We thank the 2nd reviewer for his/her detailed and insightful comments.

Major issues

- I agree with the first three major points of reviewer #1 regarding the interpretation of the Vaden et al. (2011) results. These appear to be potential misinterpretations of the results. I feel that reviewer #1 has done a thorough job of detailing these results, and thus I will not go into further detail. If the paper is to be published, I will need to be convinced that the points made by reviewer #1 are not correct, or the points made by reviewer 1 will need to be thoroughly incorporated into the revised paper.

First, we would like to thank the 2nd reviewer for leaving open the possibility that the points made by reviewer #1 are not correct. We are confident that after reading our response to the 1st referee's comments he/she will realize that the problem is with the arguments made by the 1st referee and not with our data and analysis.

In our response to the 1st referee we show in detail that **each and every** point made by the 1st reviewer is wrong. We show that he/she makes self-contradicting statements, misinterprets our data and our data interpretations, all of which were published in peer-reviewed journal publications. The 1st referee goes on to wrongly dismiss all other published data that do not fit his/her picture, choosing to freely speculate while ignoring published data that prove his/her speculations false. Please, refer to our reply to the 1st reviewer for detailed point-by-point rebuttal.

Irreversible partitioning: The conceptual framework of irreversible partitioning is physically impossible. It may be a useful means of getting behaviour that may be realistic in models (although the model results were not evaluated); however, I am uncomfortable with the concept of it.

Here is why: Lets say that reversible partition predicts that 50% of the SOM mass in one of your volatility bins should be in the aerosol phase with the rest in the gas phase. At this gas-phase concentration, the condensation and evaporation are equal, so there is no net condensation/evaporation. In the proposed irreversible partitioning construct proposed in this

paper, you follow the reversible partitioning solution if this solution is larger than the previous aerosol amount. However, if the reversible partitioning solution is lower than previous aerosol amount, the aerosols do not net evaporate to the reversible partitioning solution. This implies that there is no evaporation at all (not even just no net evaporation).

If there is no evaporation when the reversible partitioning solution is lower than the previous aerosol amount, there should be no evaporation from the aerosol in other cases too (why would it be any different now?). Yet, we know that there IS condensation to the particle as long as there are condensible particles in the gas phase (e.g. 50% of the SOM in this scenario). Why does this SOM not stay stuck in the particle? Why does the amount of SOA in the reversible solution get "stuck" to the particle but any SOM that impinges onto the aerosol above this not get stuck?

The above does not make physical sense. I realize that the authors intended the irreversible partitioning construct to be a rough means of representing the experiments (i.e. the last paragraph of the paper), but I feel that the oddness of physics should be described better.

We agree with the reviewer that the conceptual framework we used (one-way dissolution of organic vapors using Raoult's law into particle phase without oligomerization or reactive uptake considerations) to model irreversible partitioning in this paper is approximate and seems at first glance inconsistent. However, if one were to include reactive uptake/oligomerization, for which the data show evidence, then this model treatment is not far off the mark. In a reactive uptake scenario, in which the vapor pressure of the condensing molecules drops drastically by condensed phase chemistry, one-way condensation would be rather reasonable. The important assumption required for implementation of the approximate one-way condensation approach in models 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). Our model was constructed to allow us to focus on and explore the effects of non-equilibrium due to extremely slow particle evaporation, which is the subject of the paper.

Our observed non-equilibrium behavior is a direct result of the slow evaporation of SOA particles. Just to be clear, since the 1st referee seems confused with the word slow, what we mean by slow is that changes in the gas phase are much faster than the rate at which the particles

respond by evaporation. The same is clearly not true for condensation that, as the data show, is much faster.

There is no question that in the long run, to implement the right physical and chemical processes in models, we need to rethink everything starting from SOA formation and growth. We need to account for all non-equilibrium effects in SOA particles, the phase of SOA particles, and the kinetic limitations on gas-particle partitioning, as suggested for e.g. by Pfrang et al. (2011), Shiraiwa et al. (2011), and Cappa and Wilson (2011). These would require development of advanced models, which is beyond the scope of this work.

For example, Shiraiwa et al. (2011) suggest "slow bulk diffusion may change the growth of SOA particles from absorptive to adsorptive, resulting in steep concentration gradients. On the other hand, slow transport from the bulk to the surface may play an important role in the suppression of SOA evaporation (Vaden et al., 2011). Moreover, aerosol hygroscopic growth and the nucleation of cloud droplets or ice crystals can be retarded or inhibited by slow diffusion"… The authors conclude that "occurrence and properties of amorphous semisolid 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."

Cappa and Wilson (2011), for example, recently developed a new model for SOA formation that assumes that "the material that condensed to the particle phase in this step is "lost" from the system and does not influence partitioning in the next step, i.e. is converted to non-absorbing (non-partitioning) material. In the next step, further hydrocarbon is reacted, producing more gas-phase material. The total material available for partitioning in this step is then the sum of the newly formed gas phase material from reaction and the material from the previous step that did not condense (i.e. the residual gas-phase material). For compounds that partition strongly to the particle phase, the new total is effectively equal to only the material produced from gas-phase reactions, while for compounds that weakly partition to the particle phase the total is equal to the sum of the newly produced and residual gas-phase material."

Again, as mentioned in our response to reviewer 1, the S-EPM model by Cappa and Wilson (2011) uses Raoult's law for SOA formation, and then instantaneously converts it to non-absorbing SOA. The work of Cappa and Wilson (2011) shows that the S-EPM model, which

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accounts for diffusion-limited non-absorbing SOA predicts nearly the same amount of SOA formed as the traditional absorptive partitioning theory. In the revised manuscript, we added to our box model a simulation of SOA formation based on the Cappa and Wilson (2011) new model. See, for example, the figure below. Their model fits the smog chamber data and thus produces results that are very close to those produced by the irreversible partitioning model that was originally adopted in this manuscript. We include this additional comparison with the S-EPM model of Cappa and Wilson (2011) only to show that our irreversible partitioning approach starts with similar amounts of SOA formed as previous VBS models implementing absorptive partitioning, which allows us to consistently compare the effects of SOA evaporation to previous models. We are not suggesting that either of S-EPM model developed by Cappa and Wilson (2011), or our irreversible partitioning approach have solved all pieces of the puzzle.
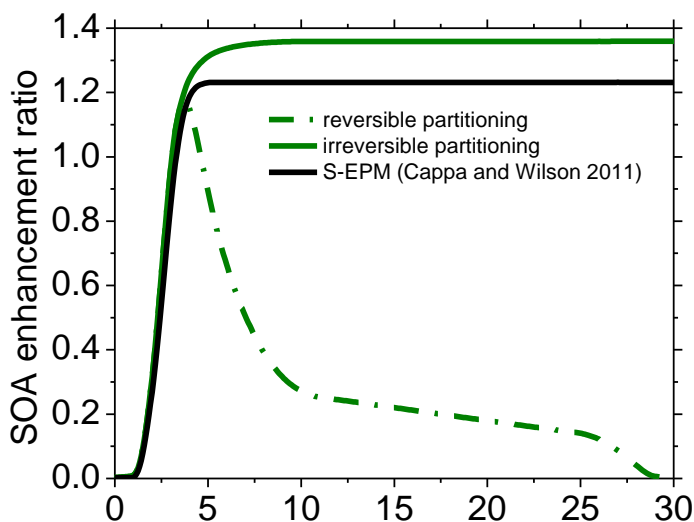
Comparison to Cappa & Wilson SOA formation model for 75% fragmentation (corresponding to Figure 4b in our manuscript)

Our goal, in this work was to investigate the effect of slow SOA evaporation on the lifecycle of SOA. 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 in the light of our new findings of "low effective volatility SOA" to

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compare its results with traditional reversible partitioning models. This approach limited, by design, the scope of the study to evaporation.

The present, irreversible partitioning was a first case study constructed by adjusting existing models to explore the effect of slow evaporation, which we observed experimentally, on the loadings of SOA in the atmosphere. One could also argue that assuming SOA as almost non-volatile, as derived by the 1st reviewer, based on our data, would be a more physically plausible model. The differences between the two, as far as evaporation goes, are minor. Non-evaporating is non-evaporating. The problem with the 1st reviewer's model is that it predicts significant changes in composition with evaporation, which Cappa and Wilson (2011) and our data unambiguously show not to be the case. In addition, the 1st reviewer's treatment of the data predicts that particle composition must be size-dependent, which again is refuted by our data. Finally, 1st reviewer's model predicts that when two identical particles coagulate to form a larger particle the composition of the larger particle must be different from the two coagulating particles, which is not true.

Current smog chamber parameters are non-linear fits using many free parameters to fit real experimental data. The problem is that a number of recent studies (Cappa and Wilson, 2011; Vaden et al., 2011; Virtanen et al., 2010) and our results all show that these empirical fits derived from smog chamber data do not properly represent actual physical and chemical properties and evolution of particles in the laboratory and in the atmosphere.

Our data clearly point to reactive uptake/oligomerization as playing an important role. Our findings are supported by vast literature showing that SOA composition includes high molecular weight compounds that are described as oligomers or polymers. Indirect methods measuring changes in volatility after thermal treatment have estimated that oligomers contribute 25-70% of the composition of laboratory SOA (Hallquist et al., 2009). Again, our measurements clearly point to reactive uptake/oligomerization as being extremely important processes to the evolution of SOA in the atmosphere. This aspect of our work has not been presented yet.

Our data also clearly show that evaporation is slow, and proceeds over timescales of days. In contrast, both smog chamber and field data show that nucleation/condensation kinetics and hence particle growth are fast relative to gas phase chemistry (Pierce et al., 2011; Presto and Donahue, 2006). These are simple facts. The model we constructed has fast condensation, governed by

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instantaneous thermodynamics, and very slow evaporation, so slow that on atmospheric time scales particles do not keep up with changes in the gas phase and are therefore not at equilibrium. The slow evaporation justifies the assumption of negligible evaporation as a good first-order approximation in 3D Chemical Transport Models, which need computationally efficient algorithms to represent complex processes. Finally, our modeling approach was used as tool to develop scientific insight into effects of our new findings on the lifecycle of SOA in the atmosphere. As we see it, the path to a comprehensive model that includes formation with reactive uptake, physical and chemical condensed phase processes, evaporation, and interaction with water vapor is arduous.

It is awkward to put down 100% functionalization approaches as unrealistic while this approach is also unrealistic. They both might work at giving better model solutions, but they certainly can not be describing the chemistry/physics that are occurring.

Here is how we see the differences: That 100% functionalization approaches are unrealistic is an established fact based on what is known about chemistry of organic vapors (Jimenez et al., 2009; Kroll et al., 2011). How far off is the assumption that 100% of products have lower vapor pressure, is not easy to estimate, as it depends on the specific chemical processes and reacting species involved. Consequently, when it is implemented in models, the magnitude of the errors it carries is not easily quantified. As an aside, the present paper can also be viewed as an attempt to estimate the magnitude of these uncertainties.

As suggested by Kroll et al. (2011), better constraints on the kinetics of key organic 'aging' reactions are needed for accurate quantification of functionalization and fragmentation reactions and their effects on SOA loadings in the atmosphere.

In this work, we focused our attention on experimental data that show that ambient SOA loses only ~20% of its mass by evaporation in 4 hours under organic vapor-free conditions. It is easy to conclude that under atmospheric conditions, with gas phase concentrations decreasing slowly, this rate would be even slower. We also provided information about the evolution of the system with aging. It shows that as particles age in our smog chamber, their evaporation in the evaporation chamber slows even further. We also provided experimental evidence on the

evaporation behavior (for over 24 hours) of SOA with 'trapped' pyrene that seems very similar to ambient SOA. We showed that aged SOA with 'trapped' pyrene evaporates even slower. All these pieces of experimental data show us that the observed slow evaporation will become even slower in the real atmosphere. Therefore, when we approximate the system as being non-evaporative, it is easy to estimate the validity of this first-order approximation in the light of our experimental data.

In this modeling work, we are only evaluating the sensitivity of our observations of non-equilibrium SOA partitioning relative to previous models. We stress that our model simulations are sensitivity studies designed to motivate the scientific community to rethink their modeling assumptions.

Other comments:

(Page 20124, Line 16) What is the basis for 75% fragmentation. Is this more realistic than 100% functionalization?

In this manuscript, we present the first sensitivity study that explores the effects of functionalization and fragmentation. We compare two cases, 75% fragmentation and 75% functionalization approaches that represent two ends of the wide spectrum of functionalization and fragmentation reactions shifting the volatility of organic vapors in the atmosphere (Jimenez et al., 2009). Implementation of sensitivity to fragmentation in our modeling approach is based on work by Kroll et al. (2011) who recently suggested that fragmentation reactions are extremely important as addition of oxygen-containing groups weakens the C-C bonds and leads to fragmentation after just 1 to 4 generations of oxidation. With 75% fragmentation, our box model simulations showed large reduction of SOA loadings by traditional reversible partitioning approach, whereas our experimentally based non-equilibrium approach predicts much higher SOA loadings and lifetimes in the atmosphere. This sensitivity study was intended to provide insight and to illustrate how non-equilibrium partitioning protects SOA from the effects of dilution and removal by gas phase fragmentation reactions. In a box model simulation, we show that SOA is shielded from effects of re-partitioning to gas phase when the surrounding organic vapors are removed rapidly in 75% fragmentation case.

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For 3-D models, we use a combination of 100% functionalizations for first 2 generations, followed by 75% fragmentation in the gas phase. Again this assumes the upper bound of fragmentation reactions based on suggestions by Kroll et al. (2011) that fragmentation reactions would become increasingly important after 1 to 4 generations of functionalization reactions. The purpose is to investigate effects of non-equilibrium partitioning behavior in 3-D model simulations as compared to traditional approaches.

(Page 20124, Line 20) How do results change if POA and SOA were allowed to mix?

In our 3-D model implementations in this work, we treated partitioning of POA as reversible equilibrium process based on work by Robinson et al. (2007). If POA and SOA were allowed to mix, in the irreversible partitioning case we would see bigger increases in both POA and SOA loadings as we are increasing organic mass, assuming that SOA partitioning is non-equilibrium. Since we were only interested in model sensitivity tests using the SOA properties derived from recent experimental observations, we decided to keep POA and SOA as two separate solutions.

Lower activity coefficient: This is saying that when in solution, the aerosols have a lower volatility (you are lowering the volatility by a factor of 5). As the other reviewer said, the VBS approach has the activity coefficients implicit in the C*s (and assumes they are constant), so you are essentially just reducing your C* values by a factor of 5.

Yes, we agree that C*s derived based on fits to smog chamber data already have implicit activity coefficients. The idea to use a lower activity coefficient was to account for the fact that our data show that the SOA matrix traps higher volatility organics, such as pyrene, DOP, DOS, and others, resulting in increase in SOA organic mass. The presence of these hydrophobic organics "effectively" lowers their vapor pressure. Moreover, our data show that when these hydrophobic organics are present, SOA formation yields are enhanced (data in preparation for publication). None of these processes are part of the current smog chamber data fits. By assuming a lower activity coefficient, we are "effectively" reducing volatility of all species, forcing a greater fraction of higher volatility species into the particle phase than that predicted by

VBS. Again, the assumption of activity coefficient of 0.2 was meant to produce easily observable results for our sensitivity study. As mentioned in our reply to the 1st referee, we are not 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 and oligomerization of organic species in particle phase.

How do the SOA properties depend on RH? Would you expect them to still be highly viscous at high RHs?

This is a very good question. We recently measured the evaporation rates of α-pinene SOA made at higher (>60%) RH in the smog chamber and studied its evaporation behavior at low RH within the evaporation chamber. We found it to be nearly identical to dry SOA. We also looked at the evaporation of α-pinene SOA made at higher (>60%) RH and studied its evaporation behavior at ~50% RH in the evaporation chamber at very long timescales, and found it to be the nearly identical to dry SOA.

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