

# ***Interactive comment on “Secondary organic aerosol production from pinanediol, a semi-volatile surrogate for first-generation oxidation products of monoterpenes” by Penglin Ye et al.***

**Penglin Ye et al.**

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Reviewer 2:

General comments:

1. What 8 m<sup>3</sup> chamber has a surface area of 12 m<sup>2</sup> (line 105)? This is off by a factor of probably about 2. The smallest surface area to volume ratio is that of a sphere, and a sphere with a volume of 8 m<sup>3</sup> would have a surface area of 19.3 m<sup>2</sup>. Likely, any chamber with this volume would have an even larger surface area (and certainly much

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larger than 12 m<sup>2</sup>). Related to this, what is the source of the estimate of 10 g in line 107?

ANSWERS: 12 m<sup>2</sup> is a typo. It should be 24. The chamber is a cubic shape. We used 0.8 g/cm<sup>3</sup> as the density of the Teflon to calculate the 1 μm thick Teflon layer mass and got 10 g.

2. How are the data points in Fig. 1 obtained, since in Fig. 2 there is a slightly decreasing trend when the concentrations reach “quasi-steady-state”?

ANSWERS: We averaged the concentrations from the time when the gas concentration got stable to right before the next injection.

3. How do you perform the stepwise injection of the compounds in Fig. 2, i.e. at each injection step does the volume of the chamber change because of constant sampling? Also, you mention the longer evaporation time of the less volatile compound: can you give an estimated timescale?

ANSWERS: We put the mixture the compounds in a flash vaporizer consisting of a stainless steel tip with a machined trough for compounds containing a resistive heating element, all inserted well into the chamber at the end of a stainless steel tube through which we passed purified, heated air. We used the purified air flow to transfer the vapors into the chamber while heating the mixture. The total sampling rate from the chamber was around 5L/min. We used 15L/min air flow to inject the organic mixture for 15 mins. It was around 40 mins between each injection. So the injection and sampling flow were almost balanced. The change of the chamber volume is very small. In this study, the evaporation time of pinanediol was around 10 minutes. We used a low heating output to avoid the thermal decomposition of pinanediol.

4. In the heating experiment (Fig. 3), how much PD do you inject into the chamber at 130°C in order to get 866 μg m<sup>-3</sup>? Have you tried to increase temperature to just 220°C to see if you can get a similar portion of bulk concentration of PD with the ones in Fig.

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2? In other words, how can you verify the possibility of pure condensation of PD on the wall or other lines at such a lower temperature? Otherwise, one would think the vapor-wall interaction mechanism is different in heating and dilution experiments.

ANSWERS: We put 20mg pinanediol in the chamber. We tried a series of different amounts of pinanediol.  $866 \mu\text{g}/\text{m}^3$  was in the middle of the gas phase concentrations we measured. We regarded pure condensation of PD as unlikely since the PD was not saturated in the gas phase. However, it is not obvious at all that this would produce a different result. For "pure condensation" the gas-phase (and condensed-phase) activities would be 1 – the system would be saturated. Consequently, there would be a condensed-phase reservoir with an equilibrium vapor pressure of the PD saturation vapor pressure in the chamber or the lines; this in turn would lead to a significant return flux when the system was dis-equilibrated by dilution. The only substantial difference would be that we would not have been able to add more PD to the gas phase, because it would have been saturated. That is directly contradicted by the data in Figures 1 and 2.

5. In the dilution experiment, you show that PD-wall partition is irreversible above 22% of the initial value, which may be true if the oxidation rate of PD is similar to the dilution rate. So how do you simulate the photo-oxidation of PD? What are the actual values of jHONO and OH level in the chamber? What is the oxidation mechanism used in the simulation: parallel or in series?

ANSWERS: The simulation here was purely experimental. The removal of PD by dilution directly simulates removal of PD by oxidation; there should be no difference to the wall-vapor equilibration because the remaining PD molecules will not "know" how their missing comrades came to vanish - whether down a drain or via oxidation. From the dilution experiment, we found the PD started to release from the chamber wall only after the PD concentration reached  $2 \mu\text{g}/\text{m}^3$ . We limited our analysis to the first 1.5 e-folding lifetimes in PD oxidation (we only use the data where the PD concentration is above  $8 \mu\text{g}/\text{m}^3$ , 22% of its initial value). For the 2D-VBS simulations we used the con-

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strained (measured) PD removal rate to drive formation of VBS products, again without direct numerical simulation of the gas-phase chemistry.

We injected PD and HONO into the chamber and turned on the UV lights to initiate the oxidation of PD with OH radicals. The OH concentration in these experiments was around  $2.4 \times 10^7$  molecules/cm<sup>3</sup> for the first hour, then dropped to around  $5 \times 10^6$  molecules/cm<sup>3</sup> afterwards.

6. If the conclusion in lines 318-320 is correct, why does Fig. 1 not have a y-intercept of 0? Also, how are you accounting for the additional loss you saw in the experiment for Fig. 4?

ANSWERS: The y-intercept is a little bit away from 0 may be due to the large uncertainty of the measurement when PD concentration was low. The decrease of PD was very slow, the loss rate is around 0.05/h. This gave a very small uncertainty when calculating the mass yield. Consequently, we just used the PTR measurement to do the calculations.

7. Around line 372, you are assuming that the condensation sink does not change as more vapor deposits throughout the experiment. How do you justify this assumption, particularly for the boundary layer? The mass transport through the boundary later is changing throughout the experiment, so the condensation sink of deposited particles also changes.

ANSWERS: We do not assume that the suspended condensation sink is a constant – we measure the suspended particle surface area, correct it for near-surface diffusion (i.e. Fuchs and Sutugen) and calculate the collision frequency of vapors with that suspended surface area. When  $\alpha=1$  this is the condensation sink, when  $\alpha < 1$  it the condensation sink is slightly larger than  $\alpha \times$  collision frequency (in the transition regime). For the chamber walls, we assume that the condensation sink to the walls is completely limited by diffusion to the chamber walls and that uptake of vapors is quasi-irreversible. McMurry and Grosjean showed decades ago that this

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will be true so long as the accommodation coefficient of vapors to the walls is larger than roughly  $1e-4$ , and in vapor wall loss experiments we have found no evidence that accommodation is delayed; consequently, vapor transfer to the chamber walls is rate limited by gas-phase diffusion in the quasi laminar boundary layer. Members of our team described this in Trump et al, Aerosol Science and Technology, 2016).

8. Can you clarify the necessity of the correction for delayed condensation? In the caption of Fig. 8, you attribute the delayed condensation to the diffusion time of vapor molecules to the surface of the particles or the wall. Do you mean the gas-phase production rate is too fast compared with the timescale to reach gas-particle-wall equilibrium, so that the instantaneous equilibrium assumption cannot be used at the initial stage?

ANSWERS: The delayed condensation will mostly affect the observed SOA mass in the early stage of the experiments, likely the first 20 mins. During this period, the equilibrium may not be obtained instantaneously.

9. Since you are comparing your experiment to a nucleation experiment in CLOUD (lines 513-520), you should justify your assumption that you used enough seed to suppress nucleation when discussing particle number concentration (line 351).

ANSWERS: This is not an assumption - we measured the suspended number concentration and no new particles appeared. We focused on the chemical compositions observed in this study to the CLOUD experiments. Because we did not observe nucleation in these experiments, the seed particles evidently provided enough surface to prevent the nucleating ELVOCs from building a supersaturation sufficient for nucleation. Members of our team modeled this for the alpha-pinene SOA case, comparing SOA production with CLOUD nucleation, in Chuang et al, ACP, 2017. However, for PD in CLOUD, the nucleation involves sulfuric acid vapor and so we cannot directly compare the nucleation results (we do not know when nucleation "should" or "should not" have occurred in our experiments given the product formation rate, suspended condensation

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sink, and consequent steady-state supersaturations of nucleating species).

10. How do you distinguish “overall SOA yield” and “instantaneous SOA yield”? It looks like Fig. 9 and Fig. 10 are plots of temporal profile of overall SOA yield.

ANSWERS: The “overall SOA yield” in the manuscript means all SOA yields we observed at different PD initial concentrations. We removed the term “overall” in the revised manuscript. The “instantaneous SOA yield” is the overall SOA yield.

Specific comments:

Line 93: Remove the symbol “ $\mu\text{g}$ ” in the citation. Lines 91-94 repeat what is more succinctly said in line 89. Line 163: I believe the unit is  $\text{m}^3$  not  $\text{m}^{-3}$ . ANSWERS: We changed those in the manuscript. Line 178: What type of neutralizer did you use?

ANSWERS: It is Po-210

Lines 199, 265, 269, 271, 306: There should not be a space before  $^{\circ}\text{C}$ . Lines 213 and 220: The period should go after “Fig” not after the number, as is done in the rest of the paper.

ANSWERS: We changed those in the manuscript.

Line 218: Why does it look like the y-intercepts for oxy pinocamphone and PD are not 0?

ANSWERS: The y-intercept is a little bit away from 0 may be due to the large uncertainty of the measurement when PD concentration was low.

Line 228/Fig. 2: The overshoot time for 2-Nonanone appears to be a lot closer to 10 minutes than to 1 min, especially for the data a little after 2 hours.

ANSWERS: We only counted the first peak as the overshoot time in the original manuscript. We changed it to “5 to 10 mins”

Lines 265 and 278-280: These sentences repeat each other but, in line 265, you say

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“factor of 10 to 30” and in lines 279-280 you just say “30-fold increase.” What happened to the range in the second sentence?

ANSWERS: It should be “factor of 30” in line 265. We changed the wording in the revised manuscript.

Line 283: The PD should be “absorbed into” or “absorbed by” the Teflon walls, not “absorbed in” them.

ANSWERS: We changed it to “absorbed into”

Line 307: Does the ratio decrease before dilution when the concentration is held constant? Otherwise, diffusion into the bulk Teflon does not make sense.

ANSWERS: The ratio also decreased at a similar rate before dilution.

Line 308: This is the wrong Zhang 2015 reference.

ANSWERS: We put in the right reference.

Line 310: There should be a space after “5.5” before “h,” as is done in the rest of the paper.

ANSWERS: We changed those in the manuscript.

Line 317: Did you try slowing the rate of dilution even more to see if there was an effect?

ANSWERS: We didn’t try a slower dilution rate.

Line 339: “as same as” should be “the same as” or something of that sort. Line 352: The font is bold.

ANSWERS: We changed those in the manuscript.

Line 352: How do you verify ignoring other dependencies? E.g. the dependence of the wall loss rate on the diameter of the particle.

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ANSWERS: The wall loss of particles also depends on the particle size. We added “without considering the size dependence particle wall loss and other effects”

Lines 384 and 386: These lines have odd spaces/indentations. Line 437: Inconsistent spacing after the equals sign. Line 474: Be consistent between “oxy-pinocamphone” and “oxy pinocamphone.” Line 466-476: It is better to represent the chemical mechanism in a scheme. Line 517: OSC needs a line above it instead of an accent mark.

ANSWERS: We changed those in the manuscript.

Line 535: Where in the supplemental material is this provided?

ANSWERS: It should be “in the following section”.

Line 536: You should probably mention this is for  $\alpha=1$  and give the justification for choosing this value of  $\alpha$  that you give in the figure captions. Lines 561, 880, and 904: “Teflon,” “summary,” and “simulation” are misspelled. Lines S26-S28: It is unclear when you switch to an explanation of method 3.

ANSWERS: We changed those in the manuscript.

Figure 3: Why is there a bump/overshoot in the Pinanediol concentration around 0.1 hours?

ANSWERS: This is probably due to a combination of chamber mixing and the fact that the heating is delivered directly through the walls - it is not unreasonable to expect a surge of material off of the walls during the initial heating shock. However, this is total speculation.

Figures 4 and S1: Why not make these A and B parts of a figure, so that they can be more directly compared?

ANSWERS: This is a good suggestion - we have combined the figures in the revised manuscript.

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Figure 5: The SMPS used in this experiment cannot detect nano-particles, so the last sentence about nucleation may not stand.

ANSWERS: We observe growth rates of the accumulation mode (seed) particles and this constrains the growth rates of nucleated particles as well (they will in general be significantly larger). During the active SOA formation period of these experiments the SOA growth rates exceeded 100 nm/h, so any nucleated particles would have grown into our SMPS detection range in 6 min or less, with a very high survival probability. While it is possible that alien nano-spacecraft were zapping the nucleated particles out of the bag before they grew into our detection window, we regard this as sufficiently unlikely to exclude it from our analysis.

Figure 7: Use another color or background for the case  $\alpha = 0.1$ . Figure 7: The solid red versus thickly shaded red are very difficult to distinguish, even when viewed in color. Figure 8: Since you already use red in the figure, it may make more sense to replace the red dashed line with another color.

ANSWERS: We recolored Fig. 7 and 8.

Figure 11: This figure is missing a legend.

ANSWERS: We added a legend.

Figure 12: Missing colorbar for contour lines.

ANSWERS: The contour lines are not colored - they are in the figure for a qualitative representation of the 2D product distribution. The quantitative representation is the sum over O:C (the 1D representation) shown in the lower panel.

Figure 13: I suggest you change “Bulk suspended” to “Particle suspended” in the legend. Figures S2 and S3:  $C_n$  is never defined. Also, in S2, the labels on the blue arrows are sufficiently far away from these arrows to be somewhat confusing. ANSWERS: We changed those in the manuscript.

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