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Atmospheric Chemistry and Physics Discussions

# *Interactive comment on* "New particle formation from the oxidation of direct emissions of pine seedlings" *by* L. Q. Hao et al.

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The authors thank for the reviewer for his/her constructive and helpful comments:

p. 8227, line 9f: Why do you need to simulate beetle attack? To which extent does this effect the patterns and the strength of VOC emission compared to outside pines. Do you have indication of emission of larger oxygenated VOC, sesquiterpenes or other large VOC? How large is the fraction of non-identified compounds?

Answer: Purpose to simulate beetle attack is to increase the total emissions of pine. According to our unpublished results beetle feeding on bark increased bark emission of monoterpenes by nearly 4-fold and sesquiterpenes by 7-fold. The total emission of MTs and SQTs from intact needles was respectively 2.8-fold and 2.9-fold higher in the

pine weevil beetles damaged plants than the undamaged plants. With Norway spruce the feeding damage on bark by pine weevils has more pronounced effects on monoterpene and sesquiterpene emissions (see Blande, J.D., Turunen, K. & Holopainen, J.K. 2009. Pine weevil feeding on Norway spruce bark has a stronger impact on needle VOC emissions than enhanced UV-B radiation. Environmental Pollution 157: 174-180). These observations suggest that beetle damage on bark make pine seedling to emit substantially more mono- and sesquiterpenes than undamaged seedlings. In the emitted pine VOCs, there was oxygenated compound of methanol with concentration less than 5ppb according to the PTR-MS measurements. The sesquiteterpenes concentrations in all the experiments were smaller than 0.05ppb. From the estimation of GC-MS and PTR-MS measurements, non-identified compounds accounts for ~10% of the total emitted VOCs.

p. 8228, line 14f: The experimental procedure became not quite clear to me. What do you mean by " Ozone and TME were kept separated until inside the chamber because of the short lifetime of OH radical. " ? It would be helpful if add the starting times for second O3 addition in Table 2.

Answer: We will revise this sentence to 'In the experiments with using TME, TME was injected into the chamber prior to the ozone addition.' We will also expand this section to give a more detailed presentation. We will add the starting time for the second ozone addition in Table 2.

Section 2.5: The authors should extent this section. It does not become clear to me how the model calculations were performed. How does the model look like, which reactions were included. The reactions should be listed in a table together with the used rate coefficients. How did you solve the reaction system?

Answer: The model is to compare the modeled result with the particle measurements so that particle formation/growth can be discussed in terms of gas-phase chemistry. This model includes three types of VOCs including TME, isoprene and monoterpenes and two oxidants-ozone and OH. Since products from OH and O3 oxidation with TME are too volatile to partition into the aerosol phase, contributions to the new particle formation are mainly from the reaction of OH/O3 with isoprene and monoterepens. However, for the experiment with using of TME, ozonolysis of TME can generate OH radical. Meanwhile, the produced OH will be consumed partly by TME as shown in Eq. (4) and (7). So usage of TME can adjust the ratio of OH to O3. All the reactions included in this model are tabulated in Table 1 column 1and Eqs.(2)-(16) with the used rate coefficients in column 2 in Table 1. Since the model concentrates on the gas-phase chemistry, we handled only the first-step reactions of OH/O3with VOCs. For contribution of the subsequent reactions after first step to the particle formation, different correction factors are applied. No gas-particle partitioning theory is included in the model.

More detailed information should be given how the gamma's in Eq. 6 and 8 were determined.

Answer: In Eq. 6, Gamma includes ozone consumptions from all the monoterpenes, isoprene and TME listed in Table 1. Similarly, for Eq. (8), VOC includes all the monoterpenes and isoprene. For Eq. (9-10), since ozonolysis or OH oxidation of TME will not contribute to the new particle formation, so they are excluded from the equation as we have stated in the MS that 'O3 and OH oxidation rates (excluding the contributions from TME) with VOCs are defined as. . ....'. So here VOCs include isoprene and all the monoterpenes. Detailed equations will be presented in the reviesed MS.

In the legend of Fig. 5 the derivation of nucleation and condensation rates from the size distribution measurements is mentioned. The procedures should be described somewhere in the experimental section 2.

Answer: Thanks for the comments. We will add one paragraph to describe how the nucleation and condensation rates are derived as below: New particles in the sub-25 nm size range are considered to be caused by formation of new particles from

precursor vapors (Dal Maso et al, 2005). So in this paper, nucleation rate (FR) was derived from the number concentration of aerosols with size less than 20 nm as function of time. The geometric mean diameters (GMD) from the direct FMPS measurements were adopted to estimate the condensational growth rates (GR) of new particle.

p. 8235, line 8f and Fig. 2: The curves could be better understood if you would indicate the time of the second ozone addition.

Answer: Will be added.

Section 3.2.2 and Fig 3. Fig 3 is of insufficient quality. The y-axis of the panels C,D should be doubled in length. The different y-axis' should be better separated. Please add the model OH concentrations to the panels D.

Answer: Quality of Fig. 3 will be improved. Modeled OH concentrations will also be added to panel D.

p. 8237, line10 ff : I don't understand this argument. Growth rate in E1a and E1c are as high as E3 with low O3 rates and high OH rates !? Please clarify and expand your explanations.

Answer: Growth rate in E1a (126 nm h-1) is 1.7-fold higher than that in E3 even if its O3 reaction rate (25.5×106 molecules cm-3s-1) is two-times lower than that in E3. Similarly, 5.5×106 molecules cm-3s-1 of O3 rate was observed in E1c, which is 9-fold lower than in E3. However, a growth rate of 25.0 nm h-1 in E1c was found, which is only 3-times lower than in E3. These results indicate that OH and O3 both play roles in involving the particle condensational growth process. In E3, OH rate is at least 25-times lower (0.72×106 molecules cm-3s-1) compared to other four cases (>18.3×106 molecules cm-3s-1). However, a high growth rate of 73.8 nm h-1 was achieved, suggesting that the ozonolysis of VOCs is more efficient for aerosol growth.

p. 8238, line 8: Mentel et al. claim no nucleation with O3 at their VOC levels. Which role plays the initial VOC concentration in your study compared to Bonn and Moortgat

2002, Burkholder et al. 2007, and Mentel et al. 2009?

Answer: In Mental et al (2009) experiments, the initial concentrations of pine emitted VOCs were 20.0, 37.5, 43.1, 43.4 and 95.1ppb. Based on their result, single particle formation threshold for pine is 9 ppb. In Bonn and Moortgat (2002) and Burkholder et al (2007), studies were focused on the roles of OH and O3 chemistry with $\alpha$-pinene and $\beta$-pinene on the new particle formation. In our cases, the initial VOC concentration levels were close to Mentel et al's. VOC oxidation products are believed to be essential to the new particle formation (Laaksonen et al, 2008). But ozonolysis alone of VOCs (removing the OH radial) does not yield significant particle formation. This highlights the importance of OH radical initiated monoterpene oxidation in the new particle formation.

p. 8239, line 13: As far as I understood m/z44 is related to carboxyl compounds (acids). These are formed in the ozonolysis reactions. What could be the reason /mechanism for m/z 44 from OH reactions ?

Answer: m/z 44 signal has also been observed in the mass spectra of SOA from OH-initiated oxidation of $\alpha$-pinene (contributing to $\sim$6-8% to the total organic signals) (Alfarra et al, 2006). OH reactions with biogenic species can generate aldehyde compounds (-CHO), which can be further oxidized to carboxylic acid (Atkinson and Arey, 2003; Jaoui and Kamens, 2003; Wisthaler et al, 2001).

p. 8239, line 26ff: Can you give a quantitative statement, how well the pattern of your average mass spectra correlate with those observed in the field observation of the same masses seems to be a little bit weak statement, especially considering the strong tendency to fragmentation of the AMS.

Answer: In the revised manuscript, Fig. 7 will show the comparison of the fragmentation patterns of aerosol products in the chamber simulations in this work with those in the field campaign. The mass spectra in this work are averaged in the first hour in E2 and ambient measurement is from two-hour averaged mass spectra during one nucleation event from 9:30AM to 11:30AM on June 1st, 2007, in Hyytiälä forest in Finland.

Good correlation (R2= 0.89) of our measurements with the ambient mass spectra indicate that the experimental results are able to reproduce the products distributions of SOA formed in the real atmosphere.

p. 8240, line 17: AMS can measure in the size range of Aitken mode ? How did you determine the density ?

Answer: FLUENT model results show that AMS allows 100 percent transmission efficiency for particles between 60 and 600 nm in diameter and partial transmission down to 20 nm and up to 2000 nm (Jayne et al, 2000). In the range of 70$\sim$100 nm of Aitken mode, AMS can provide nice volume size distributions of aerosols. The density was calculated in the same way as described in section 2.4 and 3.4.

Minor: p. 8238, line 8: There is a "in" missing.

Answer: Will be fixed.

I would suggest to give the OH concentrations in Table 1 in terms of molecules/ cm-3 not as mixing ratios

Answer: accepted.

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 8223, 2009.