Reviewer #2

We thank the reviewer for his or her overall positive assessment of the paper, and for the helpful comments and suggestions. We address specific points below.

Page 7155. Lines 5-9. Smith et al. 2012 provided evidence of liquid-liquid phase separation, but I don't think they provided information on the morphology after phase separation. Papers that have considered morphologies after phase separation include the following: [Ciobanu et al., 2009; Kwamena et al., 2010; Reid et al., 2011; Song et al., 2012]. Other papers that may be relevant for this manuscript include the following: [Anttila et al., 2007; Prisle et al., 2010].

The appropriate references were added.

Page 7155. Line 18-20. "A DMA was used to size-select 150 nm particles." I assume this refers to particles with a single charge. Do particles with a double charge play a role in these experiments and contribute to uncertainty in the results? Please discuss.

If a significant number of doubly charged particles were selected, this would result in a bi-modal size distribution after aPO uptake begins, because of the difference in growth rates between the two particle sizes. We did not observe a bimodal distribution after growth, leading us to conclude that doubly charged particles are not significant in this system.

Page 7156, line 11-13. How do the concentrations of sulfuric acid and pH used in the bulk studies compare with the concentrations and pH in the aerosol studies?

The concentrations of the bulk solutions (10M, 3M, 1M, 0.1M) were picked to roughly match the pH values predicted by E-AIM for the particles in the chamber experiments (-1, -0.5, 0, 1). The text in section 2.3.1 was augmented to clarify this.

Page 7158, Section 3.2, line 8. The units are not written correctly.

These units were corrected.

Page 7158, Section 3.2. lines 7-10. On lines 7-10, the authors compared their measured effective partitioning coefficient with the effective partitioning coefficient reported in linuma et al. It would be useful to mention the growth factor in the experiments by linuma et al. since the current study shows that the effective partitioning coefficient depends strongly on this value. Without knowing the growth factor in the work by linuma et al. it is hard to compare the results directly.

The text was changed to clarify this:
"For that study this corresponded to a volume growth factor of ~1.1."

Page 7158, Section 3.2 line 13. The authors state "this is good agreement given measurement uncertainty and the observed increase in uptake coefficient with lower alpha- PO concentrations". Please add a reference to previous measurements of uptake co- efficients or refer to Section 2.5 for further information.

The text was altered to more clearly indicate that our measured value is similar to that from Iinuma et al. (2009) and should be lower because we used a higher aPO concentration:
"This is good agreement given measurement uncertainty and our observation that the partitioning coefficient decreases with increasing αPO concentration (Fig. 5)."

Page 7159, Section 3.3. The authors used Fick's law to estimate a diffusion coefficient. In addition, they assumed that the rate limiting step for the change in the thickness of the red layer over time is molecular diffusion. First it is not clear exactly what the au- thors used for distance, x, and time, t in their calculation. Second, for the liquid-liquid phase separation process I wonder if molecular diffusion is the rate limiting step for the change in thickness of the red layer over time. The authors should give some justification for the assumption of molecular diffusion controlling the change in the thickness of the red layer. Is it possible that the reaction studied by the authors lead to a colloidal dispersion of organic-rich particles immersed in an aqueous-rich phase? This would appear as a cloudy suspension. If this is the case, then could the rate limiting step for the change in thickness of the red layer be due to coagulation of these organic-rich particles and transport of these organic-rich particles (not the molecules) by buoyancy forces. Please discuss why coagulation and transport of the organic-rich particles by buoyancy forces is not important.

The distance "x" is the depth of the colored layer and the time "t" is the duration of exposure of the sulfuric acid surface to vapor aPO at room temperature. The mass-loading of aPO in the sulfuric acid solution is low enough that phase separation does not is not evident. This can be seen by comparing the photographs of the low mass-loading case (Fig. 3a) and the high mass-loading case (Fig. 3b). Comparing the relevant timescales in the system (uptake, reaction, and diffusion), our observation of a colored layer growing slowly from the interface suggests that diffusion of organics (reactants and colored products) through the liquid phase is the rate limiting step. Due to structural similarities, we expect the diffusivities of aPO and its reaction products to be similar. However, from the results of Bleier et al. (2013) the timescale for reaction of αPO in 10M sulfuric acid will be ~5 minutes, suggesting a short reacto-diffusive length of ~0.05 cm. Therefore we conclude that aPO will react near the interface, and analysis of the depth of the colored layer can give an estimate of the diffusivity of the colored products.

Based on this assumption, we calculate a low-concentration, room temperature value for aPO products in sulfuric acid solution of $9*10^{-6}$ *cm*^{2} *sec*$^{-1}$*. This is quite reasonable, e.g. the room temperature, low-concentration limit for the diffusivity of glucose in water is* $6.75*10^{-6}$ *cm*^{2} *sec*$^{-1}$*. The fact that we calculate a reasonable value for the diffusion* *constant supports that the growth of the colored layer is due to diffusion of organics in the liquid phase.*

Finally, the organic particles posited by the reviewer would have a lower density than water (~0.9 g/ml) and a much lower density than liquid sulfuric acid (1.84 g/ml). Therefore, rather than growth in the penetration depth of the colored layer into the solution, buoyancy forces would likely lead to collection of the particles at the top of the solution, leading to coagulation and ultimately the formation of a phase-separated layer.

Page 7160, Section 3.4. Here the authors are measuring the fraction of water lost, which is the change in water content from drying normalized to the predicted change in water content assuming only sulfuric acid and ammonium sulfate. The authors ob- served that the fraction of water lost is less than unity for a large amount of organic on the particles, and from the observations they conclude that the organic component of the particle inhibited evaporation. First, more information on the drying experiments are needed. For example, what was the residence time in the dryer and what were the starting and final RH values in the drying experiment? Also, how was drying achieved and were the particles dried below the efflorescence point of the particles? Second, I wonder if there is a possible thermodynamic explanation for the author's observations rather than a kinetic explanation. For example could a large fraction of the sulfate be converted into organosulfates, which would have different hygroscopic properties com- pared to sulfuric acid and ammonium sulfate? As another example, could some of the organic still mix with the sulfuric acid and ammonium sulfate even though there is phase separation? This would change hygroscopic properties, such as efflorescence relative humidities. These possible thermodynamic explanations need to be discussed and some justification for why they are not important needs to be given.

Most of these particles have will no efflorescence behavior (pure H_2SO_4*). Only those particles dominated by* $(NH_4)_2SO_4$ *are predicted by E-AIM to become solid at the drier RH (~5%), but the high organic content present may prevent clear efflorescence behavior. By suppressing the formation of solids in our E-AIM calculations, we will have a lower estimate on the fraction of water lost. The initial humidity is that of the chamber during aPO uptake, either ~25% or ~50(+/-5)%.*

The fractions of water lost were re-calculated using E-AIM predictions for our experimental particle compositions and humidities. The fraction of water Table 1 has been updated to reflect these new values for initial volume fraction of water and fraction water lost. While the overall variability in fraction of water lost has decreased from (0.24-0.76) to (0.27-0.51) this is still a significant variability yet to be explained.

The residence time in the drier was ~7 seconds. It may be the case that on longer timescales (~1 min to several minutes) all these particles may reach equilibrium. But given the relation between particle diameter (d_p*), diffusivity (D), and equilibration time (*τ_D*):*

$$\tau_D \; \alpha \; \frac{{d_p}^2}{D}$$

the variation in the **relative** *amounts of drying is greater than would be explained by the variation in particle diameter alone. As seen in Fig. 7, the variation in final particle diameter is 152-182nm, which would only give rise to ~30% variation in equilibration timescales. The diffusivity of the particles is indeed likely to decrease with increased organic material, regardless of particle morphology. Our measurements of diffusivity in the bulk correspond to a low-concentration limit, as the uptake of gas-phase aPO to the sulfuric acid surface is a very low mass loading. In other words we measure the diffusion of aPO reaction products in sulfuric acid:* $D_{Products\text{-}Acid}$*. That we observe high diffusivity in the low-concentration limit and that particle size alone does not explain the variability in approach to equilibirum suggests that at the very least the* **effective** *diffusivity may decrease significantly with higher particle fractions of aPO-SOA.*

Another possible cause for the variation in the fraction of water loss is a change in the water activity of the particles after organic deposition. Water activity can be calculated as (Bilde and Svenningsson, 2004)

$$a_w = \gamma_w \frac{n_w}{n_w + \sum_s i_s \times n_s}$$

where γ_w *is the activity coefficient for water,* n_w *is the moles of water,* i_s *is the van't Hoff factor for solute species "s", and* n_s *is the moles of solutes "s". The variation in water activity for our systems was calculated using this equation with the molalities of for the inorganic species (including water) from E-AIM output and assuming the aPO SOA organic material to have a density of* $1\ \text{g cm}^{-3}$ *and molecular weight of* $150\ \text{g mol}^{-1}$*. The Raoult's law (mole fraction) part of the water activity expression only explains about 7% of the variation in water evaporation, much less than the factor of 2 exhibited. Thus the variation in fraction of water lost would be held in the water activity coefficients.*

The trend in water loss due to drying will be partially due to differences in equilibration timescales and the mole fractions of water present. Empirically this could be represented as a change in the water activity coefficient for particles with different amounts of aPO SOA. Given that phase separation is observed in the bulk solutions with high mass-loadings and that the O:C of the aPO-SOA is likely less than 0.7, we posit that the large variation in activity coefficients may in fact reflect the presence of an organic coating.

The text in Section 3.4 was substantially modified to include discussion of the importance of drying timescales (kinetic) and water activity (thermodynamic) considerations.

Page 7160, Page 3.4, line 24-25. This sentence could be improved for clarity. Maybe change to "the observed trend in water loss highlights the importance of phase separation in predicting water uptake/loss"?

The text now reads:
"The observed trend in water loss highlights the potential importance of phase separation in predicting water uptake/loss."

Page 7161, Section 3.5. The authors use equation 4 to estimate an uptake coefficient from their experiments. The duration of condensation (delta t) used in the equation was taken from Iinuma et al. 2009. Inuma used a different sized chamber (19 mˆ3 vs 3.5 mˆ3) and likely different experimental conditions. Why use the duration of condensation from Inuma et al.? The authors should also discuss how the uncertainty in delta t translate to an uncertainty in the experimental uptake coefficient (i.e. what is the uncertainty in the experimental uptake coefficient due to the uncertainty in the duration of condensation).

As a first approximation, we use the timescale for uptake from Iinuma et al. because in that study a static chamber is used, so the measured time to steady-state is a closer (still an upper estimate) reflection of the chemical timescale to steady state. From Eq. 4, time and uptake coefficient are linearly related. The general consistency of timescales in the work of Iinuma et al. suggests little variation with chemical parameters, but an estimate of +/-20% seems reasonable. This uncertainty is now reflected in Fig 7.

Page 7157. Line 18-20. "Iinuma et al. ran experiments with acidic and neutral aerosol, but only observe uptake at pH=0 (Lai et al. 2012)." I assume that "Lai et al. 2012" should be replaced with "Iinuma et al. 2009".
Figure 3. In Figure 3a the red layer appears to be the less dense phase (i.e. the red layer is the top layer). In Figure 3b, however, the dark/red layer appears to be the more dense phase (i.e. the red/dark layer is the bottom layer). Why the change in the location of the red layer? Also in Figure 3b, at first glance there appears to be three layers – a top red layer, a middle clear layer, and a bottom red layer. I assume the top red layer is just a reflection/optical effect? Please explain what is shown in Figure 3b. Some annotation in the figure may help, or perhaps improved images may help.

The major difference between the photos in figures 3a and 3b is the mass loading of the aPO in sulfuric acid. The mass-loading of aPO in the sulfuric acid solution is low enough that phase separation does not appear evident. Thus the observed coloration of the sulfuric acid solution in Fig. 3a is due to mainly to diffusion of the colored products. The purpose of this figure is solely to show that phase separation occurs at high mass-loading. In fact, that different products/colors are seen in Fig. 3a and 3b is consistent with the varying UV-Vis spectra in the supplemental material (Fig. S1).