

## *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 #1

Received and published: 5 February 2015

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 different 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 in-

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teresting 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  $\Delta$ Qinflow, 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.

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 $\rightarrow$ i\*OxVOC+n\*NucOX (R2)

 $BVOC+(X) \rightarrow dilution + losses (R3)$ 

NucOX+H2SO4→nanoCN (R4)

NucOX+(X) $\rightarrow$ 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. However, the mechanism fails to take into account the unreacted BVOC, which can lead to a change in the mechanism:

Qinflow→BVOC (R1)

 $BVOC+OX \rightarrow i^*OxVOC+n^*NucOX$  (R2)

 $BVOC+(X) \rightarrow dilution + losses (R3)$ 

BVOC→BVOCunreacted (R3.1)

NucOX+H2SO4→nanoCN (R4)

NucOX+(X) $\rightarrow$ 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.

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.

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.

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

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

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?

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2. UV lamp wavelength should be mentioned.

3. 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.

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 nanoparticle 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.

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?

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

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

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.

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

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.

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

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

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 31319, 2014.

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