

Review of “Real refractive indices and volatility of secondary organic aerosol generated from photooxidation and ozonolysis of limonene, alpha-pinene and toluene”

Kim and Paulson report on measurements of SOA volatility and real refractive indices for particles generated from toluene, alpha pinene (aP) or limonene via either photooxidation (all three) or ozonolysis (aP and limonene only). They find that the toluene SOA is essentially non-volatile up to $\sim 100^{\circ}\text{C}$, while aP and limonene SOA evaporate substantially above $\sim 60^{\circ}\text{C}$. The toluene SOA measurements are a new result, while the aP and limonene are consistent with literature results. They importantly find that for the generated SOA particles the real refractive index (RI) varies substantially between the different compounds and between different reaction conditions for the same compound, as they have previously observed, and they place these variations in the context of how OA optical properties are commonly treated within climate models. However, in this study I find that they offer little guidance in terms of developing generalizations that would help to relate e.g. reaction conditions or particle composition and the derived RI values.

My primary concern with this work is that I find it somewhat difficult to follow the connections that are (or are not) being made between reaction conditions, particle size, particle mass loading and particle composition and how all of these influence the derived RI values. If I am understanding correctly, the authors are arguing that composition plays a controlling role on determining the derived RI values. However, they do not provide any direct measurements of particle composition, instead seeming to use particle size as a proxy for chemical composition. Yet the particle size that results from a given experiment can depend on myriad factors and may only loosely be related to particle composition. By presenting their derived RI values vs. particle size, they seem to be leading the reader to think that there is a one-to-one correspondence between particle size and composition, even if they don't explicitly make this claim. Although particle size may be related to composition, the relationship is most certainly not straightforward and highly subject to specific experimental conditions (including the amount of precursor VOC and the rate of oxidation). The authors do provide strong evidence for the optical properties of SOA being highly variable, but it is not clear to me that these results provide any particular elucidation of the controlling factors, at least not as presented. I would encourage the authors to look for ways they can present their data similar to how they did in Kim et al. (2012), where they showed derived RI vs. HC/NO_x. I believe that this would allow for more direct connections to be made between particle composition and particle RI, even when no composition measurements have been directly made. That said, most of the results presented in the current work are extensions or repeats of previous experiments: it is really only the results from the thermodenuding experiments that are particularly new. Here, they find that there are some differences in how thermodenuding influences the derived RI values, with apparent differences between higher HC/NO_x and lower HC/NO_x conditions. This is interesting. They speculate that these differences suggest “significantly different chemical composition of SOA generated under low [vs. high] NO_x conditions,” but provide no supporting compositional evidence. How “significant” do they expect the differences to be based on the literature? Given that no direct composition measurements have been made, I suggest that a much greater link to the literature would be beneficial. It does appear that there are some differences in the volatility of the aerosol formed at higher vs. lower HC/NO_x that correlate with the RI behavior, but the authors do not refer to

this in their discussion of the optical properties, and it is only indirect evidence in any case (although should nonetheless be exploited). Regardless, I find that the differences between different conditions are often difficult to discern, at least as presented. The authors might wish to try something like graphing the mean change in RI upon thermodenuding vs. HC/NO_x (for photooxidation experiments). Or the change in RI vs. the volume fraction remaining upon thermodenuding. Something like this, I believe, would help to make the relationship with composition stand out.

Other comments:

P1951, L21: The references given here seem biased towards the authors' own work.

P1952, L1: I find the statement "We note that smaller particles (e.g. <200 nm) do not scatter much light, which presents measurement challenges and in some cases requires high mass concentrations" to unduly put emphasis on techniques that do not have the sensitivity to make light scattering (or extinction) measurements. There are techniques that are quite capable of making measurements at low concentrations, such as cavity ringdown. See for example the sensitivity of the CRD spectrometer described in Langridge et al. (2011). This instrument can easily measure particle scattering for much smaller particles. Also, this statement seems inconsistent with the mention on P1957 that the authors can reliably retrieve Ri values for particles >100 nm when concentrations are >20 micrograms/m³.

P1952, L13: The statement "By generating aerosols at higher concentration and thermodenuding them, we may obtain aerosols with the full range of volatilities, and then thermodenude them to obtain more atmospherically relevant lower volatility species" implicitly assumes that particle phase reactions do not occur that modify the particle properties, making thermodenuding a potentially inefficient method of generating atmospherically relevant particles. Note that this is true whether such reactions are enhanced by heating or not. In other words, if particle phase reactions are already leading towards the production of low volatility material, then lower volatility species may already be generated at "high" SOA concentrations. The question is then not one of volatility, but of compositional representativeness.

P1952, General: If the point of the thermodenuding is to push the particle composition back towards ambient, then why not just do experiments at lower initial concentrations? One cannot get around the issue of instrument sensitivity just by using a thermodenuder.

P1955, L24 and Fig. 1a: Looking at this figure, it appears that it took more like 1 hour to stabilize at a new temperature, yet the authors' state it takes 6-9 minutes. It would be helpful if clarification was provided.

P1959, L3: It is not entirely clear why "Reliable refractive indices were first obtained when the particles had grown to about 344nm at 13:07." What specifically limited the ability to extract refractive indices prior to this? Presumably not concentration, because this would then suggest that the thermodenuded results are unreliable. Is it the rapidly evolving size distribution during this period? Also, on P1957 the authors state that reliable measurements can be made for particles >100 nm when concentrations are >20 micrograms/m³.

General: I am not entirely convinced that the characteristic shape (i.e. the up/down behavior) that the authors observe for SOA RI values vs. particle diameter is not a result of changing instrument sensitivities.

Figure 2 and associated discussion: Khlystov and co-workers have shown that “mass fraction remaining” is potentially an unreliable metric because it explicitly depends on the associated mass loading for a given experiment. This is a result of recondensation at higher mass loadings influencing the net evaporation. Given this, it could be helpful if the authors were to color code the data by mass concentration, using a consistent color scheme through all 3 panels. This is especially important given that, based on the information in the table 1, the mass loadings for Limonene SOA were systematically higher than those for α -pinene, and the mass loadings for toluene SOA appear to have been even higher. How can the authors ensure that the differences are not simply due to different mass loadings?

P1959, L20: The authors mention that higher f_{44} values for toluene SOA compared to biogenic SOA might indicate aromatic SOA is less volatile than biogenic SOA. However, f_{44} is never defined to let the reader know what this means. In other words, the authors are using Aerodyne aerosol mass spectrometer (AMS) jargon without defining it or assuming that the reader knows that f_{44} is thought to correspond more to organic acids. In any case, the reference they cite (Chhabra et al.) says nothing *directly* about volatility of SOA. A specific reference is needed to support the contention that higher f_{44} should equal lower volatility.

P1960: Regarding the various discussion about RH effects: do the authors mean to imply that particle phase water is leading to differences, or are they assuming that there are differences in the gas-phase formation of SOA condensables? This should be stated. At these low RH's the amount of water uptake for these types of SOA are typically very, very low.

S3.4.1: I find the discussion regarding water uptake to be confusing, and the authors appear to be conflating chemical changes with size changes. Size is not important, except to the extent that it reflects that the reactions have been run for longer times and greater amounts of SOA formed, potentially with a different composition than earlier in the experiments. It is composition that matters. I find the emphasis on size to be misplaced and suggest that the authors focus on the compositional differences. As such, I suggest that the authors adopt their approach from Kim et al. (2010), in which they consider their observed RI values vs. mass concentration, instead of the approach from Kim et al. (2012), in which they also use particle size as the key metric.

S3.4.1-Toluene SOA: The values observed here do not actually seem to me to be consistent with the previous observations, despite the statement that they are “consistent with previous studies.” In Kim et al. (2010) the RI for toluene SOA formed at the same VOC/NO_x (=15) as here ranged from ~1.45-1.55. This is substantially higher than the 1.35 values reported in the current study. What is the reason for this difference? It is somewhat difficult to make direct comparisons between this work and Kim et al. (2010) because here the authors report their results relative to particle diameter while in Kim et al. (2010) they report them vs. mass concentration (which, in my opinion, is the physically more meaningful quantity in

any case; see above comment). The data from the two studies should be compared directly, perhaps in the supplemental material like the aP and limonene results.

S3.4.1-Toluene SOA: Nakayama et al. report an imaginary RI of 0.007, not 0.037 as stated. This is a very, very important distinction as Mie theory is very sensitive to changes in the imaginary RI when it is around this range. In any case, the authors should state what they believe to be their detection limit for imaginary RI values. To state that their GA retrievals give values $O(10^{-5})$ is not helpful if they cannot distinguish between 0.1 and 0.05 (as a random example).

P1964, L9: As far as I can tell, Salo et al. (2011) report a temperature of formation influence on the volatility of the formed SOA, but they in no way identify 20°C as “an important transition temperature.” The authors need to elaborate as to what exactly leads them to this conclusion. Also, here the difference in temperature between the Nov. 18 experiment and the other experiment ranges from 2-5°C, which is much smaller than the 20°C steps in the Salo et al. (2011) experiments. Given this, I am not convinced by the argument that the difference between, in particular, the Nov. 18 and Nov. 10 experiments is explainable by the different temperatures.

P1962, L22: The authors need to advance a stronger theoretical reason for the increase/decrease behavior of the real RI for both limonene and aPinene SOAs. I find the arguments put forth on the top of the next page to be weak, given the lack of actual composition data here. Their own calculations in Kim et al. (2012) indicate a monotonic increase in RI with mass concentration (and presumably particle size, but this is not shown). Is this behavior simply being driven by the particulars of whether particles are more likely to nucleate fewer, bigger particles or more, smaller particles given a particular set of reaction conditions?

P1963, L9: The authors need to provide a reference (or references) in support of the statement: “The observed TD behavior is consistent with a simple model for aerosol growth in which more volatile species are deposited on lower volatility species as the experiments progress; heating appears to simply reverse the process. This behavior is consistent with the notion that condensed species do not mix effectively, but instead layer material on as they grow,”

Figure 6: I find the presentation in this figure to be somewhat confusing. In particular, it is not clear to me what is determining the vertical height of the boxes as compared to the +/- 15% error bars. Are these +/-15% on top of the total observed range? Further, I would suggest that this figure is potentially misleading in terms of the atmospheric relevance. The authors include results from all of their experiments, which cover an extremely wide range of organic mass loadings, most of which are well above the atmospherically relevant range. What would this figure look like if constrained simply to the atmospherically relevant range of concentrations? I suppose that this, then, limits the ability to make this figure to the thermodenuder measurement here, as they are the only ones that measure optical properties for SOA anywhere close to ambient concentrations. Nonetheless, the point is well made that SOA optical properties cannot be considered a constant.

P1954, L7: “gasses” should be “gases”.

P1957, L18: “Detailed” should be “Details”

P1962, L10: Figure 4S should be Figure S4.