

We thank the reviewer for taking time to provide this detailed review, but strongly disagree with the reviewer's interpretation of our data and data published by other groups. Below we address each of the referee's points in detail. We show that each point the referee attempted to label as flawed was fully explained and was shown to be the result of the referee making flawed arguments.

Our recent laboratory and field measurements of SOA evaporation rates show that the evaporation rates of SOA particles are so slow that to first order we suggested they could be ignored. The manuscript presents a modeling study, in which we compare the atmospheric evolution of non-evaporating SOA with the traditional modeling approach that assumes instantaneous gas/particle equilibration. In addition, we present a sensitivity study that explores the effects of gas-phase multigenerational chemistry that, for the first time, includes fragmentation and functionalization reactions of organics, in box model and 3D Chemical Transport Model.

All that was needed to motivate development of a model, in which to first order SOA is treated as non-evaporating, is to cite Vaden et al. (2011) PNAS paper, in which we presented the first and only room temperature study of evaporation of size-selected ambient particles. These data show that even when gas phase organics are continuously removed, these particles evaporate extremely slowly, with 100 nm ambient SOA particles losing ~6 nm in diameter in 4 hours. Instead of looking at the ambient SOA evaporation data, the referee focused on the faster evaporation of pure SOA. However, even for pure SOA our data (Vaden et al., 2011) showed that SOA evaporates much slower than predicted based on smog chamber data. In this work, we decided to provide the reader with a more complete picture of SOA we included in the paper our interpretation of the Vaden et al. (2010) and (2011), both published in *PNAS*, a highly prestigious peer-reviewed journal. Nearly nothing new was added.

The referee virtually ignores the present manuscript and chooses instead to review the published Vaden et al. papers. We always welcome any comments about our work, including our published papers. We agree with the referee that these papers present extremely important results, whose ramifications need to be investigated in a modeling study like the one presented here. The problem, however, is that the referee misinterprets many of the measurements described thoroughly in Vaden et al. (2011; 2010), ignores other supporting studies all published

in high impact peer-reviewed journals, and does not follow the arguments in both present and past papers.

Below we address each of the referee's points. However, before we do so would like to give one illustrative example of the arguments made by the referee.

In an attempt to dismiss the results of the Virtanen et al. paper, recently published in *Nature*, the reviewer claims particles could be frozen. The reviewer sums the argument as follows: "Whether or not this is the case I do not know, but want to point out that this makes this additional evidence rather indirect and quite inconclusive." The logic seems to be that the argument does not need to be correct for it to cast doubt on published paper in *Nature*, a reputable journal. The argument was obviously wrong.

In contrast, Paul Ziemann, with whom we had many lengthy discussions about our findings, as evident by the acknowledgments in our paper, wrote the highlight for *Nature* on the Virtanen et al. paper, where he says: "The results of this study have consequences for understanding and modeling atmospheric organic aerosol and its environmental effects." and that this work represents "a finding that will lead to a re-evaluation of how they [SOA particles] are formed, and their properties and effects". Our recent papers represent our effort to provide new insights into SOA properties and behavior. Similarly, a 2011 *PNAS* paper by the Ulrich Pöschl group states: "Virtanen, however, showed that biogenic SOA particles formed in plant chamber experiments and in new particle formation events over boreal forests can adopt an amorphous semisolid state, which is in line with the observed presence of oligomers or other organic compounds with high molecular mass and low volatility in SOA (30, 31)". They acknowledge the importance of the findings and point to other papers, including Vaden et al. (2011) that support it. M. Shiraiwa et al. (2011) conclude that "occurrence and properties of amorphous semisolid [SOA] phases challenge traditional views and require new formalisms for the description of organic particle transformation and partitioning in atmospheric models of aerosol effects on air quality, public health, cloud physics, and climate."

The Virtanen paper has been out for less than a year and has already been cited 29 times, in published works, providing impetus for changes in SOA modeling. On the same point, we cited Cappa and Wilson (2011) ACP paper that like Virtanen et al. (2010) and us concludes that SOA cannot be liquid. The referee chooses to ignore the Cappa and Wilson paper, in which different

experimental approach was used to demonstrate that the evaporative behavior of SOA particles is very different from that of multicomponent liquid droplets. The authors of this paper, recently published in *ACP*, conclude that SOA must be highly viscous and not governed by partitioning theory

Are we to conclude that because the 1<sup>st</sup> reviewer speculated, providing no evidence, that these particles are frozen, all the studies citing these recent papers are also questionable?

The amount of experimental data that support these recent findings about SOA phase is rapidly growing. For example, we participated in experiments conducted by the Barbara Finlayson-Pitts group that also point to non-liquid like and non-equilibrium SOA behavior. A manuscript describing these findings (that are based on very different experimental approach) is currently under review in *Nature-Geosciences*. James Pankow, who is one of the “founding fathers” of liquid-like reversible treatment of SOA, is a co-author on this paper. A recent *ACP* by paper C. Pfrang, M. Shiraiwa, and U. Pöschl, titled “Chemical ageing and transformation of diffusivity in semi-solid multi-component organic aerosol particles” presents a modeling study that aims to take into account the new experimental findings relating to the importance of diffusivity in atmospheric aerosols. (Note that each of the papers mentioned above cite Vaden et al. (2011) in support)

The referee agrees that evaporation is slow, but perhaps does not realize that it implies that all current 3D Chemical Transport Models assume that instantaneous gas-particle equilibrium is established, which implicitly include the assumption that evaporation is faster than all other processes that affect gas/particle equilibrium, and are therefore not correct. We tried, in this paper, to present a new approach that considers our experimental findings that SOA evaporation is slow and represents the reality much better than previous approaches. The referee focused instead on whether it is possible to find organic molecules that evaporate very slowly; having found some, he/she states that evaporation is not too slow and ignores the implications. Our argument is simple, slow evaporation means that not much evaporates under atmospheric conditions and that models must account for that.

What made these measurements possible is our one of a kind, ultra-sensitive single particle mass spectrometer, called SPLAT II, and a newly developed approach to measure, for the first

time, the room-temperature evaporation kinetics of size-selected particles for over 24 hours and monitor the changes in all the SOA properties (size, composition, shape, density, and morphology).

As measurement technologies improve and generate new data, assumptions are replaced by experimentally derived evidence and SOA is not an exception. The measurements performed by SPLAT II have never been done before and the data it produced unveiled new information that we used to guide our model construction. As more data are generated and models are improved, the discrepancy between model predictions and field observations should decrease.

We request the scientific community to think holistically, examining all lines of evidence when defending or rejecting any claim or hypothesis presented in this paper. We also feel that any strong hypothesis or claim backed by solid experimental evidence, such as presented in this paper, cannot be rejected based on previous assumptions, theories, and notions.

Anonymous Referee #1

Received and published: 19 August 2011

The authors are advancing what they call “a new picture of non-evaporating, quasi solid SOA, with trapped hydrophobic organics”, which “casts doubt on all SOA gas particle mass transfer calculations based on reversible partitioning and Raoult’s law.”

This “picture” rests mainly upon authors’ interpretation of experimental results recently published by their group in PNAS (Vaden et al., 2011) and repeated, though without much detail, in this paper. The authors make the following main observations and conclusions: 1) the SOA evaporation proceeds “too slowly”, in two stages, and does not agree with the evaporation calculated using published  $\alpha$ -pinene parameterizations; therefore, SOA does not follow partitioning theory;

It is not that SOA does not respond to changes in the gas phase according to the laws of chemistry and physics. It is that when it needs to respond by evaporation, it take a very long time to do so, where long is much longer than 24 hours according to our data. In addition, the

reviewer chose to ignore the fact that evaporation of ambient SOA, measured during the CARES field campaign in Sacramento CA, was much slower than that of  $\alpha$ -pinene SOA. Our measured evaporation rates show that on atmospheric time scales SOA particles do not keep up with changes in the gas phase and are therefore not at equilibrium.

2) SOA particle evaporation is size independent; therefore, particles are highly viscous, having high resistance to mass transfer within the particles, which explains the deviation from the expected partitioning behavior;

That is not correct. Deviation from partitioning theory is because particles are not at equilibrium with the gas phase. The fact that SOA does not follow the evaporation kinetics expected for liquids indicates that it might not be liquid. If it is indeed not a liquid, it should not follow the partitioning theory developed for ideal liquids. It should and does follow another partitioning theory, but again does not reach equilibrium because of kinetic constraints.

3) hydrophobic compounds form coatings on SOA, and vice versa, which slow down evaporation; this is taken as an additional indication of highly viscous state of the particles.

This statement is simply not correct. We present a number of pieces of evidence that SOA is viscous, none of which is because hydrophobic organics form coatings. We will go over our arguments that SOA is viscous below. The simple truth is that whether it is viscous or not makes no difference to the fact that evaporation is very slow and can therefore be neglected, which is what the modeling section is all about.

We never said that the coatings by hydrophobic organics slow evaporation. We speculated in the first Vaden PNAS paper that based on the existing literature they might, but have since learned that the mechanism is very different. The surface hydrophobic organics coatings evaporate rapidly (just as expected), and their effect on SOA evaporation is due to the remaining hydrophobic organics that are trapped within the SOA particles. In fact, when this paper was sent to print we did not know the exact mechanism by which trapped hydrophobic organics slow evaporation. We have since conducted a set of experiments that provide direct evidence of the mechanism by which SOA evaporation is slowed by trapped hydrophobic organics.

Based on these points, the authors present an unorthodox modeling approach in which OA gas/aerosol partitioning is treated as a one-way process: organic species are allowed to condense onto particles, but their evaporation is prohibited. The possibility of particle phase limitations to gas/aerosol exchange is highly intriguing and has been receiving much attention recently. There is no question that such particle phase limitations could be of extreme importance for OA chemistry and gas/aerosol partitioning. However, there are still many questions related to the extent and importance of these limitations for ambient OA that remain to be addressed. The current paper, as well as Vaden et al. (2011), unfortunately, fall far short of answering these questions. I cannot recommend publishing this paper, because of the numerous errors in interpretation and self-contradicting statements. I do not believe a major revision can remedy these problems and thus recommend rejection.

The reviewer rightfully acknowledges the extreme importance of particle phase limitations to gas-particle partitioning and agrees that questions surrounding this issue need to be addressed. The referee seems to accept our measurements of evaporation rates, which directly address gas-particle exchange. It is not clear why should there be objection to a paper attempting to put these findings, that the referee has no problems with, into a modeling study. Consider the number of papers published based on particle evaporation measurements conducted for a few seconds or minutes at high temperatures in the thermodenuders. Do they provide more reliable information on gas-particle exchange than Vaden et al. (2011)?

We respectfully but strongly object to reviewer's comment that this paper has numerous errors in interpretation and self-contradicting statements. We acknowledge that the results presented in this paper and in Vaden et al. (2011) need careful thought, and that they may have been confusing to the reviewer, as evident by the fact that the reviewer misinterpreted several points in this paper and our previous PNAS papers. Below we rebut each of the issues raised by the reviewer, and request a careful re-consideration of each of the reviewer's objections.

The fact that the Vaden paper presents data that show extremely slow evaporation of ambient SOA particles (even under the conditions when gas phase organics are continuously removed) is undeniable. Our modeling of a non-evaporating SOA is based on these field observations and

does not take into consideration particle phase. The fact that the field data happen to agree with laboratory data provides support for the idea of using laboratory observations to learn about SOA properties and behavior.

Ambient SOA particles evaporate in two stages fast and slow. Evaporation is size-independent, as *we clearly defined it*. It follows evaporation kinetics very similar to that of  $\alpha$ -pinene SOA with trapped pyrene that was acquired by SOA particles during their formation by nucleation. More than 80% of the particle mass (93% of its initial diameter) remains in particle form after ~4 hours of evaporation in organic vapor free environment. Evaporation under real atmospheric conditions is expected to be slower. Based on these observations we suggested that to first degree SOA evaporation could be ignored.

Clearly, that does not mean that evaporation is zero. It means that we approximate it as such and our data indicate that it is a reasonable approximation. Moreover, it is not very difficult to estimate what error this approximation can introduce.

Consider that current models assume 100% functionalization in reaction with OH, which is clearly not correct, yet many published papers deploy it as an approximation. As long as one states what approximation one's model includes and what it is based on, the reader could and should be made aware of the errors involved.

Some SOA modeling papers state that SOA is assumed to be in ideal-like or pseudo-ideal solution. Given what we know about SOA, it would be surprising to anyone if it was ideal. How bad is this assumption? What evidence is there to support it? Based on referee's comment regarding the large uncertainty associated with smog chamber data, it is not easy to find evidence for this idea.

Many models use a single OH reaction rate constant. How important is this approximation?

We commonly accept the fact that modeling includes approximations and often unsupported assumptions, yet they serve a purpose and provide new information. In our case, the ambient and laboratory data provide the justification for our approximation of non-evaporating SOA.

The referee states at some point below that it is not surprising that when evaporation is stopped, more SOA is made. The truth is that it is not as simple as he/she makes it seem. Our paper provides a very detailed study of the issue and the referee ignores it completely.

Below I provide criticism of the main points of the paper, addressed in separate sections, and show that the observations do not contradict the partitioning theory and, in fact, tend to support it.

Our arguments are not that partitioning theory does not work. We are not saying that SOA does not follow the laws of chemistry and physics.

Let us try to clarify the point. Consider a normal atmospheric environment, in which gas phase concentrations change due to chemistry and dilution. If the gas phase changes are much faster than the SOA evaporation rate, then the particle phase cannot maintain equilibrium with the gas phase. Assume that it takes the particle more than 2 days to reach equilibrium by evaporation. On this time-scale (due to much faster changes in the gas phase) the equilibrium state itself will be changing faster than the particle can respond. It means that the particle phase never reaches equilibrium with the gas phase. Note that we made no mention of SOA formation. Our work focuses on what happens once these particles are formed and how they are expected to respond to the changing atmosphere. The same particles may respond rapidly to changing gas phase when gas-phase concentrations are high and equilibrium is reached by condensation, but slowly when the response requires evaporation. This scenario would easily fit a case, in which processes in the condensed phase play important role. If condensation is fast and evaporation is slow, it would be possible to use partitioning theory to calculate gas/particle partitioning for SOA formation, assuming equilibrium is reached, and not to describe SOA evolution in a diluting atmosphere, in which evaporation is called for. But again, even if we limit the use of partitioning theory to formation, in order for it to be accurate, it should account for the actual physical and chemical state of the particle, without simplifying assumptions of diffusively well-mixed liquid as required by absorptive partitioning theory developed by Pankow (1994) . We tried to state this idea by saying that the particle phase does not follow partitioning theory. We agree that this point needs additional clarification.

**(1) SOA evaporate “much slower” than expected and does not follow partitioning theory**

This conclusion appears to be drawn mainly from the discrepancy between the observed evaporation rates and those predicted using a volatility basis set (VBS) parameterization of  $\alpha$ -



pinene SOA from Pathak et al. (2007). This conclusion is, clearly, an unjustified generalization. The fact that the two disagree does not necessarily mean that the SOA does not follow partitioning theory.

Our point is not that SOA does not follow partitioning theory. Instead, our point is that SOA evaporates much slower than expected by models. We looked at  $\alpha$ -pinene SOA and used the available product volatilities parameters derived for this SOA. We find that our data (and similarly the data presented in (Grieshop et al., 2007; Stanier et al., 2007)) do not agree with predictions.

It is not clear what generalization the referee objects to. Again, we are not saying that SOA does not evaporate. We say that it evaporates so slow that it is never at equilibrium with the gas phase.

As far as generalizations go, we have since looked at SOA formed by oxidation of a number of different precursors and found very similar results. These data will be presented in separate publications.

For example, the VBS parameterization was derived from various, quite variable smog chamber yield data. The uncertainties in this parameterization combined with various potential experimental problems in smog chambers, such as the mass exchange with the chamber walls (Matsunaga and Ziemann, 2010), make it extremely difficult to draw any conclusions from the reported differences.

Does the referee really mean that parameters derived from smog chamber data could be off by orders of magnitude? This comment casts doubt on the utility of all smog chamber experiments that to this day are being carried in many laboratories in the world. Data from these experiments helped generate the basis of our understanding of gas and particle phase chemistry and physics in the atmosphere for many years. The reviewer completely disregarded the fact that these same parameterizations derived from fitting smog chamber data are commonly used to predict the gas-particle partitioning of SOA in 3D Chemical Transport Models (for

example, Chung and Seinfeld, 2002; Heald et al., 2005; Tsimpidi et al., 2010). Should all of these papers be retracted?

This comment is one example, in which the referee claims that data are not to be taken as evidence, when they do not fit his/her expectations.

Alternatively, this statement can be viewed as a compliment for our work. The reviewer seems to suggest that smog chamber data are unreliable and that the Vaden et al. (2011) data on evaporation provide one more reliable piece of evidence that proves that point. It is important to emphasize that we completely disagree with the referee. We do not cast doubt on all smog chamber results and agree that they are extremely useful. As a matter of fact, our point of view is that the fact that the VBS distributions derived from smog chamber data do not fit our evaporation data provides the most important piece of information about SOA. As we see it, smog chamber data are consistent with our evaporation rates.

Similarly, in the recent *ACP* paper, Cappa and Wilson reported that evaporation of particles composed of lubricating oil is “quantitatively in agreement with expectations from absorptive partitioning theory”, while  $\alpha$ -pinene SOA “appears to not be governed by partitioning theory”. The authors “postulate that this difference arises from diffusivity within the  $\alpha$ -pinene particles being sufficiently slow that they do not exhibit the expected liquid-like behavior and perhaps exist in a glassy state.” They also did not dismiss all smog chamber data, but instead demonstrated that it is possible to reconcile smog chamber aerosol growth measurements with the picture of highly viscous SOA. They showed that previous VBS fits to aerosol growth in smog chamber experiments predict very similar results to their sequential partitioning modeling approach (S-EPM) that assumes SOA is non-absorbing and does not form a solution with condensing gas-phase. However, they also noted that in their paradigm evaporation and atmospheric evolution of SOA is different from prevailing assumptions. Note that the reviewer completely dismisses the results of this study from Cappa and Wilson (2011) that we refer to in our manuscript as another piece of **experimental evidence** that is consistent with our data and data interpretation.

Most importantly, our laboratory data agree with our field data. It seems that we are all in agreement that SOA evaporation is very slow. How slow? Well, our data provide clear numbers for laboratory and ambient SOA.

Whether the evaporation is “slow” or not does not prove or disprove partitioning theory. A particle made up of compounds with low vapor pressure may evaporate very slowly even if the vapors are scavenged from the gas phase by activated carbon, as the evaporative flux is proportional to the vapor pressure. But such a particle may still follow partitioning theory. The particle size change rate is a function of particle size and the average vapor pressure of the compounds in the particle.

We agree with the reviewer that a particle made of compounds with low vapor pressure will evaporate very slowly even if the vapors are scavenged from gas phase by activated carbon. This amounts to stating that compounds with low vapor pressure have low vapor pressure.

However, fits to smog chamber data that use partitioning theory classify a very small fraction of compounds to very low vapor pressures. For example: 7-product VBS fits from Pathak et al. (2007) for low-NO<sub>x</sub> ozonolysis of 200 ppb of  $\alpha$ -pinene (similar to our experimental conditions) suggest that 96% of the particle mass exists in C\* bins between 1 to 10<sup>4</sup>  $\mu\text{g m}^{-3}$ , which is orders of magnitude higher than what the reviewer derived in his Figure 1. Thus, reviewer’s calculations of “extremely low” volatilities are inconsistent with smog chamber derived fits for  $\alpha$ -pinene SOA. In other words, the referee agrees with us.

For example, reviewer’s calculations, based on experimental data by Vaden et al. (2011), conclude that 100% of 160 nm particles with  $\alpha=1$  have an average vapor pressure on the particle surface lower than 0.1  $\mu\text{g m}^{-3}$  to start with. There is no question that there is a huge gap between smog chamber derived vapor pressure distributions and that derived by the reviewer in Figure 1 from evaporation data published by Vaden et al. (2011). In other words, the referee agrees with us.

Does the reviewer claim that from now, our evaporation data should be used to calculate the C\* distribution and all smog chamber data need to be discarded? That is an important conclusion that has far-reaching ramifications. Reading reviewer’s comments below, reveals that this is exactly what the reviewer suggests.

Keep in mind that our evaporation rates were measured under organic vapor-free conditions. Under real atmospheric conditions, there would always be organic vapors present, and

evaporation would be even slower. Under these conditions, how is one to calculate the gas particle partitioning, with the system being permanently far from equilibrium?

However, the evaporation or growth rate is only a part of the story in gas / aerosol equilibration. The gas concentration is what matters for equilibrium and the gas concentration change rate is the only important parameter. This change rate is, indeed, proportional to the particle size change rate, but also linearly depends on the particle concentration. Outside the context of particle concentration and size distribution, the size change rates do not mean much for aerosol equilibration. However, let us check how “slow” these evaporation rates actually are. The particle size change rate is driven by the average vapor pressure at the particle surface,  $C^*$ :

$$\frac{dd_p}{dt} = -\frac{4Df(Kn, \alpha)}{\rho d_p} C^* \quad (1)$$

in which  $d_p$  is the particle diameter.  $D$  is the average diffusion coefficient of evaporating species,  $\rho$  is the particle density,  $f(Kn; \alpha)$  is the Fuchs-Sutugin correction,  $Kn$  is the average Knudsen number of evaporating species, and  $\alpha$  is the evaporation coefficient. This equation is a different form of equations 1 and 3 in the supplement, in which the mass flux is converted to the size change rate and the ambient gas concentration is set to zero, as dictated by the experimental conditions, and the combined properties of different compounds in the mixture replaced by their averages. The particle sizes as a function of time can be obtained from Fig.3B of Vaden et al. (2011) and used to calculate both the evaporation rate and the term preceding  $C^*$  on the right hand side of the equation. Having calculated these, one can easily obtain values of  $C^*$  as a function of time, i.e. as the evaporation proceeds. The diffusion coefficient  $D = 0.057\text{cm}^2/\text{s}$  and the mean free path of evaporating molecules (81.6 nm) for  $Kn$  calculations were taken to be equal to those of adipic acid, a relatively small, but relevant molecule. The particle density was taken to be  $1\text{ g/cm}^3$ . The results for two particle sizes are shown in Figure 1, which can be found at the end of this document. Two values of the evaporation coefficient,  $\alpha$ , were used, 1 and 0.1, none of which are “unreasonably low”. Two observations can be made from this exercise: 1) at the beginning of evaporation, SOA particles contain substances that

12

evaporate with an average rate consistent with vapor concentration of the order of 0.1 – 1  $\mu\text{g}/\text{m}^3$ ; extrapolating to  $t = 0$  one can potentially expect values as high as 10  $\mu\text{g}/\text{m}^3$ ; 2) the vapor concentration at the surface is monotonically decreasing with time. In relation to point one, I would like to point out that C4 – C10 dicarboxylic acids have saturation vapor concentrations at 25°C in the range 0.1 - 10  $\mu\text{g}/\text{m}^3$ , C13 – C22 monocarboxylic acids 0.001 – 100  $\mu\text{g}/\text{m}^3$ , addition of hydroxyl and carboxyl groups to monocarboxylic acids leads to a decrease of the vapor pressure by 1 – 2 orders of magnitude (Chattopadhyay and Ziemann, 2005, e.g.). This means that the experimental data reported in Vaden et al. (2011) and this paper are well within the range expected for atmospherically relevant oxygenated organic compounds. The observed evaporation rates are not “too slow”!

When one states that evaporation rates are “too slow” or “not too slow” he/she need to say compared with what? When we say that evaporation is very slow or extremely slow, we explain that it is slow by comparison with what is predicted based on smog chamber data. Or better yet, slow compared to changes in gas phase concentrations (due to dilution and chemistry) under normal atmospheric conditions. This is not different from Grieshop et al. (2007) who looked at room temperature SOA evaporation in smog chamber and concluded that evaporation timescales were “surprisingly slow” compared to the predictions.

The referee used our evaporation data to calculate the vapor pressures of compounds that would have the observed evaporation rates and concluded that the data fit his/her calculation. We agree that compounds with lower vapor pressures evaporate slower. This is not an interesting point. What we mean by “too slow” is that our observations do not support the vapor pressures of compounds supposed/assumed to be in these particles. However, the referee dealt with this issue by dismissing all smog chamber data. The referee still avoids the question of equilibrium. Now that the referee agrees that evaporation rates are slow (it takes longer than a day under the conditions of organic-free gas phase), he/she needs to accept that gas/particle equilibrium is not established on atmospherically relevant time scales and partitioning theory cannot be applied.

Let us for the moment accept referee’s calculation and take the next step. To explain the data the referee was forced to come to the conclusion that these particles are composed of a mixture of organics with vapor pressures from  $C^*=1$  to  $C^*=10^{-3} \mu\text{g m}^{-3}$  and that as the particle evaporates, its composition changes. That is exactly what we expected to see before we did the

experiments. However, the data show that the mass spectra basically do not change with evaporation. In other words, the SOA composition remains constant. Cappa and Wilson (2011) observed the very same behavior for SOA particles using the thermodenuder and VUV-AMS. They reported that the evolution of the mass spectra for particles composed of lubricating oil and  $\alpha$ -pinene SOA during evaporation were dramatically different. For lubricating oil particles, the spectra exhibited distinct changes, in which the lower  $m/z$  peaks, corresponding to compounds with higher vapor pressures, disappear more rapidly than the high  $m/z$  peaks –consistent with distillation behavior of the liquid droplets and “quantitatively in agreement with expectations from absorptive partitioning theory”.

In contrast, the mass spectra of SOA particles remained essentially unchanged during evaporation even though the particles experienced significant mass loss due to evaporation. As already discussed above (and in the manuscript itself) the authors “postulate that this difference arises from diffusivity within the  $\alpha$ -pinene SOA particles being sufficiently slow that they do not exhibit the expected liquid-like behavior and perhaps exist in a glassy state.” To account for their findings, Cappa and Wilson (2011) developed a new model for SOA, in which SOA forms and hardens, rapidly converting from an absorbing form to a non-absorbing form. As a result, evaporation takes place in layers and not by volatility. Cappa and Wilson (2011) refer to the Virtanen et al. (2010) and Vaden et al. (2011) papers, pointing out that these papers support their findings. We agree. However, the referee chooses to ignore the Cappa and Wilson (2011) paper, in which they report that their mass spectra do not change during SOA evaporation.

Careful examination of our mass spectra indicates that there are only very minor changes in the mass spectra at very short times (minutes), after which the mass spectra become nearly constant. We assigned the changes that take place in the first few minutes to surface evaporation. As we reported, we also observed an increase in intensity of peaks at higher  $m/z$ s that could be interpreted to indicate a minor distillation effect. However, since the publication of Vaden et al. (2011) we found that similar increase in the intensity of mass-spectral peaks at high  $m/z$ s occurs due to aging and oligomer formation.

The referee’s analysis presented in Figure 1 indicates that in order to explain the data particles of different sizes must have different compositions. Our data do not support this conclusion. The mass spectra and densities of different size particles are identical. For the

concentration of  $\alpha$ -pinene and ozone used in these experiments the oxidation reaction is fast and particle nucleation is followed by rapid particle coagulation and growth. Based on the referee's analysis of our data we must conclude that once SOA particles coagulate and become larger their compositions must change to fit the referee's calculated  $C^*$  distributions. This is clearly not reasonable.

Furthermore, taking the referee's approach, we must conclude that what everyone thought was in these particles and hence in the gas phase based on smog chamber data is not there, which seems to be an important conclusion. However, based on Cappa and Wilson (2011) and our mass spectra, which the referee chose to ignore, we have to conclude that the referee's interpretation of the data must be seriously flawed.

It is important to keep in mind that the issue is not how fast  $\alpha$ -pinene SOA evaporates. The important issue is how fast real atmospheric particles evaporate. It is clear from our data that pure  $\alpha$ -pinene SOA particles evaporate much slower than predicted, but considerably faster than ambient particles. As a result, to explain the ambient SOA data requires  $C^*$  that are even smaller than in case of  $\alpha$ -pinene SOA, further deviating from the smog chamber data derived parameters. But then again, the referee has already dismissed all smog chamber data.

We disagree with the reviewer's comment that experimental data reported in Vaden et al. (2011) and this manuscript are well within the expected range of atmospherically relevant oxygenated organic compounds. Again, the question is not whether one can find organic compounds with low vapor pressures. "Expected" means that which was predicted from smog chamber data, accepted and used by the SOA community at large. As we keep pointing out, the referee chooses to ignore this point.

The referee keeps coming back to partitioning theory. We keep pointing out that because evaporation is very slow particles never reach equilibrium by evaporation, which means that partitioning theory cannot be used to calculate gas/particle partitioning.

To argue whether something is "too slow" or even slow is not meaningful. It is too slow or slow with respect to something. Let us instead state that it takes the particle more than few days to reach equilibrium. You can call it fast or slow, the time scale remains a few days.

To clarify this, we refer to the interactive discussions of the Pierce et al. (2011) paper. The referee B. Bonn notes:

*“Assuming  $0.01 \mu\text{g}/\text{m}^3$  would result in a saturation concentration of about  $3 \times 10^7$  molecules per ccm. Compared to a total molecule number concentration of  $2.5 \times 10^{19}$  molecules per ccm, this yields a volume mixing ratio of about 1 ppt and a vapor pressure of  $10^{-7}$  Pa. Even the di-carboxylic acids of two monoterpenes, i.e. pinic acid is in the order of five magnitudes higher in volatility ( $\sim 0.06$  Pa) (Bilde and Pandis 2001). There are certainly additional compounds which are supposed to lower the volatility such as hydroxyl-hydroperoxides and highly oxidized species. But to shift the volatility down remarkably is by far no easy task to perform especially when considering the present knowledge about identified compounds.”*

The second point, namely, the continuous reduction of the vapor concentration at the particle surface, shows that 1) the “two-stage” evaporation of SOA, which is given so much attention in this and Vaden et al. (2011) papers, is not reflected in changes in  $C^*$ , which should have occurred around 70 min.; and

It is not clear what is meant by “... given so much attention”?

All we tried to do is describe the data. We did not ascribe any meaning to it. We never talked about changes in  $C^*$ . Changes in  $C^*$  are the referee’s way of explaining the evaporation data. As we noted before, our mass-spectral data and data presented in Cappa and Wilson (2011) contradict this idea.

In addition, the reviewer ignores the other evaporation curves in Figures 4, 6, and 7 of Vaden et al. (2011). For example, Figures 6 and 7 in Vaden et al. (2011) show evaporation behavior of two distinct types of ambient SOA particles that were composed of  $\sim 88\%$  organics and 12% sulfate and were characterized by SPLAT during the CARES field campaign in Sacramento, CA. These data show that evaporation rates of ambient SOA particles were similar to SOA formed in the presence of hydrophobic organic vapors and significantly slower than the evaporation rates of pure  $\alpha$ -pinene SOA. As the referee shows, describing this evaporation behavior by VBS will require all SOA compounds to have  $C^*$  that are even lower than those shown in reviewer’s Figure 1.



2) the evaporation most probably proceeds according to a well-mixed organic solution. When discussing the "two-stage" evaporation as surprising,

We had never referred to the two-stage evaporation as surprising. "Surprisingly slow" was used by Grieshop et al. (2007). Two-stage evaporation is merely description of the data. .

the authors make a major error in assuming that a mixture of compounds with different volatilities should behave as a pure substance. In a mixture, the higher volatility substances distill first, the lower volatility last, consistent with their data as interpreted in the previous figure. The evaporative flux and the corresponding size changes are bound to slow down as the evaporation progresses, because the evaporation rate is directly proportional to the vapor pressure of the species (see the equation above). This makes the "two stage" observations unsurprising.

This comment is rather confusing. We looked at papers published by the Davis's group (Widmann and Davis, 1997) , where they study evaporation of mixed organics. Their curves look very much like our SOA evaporation curves. We were therefore not surprised to observe the "two stage" evaporative behavior; and our first inclination was to interpret the data just like the referee did. However, our data show no changes in evaporation rates (as we defined it  $(d_i/d_0)^n$ ,  $n=1,2,3$ ) as a function of initial particle size. This observation is in sharp contrast with evaporation data of multicomponent liquids presented by Davis's group, evaporation behavior predicted by our calculation (shown in Figures 3c and 7), and by the referee's calculations. Data from Davis's group (Widmann and Davis, 1997), and the referee's and our model calculations, all show that  $d_i/d_0$  decreases faster for smaller  $d_0$ .

We were surprised by the absence of the expected "distillation" effect in the mass spectra, like that shown in the Cappa and Wilson (2011) paper for the evaporation of lubricating oil, a multi component substance. As mentioned above, Cappa and Wilson (2011) point to the difference between lubricating oil and SOA as evidence that SOA is not in the liquid phase and, in their words, is not governed by equilibrium partitioning theory.

The simple answer is that what the referee shows in his/her Figure 1 exactly what we and everyone else expected to see: compounds with higher volatility evaporate faster, the mass

spectra change, and evaporation rates show the expected size-dependence that is reflected in the referee's figure. We had no reason to assume otherwise. That is not, however, what the data show.

In principle, the same data can be used to estimate a VBS which explains the observed evaporation. In the interest of space I am not going to explain the procedure.

It seems like according to the referee it is time to ignore all smog chamber data and use our evaporation data to derive VBS distributions. Are we to assume that all published papers describing smog chamber data should be retracted? Should this also include all modeling papers that rely on these results?

The bottom line is that the size-dependence expected for liquid particles, as demonstrated by Widmann and Davis (1997), the referee, and our calculations, was not observed. Similarly, the expected changes in mass-spectral intensity with evaporation were not observed by us or by Cappa and Wilson.

There is a problem with the data, however, as the evaporation rate appears, against the authors' claims, to have a very strange dependence on particle size (see the following section). This is also reflected in Fig.1 where the larger particles appear to have higher effective vapor pressure than the smaller ones.

This is a very revealing comment. All that the referee means is that if one looks at the data in the  $d/d_0$ , as we did, the data show no size dependence. However, if instead one chooses a different coordinate system and does not divide by  $d_0$ , the data show size dependence. We clearly agree. There is nothing interesting here. We clearly defined our coordinate system in the papers and referred to the behavior in that coordinate system.

Because there seems to be confusion here, in the revised manuscript we rephrase the statement and replace size independent evaporation by volume or surface fraction remaining is not a function of "initial" particle size.

What is more interesting is that the referee comes to the very same conclusion we did, namely, that the data do not exhibit the size dependence he/she expected to see for liquid droplets. We concluded that because the data for the liquid droplets look just as expected, while the SOA data do not follow the expected behavior, the data are telling us something new about the behavior and properties of the SOA particles. In contrast, the referee concludes that there is problem with the data. This provides another example in a rather reproducible pattern: When the smog chamber data do not fit our evaporation measurements, no problem, toss the smog chamber data. When the evaporation data do not fit his/her expected behavior of liquid droplets, no problem, toss the data out. When the smog chamber data do not fit, no problem, use our evaporation data to construct a new volatility distribution. Want support for particle liquidity; cite in support fits to smog chamber data. Bottom line, data are not to be trusted unless they fit unsupported assumptions.

Thus, the estimated VBS depends on the assumption of the initial particle size, and is given here only for illustration purposes. Using the fitline parameters given in the appendix to Vaden et al. (2011) and the initial particle size of 250 nm, my rough estimate is that the mean  $\alpha$ -pinene aerosol volatility was about  $0.3 \mu\text{g}/\text{m}^3$  (logmean  $0.1 \mu\text{g}/\text{m}^3$ ) and that of ambient about  $0.05 \mu\text{g}/\text{m}^3$  (logmean  $0.01 \mu\text{g}/\text{m}^3$ ) assuming  $\alpha = 1$ . Using larger initial sizes produces higher values. For example, for 500 nm the mean volatility of  $\alpha$ -pinene aerosol is about  $1.1 \mu\text{g}/\text{m}^3$ . In any case, these values are similar or higher to the range of vapor pressures recently reported values for ambient aerosols (Cappa and Jimenez, 2010) and the main take home message is: the observations can be easily explained by the conventional partitioning theory.

It is not clear what is meant by “only for illustration purposes”. Does that mean the results are unreliable, or that the fit to the data are unreliable, even though the results fit his/her expectation? Here again the referee dismisses vast amount of smog chamber papers, pointing to the Cappa and Jimenez (2010) paper reporting on the evaporation of ambient particles in support. The Cappa and Jimenez paper, much like our work on ambient SOA, finds that SOA evaporation is slow.

For fresh smog-chamber SOA we know exactly what was expected and we show it in our figures as the calculated evaporation rates. For field SOA, it can be more complicated. In our field-study, we observed the SOA form and as a result had unequivocal evidence that it was only a few hours old. Lacking such evidence, observed slow evaporation rates can be explained by invoking the multi-generation chemical processing commonly used in SOA modeling, in which the volatility of SOA decreases in the atmosphere with processing time.

But, even if we accept this explanation for the Cappa and Jimenez findings, there is still a major problem, having to do with the fact that commonly used SOA modeling assumes that the gas and particle phases are at equilibrium at all times. The referee points out that it is possible to find compounds that evaporate as slow as the  $\alpha$ -pinene SOA in Vaden et al. (2011). We never doubted that. The referee says that he is forced to give larger particles higher vapor pressures, which means that in this model larger particles have different compositions than smaller ones. This is in contradiction to our data. Again, according to the referee when two particles coalesce their composition must change to give them higher vapor pressures.

The reviewer suggests here that based on data from Vaden et al. (2011), the ambient SOA particles have a log mean volatility of  $0.01 \mu\text{g}/\text{m}^3$ . These are essentially non-volatile for most atmospheric conditions, and would not exhibit significant gas-particle partitioning in the atmosphere. In this case, applying the absorptive partitioning theory would predict similar results as our one-way irreversible gas-particle partitioning scheme, implemented in this paper.

In other words, all of us, including the referee, agree, as far as evaporation goes. Evaporation under atmospheric conditions is so slow that it can be ignored.

However, the reviewer again completely ignores the fact that SOA is considered semi-volatile in most regional and global climate models (Chung and Seinfeld, 2002; Robinson et al., 2007; Tsimpidi et al., 2010). In fact, VBS implementations in regional Chemical Transport Models have assumed that SOA is semi-volatile with volatilities continuously decreasing due to 100% functionalization (Robinson et al., 2007). This paper makes a major advance in this direction and shows that assuming SOA as semi-volatile in models is flawed.

## **2 Size-independent evaporation**

One of the central claims made in this paper and Vaden et al. (2011) is “The simple fact that SOA evaporation does not follow the size-dependent evaporation behavior expected of liquid droplets indicates that these particles are not liquid-like” (I cite this from Vaden et al. (2011), end of section Evaporation Kinetics of Pure Laboratory SOA). The problem is, the particle size dependence of evaporation kinetics comes from the Maxwell solution of diffusional flux through air in a spherical geometry (see for example equation 1 in the supplement to this paper). It has absolutely nothing to do with the phase of the particle, be it solid or liquid. This equation has been used to characterize evaporation kinetics of both liquid (such as DOP) and solid particles (such as mono and di-carboxylic acids), see for example the classic (Tao and McMurry, 1989) and many, many other papers. On the other hand, it is general knowledge that evaporation in the free-molecular regime, i.e. when particle size is much smaller than the mean free path of the evaporating species, is particle size independent. Evaporation in the transition regime, as is the case in this study, could have very weak size dependence if the size of the evaporating molecules is relatively large. Strictly speaking, one cannot draw any conclusions about the particle phase from the size dependence of evaporation for particle sizes used in this study.

We agree with the reviewer that particle size-dependence of evaporation kinetics comes from the Maxwell solution of diffusional flux through air in a spherical geometry, and is applicable to both liquid and solid particles. However, the reviewer fails to consider highly viscous internally mixed particles. Cappa and Wilson (2011) present a very clear discussion on the subject.

Consider a solid particle with a semi-volatile core that is coated by a non-evaporating solid. In this case, diffusion through the non-evaporating solid determines the evaporation kinetics. Now take a particle with identical composition except that the core is made of the non-evaporating solid and the coating is the semi-volatile compound. The evaporation of these two particles would be very different in all regimes.

We have shown through other multiple lines of evidence that diffusion within the SOA particle is extremely slow. We repeat these lines of evidence for clarifications:

1. As the referee notes, the size dependence of SOA evaporation rates do not fit those expected for liquid particles.
2. Grieshop et al. (2007) RT evaporation study shows the same size dependent (or as defined in Vaden et al. (2011) rather size-independent) evaporation behavior as we have seen.
3. Vaden et al. (2011) showed that diffusion of semi-volatile organic species, like pyrene, through SOA is extremely slow, providing direct evidence that SOA is highly viscous. We have since looked at the diffusion of a range of compounds through SOA and found them all to be very slow.
4. We produced particles with opposite layered morphologies, SOA on DOP and DOP on SOA and showed that both remain stable for many hours. The reviewer suggests that oil and water do not mix due to phase separation of two immiscible liquids despite low viscosity and fast diffusion in both liquids. In making this argument, the reviewer has completely missed the point that if one of the fluids: oil or water is lighter; it always comes over to the surface due to very fast diffusion. However, in our case, the two reverse morphologies, SOA coated with DOP and DOP coated with SOA were found to be stable for many hours indicating that DOP diffusion through SOA and SOA diffusion through liquid DOP are very slow. The density of liquid DOP at room temperature is  $0.97 \text{ g/cm}^3$  – lower than SOA density of  $1.2 \text{ g/cm}^3$  as measured by SPLAT. If diffusion was fast, we would always expect the DOP to be on surface of SOA, no matter if it was “DOP coated SOA” or “SOA coated DOP”.
5. The evaporation of DOP coated pure SOA indicates that the DOP coating evaporates rapidly, just like pure DOP, leaving behind an SOA particle with no trace of DOP, which subsequently follows evaporation of pure SOA
6. The evaporation of SOA coated DOP particles indicates that in 24 hours the DOP core does not evaporate.
7. In contrast to SOA particles formed in the presence of pyrene vapor, pure SOA particles coated with pyrene are aspherical. During their evaporation pyrene evaporates rapidly and within ~2 hours the pyrene coat is gone, leaving no trace of pyrene in the particles.

8. In Zelenyuk et al. (2010), we describe experiments conducted in the UCI flow tube that show that SOA coatings on wet  $\text{NaNO}_3$  seed particles, prevents water evaporation from these particles.
9. Changes in our mass-spectral relative intensities as a function of evaporation do not show the expected behavior for the distillation of multi-component liquid.
10. Cappa and Wilson (2011) find no changes in mass-spectral intensity as a function of evaporation and conclude that SOA must be highly viscous.
11. Cappa and Wilson (2011) report the same behavior, using different experimental approach.
12. Virtanen et al. (2010) characterize the bouncing behavior of SOA particles and conclude that SOA particles must be highly viscous.
13. Virtanen et al. (2010) use microscopy and conclude that SOA particles must be highly viscous.
14. A recent paper (under review) by the Barbara Finlayson-Pitts group, with James Pankow as a co-author, points to non-liquid like SOA behavior.

However, is the evaporation rate reported here really size independent? Surprisingly, it is not. The authors use time evolution of  $(d_p/d_0)^2$  to make this conclusion, because it appears to be independent of the initial particle size.

That is misleading. We chose this coordinate to plot the DOP data and the SOA data for comparison. We did not try to come to any conclusions; we tried to show what the data look like. In other plots, we chose to plot the very same data in the coordinates  $(d_p/d_0)^3$  vs. time for the direct comparison to the volume fraction remaining used in the Grieshop et al. (2007) study.

Again, a priori we expected to see exactly the same things that the referee is expecting to find in these data. We assumed that these particles are liquid and comprised of a mixture of organics

with a range of volatilities calculated from smog chamber studies. We had no reason to expect otherwise. The data indicate that these assumptions were wrong.

However, for judging the effects of diffusional limitations within a particle, which could lead to size independent evaporation, one needs to investigate  $dp/dt$ , not  $(dp/dt)^2$ . If  $(dp/dt)^2$  is size independent,  $dp/dt$  is necessarily size dependent.

This cannot be correct. If  $(d_p/d_0)^2$  is size-independent, then so is  $d_p/d_0$ .

For example, the evaporation rate (nm/min) of 251 nm particles is 1.57 times faster than that of 160 nm particles. Inspection of individual points in Fig.3B of Vaden et al. (2011) shows that, indeed, 251 nm evaporate on average 1.65 times faster. The evaporation rate is clearly not size independent, in fact it appears to be proportional to the particle size.

It is size-independent as we defined it. It is not size-independent as the referee defined it. It is not a meaningful argument. The main point is that it does not behave as predicted for the liquid droplets. It is for that reason that the referee concludes: “there is a problem with the data”.

The observed size dependence is quite curious, because it contradicts the basic diffusional transport theory.  $dp/dt$  should be either size independent, as in the free molecular regime, or be inversely proportional to  $dp$ , as in the continuum regime, i.e. the rate is slower at larger sizes. The transition regime has a dependence on size that is between these two limiting cases, but under no circumstances should it be increasing with particle size.

Also please note that the observed increase with size cannot be explained by mass transfer limitations in the particle phase. If the diffusion within particles is much slower than the diffusional exchange with the gas, the evaporation behavior will follow that of the free-molecular regime, i.e. be size independent.



First, it is important to point out that the reviewer defines the size-independence very different than it was done in Vaden et al. (2011). What the reviewer seems to suggest is that depending on the regime,  $d_p$  vs. time for particles with different sizes or  $d_p^2$  vs. time will look like a set of parallel lines. For single component droplets, these lines will have a constant slope, while for the multicomponent droplets, the slope will be changing with time. What he/she suggest will look size-independent will be size-dependent in our coordinates ( $(d_p/d_0)^n$  vs. time, where  $n=1,2,3,\dots$ ). Smaller **liquid** droplets will lose larger fraction of their volume per unit time than large particles.

Now, why should highly viscous particles behave as if they are in the free-molecular regime? The referee seems to suggest that because evaporation rates in the continuum regime are determined by diffusivity in the gas phase, evaporation rate in the free-molecular regime must depend on diffusivity in the condensed phase.

The reviewer's next logical step seems to be that if we claim that our evaporation kinetics rates are determined by diffusion in the condensed phase they should look like the free-molecular regime. The fact that they do not, raises a flag for the referee.

However, is it correct that evaporation rates in the free-molecular regime depend on diffusivity in the condensed phase? This is definitely not the case. We would refer the reviewer again to the work by the Davis group (Widmann and Davis, 1997) who extensively studied the evaporation of single and multicomponent droplets under different regimes, including when a multicomponent droplet evaporates into a vapor-free medium. In the latter case, it is necessary to know the diffusion coefficients in the surrounding gas, the vapor pressures of the individual components at the temperature of the drop, and the activity coefficients for each of the species present (Widmann and Davis, 1997) .

It seems that according to the referee, two particles of identical size and vapor pressure would have very different evaporation rates in the free-molecular regime, if one is a solid and the other a liquid, since their viscosities are different by a factor of  $\sim 10^{14}$ . In contrast, the same particles, according to the referee, would have identical evaporation rates in the continuum regime. This is clearly not a valid argument.

The referee ignores the possibility of highly viscous particles composed of a mix of molecules with different vapor pressures. As the molecules at the surface evaporate, they leave behind a surface coated with low volatility compounds, which is consistent with the layered evaporation picture presented in Cappa and Wilson (2011).

Here are the simple facts: We tested the system with DOP and DOS. It quantitatively gives the correct size-dependent behavior and the correct vapor pressure.

We then apply the system to SOA particles of similar sizes and the data are the data. They are in very good agreement with the room temperature evaporation kinetics observed in Prof. Neil Donahue group. Their SOA evaporates slightly slower than ours does, which can easily be explained by the difference in technique, including the effect of smog chamber walls. They concluded that SOA evaporation is “surprisingly slow”. The problem is that they stopped just before the slow evaporation stage begins, because of poor signal to noise.

The DOP and DOS data clearly show temporal evolution of the line shape of size distributions due to differences in evaporation rate of smaller and larger particles. Keep in mind that these are very small differences between particle sizes (with initial FWHM of 5-7%), yet they are clearly observable. This is not what the SOA data show! The SOA size distributions maintain constant line shape with evaporation. The same behavior was seen in Grieshop et al. (2007) evaporation experiment, for which the line shape does not change due to evaporation.

Bottom line, the data are the data. Our conclusion that SOA evaporation does not follow that expected for liquid particles remains and the referee agrees. Then, he/she concludes, “There is a problem with the data”.

This is exactly the point the authors are extensively exploiting to link the size “independence” to intra-particle transport limitations. This is, however, clearly not the case for the data reported here. One can only speculate about the reason for this strange size dependence. Could it be an artifact due to the counting efficiency of SPLAT which decreases with size (100 nm is approximately the size of 50% counting efficiency), or due to density changes during evaporation? I am curious to read the authors’ interpretation.

This comment is rather baffling, since particle counting is not used to measure evaporation? We are following single particle evaporation kinetics, as described in details in Vaden et al. (2011). It is a good example of the differences between the referee's and our approach to data. Particle evaporation rate is determined from changes in particle size. It has absolutely nothing to do with particle counting. It is hard to see how this simple procedure can be so misconstrued. Yet, the referee comes to the conclusion that "One can only speculate", which is clearly not correct. We do not need to speculate. We know exactly how evaporation is quantified, and provide clear description of the experimental procedure with illustrative figures in Vaden et al. (2011).

### **3 Phase separation as "evidence" of particle viscosity**

This is one of the strangest conclusions the authors make in this paper and in Vaden et al. (2011). For example, SOA formed on DOP seeds and SOA coated with DOP exhibit a "layered" structure with the coating material (be it SOA itself or DOP) being on top of the particle. From this the authors conclude (p.20114, l8): "The fact that mixed SOA/DOP particles with two reverse morphologies were found to be stable for many hours indicates that diffusion through SOA must be very slow." Phase separation of two immiscible liquids in equilibrium, such as water and oil, is very well understood and is due to molecular-level interactions, despite low viscosity and fast diffusion in both liquids. Phase separation could also be present in a system where the equilibrium state is a single phase, but the approach to equilibrium is very slow due to very slow diffusion, as the authors seem to favor. But how can the authors choose one explanation over the other? The fact that the two interacting species (SOA and DOP) have very different states of oxygenation and polarities suggests that an equilibrium phase separation such as for oil and water is plausible.

The referee clearly misunderstood the point. The issue is not phase separation, but stability of the two reverse morphologies: both "SOA coated DOP" and "DOP coated SOA" remain stable for many hours. Water and oil are immiscible and exist in separate phases, but if the oil is lighter

than water, it will always diffuse, very fast, to the surface. Thus, regardless of whether one places “oil on water”, or “water on oil” to start with, the lower density fluid will always diffuse and reside on the surface of denser fluid. The only explanations why our two reverse morphologies “SOA coated DOP” and “DOP coated SOA” remain stable for many hours is slow diffusion through SOA.

The contrast between this referee and the two referees of Vaden et al. (2010) PNAS paper, in which the discovery of these two stable morphologies was first reported, could not be starker. While the present referee claims that, nothing can be learned from the fact that particles with opposite morphologies are stable for many hours, the original referees pointed to the significance of this discovery.

As already mentioned above, since the two Vaden et al. PNAS papers we studied evaporation behavior of DOP/SOA particles with two reversed morphologies, and showed it to be extremely different.



















In fact Asa-Awuku et al. (2009) showed that  $\alpha$ -pinene SOA (the same SOA used here) did not become internally mixed with lubricating oil over a few hours, but it did with diesel exhaust which was slightly more polar. This strongly suggest that the morphologies observed by the authors are explainable by equilibrium arguments.

The Asa-Awuku et al. (2009) results have no bearing on our argument. The point we made is not that oil and water do not mix. The point was that SOA can be on top of DOP and DOP can be on top of SOA for long time, as long as we observed these particles.

There are many, many problems with the analysis of how the coated particles behave in the experiments. For example, to cite Vaden et al. (2011): “Importantly, the particles composed of pure coating materials (DOP, DOS, or PY) exhibit drastically higher evaporation rates” than particles coated by these same materials. It is strange that these coatings do not seem to evaporate. If something forms a coating, it means it does not dissolve in the rest of the material but forms a separate phase on the particle surface with many molecular layers. This implies that the coating should behave more or less as a pure substance and thus evaporate with the same rate.

Indeed, the coatings deposited by condensation of supersaturated DOP or pyrene on top of pure SOA core particles practically evaporate as pure compounds followed by the evaporation of the SOA core. On other hand, SOA particles that form in the presence of DOP or pyrene vapors acquire the hydrophobic organics during their formation, and the morphological distribution of these organics in the SOA particles, and the properties of the resulting particles are very different. Below is a table that shows some of the different particle types we made and characterized their evaporation for over 24-hours. For many of them we looked at aging behavior as well (much of this has not been published yet). From left to right: 1) Pure SOA: evaporates in two stages (faster and slower), losing ~75% of its volume after 24 hours of evaporation. 2) Pure SOA coated with (liquid hydrophobic) DOP that was deposited by condensation of supersaturated DOP vapors as described in Vaden et al. (2010). The DOP forms a thick coating layer (with the DOP volume being larger than that of the SOA core) that evaporates in less than 2 hours, leaving no trace. The remaining SOA follows evaporation of pure SOA. 3) SOA formed in the presence of DOP vapor. These 150 nm SOA particles have a thin (~ 4 nm) DOP surface coating and have ~20% of the DOP trapped inside the particles as evident from Figure S1 in Vaden et al. (2011). The surface coating evaporates in minutes and the relative amount of remaining DOP barely changes in 24 hours, as the particle evaporates layer-by-layer. These SOA particles evaporate slower than pure SOA particles. 4) DOP core coated with SOA that was clearly formed in the presence of DOP vapor. The particles have a DOP core, SOA coating, in which DOP is trapped, and a very thin DOP coating on the surface. The DOP coat evaporates in minutes and SOA evaporates identical to SOA with DOP trapped inside (type 3). The DOP core remains constant over 24 hours. 5) Pyrene (solid hydrophobic organic) coated pure SOA deposited by condensation of supersaturated pyrene vapors on top of pure SOA core. Pyrene forms a nodule on the SOA and the particles become aspherical. During evaporation, the nodule disappears in less than 2 hours, leaving no trace of pyrene. The particles become spherical again and evaporate just like pure SOA. 6) SOA formed in the presence of pyrene vapor. These particles have a very thin pyrene coating and pyrene trapped inside. The coating layer evaporates in minutes and the rest of the pyrene evaporates slightly faster than the SOA. SOA with trapped

pyrene evaporates much slower than pure SOA. As we said above, we looked at the effect of aging and found that in all cases it slows evaporation.

| type \ evaporation | ①                                                                                 | ②                                                                                 | ③                                                                                 | ④                                                                                  | ⑤                                                                                   | ⑥                                                                                   |
|--------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
|                    | pure SOA                                                                          | DOP coated SOA                                                                    | SOA formed in presence of DOP vapor                                               | SOA coated DOP                                                                     | pyrene coated SOA                                                                   | SOA formed in presence of pyrene vapor                                              |
| t=0                |  |  |  |  |  |  |
| 1 to 2 hours       |  |  |  |  |  |  |
| 24-hours           |  |  |  |  |  |  |

The reviewer seems to be confusing two very different particle mixing states: 1. Coated particles, where for example DOP resides only at the surface of SOA particles (type 2) in the Figure above. 2. SOA particles formed in the presence of DOP vapors, where DOP is incorporated in the SOA particle bulk due to adsorption on molecular clusters of SOA species during their nucleation, coagulation and growth (type 3 labeled as “SOA formed in the presence of DOP vapor”). Note that DOP does not get into particle bulk by diffusion from surface of “fully grown” SOA; rather it gets incorporated in the bulk as it is adsorbed on molecular clusters of SOA species during the process of their “growth”.

In fact the figure above shows that when DOP coats pure SOA particles, (type 2), it completely evaporates very fast at the same rate as pure DOP. This is exactly what the reviewer predicts above, for DOP on surface of SOA.

However, when DOP is incorporated within the bulk of SOA particles, it is present within the SOA particles bulk, cannot diffuse out, and persists even at the very long evaporation timescales of over 24 hours. The behavior with pyrene is the same. When pyrene is used to coat pure SOA

is evaporates fast, leaving pure SOA behind. When SOA is made in the presence of pyrene vapor, pyrene is trapped inside the SOA, diffusing out slowly.

SPLAT measurements have unambiguously resolved this sharp contrast in evaporation behavior of DOP and pyrene depending on whether DOP or pyrene is present on SOA particle surface or within particle bulk. This comparison again proves the extremely slow diffusion of DOP within the SOA particles. We use  $\alpha$ -pinene SOA and DOP and pyrene as examples, but have by now looked at other SOA precursors and other hydrophobic substances and their mixtures.

The values for the coating thickness given in Vaden et al. (2011) correspond to about 8% by volume of, say, DOP. Yet the authors observe 30% mass loss during the “fast” evaporation stage, with a significant fraction of DOP still remaining even at the end of the “slow” stage. This implies that at least 20% of SOA mass, despite its “high viscosity”, managed to get through the coating and into the gas, contradicting the slow diffusion claims.

This comment was just addressed above. Some of the DOP (~80% is on the surface and it evaporates fast and completely. 20% of the DOP is trapped inside for 24 hours as particle evaporates layer-by-layer with relative fraction of DOP unchanged (Vaden et al. (20110, Figure S1).

The authors also seem to suggest that polymerization may contribute to slowing down of, say, DOP evaporation. If DOP forms a coating, as they say in the paper, it apparently does not dissolve in the “highly viscous” SOA matrix. Then, how do molecules from this coating manage to get inside the matrix to be unable to evaporate anymore?

The reviewer has again completely misunderstood the data. DOP molecules do not get into the “highly viscous” SOA matrix by diffusion from surface of “fully grown” SOA. Rather, when SOA is formed in the presence of DOP vapors, these vapors adsorb to clusters of SOA particles as they are forming. As these clusters grow bigger in size by coagulation, the process traps the

DOP vapors within the SOA particle bulk. This is schematically shown in the figure above as type 3 particles.

In contrast, when we pass “fully grown” pure SOA particles over DOP vapors, the SOA particles are coated by DOP vapors. This is schematically illustrated as type 2 particles above and fully discussed by Vaden et al. (2010).

Even if we assume that they do, which would contradict the coating hypothesis, another problem arises. If there is enough time to get DOP inside the SOA during the long experiment/evaporation times, this time should be just as sufficient to get it back out. The authors’ claims, in this respect, are again self-contradictory.

Again, there is nothing self-contradictory in our claims here, as DOP did not get inside fully-grown SOA particles by diffusion. Rather, DOP adsorbs to SOA becoming trapped within the SOA bulk during particle formation and growth. This is not due to diffusion of DOP within SOA. See discussions above for more details.

If these contradictions are not sufficiently convincing, please check p. 20114, l.10: “Similarly, we recently found that pyrene, a solid polyaromatic hydrocarbon (PAH), does not dissolve in pure  $\alpha$ -pinene SOA and forms instead a localized nodule on top of the SOA particle.” So, pyrene forms a localized nodule on top of SOA and yet the polymers inside the SOA particle somehow convince it not to evaporate. I wish the authors could provide a hypothesis for the mechanism underlying these observations.

The explanation for pyrene is same as for DOP. The reviewer has again confused the two very different mixing states: Particles type 5 and 6 in the figure above.

Type 5 particles have a localized nodule of pyrene on the surface of “fully grown” size-selected pure SOA particles. This pyrene nodule was deposited by condensation of supersaturated pyrene vapors on top of a pure SOA core. In type 6 particles pyrene is incorporated within bulk of SOA due to adsorption of pyrene on molecular clusters of SOA during SOA formation, leading to the trapping of pyrene within SOA. In the second case (type



6), the concentration of pyrene vapor in the reaction chamber was at or below pyrene equilibrium vapor pressure.

Again, the Figure above schematically shows that when pyrene forms a localized nodule on surface of fully-grown pure SOA particles (particles type 5), it evaporates very fast, leaving no trace, and its evaporation behavior is the same as what would be expected for pure pyrene. The evaporation of the remaining SOA core then follows the evaporation of pure SOA. On the other hand, type 7 particles represent the case in which pyrene gets incorporated within the bulk of SOA particles during their formation. Please note again that this pyrene did not diffuse from the surface. It was incorporated within bulk of SOA, as pyrene vapors were present during SOA formation. ~7% of the pyrene is found on/near the particle surface and evaporates very fast, while the rest (~93%) is trapped inside and diffuses very slowly through the viscous SOA during particle evaporation. Figure S1 in Vaden et al. (2011) shows that the relative intensity of the pyrene parent ion peak in the type 6 particles decreases slowly such that ~50% of it remains even after 25 hours of evaporation. In addition, the presence of pyrene within the SOA bulk has significant effect on the evaporating rates of these particles (type 6, for clarity). – These particles lose only 20% of their volume (~7% of their size) after 25 hours of evaporation.

One may ask about the significant amounts of DOP and pyrene (20–50% of the initial mass) remaining in the “second stage” of evaporation (see Fig.S1 in the supplement to Vaden et al. (2011)). However, one should also note that the authors in actuality do not show the DOP and pyrene concentrations, but rather the mass-spec peak abundances, which they use as a proxy for these substances. Nothing is said about the abundance of the corresponding peaks in the pure SOA or whether or not any corrections were made for these potentially interfering peaks. Even if they were corrected for, it is still possible that chemical reactions (which were apparently still ongoing) were producing peaks with the same  $m/z$ .

First, it is a common practice to follow the relative intensity of the characteristic peaks to monitor changes in their abundance. In addition, we show how particle volume is changing with the evaporation time.

Most importantly, here again, the referee provides some completely unsubstantiated speculations about some reactions that continue to form DOP and pyrene peaks. Note, for example, that Figure S1 in Vaden et al. (2011) shows changes in the relative intensity of pyrene parent ion peak as function of evaporation time, so it is not clear which “apparently still ongoing” reactions reviewer is referring to. This comment by the referee is baffling.

In the experiments, in which DOP or pyrene were deposited on the surface of pure SOA (particles type 2 and 5), the coating thicknesses were such that the volume of the coating substance was a few times larger than volume of the SOA core. The temporal evolution of the mass spectra of these particles shows that the DOP and pyrene peaks disappear completely after ~2 hours of evaporation and the remaining SOA core follows evaporation kinetics of pure SOA. In contrast, Figure S1 in Vaden et al. (2011) shows very different temporal evolution for particles type 3 and 6 that were formed in the presence of DOP or pyrene vapors. Both, the evaporation rates and mass spectra exhibit very different temporal behavior. Vaden et al. (2010) described in detail the mass-spectral signatures at different laser powers for pure SOA, pure DOP, and layered SOA/DOP particles with two reversed morphologies and different coating thicknesses.

Similarly, for pyrene – when pyrene was absent in the experiment, the intensity of its parent ion peak ( $m/z=202$ ) was zero. In the presence of even small amounts of pyrene, it is high due to its high ionization efficiency.

Since the studies described in the two PNAS papers we conducted a large number of experiments using different SOA precursors and different hydrophobic organics. They all behave remarkably similar and most importantly, similar to the ambient SOA particles we characterized. In all cases particles do NOT reach equilibrium with the gas phase even after they evaporate for over a day under organic vapor-free environment.

In the present manuscript, we provided simple evidence-based explanations for all our observations and refrained from unsupported speculations.

Another self-contradiction to the high viscosity claims can be found in the paragraph starting at the end of p.20115 of the current paper. "The authors state that their recent unpublished calculations of diffusivities in SOA lead to SOA particle coalescence times (i.e. to form a

spherical particle after two particles coagulate) “that are on the order of seconds to minutes”. So, their own experimental data suggests that seconds or minutes could be sufficient to move the bulk of the material, not just a few molecules, on length scales of the particles size.”

Bulk movement of a fluid can be much faster than diffusion through it. Two particles drawn together by surface tension can coalesce in far shorter time than something on the inside can diffuse out. It seems that the reviewer confuses the idea that volatiles (e.g., pyrene) escape by diffusion through a viscous SOA with the idea that the particle shape changes by diffusion of the molecules making up the balance of the SOA. Coalescence is not driven by diffusion of the SOA (which would be quite slow), but by bulk movement driven by surface tension.

"If one is not convinced by this argument that this is a contradiction, let us estimate the diffusion coefficients that would explain such coalescence times using Friedlander and Wu (1994) formula

$$\tau_c = \frac{kTR^3}{16v_m D\sigma} \quad (2)$$

in which  $\tau_c$  is the characteristic coalescence time,  $k$  is the Boltzmann constant,  $R$  is particle radius,  $v_m$  is molecular volume,  $\sigma$  is the surface tension, and  $D$  is the diffusion coefficient. Taking  $R = 100$  nm,  $\sigma = 30$  mN/m, and estimating  $v_m$  as  $M_w/(\rho N_A)$  (in which  $M_w = 150$  g/mol,  $\rho = 1$  g/cm<sup>3</sup>,  $N_A = 6.02 \times 10^{23}$ ), we obtain values for the diffusion coefficient  $D$  being  $3.45 \times 10^{-14}$  m<sup>2</sup>/s, if  $\tau_c = 1$  s, and  $5.75 \times 10^{-16}$  m<sup>2</sup>/s, if  $\tau_c = 1$  min. Characteristic diffusion times in the particle phase are given by (Seinfeld and Pandis, 2006):

$$\tau_d = \frac{R^2}{\pi^2 D} \quad (3)$$

Thus, the above coalescence timescales correspond to timescales of diffusion inside the particles of 29 ms and 1.76 s. And yet the very same paragraph is started with the “extremely slow diffusion” mantra. If seconds are “extremely slow”, then I do not know what would be “fast” in comparison to the atmospheric life times of the order of a week. In fact, the authors statements are consistent with SOA particles that are indeed liquid and with characteristic diffusion time scales in the particles that are negligible!

The cited model by Friedlander and Wu (1994) was developed to apply to solids, which change shape due to diffusive hopping of molecules; it does not necessarily apply to situations of bulk flow in fluids. Moreover, by using this model the referee assumes that the average (self) diffusivity of the molecules making up the solid is the same as the probably much higher diffusivity of volatiles through the SOA.

A more appropriate model (i.e., the physics make sense while the results comport with experimental observations) gives the fluid viscosity,  $\eta$ , as  $\sigma\tau/R$  and then uses the Stokes-Einstein relation to derive the diffusivity of volatiles through this fluid. Such a model allows for both coalescence times short enough to be consistent with experimental data and diffusion times on the order of many hours as also seen in the experiments.

This point provides another illustration of the differences between the two approaches, the referee's and ours. The referee chose to use intuition to come to his/her first conclusion and then to fortify his/her flawed argument with a quantitative argument using the wrong equation. In our effort to understand how ALL SOA properties (evaporation rates, mass spectra, morphologies, shape, diffusivity, viscosity, and coalescence times) come together to yield a consistent picture, we decided to consult with Dr. Evan Abramson from the University of Washington, who has dedicated his research career to developing new methods for measuring the viscosity of substances under wide range of conditions. With him we developed the understanding of the relationship between our measured data and the properties of the substances we investigate.

#### **4 What about the “evidence” from other studies?**

The above discussion shows that all (please note – all) of the experimental “evidence” for the “highly viscous, non-partitioning SOA” provided by the authors is, unfortunately, deeply flawed.

Thus far, we have not seen a single flawed argument. Each point the referee attempted to label as flawed was fully explained and was shown to be the result of the referee making flawed arguments.

However, the authors list a few recent studies, which they say confirm their statements. For example, Virtanen et al. (2010) reported bouncing of particles in Electrical Low Pressure Impactor. Salcedo et al. (2006, 2007) reported bouncing of SOA particles in the AMS. While I do not pretend to make any definitive conclusions, I would like to point out that the two instruments share one common feature: expansion of air into (near) vacuum, which could lead to particle freezing due to adiabatic cooling, which potentially could explain the bouncing. Whether or not this is the case I do not know, but want to point out that this makes this additional evidence rather indirect and quite inconclusive.

Before we discuss this comment, we note that the reviewer chooses to forget/ignore the Cappa and Wilson (2011) paper that describes work conducted at high temperature. Why?

Compare this referee's comment on the Virtanen et al. (2010) paper to the comment taken from the Shiraiwa et al. (2011) PNAS paper (with Ulrich Pöschl and Thomas Koop, as co-authors). "Virtanen et al. (2010), however, showed that biogenic SOA particles formed in plant chamber experiments and in new particle formation events over boreal forests can adopt an amorphous semisolid state, which is in line with the observed presence of oligomers or other organic compounds with high molecular mass and low volatility in SOA (Hallquist et al., 2009; Kroll and Seinfeld, 2008) . The same paper references our Vaden et al. (2011) paper as well. One dismisses the data by unsubstantiated speculation, the other points to the fact that it is consistent with many other published data.

This represents a rather reproducible pattern, when the referee does not like published data he/she casts doubt on it by speculation. Consider the following logic used by the reviewer: (1) Parameters derived from smog chamber data, assuming the particles are liquid, fit smog chamber data. (2) It means that these particles must be liquid, because the model fit the data. (3) The derived parameters do not fit the experimental data. (4) No problem, referee suggests that smog chamber experiments have huge uncertainties and their results should not be used.

The case here is not different. In this manuscript and in our previous papers we present results for particle shape measurements. In this manuscript we say that ambient SOA particles

mixed with sulfate are spherical. In a previous paper we described measurements of SOA-coated NaCl particles, which we also found to be spherical. We are the only group that characterized SOA particle shape showing them to be spherical. We discuss in this manuscript the sphericity of coagulated SOA particles. Each of these examples was carried out with SPLAT that uses an inlet lens identical to that used in the AMS in Salcedo et al. (2007; 2006). The referee read at least some of these, yet chose to ignore the information and speculate. There is an enormous amount of work put into our studies and their interpretation. We worried about particle freezing and evaporation in the lens, performed experiments on the subject and published the results (Zelenyuk et al., 2006). We also performed heat transfer calculations that show that at the 2 torr pressure inside the lens particles return to room temperature. Furthermore, a number of studies that use AMS reported significantly (3-4 times) higher collection efficiency for the particles sampled at high relative humidity, due to their liquid phase and reduced bounce. This is yet another proof that these particles do not freeze. The referee dismisses all this hard work by unsubstantiated statement like the one above. Something here seems unreasonable.

The lowest pressure in ELPI, used in the Virtanen et al. (2010) paper, is over 30 times higher than in the aerodynamic lens. There are no supersonic expansions here. The authors of this study examined the bouncing behavior of both SOA and liquid droplets, to show that the two behave very different under the same experimental conditions. This comment by the referee, like all other speculations, turns out to be false.

The point is that we work hard to get at the information by running careful experiments and modeling. We try to find explanations for our observations to take into account **all** available data.

On the other hand there have been countless studies in the past decades that show that many SOA systems follow, or at least can be approximated to a good degree by the Pankow partitioning theory. The authors appear to ignore much of the previously published evidence that is inconsistent with their interpretations, such as the Asa-Awuku et al. (2009) study discussed earlier.

That is another interesting comment. Earlier in the review the referee did not just cast doubt on all smog chamber experiments, but out-right dismissed their results. He/she even suggested

ignoring these data and using our evaporation data, which the referee claims also have problems, although it is unclear what that means, to derive volatility distributions. Here the referee chides all who accept the idea that these particles are not liquids, which includes Ulrich Pöschl, Virtanen, Cappa, us, and others, for ignoring fits to smog chamber results.

Cappa and Wilson (2011) present a new paradigm for SOA, in which they assume SOA to be non-liquid, not governed by the traditional partitioning theory, and demonstrate that their model can be used to reproduce smog chamber data. Does the referee conclude that SOA cannot be liquid because smog chamber data can be fit under the assumption that SOA rapidly hardens?

The only experimental paper the referee offers as proof that these particles are in the liquid phase is the Asa-Awaku et al. (2009) study, in which they generated and analyzed mixed SOA/POA particles to conclude that they are in a single phase. The referee concludes that a single phase solution can form only if the SOA is in liquid phase.

Is that really true?

Consider NaCl particles at zero RH, which we all agree are solid. Now add water vapor, increasing RH to above the NaCl deliquescence point, and solution droplets form. The water and NaCl form a single phase. That clearly is not proof that NaCl is liquid. All it says is that NaCl is soluble in water. ,

If SOA dissolves in POA, as claimed in Asa-Awaku et al. (2009), then the SOA/POA story could be as simple as that of NaCl and H<sub>2</sub>O; highly viscous SOA mixed with liquid POA “solvent” and forms single-phase particles.

As I have shown above, the data presented by the authors, despite their claims, actually favors the assumption of liquid SOA, which is well-mixed unless there is phase separation due to large differences in polarity between its components.

Nowhere in the referee’s comments is there a note that shows that our data support the notion that SOA is liquid. Asa- Awuku et al. (2009) are the only experimental data the referee attempted to cite as support for liquid SOA, and as we showed above, his/her logic could be used to

conclude, that NaCl is a liquid. It is not sufficient to state that our data favors liquid SOA, one has to point to the data and explain how it fits the assumption of liquid SOA.

When he/she fails to fit our data based on the assumption that these particles are liquid, the referee concludes “there is a problem with the data”. Therefore, our work proves SOA is a liquid, once one discards the data.

5 One-way condensation model approach Given the above discussion, it is obvious that the modeling approach proposed in this paper has no theoretical or experimental foundation.

This statement is very confusing. Throughout this review, the referee agreed that SOA evaporation takes days to come to equilibrium. Nowhere in the entire review is there a comment suggesting that our data support the assumption used by all SOA modeling that gas/particle equilibrium is maintained at all times. To implement the partitioning theory there is need to assume that the system establishes instantaneous equilibrium.

Moreover, the referee trusts our data to the point that he/she suggests replacing published fits to smog chamber data, which clearly attribute a much higher fraction of organics to higher volatility bins, by volatility distributions, generated using our evaporation data instead.

We conclude that the referee must agree that evaporation takes days and that SOA is comprised of very low volatility compounds as per his/her Figure 1.

It looks like we all agree that very little SOA evaporates in the atmosphere in 24 to 48 hours (the referee sure seems to), so then what is wrong with putting it into models?

One can, of course, argue that a one-way partitioning could be applicable in general, if the condensing species reacts rapidly with the particle producing significantly less volatile material.

This is again a very confusing statement. Above, the referee stated, “There have been countless studies in the past decades that show that many SOA systems follow, or at least can be approximated to a good degree by the Pankow partitioning theory.” Here the idea of changing it to reactive uptake is discussed as a reasonable approach. Is the referee suggesting that it might be true that these SOA particles are not liquids that follow Pankow partitioning theory? Should all



these papers be ignored or treated as evidence? But then again the referee stated above that no smog chamber studies are reliable. The simple answer is that in our opinion, which is based not on speculation, but on solid data: there is clearly need to change our picture of how SOA is made and how it evolves in the atmosphere. Again, this conclusion is based on data obtained by us, some of which is published, and some of which is more recent and hence not published yet, and supported by recent work from other groups. Consider Cappa and Wilson (2011), for example, they offer a new SOA formation mechanism that tries to address the non-liquidity of SOA and reconcile it with the decades of smog chamber measurements. The road is long and arduous. It will take some time to get there As of now, James Pankow himself is our co-author on the manuscript by Barbara Finlayson-Pitts group (under review in Nature-Geosciences) that also points to non-liquid like and non-equilibrium SOA behavior.

The reviewer, however, seems to dismiss any experimental evidence that does not fit his picture of liquid SOA that is in the thermodynamic equilibrium with the gas phase.

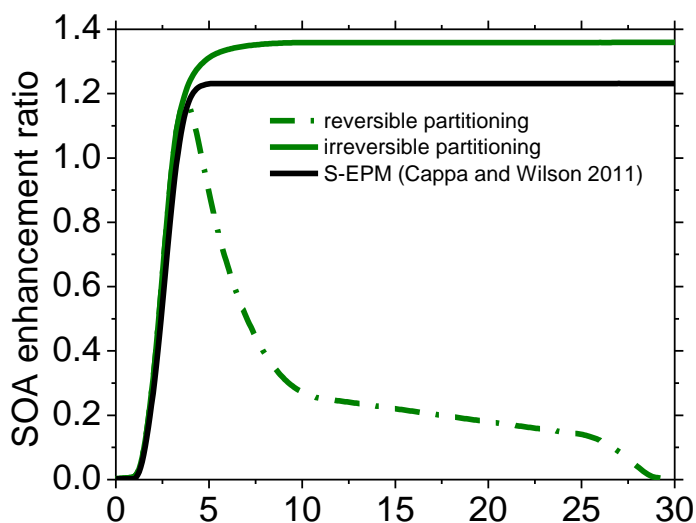
This, however, would require a modification to the chemical mechanisms used in the model, not to mention the need for their experimental verification. Since this is clearly not the subject of this paper, I will set it aside and instead point out some of the remaining problems with the paper.

This is a very interesting comment, whose content is not new for us. We understand that SOA formation has to be modified as well. We mention this point in the paper. Cappa and Wilson (2011), for example, developed a new model for SOA formation (that fits the smog chamber data), in which SOA forms and hardens, rapidly converting from an absorbing form to a non-absorbing form. Our goal was to investigate the effect of slow SOA evaporation on the kinetics of particle evolution. Our goal was not to fit Mexico City SOA. We decided that a simple approach would be to use a model that was tuned/parameterized to fit field data, adopt its method for making SOA, and let the SOA evolve under instantaneous equilibrium conditions to compare its results with non-evaporating SOA. This approach limited, by design, the scope of the study to evaporation.

Just a comment on the SOA formation model we adopted: Current smog-chamber derived parameterizations and the recently developed VBS approach account for SOA formation due to semi-volatile/intermediate-volatility organic compounds (SVOC/IVOC) from several unidentified or missing anthropogenic and biomass burning precursors in addition to biogenic SOA (Robinson et al., 2007). These parameterizations do a reasonable job predicting SOA formation in the smog chambers at short timescales of a few hours, but are subject to several uncertainties when applied at much longer timescales of days in the real atmosphere. These uncertainties include physical and chemical evolution of SOA in the atmosphere, which have not been comprehensively evaluated. The new findings about SOA properties and evaporative behavior explains the extremely “low effective volatilities” observed for both freshly formed and aged-processed SOA in the atmosphere (Cappa and Jimenez, 2010; Pierce et al., 2011). These “low effective volatilities” are due to diffusion limitations of higher volatility organics trapped within the SOA matrix. Once these higher volatility species reach the surface of SOA they rapidly evaporate in vapor-free environments completely in agreement with expected partitioning behavior, as our experimental data show for surface pyrene, DOP, DOS and a variety of other organics. To the best of our knowledge, our data are the first ever to experimentally measure the diffusivity of hydrophobic organics within the SOA matrix, and we expect these data to be of immense scientific value. Pankow (1994) clearly stated that application of absorptive partitioning theory to OA is based on the fundamental assumption that all organic species form a diffusively well-mixed solution in SOA. Our data clearly showed that diffusivity within SOA matrix is extremely low and hence the absorptive partitioning theory does not govern the atmospheric evolution of SOA.

Most recently, we added to our box model, a simulation of SOA formation based on the sequential partitioning model (S-EPM) developed and presented in Cappa and Wilson (2011). See, for example, the figure below. This new model fits the smog chamber data and thus produces results that are very close to those produced by the formation model that was originally adopted in this manuscript. Most importantly, it is consistent with our new SOA picture: non-liquid SOA that is not governed by equilibrium partitioning theory and evaporates so slow that evaporation can simply be ignored. The important assumption implicit in both modeling approaches: the irreversible partitioning approach in our paper and S-EPM model by Cappa and

Wilson (2011) is that timescales for conversion of SOA to diffusion-limited or non-volatile SOA are much shorter than other atmospheric processes, which is justified based on experimental data i.e. SOA residence times of few minutes in experimental system of Cappa and Wilson (2011). In addition, while there is small difference between the two models in terms of amount of non-volatile SOA formed, both approaches clearly demonstrate the large differences in the properties of SOA as compared to the traditional reversible partitioning models during SOA evaporation.



**Comparison to Cappa & Wilson SOA formation model for 75% fragmentation (corresponding to Figure 4b in our manuscript)**

For example, the data presented in the paper show that the one-way approach is clearly wrong, because a significant fraction of SOA (namely, 40%) in the reported experiments evaporates within two hours (p.20116, l.8).

The reviewer misses some very important points here.

1. The reviewer chooses to ignore the ambient data, in which under organic vapor-free conditions evaporation is much slower. It looks very much like the evaporation of

SOA formed in the presence of pyrene or a mixture of hydrophobic organics. These particle types lose less than 20% of their mass by evaporation in 24-hours.

2. Most of that loss is within the first 100 minutes or so. Later evaporation becomes very slow.
3. All our experiments look at evaporation of SOA under vapor-free conditions. In the ambient atmosphere, where dilution rates are slow, there are always organic vapors present surrounding the SOA particles, hence evaporation in the ambient conditions is expected to be slower than what we observed.
4. Consider that the observed loss of 20% of volume for the 100 nm ambient particles translates to a 6 nm change in diameter. Hence, our approximation says that in the real atmosphere, where evaporation is even slower, it can to first degree be ignored.
5. When we use these data or the data produced by SOA formed in the presence of pyrene or a mixture of hydrophobic organics we find that more than 80% of the particle must be comprised of organics with  $C^*$  smaller  $\sim 2 \times 10^{-3} \mu\text{g}/\text{m}^3$ . In other words, they nearly stop evaporating.
6. Evaporation rate slows with time due to aging.
7. Are other approximations, like 100% functionalization, instant equilibration, a single value of OH rate constant for all organics, and others, are accurate, or are they worse? Moreover, we provide direct information on the degree of approximation.
8. It is true that significant fraction of pure  $\alpha$ -pinene SOA evaporates after 24 hours in our organic vapor-free conditions. However, this is still orders of magnitude slower than instantaneous. Moreover, in our modeling work, we are focused on ambient SOA. Pure  $\alpha$ -pinene SOA in the laboratory clearly evaporates losing 75% of its initial volume in 24 hours, but aged SOA particles with trapped hydrophobic pyrene vapors (pyrene vapors get adsorbed on molecular cluster of SOA during formation and get trapped in bulk of SOA) lose just 11% of their volume in 24 hours (Vaden et al., 2011). In addition, 100 nm ambient SOA particles containing 88% organic mass characterized during CARES field campaign in Sacramento, CA in June 2011, showed an evaporation behavior similar to SOA with trapped pyrene, and lost just

~17% of their volume in 208 min of evaporation under organic- vapor-free conditions and at later times evaporation significantly slows down.

There is a very strange argument given for the necessity of high accommodation coefficient during condensation based on the modeled growth rate of 10 nm particles. An arbitrary difference of 1  $\mu\text{g}/\text{m}^3$  in the gas concentration is chosen to drive condensation. Why not 0.001 or 100, why equal for all volatility bins?

The 10 nm particles in this calculation were assumed to be non-volatile. Thus, there was just 1 non-volatile bin, not many bins as the reviewer thinks. Assuming non-volatile SOA particles during nucleation and growth of freshly formed SOA is also supported by recent work by Pierce et al. (2011), where they found volatility of freshly nucleated SOA was less than  $10^{-3}$  to  $10^{-2}$   $\mu\text{g}/\text{m}^3$ .

From the work of Pierce et al. (2011), we estimated average concentrations of condensable precursors based on observed mean growth rate of  $3 \text{ nm hr}^{-1}$  for 3 nm initial size particles, and the measured change in total organic aerosol mass ( $\sim 0.5$  to  $1 \mu\text{g m}^{-3}$ ), to be even smaller than  $1 \mu\text{g m}^{-3}$ . Our analysis of their treatment yields condensation coefficients much higher than 0.001, which is in sharp contrast to evaporation coefficients  $\sim 0.001$  or lower (Figure 2a), required to explain our data. The rationale was that once all condensable organics eventually condense, they would result in much higher SOA than observed, if one uses a condensation coefficient of 0.001 to calculate the amount of condensable organics for the observed growth rate. We confirmed the logical validity of this approach through personal communications with Dr. Jeffrey Pierce who is the main author in that study. Figure 2b is used just to demonstrate the large effects of condensation coefficients on growth of ultrafine particles, which is also reflected in the detailed model calculations by Pierce et al. (2011). In addition, Presto and Donahue (2006) used high resolution PTR-MS and SOA yield measurements and showed that nucleation/condensation kinetics were not rate limiting even at low organic concentrations in the smog chamber.

Since 10 nm initial particle size is used, the growth, at least initially, is in the free molecular regime and the growth rate is proportional to the product of the excess vapor concentration

and the accommodation coefficient. The effect of the two on the growth rate can not be separated. Thus, after making an arbitrary assumption about the driving force for condensation one can not draw any meaningful conclusion about the accommodation coefficient.

We agree that effects of excess vapor concentration and the accommodation coefficient on particle growth rate cannot be separated just by looking at growth rate of non-volatile SOA particles. However, in light of our calculations, based on the Pierce et al. (2011) modeling study, our assumptions of  $1 \mu\text{g m}^{-3}$  constant driving force is on the higher end of observed growth rate of freshly nucleated particles due to organics, as discussed above. Finally the point of Figure 2b is that condensation coefficients are much higher than evaporation coefficients which are also supported by both smog chamber and field studies of particle nucleation and growth (Pierce et al., 2011; Presto and Donahue, 2006).

The effects of free-molecular and transition regimes on particle growth are reasonably captured by equation (1) presented in the Supplementary Information. In this work, we assumed a constant excess vapor concentration of  $1 \mu\text{g m}^{-3}$  and evaluated the extreme importance of accommodation coefficient on particle growth rate which has also been well documented by a recent study by Pierce et al. (2011).

I do not understand the purpose of the activity coefficients used in the model. The VBS approach explicitly assumes that activity coefficients, if they are independent of the mixture composition, are incorporated into  $C_{\text{sat}}$  values of the volatility bins (Donahue et al., 2006). The authors use an arbitrary, constant activity coefficient of 0.2, which simply means that they shift the volatility bins by a factor of 0.2 towards lower volatility. There is no surprise then that the modeled OA concentrations go up. It would be also interesting to hear justification for the value of 0.2. Cappa et al. (2008) reported activity coefficients that were “ $< 1$  for the lower-molecular-weight diacids but  $> 1$  for the heavier diacids.” Saleh and Khlystov (2009) have shown that binary mixtures of diacids could exhibit activity coefficients values above 1, while adipic acid in an ambient aerosol matrix showed activity coefficients below 1, all significantly dependent on the mixture composition.

As we have acknowledged earlier, that a fully robust modeling approach which accounts for observed near-irreversible partitioning of SOA needs to account for several processes including reactive uptake and oligomerization in the particle phase, as also shown by several recent studies (for example, Pfrang et al., 2011; Pierce et al., 2011). In the experimental work by Vaden et al. (2011), we saw that complex molecular interactions with trapped hydrophobic organics leads to lower evaporation rates and higher SOA formation yields as compared to yields measured in the absence of these organics. Cappa et al. (2008) suggest that C3-C7 diacids are most relevant to ambient loadings and Figure 2A in Cappa et al. (2008) shows activity coefficients lower than 1 for most of these atmospherically relevant diacids. In any case, the assumption of activity coefficient of 0.2 is basically to show how one could “adjust” the vapor pressure of semi-volatile organic compounds to account for these complex molecular interactions between the PAHs and SOA. It is also possible to view this correction as a method for taking into account reactive uptake that leads to incorporation of high volatility organics in the particle phase as suggested by several studies (Cappa et al., 2008; Hallquist et al., 2009; Kroll and Seinfeld, 2008). By no means, are we claiming that this low activity coefficient should be universally applied to models. In contrast, we are suggesting revision of all current model formulations accounting for reactive uptake of organic species in particle phase.

It was an example meant to investigate the effect of evaporation on SOA formed under these conditions. Again, the modeling study focuses on evaporation in a comparative study.

The modifications to the aerosol partitioning scheme, such as one-way condensation and an arbitrary shift of the VBS to lower volatilities by using an activity coefficient of 0.2, unsurprisingly cause the model to predict higher OA concentrations. Setting aside the lack of any justification for these modifications, there is still no proof of the model performance, because there is no experimental verification provided in the paper.

Again, in sharp contrast to the referee’s comments, we have extensively defended all experimental claims made in this manuscript and already published work. 1-way condensation is an approximate model approach to account for observed near-irreversible particle formation and very similar to the Cappa and Wilson (2011) approach that assumes that “the material that

condensed to the particle phase is “lost” from the system and does not influence partitioning in the next step, i.e. is converted to non-absorbing (non-partitioning) material”. Lower activity coefficient is just used to explore how reactive uptake of higher volatility species affects particle evolution as compared with traditional reversible partitioning approaches. Future model formulations need to replace current models with irreversible reactive uptake for SOA particle formation in the atmosphere.

- Cappa, C. D., Lovejoy, E. R., and Ravishankara, A. R.: Evidence for liquid-like and nonideal behavior of a mixture of organic aerosol components, *Proc. Natl. Acad. Sci. U. S. A.*, 105, 18687-18691, 10.1073/pnas.0802144105, 2008.
- Cappa, C. D., and Jimenez, J. L.: Quantitative estimates of the volatility of ambient organic aerosol, *Atmos. Chem. Phys.*, 10, 5409-5424, 10.5194/acp-10-5409-2010, 2010.
- Cappa, C. D., C. C. D., and Wilson, K. R.: Evolution of organic aerosol mass spectra upon heating: implications for OA phase and partitioning behavior, *Atmos. Chem. Phys.*, 11, 1895-1911, 10.5194/acp-11-1895-2011, 2011.
- Chung, S. H., and Seinfeld, J. H.: Global distribution and climate forcing of carbonaceous aerosols, *J. Geophys. Res.-Atmos.*, 107, 4407 10.1029/2001jd001397, 2002.
- Grieshop, A. P., Donahue, N. M., and Robinson, A. L.: Is the gas-particle partitioning in alpha-pinene secondary organic aerosol reversible?, *Geophys. Res. Lett.*, 34, L14810 10.1029/2007gl029987, 2007.
- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prevot, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155-5236, 2009.
- Heald, C. L., Jacob, D. J., Park, R. J., Russell, L. M., Huebert, B. J., Seinfeld, J. H., Liao, H., and Weber, R. J.: A large organic aerosol source in the free troposphere missing from current models, *Geophys. Res. Lett.*, 32, L18809 10.1029/2005gl023831, 2005.
- Kroll, J. H., and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, *Atmos. Environ.*, 42, 3593-3624, 10.1016/j.atmosenv.2008.01.003, 2008.
- Pankow, J. F.: An absorption model of the gas aerosol partitioning involved in the formation of secondary organic aerosol *Atmos. Environ.*, 28, 189-193, 1994.
- Pathak, R. K., Presto, A. A., Lane, T. E., Stanier, C. O., Donahue, N. M., and Pandis, S. N.: Ozonolysis of alpha-pinene: parameterization of secondary organic aerosol mass fraction, *Atmos. Chem. Phys.*, 7, 3811-3821, 2007.
- Pfrang, C., Shiraiwa, M., and Poschl, U.: Chemical ageing and transformation of diffusivity in semi-solid multi-component organic aerosol particles, *Atmos. Chem. Phys.*, 11, 7343-7354, 2011.
- Pierce, J. R., Riipinen, I., Kulmala, M., Ehn, M., Petaja, T., Junninen, H., Worsnop, D. R., and Donahue, N. M.: Quantification of the volatility of secondary organic compounds in ultrafine particles during nucleation events, *Atmospheric Chemistry and Physics Discussions*, 11, 14495-14539, 2011.
- Presto, A. A., and Donahue, N. M.: Investigation of alpha-pinene plus ozone secondary organic aerosol formation at low total aerosol mass, *Environ. Sci. Technol.*, 40, 3536-3543, 10.1021/es052203z, 2006.



- Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking organic aerosols: Semivolatile emissions and photochemical aging, *Science*, 315, 1259-1262, 10.1126/science.1133061, 2007.
- Salcedo, D., Onasch, T. B., Dzepina, K., Canagaratna, M. R., Zhang, Q., Huffman, J. A., DeCarlo, P. F., Jayne, J. T., Mortimer, P., Worsnop, D. R., Kolb, C. E., Johnson, K. S., Zuberi, B., Marr, L. C., Volkamer, R., Molina, L. T., Molina, M. J., Cardenas, B., Bernabe, R. M., Marquez, C., Gaffney, J. S., Marley, N. A., Laskin, A., Shutthanandan, V., Xie, Y., Brune, W., Leshner, R., Shirley, T., and Jimenez, J. L.: Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite, *Atmos. Chem. Phys.*, 6, 925-946, 2006.
- Salcedo, D., Onasch, T. B., Canagaratna, M. R., Dzepina, K., Huffman, J. A., Jayne, J. T., Worsnop, D. R., Kolb, C. E., Weimer, S., Drewnick, F., Allan, J. D., Delia, A. E., and Jimenez, J. L.: Technical Note: Use of a beam width probe in an Aerosol Mass Spectrometer to monitor particle collection efficiency in the field, *Atmos. Chem. Phys.*, 7, 549-556, 2007.
- Shiraiwa, M., Ammann, M., Koop, T., and Poschl, U.: Gas uptake and chemical aging of semisolid organic aerosol particles, *Proc. Natl. Acad. Sci. U. S. A.*, 108, 11003-11008, 10.1073/pnas.1103045108, 2011.
- Stanier, C. O., Pathak, R. K., and Pandis, S. N.: Measurements of the volatility of aerosols from alpha-pinene ozonolysis, *Environ. Sci. Technol.*, 41, 2756-2763, 10.1021/es0519280, 2007.
- Tsimpidi, A. P., Karydis, V. A., Zavala, M., Lei, W., Molina, L., Ulbrich, I. M., Jimenez, J. L., and Pandis, S. N.: Evaluation of the volatility basis-set approach for the simulation of organic aerosol formation in the Mexico City metropolitan area, *Atmos. Chem. Phys.*, 10, 525-546, 2010.
- Vaden, T. D., Song, C., Zaveri, R. A., Imre, D., and Zelenyuk, A.: Morphology of mixed primary and secondary organic particles and the adsorption of spectator organic gases during aerosol formation, *Proc. Natl. Acad. Sci. U. S. A.*, 107, 6658-6663, 10.1073/pnas.0911206107, 2010.
- Vaden, T. D., Imre, D., Beranek, J., Shrivastava, M., and Zelenyuk, A.: Evaporation kinetics and phase of laboratory and ambient secondary organic aerosol, *Proc. Natl. Acad. Sci. U. S. A.*, doi: 10.1073/pnas.1013391108, 2190-2195, 2011.
- Virtanen, A., Joutsensaari, J., Koop, T., Kannosto, J., Yli-Pirila, P., Leskinen, J., Makela, J. M., Holopainen, J. K., Poschl, U., Kulmala, M., Worsnop, D. R., and Laaksonen, A.: An amorphous solid state of biogenic secondary organic aerosol particles, *Nature*, 467, 824-827, 10.1038/nature09455, 2010.
- Widmann, J. F., and Davis, E. J.: Evaporation of multicomponent droplets, *Aerosol Sci. Technol.*, 27, 243-254, 10.1080/02786829708965470, 1997.
- Zelenyuk, A., Imre, D., and Cuadra-Rodriguez, L. A.: Evaporation of water from particles in the aerodynamic lens inlet: An experimental study, *Anal. Chem.*, 78, 6942-6947, 10.1021/ac061184o, 2006.
- Zelenyuk, A., Ezell, M. J., Perraud, V., Johnson, S. N., Bruns, E. A., Yu, Y., Imre, D., Alexander, M. L., and Finlayson-Pitts, B. J.: Characterization of organic coatings on hygroscopic salt particles and their atmospheric impacts, *Atmos. Environ.*, 44, 1209-1218, 10.1016/j.atmosenv.2009.11.047, 2010.