**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Reformulating the atmospheric lifecycle of SOA based on new field and laboratory data" *by* M. Shrivastava et al.

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 α-pinene parameterizations; therefore, SOA does not follow partitioning theory; 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; 3) hydrophobic compounds form coatings on SOA, and vice versa, which

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slow down evaporation; this is taken as an additional indication of highly viscous state of the particles. 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 can not 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.

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.

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 α-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. 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

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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.

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. 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^*:

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

in which d_p is the particle diameter. D is the average diffusion coefficient of evaporating species, ρ is the particle density, $f(Kn, \alpha)$ is the Fuchs-Sutugin correction, Kn is the average Knudsen number of evaporating species, and α 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 $D = 0.057cm^2/s$ 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 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, α, 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 evaporate with an average rate consistent with vapor concentration of the order of 0.1 − 1 μg/m^3; extrapolating to $t = 0$ one can potentially expect values as high as 10 μg/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 μg/m^3, C13 − C22 monocarboxylic acids 0.001 − 100 μg/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"!

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

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. 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. 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 α-pinene aerosol volatility was about 0.3 μg/m^3 (logmean 0.1 μg/m^3) and that of ambient about 0.05 μg/m^3 (logmean 0.01μg/m^3) assuming $\alpha = 1$. Using larger initial sizes produces higher values. For example, for 500 nm the mean volatility of α-pinene aerosol is about 1.1 μg/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.

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.

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. However, for judging the effects of diffusional limitations within a particle, which could lead to size independent evaporation, one needs to investigate d_p/d_0, not $(d_p/d_0)^2$. If $(d_p/d_0)^2$ is size independent, d_p/d_0 is necessarily size dependent. 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.

The observed size dependence is quite curious, because it contradicts the basic diffusional transport theory. dd_p/dt should be either size independent, as in the free molecular regime, or be inversely proportional to d_p, 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. 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.

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. In fact Asa-Awuku et al. (2009) showed that α-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.

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.

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.

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? 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. 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 α-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.

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.

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. 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:

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

in which τ_c is the characteristic coalescence time, k is the Boltzmann constant, R is particle radius, v_m is molecular volume, σ is the surface tension, and D is the diffusion

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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^3, $N_A = 6.02 \times 10^{23}$), we obtain values for the diffusion coefficient D being 3.45×10^{-14} m^2/s, if $\tau_c = 1$ s, and 5.75×10^{-16} m^2/s, if $\tau_c = 1$ min. Characteristic diffusion times in the particle phase are given by (Seinfeld and Pandis, 2006):

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

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!

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. 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.

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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. 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.

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. 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, 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.

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).

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 μg/m^3 in the gas concentration is chosen to drive condensation. Why not 0.001 or 100, why equal for all volatility bins? 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.

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_{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.

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.

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Interactive comment on Atmos. Chem. Phys. Discuss., 11, 20107, 2011.
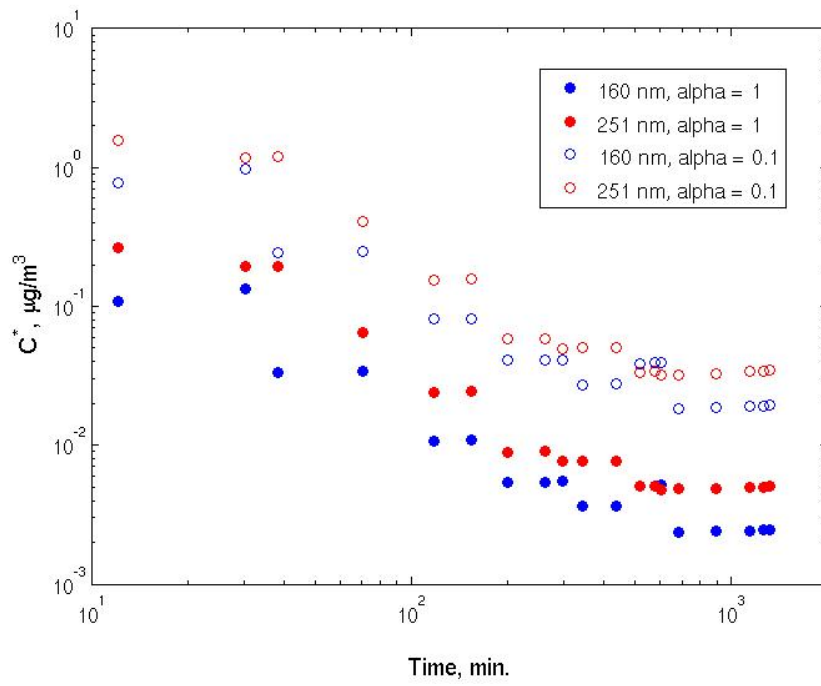
Fig. 1. Average vapor concentration at the particle surface (i.e. saturation concentration of evaporating compounds) during evaporation of alpha-pinene aerosol as derived from Fig.3B in Vaden et al. 2011

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