**Atmospheric
Chemistry
and Physics
Discussions**

Interactive
Comment

Interactive comment on "Ambient new particle formation parameter indicates potential rise in future events" *by* B. Bonn et al.

B. Bonn et al.

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General:
We thank both reviewers to have made their detailed comments on the present manuscript in *Atmos. Chem . Phys. Diss.* for improvement. Especially reviewer no. 2 provided a lot of very useful remarks that, if addressed and accepted, will improve the former manuscripts quality and reduce misunderstanding. This we would like to acknowledge kindly.

Some of the comments refer to a clear lack in description of the used nucleation parameters so that the argumentation could not be followed in detail. Others focus on the detailed description of the individual parameter parts such as Guenther algorithm which is actually the pool emission, not the direct emission from "online"; production. In the revised version we extended Section 2 from two to about four pages (p. 4-8), i.e.

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doubled the size. Therein we now start with description of the particle formation rate at about 1.2 nm in cluster diameter according to Bonn et al. (2008). Next to that the organic nucleation parameter *org. NP A* is extracted from the formation rate equation. The other nucleation parameters *org. NP B*, *NP A* and *NP B* are further developed out of the formation rate equation and reasonable assumptions for parameters not understood well currently or hard to measure. In Section 3: The nucleation parameters are now all included in the figures and their discussion. With this we hope to have built easy to follow basics in order to discuss their future behaviour in Section 4.

Additionally we have stressed now the exact meaning of individual parameters such as the empirical temperature dependency of terpene emissions after Guenther et al., which describes the release of preformed and stored molecules in the ecosystem.

The argument of language improvement was considered carefully.

For the revised version, we seek to have improved these serious remarks in order to allow both, i.e. the detailed understanding of our present study and the acceptance for final publication in Atmos. Chem. Phys. In the following we tackle the individual points of both referees individually and explain the changes applied to the revised manuscript. Therefore we discuss the comments of the anonymous reviewer no. 1 first and the remarks of reviewer no. 2 afterwards.

Response to reviewer no.1:

General - The reviewer highlighted that nucleation by organics is under heavily investigation and discussion but that the present study is highly speculative. Both is correct, although the word "highly" could be omitted in here meanwhile. But any other study regarding the atmospheric nucleation process are as well, since we are unable to exactly know and describe all different trace gas molecules and their atmospheric interaction during the nucleation process. We clearly lack of direct chemical analysis of the initial clusters for at least the next decade and each scientist aims to explain

the observations by reasonable theories from the present knowledge of the molecular processes. Nevertheless, we did this very carefully and always intercompared with the real atmosphere. Because of the complex nature of the atmosphere and the inhomogeneous distribution of the relevant trace gases the usage of mast measurements and box model approaches reveal strengths but also weaknesses. After comparison between the individual nucleation parameters to be explained much more in detail this time and aerosol datasets we are rather convinced that a comment on the future behaviour of atmospheric nucleation can be made, not of the exact nucleation number in 50 years but of its order of magnitude. However, in order to make a future prediction and to estimate the effect of a rise or a drop in number this approach is needed and reasonable, although there is certainly agreement to the fact that this is no final proof of any hypothesis and that future work is definitely needed.

Major concerns- We used the term "terpenes" in this study to include both possibilities, i.e. mono- and sesquiterpenes. Although sesquiterpenes are by far more likely to act as nucleation precursors than monoterpenes, we cannot exclude a potential monoterpenoid, not yet included in the detailed investigations. In order to make this approach applicable to a broader possible range we name both but use the most likely precursor, the sesquiterpene caryophyllene for detailed intercomparison. The variation of importance for different terpenes with respect to nucleation is due to the individual terpene structure and reactivity as well as the fact that each terpene as each alkene has three potential routes, once it reacts with ozone: (a) the ester channel (usually of minor importance), (b) the hydroperoxide channel (OH production) and (c) the stabilization. From laboratory studies (Bonn et al., 2002; Bonn and Moortgat, 2003) it is obvious that the stabilization is the path of relevance. The formation of the so called stabilized Criegee intermediate (sCI) is therefore the relevant nucleation precursor that is predominantly destroyed by reacting with ambient water vapour, but reacts with a multitude of other compounds as well. Its lifetime can be shortened and nucleation reduced until being suppressed if one adds water vapour or an organic acid (Bonn et al., 2002). Thus the most efficient terpene precursor at the current state of

knowledge is a terpenoid almost exclusively with ozone with a high reaction velocity that has a predominant stabilization pathway, which is being named "stab. frac" in the manuscript.

Regarding the **effect of water vapour on the described nucleation** described and if this effect is strong enough, the following has to be said. There is a clear difference between July and August in water vapour and in the opposite way for the occurrence of nucleation events. However, there might be a) an additional effect of acids, formed at highest radiation intensity during summer and b) of modified terpene emission. From the dataset of Hakola et al. (2006) and Tarvainen et al. (2005) it is obvious that on average the pool effect of the Guenther empirical algorithm can be described with a β coefficient of 0.17 K^{-1}. However, this is an average of a scatter plot. Comparing the emissions to water flows in trees (sap flow) the sesquiterpene flow fits quite linearly with the water vapour flux according to its water solubility (Henry's law) until the storage pools reduce. In autumn these pools seem to recover. The reason for this remains unclear. Therefore, the reduction effect in nucleation event numbers during July might partly be caused by that.

OH (or UV B): Why do we need UV B radiation as a proxy for nucleation? Is ozone not doing the job sufficiently well? Clearly we need both. The ozonolysis of terpenes serves as a source for reactive nucleation cores but no compound is able to condense or partition because of the lack of gaseous non-volatile compounds concentration and organic material in the aerosol phase. The correlation of particle formation rates with sulphuric acid indicates that there is a need for OH-derived compounds such as probably reactive compounds that activate the nuclei. That's why we need both. If one is missing the process is either rather slow or doesn't work at all. Nevertheless, if we really require sulphuric acid to be present or a different compound reacting with OH and having a sufficiently short lifetime remains elusive. That is why we focus on OH and therefore UV B.

Sesquiterpene emission formulation: This point is well made. We know remarkably less about sesquiterpene emission than about monoterpene emission. The pool

(temperature) and the light effect are both discussed among scientists. However, light dependency seems to have only a small impact. Because of these uncertainties, we formulated the terpene emission rather broadly with variation between mono- and sesquiterpene pool effects, which seem to dominate the behaviour and are currently used very similar in the global model MEGAN (Guenther et al., 2006). By doing so, we hope to approximate the maximum uncertainty range by upper and lower limits.

And again the emission and the nucleation effect: Please note that both aspects need to be combined with the suppressive effect of water vapour and acids. In this case two maxima appear, i.e. during spring and autumn in Finland.

Particle formation at Taunus Observatory: We definitely do not follow the cluster or very early particle formation rate but the one at 10 nm. Because of the fact that no 10 nm particle is of primary origin, each ultrafine particle had to grow to 10 nm in mobility derived diameter from the molecular size on earlier. Thus, if we compare a nucleation parameter with the formation rate at 10 nm there has to be a temporal shift between both that is dependent on the speed of particle growth. Now let's focus on the two different organic parameters org. NP A and org. NP B. NP A describes the efficiency of a terpene molecule to be used as a stabilized Criegee intermediate for new particle formation. If the ratio sCI to terpene concentration is small, it is difficult to activate the sCI to a nucleus. If this ratio is large it is much easier. However, this is a ratio only, which is independent of the actual terpene concentration. Thus even if one calculates a ratio of 0.001, i.e. the sCI concentration is one per mill of the terpene one, it becomes rather useless, if there is a terpene concentration of 1 molecule per cm3. The org. NP B therefore takes into account the pool effect of the Guenther expression, since terpene emissions predominantly stem from pools in the trees rather than from online production that is too slow. It does not take into account vertical and horizontal mixing since this is rather complex in this kind of terrain. Because of this one expects parameter org. NP B to be a measure for direct formation of nuclei. On the contrary org. NP A is a longer term production parameter since the nuclei are not destroyed or activated instantaneously. This is why there are shifts between different

parameters and particle number concentrations close to 10 nm in mobility derived particle diameter.

Capture of only one maximum in Hyytiälä: This is true, but the secondary maximum gets tentatively captured by the parameter NP A. There is a clear lack of understanding of the OH-derived compound, which might help solving this issue. Nevertheless the most important one is found and the annual behaviour regained. One point to be made is that during 2004 one finds this bimodal behaviour, while for other years a similar picture as shown in the study is obtained.

Therefore, although speculative this method is valid at the current stage, not for addressing the exact increase in number but to identify sources and to estimate the general future behaviour. Future measurements are certainly needed, but this stage provides another step of understanding and its publication serves as a support to the overall identification process of atmospheric nucleation in boreal forest regions.

Detailed points - p. 675, l. 27: The word "reading" is definitely wrong. It should be "regarding" and will be corrected in the revised version. Thanks.

p. 676, eq. 3: "stab. frac." explanation. This is explained in detail as other issues in the revised version.

p. 677, eq. 7: Physical dimensions of these NPs: Since organic NP A and B are ratios they are dimensionless. NP A multiplies this dimensionless number by UV B leading to a unit of W m-2. NP B is similar.

p. 678, l.2: Hard to figure out on this page. Probably the reviewer means the following page. We have inserted the year 2008.

p. 679, l. 14ff: The revised version will take care especially of careful explanations of the nucleation parameters and the reasoning within the discussion as explained in the "General response" above.

p. 679, l. 22f: There is no mentioning of monoterpenes. We use the beta coefficient of the empirical Guenther description of the pool effect on emissions of monoterpenes as a lower limit for the emissions since sesquiterpenes show a much steeper increase

with temperature. The change in NP B compared to NP A with temperature is efficiently caused by the pool derived effect.

p. 680, l.11: Correct. This is changed now.

p. 683, l. 24: Correct. This needs to be "trustworthy" predictions.

Response to reviewer no.2:

General- As the first one the second reviewer points out the need for a better description of the new parameters used and an intensified discussion about the results obtained. Both comments are justified and have been taken care of in the revised version in detail. Also the advice to seek support from a native English speaker was considered in order to minimize misunderstandings and to allow a better following of the points discussed. A detailed description of the individual changes made will be placed below the comments on the reviewer remarks.

Specific comments- Section 2: **Origin of nucleation parameter *NP B* and the need for terpenes**. As it was shortly explained above because of the remarks of the other reviewer, there is a need for terpenes. The nucleation parameter *NP A* describes the efficiency or availability of stabilized Criegee intermediates (sCIs) per molecule of terpene present in the air. The lower the ratio of sCIs to terpenes the harder it becomes to activate an sCI and to form a new cluster. Therefore, it represents a nucleation probability per terpene molecule present. It does not necessarily include terpenes only the availability, if a terpene molecule is present. Consequently, terpenes are needed and included by the pool dependent emission factor according to the empirical Guenther algorithm. This is explained in detail and units and is provided in the revised version. As indicated already for the first reviewer section 2 is now extended to twice its former size and explains the origin and the meaning of the individual nucleation parameters used in the study.

p. 677-678: **UV B approximation by 1% of global radiation.** Excellent point made. We included a new additional Figure 3 a plot for Hyytiälä in Southern Finland, where both can be intercompared. Regarding the discussion of uncertain emission factors, stability fractions and reactivity of the most important terpenes clearly more emphasis will be put in explaining the applied ranges, most likely values and the resulting uncertainties.

p. 677, l. 18: **Terpenes present in sufficient amounts.** This expression on p. 677 refers to different limiting situations. For instance if terpene-ozone reactions are needed in combination with an OH-derived compound, terpenes can be present in sufficient amounts if OH is pretty low and therefore nucleation is rather suppressed. Otherwise the more terpenes are present and converted by ozone the higher the nucleation rate.

Section 3.1: **Misunderstandings.** The text has been reformulated and some aspects were inserted to make understanding much straighter forward. "Secondary sources" means gaseous precursors such as reactive hydrocarbons that produce secondary aerosol material in contrast to the primary aerosol sources such as combustion. As the reviewer pointed out correctly, this expression referred to the biogenic emissions. Anthropogenic hydrocarbon concentrations are increasing, when the wind is coming from the direction of Frankfurt, for which nucleation is found to be minimal. The wind direction is certainly important predominantly via pollution coming from the Southeast and much cleaner conditions with respect to the Northwest, where nucleation is observed more often and more intense.

Lines 13-17: Sure. Thanks for the good suggestions. The revised version will take much more care of this.

The nucleation parameter *NP B* is now shown as well and as mentioned above discussed much more to explain the individual contribution of several aspects to the nucleation process. In general more emphasis is been put to include all formulated parameters within the discussion.

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L. 19-22: In a general way *NP A* does express the contribution by terpenes to the nucleation process because of the need for ozone and the suppressing effect of water vapour, although the terpenes concentration is not directly included. As stated above *NP A* describes the availability of sCIs per terpene molecule or efficiency of terpene molecules in the atmosphere to produce nucleation precursor molecules.

L. 22: It should be "nucleation parameters", since we refer to their difference in magnitude. The magnitude of emission and the temperature dependency is the crucial point here. Therefore we include the minimum emission factor (monoterpenes with β = 0.09 K^{-1}) and the two maximum emission factors from Hakola et al. (2006) (sesquiterpenes with β = 0.175 and 0.201 K^{-1}) as most likely range.

L. 23-26: The nucleation parameter *NP A* will be shown for Hyytiälä as well because it was referred to both sites, i.e. the Taunus site and Hyytiälä.

Humidity data: The effect of humidity or in detail water vapour on the nucleation process is known and published by Boy and Kulmala (2002), Hyvönen et al. (2005) and Lyubovtseva et al. (2006). A reference to the seasonal dependency is been included now in the supporting online information.

Section 3.2, l. 7-19: **Mismatch of nucleation parameters with observations - explanations and Guenther algorithm.** OK, the discussion will be made in much more detail so that no misunderstanding should occur again. It is certainly true that the empirical Guenther algorithm has been developed at warmer temperatures and therefore fits much better under these conditions. However, regarding sesquiterpene emissions it seems it's the only one available so far. But I agree that different emission factors regarding temperature might be very useful. This will be done.

L. 9-10: **Mismatch in August and July.** Correct. The effect of trace gases and formaldehyde was not included since the basic concept behind this study was to propose an easy to handle nucleation parameter. Ozone, temperature and water vapour are common parameters recorded. However trace gases such as organic acids are not. A complete nucleation mechanism description would probably do a better job, but this is only possible for selected days with all the individual datasets available.

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Section 3: Revised Fig. 3 and more emphasis on the organic NP B. We will correct this and define the "scaled" in detail. "Scaled" in this context expresses the need for additional factors because a value of *organic NP B* = 1 does not necessarily mean that the formation rate is unity.

Figures: Thicker lines will be made. The caption got lost at Copernicus and was mentioned in the first check, but wasn't corrected in the (old) online version. I beg your pardon for that mistake.

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