the revision.

Sect. 2.3:

1. It is not clear how the SO2 level in the reaction chamber was controlled? Is it from the background air or from extra feeding to chamber?

No additional SO2 was added to the chamber. The sulphuric acid was formed by the oxidation of the residual SO2 in the purified air in the chamber, and it was estimated to be tens of ppb.

2. UV lamp wavelength should be mentioned.

It is given in section 2.1: *OH radicals were generated by ozone photolysis (internal UV lamp, Philips, TUV 40W, λmax = 254 nm, J(O1D) ≈ 2.9 10−3s−1).* We will clarify the wording to make it clear that this is the lamp.

Three representative types of tree species were applied for the study. But it was still unknown the amount of tree seedlings, their composition and if the same seedling group was used for all the experiments.

One seedling of each tree species was used. This information has been added to our revision.

Sect. 2.4: Five equations are described to derive the aerosol formation rate, whilst the authors also assume the rate of formation at the detection limit of PSM as the nanopar- ticle formation rate. Following which, three size ranges from three particle counts are mentioned for the analysis. The description in text is confusing. I recommend the authors to describe in more details how the formation rate was determined.

The section detailing the determination of the particle formation rate will be rewritten in our revision. The details of the revision are given in our response to Reviewer 2, who raised concerns on the methodology of determining the formation rate.

p31331 L19-20 and Fig. 4(b): The particle formation rate was increasing along with monoterpene concentration under around 1.5 ppb, however, a higher monoterpene concentration than 3 ppb doesn't lead to a faster formation rate. So what are the possible explanations?

This is one of the key points. Increasing the influx of VOC into the chamber lead to a decrease in sulphuric acid concentration in the chamber, which in turn reduced the amount of particles formed. This lead us to establishing that in our experiments, both H2SO4 and organics are needed for nucleation.

p31336 L17-19, the parameters in R3 and R5 should be explained.

The explanation of the parameters in the set of equations has been improved. γ_{BVOC} and γ_{NucOx} stand for the total loss rate of BVOC and NucOx, respectively, and by loss we mean either losses to walls or dilution, or to chemical pathways that do no lead to particle formation.

p31337,L13-14, for eq. (11), it is worthy to define K= n*kj/i*Y,NucOx

We have added this definition to the revised version.

p31340, L1-2, In high NOx condition RO2 reacts dominantly with NO, producing RO radicals. Do the author indicate that RO2 radical favors new particle formation while RO doen't? Please explain more.

Our experiments were performed at low-NOx conditions. However, as per comments of Reviewer 2, reconsidered the statement presented here and have removed the suggestion that no oxidation would be needed.

p31339,L7, an approximate reference should be cited for the argument '. . .the order of 10e-10'.

We have added a reference here. (Weber RJ, et al. (1996) Measured atmospheric new particle formation rates: Implications for nucleation mechanisms. *Chem Eng Commun* 151:53–64)

p31340, L1-3, the argument 'However, the data would also support a hypothesis in

which no oxidation of the BVOC is needed, with nanoCN formation occurring directly by the interaction of a compound emitted by plants in proportion of their total BVOC emission' is misleading and should be deleted from the manuscript. Please read the major comments.

We have revised this section according to the comments of both reviewers, including removing the sentence mentioned above.

Table 2. Does it enhance the coefficients by varying the exponent of [H2SO4]?

Yes, the correlation could be enhanced somewhat by increasing the exponent of both the QOrganic and H2SO4. However, with a dataset of this size, we feel that one should keep the fit parameters to a minimum to avoid overfitting, and therefore, we did not use the exponents as free fit parameters.

Fig. 5 Should indicate clearly the red points are from a-pinene experiments, otherwise the figure is quite misleading.

We have added an indication to the figure

Technical corrections:p31322, L11, nanoCN should be given full name for the first time mentioned. p31325, L5, SD, provide the full name.Fig. 3 Caption for green curve is missing.Fig. 4 The markers are too small and difficult to distinguish them.

We thank the reviewer for pointing out these issues, and we will address these in the revised manuscript.

Reviewer 2

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.

We thank reviewer 2 for the work in carefully reading and commenting our manuscript. The comments are very valuable, and although the recommendation for publication was negative, we hope that by addressing the major concerns raised, we may be allowed to submit a revised manuscript for consideration. In reading the comments, we found 3 major concerns, which we will address first; the rest of the comments will be replied to after these.

Major comments:

Concern 1: The approach and parameterization

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.

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).

The reviewer is correct in stating that the approach that we are presenting here is not a fundamentally new approach. As mentioned by the reviewer, our results can be explained by essentially the same mechanism as given previously in other work, but we study the reaction paths that are essential in our experiments. However, we want to point out that our aim in this approach was to present the particle formation rate in terms of directly measured quantities. We think that this may be a useful approach, as for example OH radical concentrations are rarely measured, but instead estimated from solar irradiation values. Our analysis of the reaction system also shows that depending on the conditions, and the relative magnitudes of the sources and sinks and the dominating reaction pathways, the correlation with different measurable quantities may change.

We also hope that the approach that we show here may be of some help to modellers. BVOC concentrations can be difficult to model in the atmosphere, and emissions from trees are often measured directly. Using emission strength instead of concentration in the parameterization could possibly avoid difficulties in predicting concentrations, and thereby improve modeling approaches of boundary layer particle formation.

We also want to point out that the BVOC measurements were actually of sufficient quality, but as most of BVOC in the reaction chamber were reacted away, there was very little signal to be measured, leading to the poor correlation.

Should we get the opportunity to submit a revised manuscript, we will revise the section describing the rationalization of our results, and the thinking behind it. We will also emphasize the fact that the mechanism itself is not new.

Concern 2: deriving the nucleation rate

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.

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 par- ticles 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 ex- pected 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 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.

The reviewer raises a very important point. It is indeed true that using the three channels, without knowing the size distribution inside the channels, could lead to significant error in determining the formation rate. In our case, this is however, mitigated by the fact that we have used relatively slow-changing size distribution (close to steady-state) situations to estimate J. In the following, we will give a detailed description of the determination of J.

As stated in the paper, the formation rate formula is, after solving Eqs 2-4,

$J = dN_1/dt + dN_2/dt + dN_3/dt + Co_1N_1 + Co_3N_3 + Co_3N_3 + w_1N_1 + w_2N_2 + w_3N_3 + \gamma(N_1 + N_2 + N_3)$

Where N_i stands for number concentration in the ith size class, Co_i stands for the coagulation sink of size class i (given by summation in Eq 5) , w_i stands for the wall loss of size class i, and γ is the dilution rate.

Here, size class 1 is 1.6-7 nm, size class 2 is 7-15 nm, and size class 3 is >15 nm. We have no direct information on the shape of the size distribution in size classes 1 and 2, but we have full size distribution information for size class 3. As the reviewer states, the parameters Co_i and w_i are size-dependent, and averaging them over the whole size range may lead to errors.

For coagulation, instead of knowing the exact size distribution inside the size channels, it is equivalent to find the size of particles inside the size channel that would lead to the same coagulation loss rate Co_iN_i if all particles in the size class were replaced by particles of this specific size. This is conceptually similar to finding the Condensation Sink Diameter (CoSD, Lehtinen et al., 2003) for the size interval, but instead for the coagulation sink.

In steady state, the size distribution shape of small particles is determined by the growth rate and the loss rates of the particles. Basically, it resembles an exponential or second-order polynomial function. As we had information on the total number in each size class and also distribution information on the SMPS, we could estimate the size distribution using a fit estimate, and from those we could calculate the CoSD. We performed fits using 1st and 2nd order polynomials, and found that the CoSD varied very little for the smallest size class, being 3.0±0.1 nm. The little variation stems from the relative similarity of the studied events, and the steady-state condition. Based on this we estimate that using a CoSD of 3.0 nm for Eq (5) will give reasonably good results (the error being of the order of ca 20%, and if the estimation is off, the error would be consistently in the same direction for each experiment, which would not affect our fitting of the coefficient K.

For wall losses, the loss coefficient could be estimated from and experiment where particles never reached the CPC detection limit. When UV lights were turned off, particle formation is also stopping (sulphuric acid was depleted) but particle number diminished by dilution and wall scavenging (and minimally by coagulation). As dilution is known from direct measurement of the flows, the wall loss rate can be estimated from this experiment for size class 1. The wall loss coefficient for size class 2 was estimated assuming that it proportional to the diffusion coeffient as given in Verheggen and Mozurkevich (2006).

Coagulation loss rates and wall loss coefficients for size class 3 could be estimated directly from the size distribution and using the diffusion coefficient calculation. However, it was evident that for these larger particles, dilution was the main loss pathway.

In our revision, we will improve the section describing the formation rate calculation to include the above-mentioned clarifications and additions, as well as add a uncertainty analysis to both the formation rate calculations as well as the fitting of parameter K. To avoid confusion, we also like to point out that our plant chamber-reaction chamber system does not include a flow tube, but the reactor can instead be thought of a countinuous stirred tank reactor (CSTR).

References: Lehtinen, K. E. J.; Korhonen, H.; Dal Maso, M. and Kulmala, M. (2003): On the concept of condensation sink diameter. Boreal environment research 8, p. 405-412.

Verheggen and Mozurkewich: An inverse modeling procedure to determine particle growth and nucleation rates from measured aerosol size distributions Atmos. Chem. Phys., 6, 2927-2942, 2006

Concern 3: Applicability to the atmosphere

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 reasons I cannot really recommend this paper for ACP.

We will clarify this section in our possible revision. Our purpose on page 31342 is to highlight an important difference between chamber and ambient studies, namely the presence of walls as sinks for condensing and nucleating vapours. Our condensation sink in the experiments was actually quite close to some atmospheric situations, and as we have stated, the wall effect might be taken into account by scaling the CS. This would, however, require better estimates and variation of the wall sink, which we feel is outside the scope of this paper. Regarding the OH influence on the production rate, this is in a manner included in R3.

Our results fit ambient observations in terms of observable quantities, and our aim is to show the applicability of the H2SO4-organic mechanism for real tree emissions in controlled conditions. Chamber studies of course carry with them the difficulty of matching all conditions for the ambient, and in our revision we will improve this section to show the possible differences between the chamber and the real boreal forest.

Other issues:

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 reac- tion 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?

The difference between the concentrations in the plant and reaction chambers in caused by two reasons: firstly, the outflow from the plant chamber is mixed with the ozone flow, which causes dilution; secondly, ozonolysis consumes some of the BVOC. However, in the zero-O3 experiment no O3 was added to the chamber, but the dilution flow was kept constant to keep the flows as similar as possible. Therefore, the difference between the concentrations is not caused by oxidation but only by dilution. The difference in the concentrations is exactly the dilution ratio. In the revised version, this is explicitly stated.

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 monoter penes 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?

This is a good point. Firstly, we want to note that the nucleation seen in UV off periods is very low: the PSM saw a few hundred particles, and the wall and dilution loss rates basically mean that hardly any particles would reach the 7-nm size limit unless they grew really fast.

This is not the first time that the OH-O3 distinction for particle growth has been made. Hao et al (2010) came to a similar conclusion in their study. OH and ozone reactions lead to different reaction products, and while products with low enough volatility for growth are produced from ozonolysis, these same compounds do not necessarily lead to particle formation. However, considering the issue more closely, it might be that both ozonolysis and OH is required for fast particle growth, but the OH-signal is lost due to the quick variations of the concentrations. Therefore, only the O3-correlation can be observed from the data.

We agree with the reviewer on the issue of the measurements of BVOC and oxidants in the reaction chamber; the issue is the same for the growth case too, except that at the start of the experiment, more BVOC is present, which helps with PTR-MS measurements. The analysis of the data was performed in this manner following similar data analysis in e.g. Paasonen et al., and we show the results because clear dependency can be seen. For the nucleation case, no such dependency could be observed.

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.

The omission of the Riccobono paper is a glaring on in the reference list of our manuscript, and the revised manuscript will discuss the implications of our data also from this viewpoint.

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.

In the revised manuscript, we have revised this statement. Our aim was to discuss the fact that there are still significant uncertainties on the identity of the BVOC that actually cause nucleation, as it has been shown before (eg. Mentel et al, 2009, and Kiendler-Scharr, et al 2009) that the mixture of BVOC can play a significant role in particle formation.

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

Yes, these lamps were also on during the experiments.

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

The growth rate C_m here is defined as GR/Δdp, where GR is the diameter growth rate of particles in size class *i*. This has been clarified in the revised manuscript.

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.

The rise time of the two different instruments were compared.

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.

As we have already stated, the reaction chamber is not a flow tube, but a reaction volume to which a steady flow of BVOC and ozone is directed. As reactions and aerosol formation occur in the chamber, the concentrations of different compounds will change, and the system will find a new steady state. Here, we define a steady state as a situation where concentrations change slowly with respect to the fastest reactions (eg. OH-reactions). The most likely reason for the increase is the increase of the OH concentration during the experiment, which in turn can be explained by eg. the presence of a slow-reacting OH-scavenger (for example carbon monoxide, CO), which is slowly depleted during the experiment.

The reviewer is right in stating that for some experiments, the formation rate calculation was done closer to the beginning of the experiment than for most events. However, in all cases the particle distribution can be considered to be in steady-state, as well as the OH-O3-BVOC –gas phase system. Figure 2 is unfortunate in this respect, because it covers such a long period and the individual experiments are not easily seen. In our revision, we will improve the figure in this respect.

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

The references have been added to the text.

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

We have improved the figure according to the reviewer's wishes in our revision.

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.

As was discussed with the major comments, we will update this figure to also show the uncertainty ranges.

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 nucleation rate in the no-BVOC case can be explained by the higher sulphuric acid concentration. Of course, the proposed mechanism of BVOC*H2SO4 would indicate zero nucleation. However, with the exception of possibly the CLOUD chamber at CERN, it is extremely difficult to totally remove all organics from the flow using conventional methods; therefore, we assume that trace amounts of organics may be present during the experiment, leading to nucleation. Essentially no growth was observed, and the nucleation could be seen only in the PSM.

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.

The scale is correct except for the caption, which should read ln(H2SO4) The scale hase been changed to log10(h2so4), which is more logical.

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

The figure has been improved to show the inclusion of points in the fit.

Page 31358 Figure 6: Which are the a-pinene experiments in Figure 6?The different experiments are not indicated

We will revise the Figure 6 to indicate the different experiments.