Major Problems with the Referee's Comments Remain

In the original review, the referee laid-out a very lengthy list of problems he/she had with all experimental data that did not agree with his/her unsubstantiated assumptions of what SOA particles look like. As we showed in our reply, the problems are not with the data, but rather with the referee's severe misinterpretation of the data, with his/her flawed speculations about how the data were acquired, and faulty suggestions about artifacts that he/she thought might affect the data. The referee misinterpreted our and others experimental results to conclude that the data prove his assumptions correct, to later dismiss the same data claiming that "there is a problem with the data." We methodically addressed his/her long list of arguments and showed them all to be wrong.

Here the referee sets the stage by referring to a scientific issue as a fight between two camps: "the slow evaporation / high viscosity camp, and the liquid particles / fast evaporation camp." We do not "define two camps", and choose instead to focus our attention on the data, data interpretations, and their implications. As in the first review, the referee ignores nearly all the evidence we presented in the paper and in the reply, misinterprets the data he/she chooses to look at, and disposes of all supporting data from other groups by labeling it indirect. He/she puts forward a new theory, in which we prevent particles from reaching equilibrium by removing the gas phase organics in our evaporating chamber. In other words, in his/her point of view slow evaporation is not a property of these particles, but a reflection of some sort of a trick we play. (Removal of gas-phase organics with denuders is commonly used to measure particle volatilities/vapor pressures.)

The referee states that the assumption of equilibrium is derived from partitioning theory. While this makes it seem as if the assumptions are nothing more than an extension of a sound theory, it is clearly not the case. Assumptions are made, due to lack of data, to justify application of a particular theory and the SOA field is no exception. When the Pankow (1994) partitioning theory for SOA was developed, no experimental data on SOA phase and evaporation rates were available. As a result, simplifying assumptions of diffusively well-mixed particle phase SOA that is at equilibrium with the gas phase were made. Data recently acquired by a number of groups show that these simplifying assumptions are not valid. The referee further states that partitioning theory is used to calculate kinetics, which is clearly also not the case. Partitioning theory applies

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to state of equilibrium only. Kinetics is calculated from mass transfer rate equations.

The referee seems to finally agree, "the physical state of particles" has "dramatic implications", and that if one accept the experimental evidence that these particles are highly viscous, then the Pankow partitioning theory (Pankow, 1994) does not apply and *all* needs to be rethought. The reviewer however dismisses the possibility by ignoring *14* pieces of data, including the fact that we measured the SOA viscosity.

Similarly, the referee seems to finally realize, from our reply that if one accepts the experimental evidence that evaporation is slow, relative to the timescales of atmospheric evolution, it will lead to the conclusion that the system is not at equilibrium and partitioning theory cannot be applied. Here again, the referee dismisses the data (including those for ambient SOA particles), claiming that nobody knows how to extrapolate laboratory measurements to the real world. Does the referee really mean that one should ignore laboratory data and models based on laboratory data that were interpreted using unsubstantiated assumptions? But, all current SOA models that assume liquid droplets at equilibrium with the gas phase that the referee seems to accept are based on laboratory data that were interpreted on unsubstantiated assumptions.

Before we continue we would like to present evidence #15, which we refrained from discussing before, attempting to leave it for a separate publication. In a study by Widmann et al. (1998), of the evaporation rates of particles, the authors note that their "prior studies indicate that multicomponent evaporation rates can be predicted for systems containing relatively low molecular weight compounds, but the presence of high molecular weight components complicates the evaporation process." They showed, for example, that an addition of only 0.76 wt% of high molecular weight polymer additive (PMMA) has dramatic effect on the evaporation of liquid TEP microdroplets. They begin by deriving an equation for the evaporation of TEP that take into account the presence of the polymer in the droplet. As it turns out the equation is much more complicated than that for evaporating liquids. The bottom line is that even with this equation they fail to explain their data.

Widmann et al. (1998) concluded that PMMA accumulates at the surface of the droplet as the solvent evaporates and the "evaporation rate exhibits a large decrease that is likely governed by the rate at which solvent molecules diffuse through the polymer matrix."…"The partial pressure

of TEP appears to be much lower than that predicted from conventional vapor/liquid thermodynamics." The authors report that the experimentally observed evaporative behavior is "not consistent with application of Raoult's law or Flory-Huggins theory. It is likely that some other interfacial phenomenon influences the evaporation rate." The same study also shows that addition of small amount of polymer to TEP increases the solution viscosity by orders of magnitude. We will return to the results of this study later in our reply.

Note that the referee keeps treating SOA particles that are known to contain some fraction of oligomers/polymers as if they are liquid droplets composed of small organic molecules.

However, the 2nd review signifies a major change in the referee's attitude towards the subject, the definitive statements "it is liquid", and "evaporation is not too slow" have been replaced by "it is the $64 million question".

I thank the authors for providing a very detailed reply to my review. I would like to reiterate that I fully share the authors' interest in the questions discussed in the manuscript and think them of extreme importance to our field. This is exactly why I would like to see these questions addressed with utmost care and I hope the authors appreciate that. The authors seem to define two camps in discussing these important topics: the slow evaporation / high viscosity camp, and the liquid particles / fast evaporation camp. However, the review is not taking sides in such a hypothetical debate as the issues are much more complex than that dichotomy, but rather is trying to point out inconsistencies or aspects that need to be improved in their interpretation, if they want to convince the scientific community of the soundness of their approach.

The referee opens with an attempt to ascribe to us a point of view that could not be further from the truth. We see it as a scientific issue that needs to be resolved on the merits of the data. It is not about a fight between two camps that hold different *beliefs*, as the referee seems to imply.

Our work is not based on beliefs or assumptions, we present *experimental data* and refer to literature, in which *experimental data* are presented. We calibrate our instruments, and test them with known compounds before they are used to investigate something new, like SOA. We then check for consistency between multiple pieces of data, published by others and produced in our laboratory. Note that we tested our system with DOP and DOS, Cappa and Wilson (2011) used

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lubricating oil, and Virtanen et al. (2010) used solid and liquid particles to test the systems. In all cases multiple pieces of data were collected and examined before conclusions were reached. Compare this effort to that of coming up with unsupported assumptions or speculations.

We presented a list of *14* separate pieces of *experimental evidence*, from multiple sources, acquired by variety of independent methods - all indicating that SOA is highly viscous. In contrast, the referee attempted to present 1 experimental paper (Asa-Awuku et al., 2009) that he/she interpreted incorrectly to indicate that SOA is liquid. We showed that the referee's flawed logic could be used to prove that NaCl particles are liquids at zero RH. Moreover, from personal communication with the authors of Asa-Awuku et al. (2009) paper we learnt that they did not, and do not interpret their results to indicate that SOA is a liquid. Yet, the referee had no doubts that this single experiment proves that assumption of liquid SOA is correct and could be generalized to all SOA in the atmosphere.

The referee looks at the same data that others and we used to conclude that SOA could not be liquid, to reach the opposite conclusion and without a doubt states: "despite their claims, (their data) actually favors the assumption of liquid SOA". In a separate statement: "In fact, the author's statements are consistent with SOA particles that are indeed liquid and with characteristic diffusion time scales in the particles that are negligible!" Note that the referee casts no doubt about the quality of our data when he/she thinks, incorrectly, it could be used to conclude that SOA is liquid.

However, later on, in the same review, when the referee concludes that the data do not fit the assumption of liquidity, he/she states: "There is problem with the data". How could faulty data be used to prove unequivocally that SOA is a liquid?

The referee's attitude towards other, independent studies that use *experimental data* to conclude that these particles cannot be liquid, is to cast doubt on the experiment by Virtanen et al. (2010) by speculating that the particles could be frozen, claiming that whether his/her speculation is correct or not, is immaterial. In his/her point of view, the fact that he/she was able to speculate means that the data are useless. However, when the same study presents two additional pieces of supporting evidence that could not be dismissed by the referee's faulty speculation, he/she chooses to ignore it. A third experimental study by Cappa and Wilson (2011) that comes to the very same conclusion was simply ignored.

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We do not see this as a fight. When we started, we accepted the prevailing assumption that SOA is liquid and as a result struggled for months to interpret our experimental data. To begin with, we repeated the experiments a number of times and retested the experimental setup and approach with known systems. As shown in Vaden et al. (2011), the same experimental setup showed the expected droplet evaporation kinetics for pure component liquid DOP and DOS particles, with the expected size dependence, i.e. smaller particles evaporated faster than larger particles. The data show that SOA behaves very differently. Cappa and Wilson (2011) spent two years trying to come to grips with their experimental observations, before they concluded that the assumption of SOA liquidity might be wrong and all pieces fell in place and became consistent with observation by other groups, including ours.

The referee states: "I fully share the authors' interest in the questions discussed in the manuscript and think them of extreme importance to our field. This is exactly why I would like to see these questions addressed with utmost care". Yet, he/she chooses to discard and misinterpret all experimental data that shows his/her assumptions wrong. If these issues are important and need to be discussed by the community, this paper deserves to be published to make this discussion possible. He/she misinterpreted the Asa-Awuku et al. (2009) experimental results, misinterpreted our experimental results on too many points to count, speculated incorrectly about Virtanen et al. (2010) experiments, ignored two other independent pieces of experimental data by Virtanen et al. (2010) presented, and ignored (again) the Cappa and Wilson (2011) experimental results all together.

Each of the referee's choices and actions serves one purpose, which is to advance the *belief* that these particles are liquid; suggesting which of the two "camps" the referee belongs to.

The length of the reply requires some time to digest and I would be happy to provide my detailed analysis in due time. However, several major points that I have raised in my review remain unanswered by the authors' reply and I hope they will take time to revisit them in a follow-up reply, if they wish to do so. Below I provide only a few examples that illustrate why I think the questions have not been answered.

This statement is confusing. We agree that the referee did not spend the time required to

consider properly ~50 pages of text we sent in reply to the two referees, as evident from his/her 2nd review. Never the less, the referee comes to the conclusion, "Major problems remain". Below we address each point he/she made in detail. We assume that the referee accepts that countless criticisms, speculations, wrong data interpretation, the use of wrong equations, and new theories he/she presented in the 1st review have been addressed properly and what remains is is this new review.

However, before we proceed to address these new comments, it is important to keep in mind that in our rebuttal of the 1st review we showed each of the referee's comments/criticisms to be wrong.

In the reply the authors appear to alternate between two arguments, which are not necessarily connected and which have dramatically different implications for gas/aerosol partitioning. One argument is that the evaporation rates are so slow that they can be neglected in the chemical transport models. This argument does not require any knowledge of the particle physical state, intra-particle transfer limitations, etc. and does not necessarily contradict partitioning theory.

We are glad to see that the referee agrees that the fact that only a small fraction of the particle evaporates does not rely on particle phase.

Please note, I talk about validity of the theory, not validity of the assumption of equilibrium as derived from that theory. These are two very different things, which the authors seem to frequently confuse (see for example page 5, reply to #2).

We are glad to see that the referee accepts that the validity of the theory that relates to the state of equilibrium has nothing to do with how fast one gets to equilibrium.

Although, it is not clear how the assumption of equilibrium can be derived from that theory. Assumptions are not derived from theories. In the absence of data, researchers often make assumptions, which may turn out to be either correct or incorrect, but they cannot be derived from theories. Let us clarify this again. We never cast doubt that the particles obey the laws of

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chemistry and physics. What we said is that evaporation is slow, where slow refers to slower than typical atmospheric processes, like reactions with OH and dilution. If the particles need to respond to changes in the gas phase concentrations by evaporation, which our data show is slow relative to atmospheric processes, they cannot maintain a state of equilibrium with the gas phase, and particle composition cannot be calculated under the assumption that particles are at equilibrium.

For example, because in the evaporation chamber organic vapor concentration is zero, in the equilibrium state particles should completely evaporate. Yet, our data show that even after 24 hours in the chamber the significant fraction of particle's volume remains. What partitioning theory could be used to predict this behavior? Assuming these particles have non-zero vapor pressure, partitioning theory tells us that the final state must be zero particle mass, providing no information about how long it takes to get there.

In summary, our point is that all particles, including SOA, follow the laws of physics, but SOA particles evaporate at a rate that is slow by comparison with the rate at which the gas phase concentrations are changing. As a result, the particles are not at equilibrium with the gas phase.

The second argument involves the physical state of the particles, which the authors derive from the size dependence of particle evaporation, stability of two-phase particles, and back up with indirect evidence from other studies.

We tried to be very clear and numbered the arguments regarding particle phase. While the list includes *14* arguments, the referee chose to state that there are only two of them. The list even includes mention of direct measurement of molecules' diffusivity in SOA, from which we calculated the SOA viscosity. It is not possible to get more detailed than that. As we pointed out in our reply, we teamed up with Dr Evan Abramson whose research, for the past 20 years, has been centered on the study of viscosity of materials under different conditions. The referee ignores our long list and dismisses supporting experimental evidence from other groups by labeling them as being "indirect". In the previous review, the reviewer dismissed some of the data based on faulty argument that the particles could be frozen in the study by Virtanen et al. (2010). When shown that they were not, the evidence became "indirect". There are three

independent pieces of experimental evidence in Virtanen et al. (2010) Nature paper, all directly pointing to the same conclusion. What is indirect about the Cappa and Wilson (2011) study? They came to the conclusion that the particles are not liquid based on mass spectroscopic data. Are mass spectroscopy and microscopy indirect science?

In addition, Widmann et al. (1998) measured the viscosities of liquid TEP mixed with very small amounts of PMMA polymer directly and showed that even small increase in the concentration of polymer additives results in drastic increase in the viscosities of these mixtures.

This argument (i.e. inhibited intra-particle transport) does not necessarily require particle evaporation to be slow. For example, the Cappa and Wilson (2011) study referred to by the authors was performed at a very short residence time (15 s).

We never equated slow evaporation with viscosity as a rule. Many solid materials have high vapor pressures and consequently evaporate fast. As it happens, SOA is highly viscous and evaporates very slowly and the two happen to be coupled in a complex way. Widmann et al. (1998) provide very nice example how the presence of small amount of high molecular weight polymer increases viscosity and affects evaporation kinetics.

It is not clear what the point of short residence time in the Cappa and Wilson experiment has to do with particle phase or evaporation kinetics. Is the referee trying to say that we should note that some of the □-pinene SOA particles, that are not liquid, partially evaporate at high temperatures in a short time? Nobody doubts that evaporation rates increase with temperature. That is why thermal desorption is used. In the manuscript, we cited another study by Cappa and Jimenez (2010), in which they observed nearly complete evaporation of ambient organic aerosol in the thermodenuder-aerosol mass spectrometer (TD-AMS) in Mexico City and Los Angeles. In that study temperature was raised to >200C, and residence time was short, yet the author conclude that under atmospheric conditions these particles will not evaporate.

This is the first time the referee acknowledged the existence of the Cappa and Wilson (2011)study, but here again refrained from citing it for what it is: an experimental study that provides evidence for the non-liquidity and high viscosity of SOA. What is most remarkable about this study is that they show that even at high temperature SOA remains highly viscous.

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The most important aspect of the referee's paragraph above is the fact that it seems like, here, for the first time, the referee agrees with us that these particles are not liquid.

However, this argument does have dramatic implications for application of the partitioning theory to calculations of kinetics of different processes involving particle/gas exchange.

Yes, we agree, that these findings have dramatic implications. This is what we have been saying all along. We are not clear, however, what is meant by partitioning theory used to calculate kinetics. Is it not true that partitioning theory is applicable only to thermodynamic equilibrium? How does one use an equilibrium theory to calculate the kinetics of a system that is not at equilibrium?

It implies that the bulk aerosol composition, as used in the Pankow theory, cannot be used for calculations of vapor pressures at the particle surface. Viscosity and diffusivity are linked; if particles are highly viscous, the intra-particle diffusion is slow. If the intra-particle transport is sufficiently limited, then the surface becomes virtually decoupled from the bulk with all the implications for evaporation kinetics and chemical reaction kinetics.

Again, yes, we agree. It seems like the referee finally understands and accepts the consequences of our experimental findings. This is what we have been saying for a while. Here the referee takes the next step and notes that even if we ignore the issue of equilibrium for the moment, the fact that these particles are very viscous means that the assumption that they are well mixed, liquid-like does not hold and we need to find a new way to treat this system.

Recent work by Dr. Pöschl's group points out that we may need to replace in SOA the assumption that particles form and grow by absorption into liquid-like matter by adsorption to account for the particle high viscosity. Cappa and Wilson (2011) present a new SOA formation model, that we keep citing and the referee thus far ignored. In this model (that fits smog chamber data) particles harden rapidly becoming non-absorbing.

Again, the Widmann et al. (1998) study showed that when a very small amount of polymer added to liquid droplet, the polymer concentration rapidly increases at the droplet surface as the solvent evaporates. As a result the "evaporation rate exhibits a large decrease that is likely governed by the rate at which solvent molecules diffuse through the polymer matrix."…"The partial pressure of TEP appears to be much lower than that predicted from conventional vapor/liquid thermodynamics." The authors report that the experimentally observed evaporative behavior is "not consistent with application of either Raoult's law or Flory-Huggins theory."

One should bear in mind, however, that reaching thermodynamic equilibrium is still possible, if the intra-particle transport times are shorter than the atmospheric time scales.

This is exactly what we have been saying for a while. Note, here evaporation rates are ignored for the moment and we focus only on the question of whether the particles are completely mixed, which depend only on diffusion rates.

Whether or not this is the case with ambient OA is the sixty four million dollar question.

We guess, we can claim sixty four million dollars. As we keep saying, we measured the SOA viscosity. It is odd that the referee never bothers to inquire as to what viscosity we measured for SOA.

The referee is again taking the point of view that laboratory data cannot be used to learn about particles in the real atmosphere, ignoring the fact that all current SOA modeling is based on laboratory data and unsupported assumptions. The referee seems to claim that because he/she does not know how to extended our and others laboratory findings to the real atmosphere, they should be simply ignored and models based on laboratory studies and unsupported assumptions should be kept.

Nevertheless, here is what we have done so far to connect laboratory particles with ambient particles. We showed that ambient particles behave very similar to our laboratory particles that were formed in the presence of hydrophobic organic vapors. We showed that the evaporation of laboratory particles is the same at zero and ~50% RH.

In contrast, the referee uses the fact that smog chamber data can be fit with Pankow's parametric formulation as proof that all atmospheric SOA particles are liquids. However, Cappa and Wilson showed that the same data could also be fit with their model, in which SOA particles are not liquids.

The fact that the referee favors models that are based on laboratory studies and unsupported assumptions that he/she has no problems extending laboratory findings to the field. The problem is only with extending data that prove his/her unsupported assumptions wrong.

However, setting aside the questions about the underlying evidence, some of which I will briefly address below, the proposed modeling approach still does not agree with basic physics. For example, the authors confuse evaporation rate with equilibration time scales. Quoting their response "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?" A slow evaporation rate under artificial conditions does not imply a longer equilibration time in real atmosphere. As a matter of fact, because organic vapor builds up in real atmospheric conditions, as the authors rightly point out, equilibration can be quickly attained, unlike in their experimental conditions where equilibrium is impossible to achieve due to the continuous stripping of vapor. Also, note that unlike evaporation rate, equilibration times do not depend on vapor pressures (see Seinfeld and Pandis, 2006). Thus, the first argument (i.e. that the models are wrong because aerosol never reaches equilibrium due to slow evaporation) simply does not hold.

The referee seems to suggest that because we strip away the organics from the gas-phase, equilibrium becomes unreachable. That is a rather remarkable argument, as it implies that one can create metastable particles, or bulk material for that matter, in which the condensed phase is prevented from coming to equilibrium by evaporation because the gas phase has completely been stripped away. Does it imply that if the denuder did not work perfectly and a small fraction of the organic molecules remained in the gas phase, evaporation would be faster? It seems like the next logical argument is that the more organic vapor remains, the faster the evaporation rate would be.

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Clearly, the referee means to say that the rate at which equilibrium is approached could be faster because equilibrium is not far off. However, is it not true that if the driving force were reduced, the evaporation rate would slow down?

The equation below describes the evaporation rate and its dependence on the difference between the equilibrium vapor pressure of the evaporating substance and the background pressure. In our set-up, the second term is set to zero. In the real atmosphere, the pressure is not zero and evaporation rates are slower.

$$\frac{dm_A}{dt} = -\frac{4\pi a D_{AG} M_A}{R}\left[\frac{p_A^0(T_a)}{T_a} - \frac{P_A^\infty(T_\infty)}{T_\infty}\right], \tag{1}$$

where m_A is the mass of the drop, a is the drop radius, D_{AG} is the diffusion coefficient of the vapor, A, having molecular weight M_A, in stagnant gas, G. The temperature at the surface of the drop is T_a, R is the gas constant, $p_A^0(T_a)$ is the vapor pressure of the liquid at temperature T_a, and $p_A^\infty(T_\infty)$ is the partial pressure of vapor in the bulk gas at temperature T_∞.

All the referee needs to do is to use the equation, which is the same as he/she has been using throughout, except that the second term was set to zero.

Indeed, if we look at the data presented in Grieshop et al. (2007), where evaporation was induced by dilution, we find that evaporation was a factor of two slower than in our chamber where nearly 100% of the organic vapors were continuously removed. It is not surprising to find that slower driving force in Grieshop et al. (2007) caused slower evaporation than in our experiments. Keep in mind, evaporation rate is zero at equilibrium.

The reviewer refers to an equation in Seinfeld and Pandis stating that timescale to attain equilibrium is independent of vapor pressure and hence particle properties. The timescale equation in that chapter refers to changes in gas phase concentration and equilibrium of gas phase. It does not apply to particle evaporation or timescale for particles to attain equilibrium.

Note that particles are much more complicated than gas phase, and timescale for particle equilibrium depends on the particle properties. In the same chapter, the mass transfer or flux equation between gas and particle phase clearly shows that evaporation rate depends on the vapor pressure of species in the particle phase. In fact, the referee used our measured evaporation rates to calculate particle effective vapor pressure. The evaporation rate in our chamber is a measure of the rate at which particles approach equilibrium, which in our case is complete evaporation. If evaporation rates are unrelated to particle vapor pressure, how did we calculate the DOP vapor pressure from its measured evaporation rate? This is a commonly used method for measuring vapor pressures. The equation above shows that the rate, in real units of time, at which particles evaporate, clearly depends on the vapor pressure. Equilibrium is reached when the pressure of the evaporating compound in background or bulk gas equals the equilibrium compound vapor pressure in the particle. It is not clear what the referee is attempting to say by bringing the Seinfeld and Pandis reference, in which the timescale equation is written for equilibrium of gas phase species.

If one takes the second argument, the model has a major problem too. The equations provided in the Appendix do not hold for condensation (see eq.2 there), because the bulk composition is still used, which by the accepted definition of the problem is not accessible due to the very slow intra-particle diffusion. The authors' reply, unfortunately, does not resolve these problems.

This is true but we did not ignore this issue, as the referee seems to imply. We briefly discussed this issue in the manuscript and plan to expand on it in the revised version. The 2nd referee brought it up and we provided in our reply an explanation as to why we chose to use this approach. Here is a repeat of the some of these points:

1. The paper presents a comparative study with traditional SOA modeling and focuses on evaporation and not on SOA formation. To make comparison simpler, we wanted to keep all other aspects in the two models the same.

2. In addition to evaporation, we present a sensitivity study related to functionalization and fragmentation, to which the referee pays no attention. Modeling studies that use fits to smog

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chamber data to calculate SOA evolution predict nearly complete evaporation of SOA, which is in contrast to field measurements (Heald et al., 2005). Recent modeling studies fight SOA evaporation by using un-realistic assumptions of 100% functionalization, producing in the process significant amount of SOA (Dzepina et al., 2011). However, it is now widely recognized that gas-phase fragmentation reactions are extremely important and should be included in Chemical Transport Models (Kroll et al., 2011). Our paper presents sensitivity studies implementing fragmentation, for the first time, in both box models and 3D Chemical Transport Models, providing important scientific insights. Most importantly, we show that if traditional models were to include fragmentation as they should, they would predict significantly lower SOA loadings, greatly increasing discrepancy with field data. We show that our experimental observations of a nearly non-evaporating SOA would resolve this issue. Is this not an important finding that deserves to be published?

3. We point out in the manuscript that the next step must include a new method to model SOA formation. We and many others agree that the new experimental findings point to a need for major revisions in *all* aspects related to SOA modeling, including formation, evaporation, evolution, etc. In other words, we know what needs to be done and is therefore being done now. It just will take some time. Does the referee imply that because not all aspects of SOA modeling were solved in our first modeling paper, all the issues that the referee notes are important and need to be discussed should not be published?

4. We pointed out that if we use the Cappa and Wilson SOA formation model, that is consistent with non-absorbing, viscous SOA, and fits smog chamber data, differences in how much SOA is made are small (see the figure in the reply to referee # 2. A similar figure will be added to the revised manuscript.

The authors appear to be still confused about the size dependence of evaporation kinetics. In the free molecular regime dd_p/dt is size independent. Integrating leads to $d_p = d_0 - At$. Presenting it in the form of d_p/d_0 one gets $d_p/d_0 = 1 - At/d_0$ and, to compare to the graphs used in the paper, $(d_p/d_0)^2 = (1 - At/d_0)^2$. The same holds for any other power, with d_0, the initial particle size, still remaining in the right hand side. In the continuum regime $(d_p/d_0)^2$ also strongly depends on d_0, which the authors know very well according to Vaden et al. (2011). Thus, my argument

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still stands: the free-molecular regime does not produce the kind of data the authors observe, nor does the continuum or transition regime, and independently of the type of material that the particles are composed of, be it liquid, solid, or glass. It does not matter how the authors define size independence: their data contradicts the basic transport theory.

Here the referee again attempts to cast doubt on the validity of the entire data presented in Vaden et al. (2011), because he/she cannot fit one aspect of our data with his/her simple and again wrong equations. This is clearly not new for us nor is it new for anyone who read Vaden et al. (2011), which clearly includes the three referees of Vaden et al. paper. As the referee noted in the first review this is an important observation that we were the first to discover. Unlike the referee, we have concluded that the fact that the data do not fit this simple equation, tell us that these particles are complex and that processes in the particles, like diffusion and oligomerization, must play an important role. The referee again, instead of using the data to learn about SOA, chooses to toss the data out.

Here are the simple facts:

1. The system was tested on DOP, and DOS, it produces *quantitatively* the correct vapor pressures, evaporation kinetics, and size dependence.

2. The system applied to SOA produced the data presented in Vaden et al. (2011) and in the present manuscript. It indicates very different behavior than that expected for multicomponent droplets composed of small molecules (in any regime).

3. Davis's group (Widmann et al. (1998) studied the evaporation of particles composed of a liquid organic solvent mixed with a tiny amount of polymer and found that the evaporation kinetics changed. It became significantly slower, straight lines became curved, and the size dependence changed. In addition, the measured viscosity of these mixed solutions was shown to increase drastically with small increase in polymer content. As we mentioned above, Widmann et al. (1998) showed that the partial vapor pressure of the solvent "appears to be much lower than that predicted from conventional vapor/liquid thermodynamics" and the observed evaporative behavior is "not consistent with application of Raoult's law or Flory-Huggins theory.

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They wrote very different equations (more complicated than those the reviewer used) for the rate of particle evaporation that account for the presence of non-volatile additives. They show that with evaporation the concentration of polymer at the particle surface increases creating a gradient. Despite considering all these phenomena, they failed to provide quantitative explanation for the observed evaporation behavior. They speculate that the polymer they use could be surface active and that unaccounted for "interfacial phenomenon influences" might need to be included. Note that despite the fact that they were unable to provide a detailed, quantitative explanation for their data, the paper was published. The referees of that paper did not conclude that because the evaporation does not follow some simple wrong equation the paper should not be published.

It is important to point out that SOA represents significantly more complicated system than that studied in Widmann et al. (1998). SOA is a highly viscous mixture that contains many components with various vapor pressures, including high molecular weight oligomers/polymers with extremely low vapor pressures, the presence of which were shown by a number of research group, including ours. As semivolatile components near the particle's surface evaporate, the concentration of high molecular weight components near particle surface increases and further evaporation is determined by the rate of diffusion through this polymer. Moreover, our data indicate that the relative amount of the oligomers in SOA particles increases with particle aging, providing an additional complicating process. The referee chooses to ignore it all and to use simple equations that do not fit the problem at hand, discovering that the wrong equations do not reproduce the data he/she does not conclude that his/her assumptions are incorrect, but rather that the data need to be tossed out and not see the light of day.

4. Grieshop et al. (2007) measured the evaporation kinetics of SOA at RT by looking at changes in SOA size distributions upon dilution. As expected, their evaporation rates are slightly slower than ours are. We mentioned this point in our 1st reply to the referee, but he/she seems to ignore it.

5. The Figure below shows a comparison between the Grieshop et al (2007) data (red) and the evaporation predicted based on the referee's equation, which we used for DOP and DOS. As far as size dependence, the Grieshop et al. data that were obtained by different method than
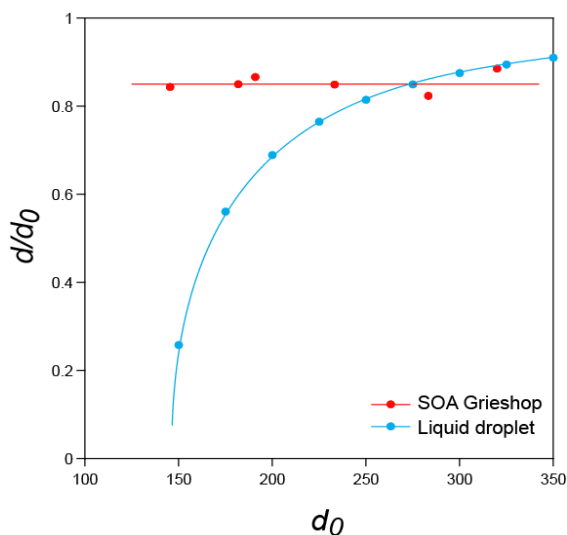
Figure 1. Calculated ratio of particle diameters after 2.5 hours of evaporation and original diameters from Grieshop et al. 2007 evaporation study (red). The same ratio calculated for liquid droplets like DOP.

ours are clearly in perfect agreement with our data and do not agree with the referee's equation. Is the referee to conclude that there is something wrong with these data as well?

6. We discussed the observed size-independence with Peter McMurry and with Paul Ziemann, after carefully examining the experimental set-up and the data we produced for the known compounds. They expressed complete confidence in our data and concluded that they contain important information. The point is that instead of following the referee's advice and discarding the data because they do not look like the reviewer expects them to, we all agree that the data are telling us something important.

7. The kinetics of oligomer formation and fragmentation, diffusion in highly viscous domain, and evaporation could be complicated. Although, we are working on a new set of experiments that may shed light on the subject. We repeatedly point out that SOA is composed of a complex mixture of compounds some of which are large oligomers, some are smaller, and some are monomers and individual molecules with different vapor pressures. We do not claim to be able to explain all of it to the last point. – Just a reminder, Davis's group (Widmann et al., 1998) could not explain their TEP data, for droplets that contain less than 1 percent of polymer. Note that the Davis data were obtained with the same experimental setup that was used for many years to successfully study kinetics of evaporation of different particle systems, including, multicomponent droplets. When new surprising results were obtained, they were not tossed away just because the observed evaporative behavior is "not consistent with application of Raoult's law".

The referee seems to imply that because he/she cannot explain this aspect of our (and others) data we should not get to publish any of it.

Keep in mind that everything we know about SOA comes from smog chamber studies that were fit with absorptive partitioning theory under the assumption that these particles are liquids and at equilibrium with the gas phase. This formalism was then extrapolated to the field. The referee seems to accept this approach, despite having to use laboratory-based data created under artificial conditions. All we have done is to replace unsupported assumptions by real experimental data. It is hard to understand why the referee would object to that.

The referee seems to imply that one should hold on to models developed based on smog chamber data and unsupported assumptions, even though these assumptions were shown by recent laboratory experiments to be wrong, just because he/she is not 100% sure how to extend what was found in these laboratory experiments to the field. In other words, models based on assumptions known to be wrong are better than evidence-based models.

Note that the referee chooses to ignore the fact that we presented ambient data on SOA evaporation measured during the CARES field campaign in Sacramento, CA as well.

Considering that the greatest priority in the SOA community is to find a way to explain persistent discrepancies between field observations and current models of SOA formation and evolution (Hallquist et al., 2009), the referee's approach of dismissing all experimental data that do not fit his/her models is especially puzzling. Taking his/her, approach would mean claiming that there is something wrong with the field measurements and not letting these experimental field papers to be published.

To explain field data, models resort to using the assumption of 100% functionalization. While this assumption is commonly used, it is well known to be wrong. Does the referee give us credit for addressing this issue, or claims instead that because we do not yet know what exact branching ratio to use, our sensitivity study on the subject should not be published?

The referee ignores the simple fact that the assumption of instantaneously established equilibrium is just an assumption. There are no data to support this assumption. Now, however, newly acquired data show this assumption to be wrong and it is time to reconsider the models and their assumptions. There is nothing wrong with that.

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The referee ignores the fact that the assumption that these particles are liquids and that they obey Raoult's law is just an assumption. There are no data to support it. Now that new data show it to be wrong, we have to reconsider this aspect of the models as well. Nothing wrong with that either.

The new discussion of the coating experiments provided in the reply was very informative. Unfortunately, neither the current manuscript nor Vaden et al. (2011) had as detailed a description of which classes or morphology of particles were used for which graphs. New information notwithstanding, the arguments remain unconvincing. The authors state, for example that "the lower density fluid will always diffuse and reside on the surface of denser fluid" (top of page 28) which apparently comes from the buoyancy considerations. The question, however, is: how does it work for a spherical particle: what is top and what is bottom with respect to the center? Is it possible that there are multiple stable or metastable states, and that the change of configuration is not kinetically limited?

We agree with the reviewer - one of these particle morphologies is metastable. Particles are stuck in that metastable i.e. non-equilibrium morphology, because the diffusion kinetics to transform them to the stable phase is very slow. That is exactly what we have been saying for a while.

Here again, the referee chooses to focus on one piece of evidence, feeling that if he/she could come up with some alternative explanation, the new picture, in its entirety, of what SOA particle look like will disappear. It does not work that way in science. There are many pieces of evidence produced by others and us, we laid out 14 of them, and they all must (and do) tell the same story. Note for example, the DOP-core of SOA coated DOP particles does not evaporate, yet a thick layer of DOP deposited on the surface of SOA particles evaporates in less than 2 hours. Why? Answer: Because it cannot diffuse through the viscous SOA. We laid out 14 pieces of information they all have to tell the same story; we do not get to pick and choose. As we mentioned above and in the previous reply, we did measure diffusivity in SOA and calculated the SOA viscosity. The results of these measurements were presented at recent meetings and will be described in detail in a separate manuscript in preparation. The referee seems to have no interest

in the results of these measurements.

A 4 nm coating on a 150 nm particle is ~8%. Why then do the authors think that the particles have ~20% of DOP trapped inside (middle of p.29 under #3)? What happened to the other 72%? Why is it that DOP dispersed inside SOA particles does not seem to evaporate together with the SOA material, etc., etc.?

The referee again tries to interpret our data and again gets it wrong. The fraction of the DOP mass-spectral signal (f_{DOP}) is: $f_{DOP} = SI_{DOP}/SI_{total}$, where SI_{DOP} and SI_{total} are the DOP MS signal intensity and the total MS intensity, respectively. At each point in time we calculate f_{DOP} and use these values to calculate $f_{DOP}(t)/f_{DOP}(t=0)$. At $t=0$ this ratio is 1. As the surface DOP evaporates rapidly, the ratio drops to 0.2. We conclude 80% of the DOP was on the surface and 20% of DOP is stuck inside the bulk SOA. Now as the SOA evaporates, so does the DOP, with the ratio remaining at 0.2, indicating that DOP that is stuck inside evaporates at the same rate as the SOA. Just like in the Cappa and Wilson experiments, particles evaporate layer-by-layer.

For pyrene (and other PAHs) we find that less than 10% of pyrene is on the surface, and the pyrene that is stuck inside the bulk SOA evaporates slightly faster than the SOA, but orders of magnitude slower than pyrene deposited on the surface of pure SOA particles.

As stated above, I will be happy to provide a detailed analysis of the authors' reply, but I hope the authors could revisit at the very least the points that I mentioned above. If the authors wish to do so, I would kindly ask to please refrain from attributing their logic and interpretations to me. No, I do not "trust their data" (middle of p.40), because I think it contradicts basic evaporation kinetics (see section 2 of the review);

Does that mean the referee does not trust any of our data? For example, does the referee not trust the evaporation of DOP that reproduces known vapor pressures? Does the referee suggest that SOA particles could be evaporating orders of magnitude faster than what we measured because he/she could not fit the size dependence assuming they are liquid particles?

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We assume then that the referee does not trust the Grieshop et al., (2007) as well. These data were taken by the same the group that took the data presented in the Asa-Awuku et al. (2009) that the referee wrongly interpreted to prove that SOA is liquid. Alternatively, should we assume that the Grieshop et al., (2007) data showing identical size dependence and slower evaporation are reliable but ours are not?

How does the reviewer explain the fact that the two studies conducted by different groups using very different approaches yield identical behavior? Does he/she think that this just a coincidence? Alternatively, does he/she think that both papers are wrong and should not have been allowed to be published?

Does the referee now trust the Virtanen et al. (2010) data, after we showed that these particles were not frozen? What about the Cappa and Wilson (2011) data? The referee used it here to show that at high temperatures some SOA can evaporate fast. Does that mean that their conclusion that SOA is highly viscous and, in their words, is not governed by equilibrium partitioning theory is acceptable? The referee cited the Cappa and Jimenez (2010) data showing slow evaporating ambient SOA. Does that mean he/she trusts that data? Just like the Cappa and Wilson (2011) study, they observed fast and nearly complete evaporation of ambient SOA particles in the thermodenuder but concluded that very large fraction of ambient SOA would never evaporate at ambient conditions. There are countless papers reporting on SOA evaporation in thermodenuders all reporting that SOA evaporation is slower than expected, are they all suspect? What about Stanier et al. (2007) TDMA study of the volatility of α-pinene SOA, mentioned in our manuscript?

All of these studies are consistent with our findings and the new picture of SOA.

nor did I ever suggest replacing the existing VBS data with the authors data;

Here is the citation from the first review: "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." We are sorry if we misinterpreted this statement. The referee discarded the smog chamber based VBS stating "For example, the VBS parameterization was derived from various, quite variable smog chamber yield data. The uncertainties in this parameterization

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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." Note we are talking about differences that are orders of magnitude. He/she then used our data to calculate C* as a function of time, noting that the entire distribution could be calculated from our data. We assumed that this is what the referee meant.

nor did I ever agree that slow evaporation under the artificial experimental conditions necessarily means that equilibrium cannot be achieved in atmospherically-relevant timescales (see section 1 of the review);

Again, the entire SOA field is built on the idea that experiments conducted in the lab can be used to model field observations. Moreover, the referee ignores that some of our measurements were conducted on real ambient SOA that we characterized with unprecedented detail. Most of the understanding of SOA properties and behavior and its modeling are based purely on laboratory generated and characterized particles under controlled conditions which the referee calls artifical.

nor do I think that I neglect or contradict the available smog chamber data, one could actually point out that it is rather the authors' data that contradicts it,

Again, we must have misinterpreted the following simple statement: "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." What the referee chose to say here about smog chamber data seems to cast doubt on their utility to generate VBS distributions. As the referee notes, the fact that smog chamber based VBS distributions predict evaporation rates orders of magnitude faster than we observe provide no

useful information because the smog chamber data are so unreliable. Does the reviewer now suggest we should use these data and draw conclusions from the discrepancy?

if one considers that much of the smog chamber data was collected at or near room temperature, etc., etc. These straw men that the authors attack have very little to do with my arguments.

We are not following this statement.

I would also like to remind the authors that I am reviewing their manuscript and not several other papers, some unpublished, which they bring up as their arguments. In my review I had to revisit Vaden et al., because the current manuscript relies heavily on it, a fact the authors acknowledge in the reply, but somehow fault me for it.

I thank the authors for reminding us of the high reputation and impact factors of some of the cited journals. However, I would like to point to a study showing a significant correlation between the journal impact factor and the number of retractions, which is briefly discussed in Science, V333, p.924. And in conclusion I would like to quote Galileo Galilei "In questions of science the authority of a thousand is not worth the humble reasoning of a single individual." Appeals to authority are still a logical fallacy.

We have no problems discussing the Vaden et al. papers. We agree that they present extremely important information. In fact, we had many discussions with many prominent scientists in the field before and after these papers were published. However, we must say that during these numerous scientific discussions, we never had encountered so many wrong arguments, data misinterpretation, disregard to the data, baseless speculations, etc. We have not tried to claim that because one journal has higher impact factor than another, it is more likely to present studies that are closer to the truth.

We all make mistakes and we all learn as more data become available. The most important difference between our point of view and that of the referee is that we develop our point of view based on *real data* (ours and others), and not on assumptions. We began this work like every one

of us in the field, accepting prevailing assumptions about phase, volatilities, and hence evaporation rates, functionalization, and fragmentation. Looking at the data with great care caused us to slowly change our point of view, while the referee chose to speculate and look for reasons to toss the data away and keep unsupported assumptions. One does not get to speculate stating: "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." and toss away data collected by reputable scientists.

We all work very hard to build our tools, test and calibrate them to assure they are free of artifacts and that they are reliable. We then spend countless hours analyzing the data, going back to the laboratory to test our ideas, and retest the system. To callously dismiss all this hard work by a mere speculation on a subject that we happen to have carefully considered a few years ago, tested with numerical simulations and experimental works, and published a paper on the subject is downright painful.

Cappa and Wilson spent two years thinking about their data, we spent more than a year thinking about our data that took many months to obtain, repeat, and analyze. In contrast, the referee took less than a day to write his/her second review of more than 50 pages of text.

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