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Atmospheric Chemistry and Physics Discussions

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.

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Reviewer 1:

General:

1. PTRMS calibration The authors used PTRMS measurements to calculate the amount of pinanediol oxidized by OH radical in order to derive the mass yields of SOA produced. A recent study (Pagonis et al., AMT, 2017) has found that gas-wall partitioning of semi-volatile organics in Teflon tubing and inside the PTRMS could cause

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significant delays (up to two hours) in instrument response to step-function changes in the concentration of the semi-volatile compounds being measured. As shown in Fig. 2, the authors in this study may have observed similar PTRMS response to the step-wise increases in the injected pinanediol in the chamber. This observation points to a very important factor that might lead to a large uncertainty in the calculated SOA yields, i.e., PTRMS calibration. The authors are suggested to describe in details how exactly PTRMS sensitivity to pinanediol was determined. If pinanediol standard was used, how was the vapor concentration calculated, and how was the vapor wall loss in the instrument accounted for?

ANSWERS: We determined the PTRMS sensitivity to pinanediol by comparing the PTRMS signals with the pinanediol concentrations inside the chamber. We measured the pinanediol concentration using TD-GCMS. We collected samples by drawing chamber air through Tenax® TA filled glass tubes. We used pinanediol in methylene chloride solution with different pinanediol concentrations as the GCMS calibration standard.

Our sampling setup is different from the study Pagonis et al., AMT, 2017. We used a steel sampling tube and heated the line to 60oC. We wanted to minimize the loss of pinanediol to the sampling tube wall or inside the instrument. We found the PD signals dropped to near to zero immediately after we disconnected the sampling tube from the chamber.

2. Dilution experiments Although the authors state that rapid gas-wall equilibrium partitioning of pinanediol (10-15 min?) was achieved in the chamber, no evidence could be found throughout of the manuscript. On the other hand, based on what is shown in Figure 2, it seems like there is a slowly decreasing trend in the measured concentration following each pinanediol injection. How did the authors define exactly the time it takes to reach gas-wall equilibrium partitioning? The authors attribute the missing spike and the slow increase in the pinanediol signal upon a succession of standard injection to the slow equilibration of the PTRMS sampling line. This might also be the reason for the observed PD:AN ratio during the dilution experiment. How long does it take be-

tween the PD/AN injection and the onset of dilution? Is it possible that the PTRMS sampling line was far from equilibration with the pinanediol vapor in the sampling air during the entire dilution experiment (or at least the very first few hours)? If this is the case, then the sampling line could possibly act as a constant sink of the pinanediol vapor and the amount evaporated from the wall upon dilution of the chamber might be compensated by that deposited onto the sampling tubing. Have the authors thought about why the PD/AN ratio only started to increase after 5 hours of dilution (or the PD concentration dropped below 2% of the initial concentration?) This gas-wall partitioning behavior seems very inconsistent with the observation from the heating experiment.

ANSWERS: The 10-15 mins timescale was calculated for SVOCs in the chamber in our previous paper (Ye et al., 2016a), and also observed by Krechmer et al (Krechmer et al., 2016). In Fig. 2, the slow increase was caused by three factors, the injection time (15mins), the chamber mixing time (5-10mins), and the gas wall partitioning equilibration time (10-15mins). These three factors overlapped each other and could not be determined individually. However, we have very strong evidence from both direct observations of H2SO4 vapor loss as well as SVOC loss from coated particles, as reported in Ye et al., 2016a, that the intrinsic chamber-wall collisional timescale is 10-15 minutes for compounds with the molecular weights of interest here, including analogues to PD such as oleic acid. Even the differences in timescales (10 min for H2SO4, 15 min for heavier organics) are consistent with theoretical expectations. PD has a higher vapor pressure than most of the SVOCs employed in Ye et al., 2016a, though it is near the high end of the range employed there. It would be very surprising if the PD equilibration timescale were significantly longer and impossible for it to be shorter (the vapor-wall collisional timescale is a lower limit).

We waited around one hour between the PD and acetonitrile (AN) injection and the onset of dilution. If PTRMS sampling line was far from equilibration with the pinanediol vapor in the sampling air, we should observe a very low signal during the injection followed by a steady increase for the hour before we started the dilution. We only ob-

served the continuous decrease after dilution started. Given that both the PD and AN signals both dropped significantly during the dilution experiment (that was the point) and that we are very confident that the AN is a truly passive tracer in both the chamber and the PTRMS and its sampling line, it would take an extraordinary confluence of events for the ratio of the two signals to remain almost perfectly constant without that reflecting a true passive dilution in the chamber itself. It seems not likely that the PTRMS sampling line is far from the equilibration, and thus our conclusion is that the actual gas-phase concentration of PD in the chamber declined during dilution consistent with passive dilution and thus no return flux from PD absorbed or adsorbed to the chamber walls.

That being said, there is an obvious inconsistency in the complete set of observations; nothing can equilibrate without a balance of forward and reverse fluxes, and we have ample evidence of significant PD loss to the chamber walls that non-the-less resulted in a constant PD gas-phase signal proportional to the amount of injected PD. Those are the hallmark signatures of equilibration, as pointed out by Matsunaga and Ziemann. The heating experiments confirm that a large fraction of the PD did indeed partition to the walls. We are fully aware of the inconsistency here, and yet the scientific question of SOA formation from SVOCs in general and PD in specific is pressing. We are still trying to get a good explanation of the different gas-wall partitioning behavior between the dilution and heating experiments. One possible reason may be the evaporation energy of the pinanediol on the chamber wall. The evaporation rate became much higher after heating up the chamber. Then we observed the increase of the pinanediol concentration in the gas phase; however, this does not solve the evident inconsistency at room temperature. Consequently, we adopted the practical and empirical approach of using the dilution experiments as a controlled test to mimic PD loss via chemical reaction. In this way we are comfortable that we can constrain the total amount of PD oxidized during the experiment, which is absolutely essential for a mass yield determination, but in an abundance of caution we restricted our analysis to the period when at least 20% of the PD remained in the chamber (a factor of 10 more than the point where

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the dilution experiments showed signs of disequilibrium).

3. Vapor wall loss correction The authors used a single wall condensation sink (0.063 min-1) measured for SVOCs in the CMU chamber to account for wall losses of vapors across all the volatility range, including LVOCs. While the time for establishing gas-wall equilibrium might be similar (say 10-15 min) for different organic vapors, it has been shown, by many studies, that the amount of organic vapors that reside in the chamber wall phase upon equilibrium depends on the vapor pressure (e.g., Matsunaga and Ziemann, 2010; Zhang et al., 2014, Krechmer et al., 2016). Here by comparing the vapor condensation rate to the wall vs. particles to evaluate the underestimation of SOA yields due to vapor wall loss may bare large uncertainties, as the amount of organic vapors in the wall upon equilibrium partitioning as a dependence of vapor pressure is not accounted for.

ANSWERS: The organics in the SOA are mostly SVOCs, LVOCs and ELVOCs. These organics equivalent saturation concentration in the wall upon equilibrium are more than milligrams/m3, which is far higher away for the concentration we used in this study. We also used seed concentrations high enough so that the collision timescale to the suspended seeds was more than an order of magnitude higher than the collision timescale with the walls, as discussed in the paper. These two things combined mean that the very large majority of condensable vapors (LVOCs and SVOCs) that encountered the walls should remain there (the equilibrium fraction was < 0.001) but also that most of the SVOCs and all of the LVOCs should have remained on suspended particles for at least a significant portion of the experiment (the other way to think of this is that the steady-state excess saturation between the gas phase and the particles was relatively high during PD oxidation, so the net flux to the suspended particles was close to that of a truly non-volatile constituent. For these reasons we modeled the loss of the SOA vapors to both the chamber walls and the suspended particles as quasi-irreversible. This is definitely an approximation, but our objective is to set up experimental conditions where we are not reliant on uncertain model parameters (i.e. the exact volatility

and wall partitioning constants) of condensable species.

4. Accommodation coefficient The accommodation coefficient is widely used to represent the probability of a vapor molecule sticking onto an organic particle surface. However, the accommodation coefficient used in Equation 3 in this study is essentially an effective accommodation coefficient, as the particle-phase diffusion process needs to be accounted for. Many studies have found that under dry conditions, the phase state of a-pinene SOA is more like semi-solid, implying that the particle-phase diffusion might be the rate limiting step in the overall gas-particle partitioning process. Please comment on the range of accommodation coefficient (0.1-1) chosen here. ANSWERS: The ELVOCs are extremely low volatility and will stick on the surface when colliding with the particle unless the true mass accommodation coefficient is less than 1. Condensed phase diffusion limitations would cause a substantial activity gradient within the particle, but if the gas-phase activity (the saturation ratio) is » 1, no condensed-phase activity gradients can significantly influence the microphysics (since the condensed-phase activity is the mole or volume fraction depending on the thermodynamic formulation, for all but very small particles < 10 nm or so with significant curvature). Our conclusion here is that the condensable PD products include a large fraction of ELVOCs, which is also strongly indicated by the new-particle formation experiments at CLOUD.

We have looked and looked and looked for indications of substantial diffusion limitations for SVOC mass transfer between SOA particles, and thus far this has been a rare occurrence. From the literature (Saleh et al., 2013), members of our research team found the accommodation coefficients of alpha-pinene SOA to be $>\sim 0.2$. Other members of our team have explored interactions of suspended SOA populations using isotopically labeled precursors and single-particle measurements (Robinson et al, J Phys Chem, 2013; P. Ye et al., J Phys Chem 2014; Q. Ye et al PNAS 2016; Q Ye et al., Chem, 2018). In no case, for experiments spanning the full range of RH, have we found evidence for substantial delays to vapor exchange between particle populations involving SOA formed from alpha-pinene. While we have not directly studied PD prod-

ucts using this method, we regard the alpha-pinene experiments as a useful analogue. For this reason, we treated two limiting cases, alpha = 0.1 and 1.

Minor: 1. Line 211: Specify how long it takes between the chemical injection into the chamber and the measurement of their concentrations by PTRMS/GCMS. What is the chamber mixing timescale?

ANSWERS: The injection time was 15 mins. Tenex tube samples were collected at 15 mins after the injections were completed. PTRMS was sampling all the time. The chamber mixing time is 5-10 mins.

2. Line 252: Please show evidence for the 'rapid vapor-wall equilibrium' observed in the experiments.

ANSWERS: We observed the rapid change of the SVOC concentration change in the gas phase due to the saturation concentration change caused by the temperature vibration in our previous paper (Ye et al., 2016a)

3. Line 295: Again, specify the time duration between chemical injection and the onset of chamber dilution.

ANSWERS: It was around 1 hour

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