Response to Reviewer Comments on "Evolution of organic aerosol mass spectra upon heating: implications for OA phase and partitioning behavior" by C. D. Cappa and K. R. Wilson

We thank the reviewers for their insightful and useful comments and suggestions.

Reviewer comments are given as normal text. Our response is italicized.

Referee #1

Data evaluation: The calculation of the volume loss from the SMPS data takes into account the volume loss of the aerosol as a result of the shrinkage of the individual particles, while the possible full evaporation of a part of the particles is not considered. Especially in the case of the alphaP aerosol with a median particle diameter of only 92 nm, it is probable that the smaller particles fully evaporate due to the Kelvin effect. Moreover, as a consequence of the heating/cooling in the thermodenuder, recondensation of a part of the volatilized material can occur and alter the size distribution of the particles. Therefore, an alternative evaluation should be attempted that takes into account the partial loss of particles because of full evaporation or, at least, evidence should be presented showing that this process can be neglected.

The loss of particles due to full evaporation can be evaluated by considering how the shape of the size distribution (i.e. σ_g) changes with TD temperature. If small particles are preferentially completely evaporating due to the Kelvin effect, then we would expect to see the σ_g change substantially as the TD temperature increases, perhaps expecting the distribution to first widen (as the small particles shrink to a greater extent than the big particles) before narrowing (as the small particles disappear completely). We find that the σ_g values for the alpha-pinene (aP) aerosol change by a only a small amount, being 1.53 at room temperature and decreasing to 1.48 at the highest temperature. This shift towards slightly larger σ_g values does appear to occur systematically with increasing temperature, although we see no evidence in the size distribution scans for significant loss of the smaller particles in the size distribution. This is shown in the following figure (which we have not included in the manuscript).
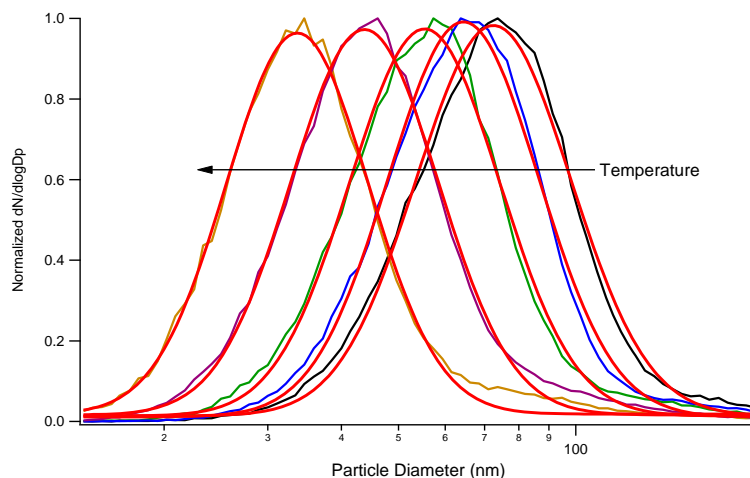
We have however added the following sentence in section 3: "The distribution width, σ_g, only changes slightly from low to high T_{TD}, indicating that preferential loss of small particles is not significantly influencing our results."

Recondensation is always a concern in TD studies, especially in experiments performed at "high" mass loadings, as was done here. Yet, there is no strong reason to think that recondensation would be significantly different between the aP and lubricating oil (LO) system. Further, we note that our general results (namely, that LO aerosol is more volatile than aP aerosol) is consistent with other experiments that employed a thermodenuder (e.g. (Huffman et al., 2009)). Finally, we note that the evaporation model used to quantitatively interpret the observations (Cappa, 2010) does account for recondensation. Thus, we do recognize that recondensation is not a process that can be neglected, but is at least a process that can be and has been accounted for. Further discussion of this topic is given in R1.4.

R1.2: One puzzling finding of this study is that the evolution of the VUV photoionization mass spectrum of the alphaP aerosol showed no distinct changes with temperature as would be expected from absorptive partitioning theory. The authors postulate that this behavior arises from the alphaP particles existing as in a glassy state. They present a conceptual model wherein the secondary OA is formed and then rapidly converted from an absorbing to a non-absorbing form. One difficulty of this model is that the thus formed particles should be "composed of sequential layers that have differing composition, with a greater fractional amount of higher volatility material in the outer layers than in the inner layers" as the authors state themselves. If this is the case, the evolution of the VUV mass spectrum should be temperature dependent because the outer higher volatility material should evaporate first.

We recognize the difficulty identified by the reviewer as an explicit limitation of the model as presented and applied to our observations. There is indeed an inconsistency with our observations. However, we believe that we have made clear this limitation through statements such as "We emphasize that this is a conceptual model meant to demonstrate that traditional absorptive partitioning theory is not the only theory capable of describing aerosol growth experiments and that the S-EPM is not a definitive physical representation of the processes occurring in the experiments described here" at the beginning of Section 3.4 and the paragraph on P. 28450 (lines 12-26):

"One potential difficulty associated with applying the S EPM to the interpretation of the αP results in this study is that the S EPM, unlike the equilibrium model, could lead to a situation where the thus formed particles are composed of sequential layers that have differing composition, with a greater fractional amount of higher volatility material in the outer layers than in the inner layers. This is a result of the "shell-by-shell" formation in the S EPM, whereas in the equilibrium model it is assumed that the particles are well-mixed at all times. (Although we note that there is nothing inherent to the S EPM that requires shell-by-shell formation, only that the absorbing material is converted to a non-absorbing phase.) However, the observations suggest that the αP particles are homogeneous, yet highly viscous such that the particle composition does not change during evaporation. As such, we reiterate that the S EPM is not meant to provide an exact representation of the physical processes that actually occur in our experiments, but only to demonstrate that aerosol growth measurements can be modeled within a

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conceptual framework that allows for transformation of the particles from a liquid-like to glassy phase on some timescale."

Furthermore, we believe that the sequential partitioning model is a useful to the discussion, despite its limitations, because (as we state above) it "demonstrate[s] that aerosol growth measurements can be modeled within a conceptual framework that allows for transformation of the particles from a liquid-like to a" non-liquid like phase.

R1.3: Another major difficulty of the presented explanation is that the glassy state should persist up to temperatures as high as 130C. However, the glass transition temperature (Tg) depends among other factors on MW. Hydrophilic substances with MW < 200 have typically Tg close to room temperature or below (e.g. glucose: MW = 180.16, Tg = 303 K ; citric acid: MW = 192.13, Tg = 283 K; tartaric acid: MW = 150.09, Tg = 289 K, glycerol: MW = 92.1, Tg = 180 K; all values from Craig et al., Int. J. Pharm., 179, 179–207, 1999). The alphaP aerosol with virtually all observed MW < 200 should therefore be present as a liquid even at RT. Nevertheless, the viscosity of these particles might be high rendering diffusion slow although the particles are not in a glassy state. Such a discussion of Tg should be added to the manuscript.

We have revised the manuscript to include explicit discussion of T_g values for individual compounds, both the low MW species here as well as for longer polymeric compounds (see comment R2.8). We have also revised the manuscript to emphasize that, as the reviewer points out, high viscosity/slow diffusion is key and that specifically calling the particles "glassy" is an assumption.

R1.4: Recondensation and redistribution of material between aerosol particles is expected to be very fast for semivolatile species that partition strongly to the gas phase. Marcolli et al. (Atmos. Chem. Phys., 4, 2593–2599, 2004) estimated that equilibration times for hydrophobic species with MW up to ca. 250 and highly hydrophilic species with MW up to ca. 100 show equilibration times of less than 1 s. This is fast enough for considerable recondensation already at the end of the heating zone even before the diffusion denuder is reached. The alphaP aerosol contains a large fraction of components in this low molecular weight range (the volatility basis set shows the largest stoichiometric yields (alpha) for C* = 1000 and 10000 microgram/m3). Therefore, the effect of recondensation of the aerosol within the thermodenuder has to be considered. The effect of such recondensation might be that the low MW fraction would show low net evaporation. Fast recondensation affecting the composition and size distribution of the particles could offer an alternative explanation why the alphaP aerosol mass spectrum is essentially unchanged as a function of evaporation temperature and why such high temperatures are needed to evaporate the alphaP aerosol.

The connection between MW and equilibration times identified by Marcolli et al. has more to do with differences in vapor pressure between species of different MW (for the same functional groups) than it does with the direct effect of MW on evaporation/condensation rates. For example, Figure 2 in Marcolli et al. (2004) (reproduced below for convenience) shows this explicitly. Note the horizontal dashed lines, which indicate that equilibration time is more related to vapor pressure than it is to MW. The dependence on MW occurs primarily because, for an organic compound of a given type (e.g. a

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hydrocarbon), there is a direct correspondence between MW and vapor pressure. As such, we do not believe that differences in recondensation resulting from MW differences between LO and aP aerosol can explain the observations. Further, we note that recondensation is explicitly considered in the evaporation model that was used to model the observations.
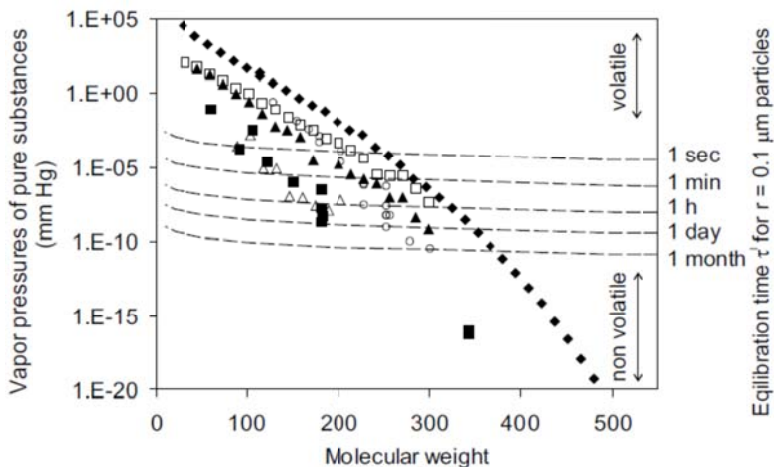
R1.5: Fig. S-1 in the supplement gives an interesting comparison between EI-AMS and VUV-AMS. It should be included in the main text.

This has been done.

R1.6: Section 2.2.1: The preparation of the lubricating oil aerosol should be explained in more detail, especially, the "filter-based diluter".

This has been done.

R1.7: Section 3: The volume fraction remaining is evaluated solely based on the changes in the particle size. This evaluation assumes that the whole mass or volume loss of the aerosol is due to the decrease of particle diameter. However, there is also the possibility of mass loss due to decreasing number of particles. This effect should be evaluated by comparing the number concentration of aerosols that passed through the TD at RT and at elevated temperature. Such an evaluation should be feasible because the dependence of particle number loss on temperature in the thermodenuder is rather small (Huffmann et al., 2008). The authors might also show a figure with SMPS spectra of LO and alphaP aerosols that passed the thermodenuder at RT and at elevated temperature.

The reviewer is correct that particle number loss can and do additionally contribute to mass loss. However, we believe it is important to recognize that this particle number loss is not an evaporative loss, and thus contains no information on the aerosol volatility. By using the particle size decrease, we are able to effectively determine how the particle mass would have changed if there were no particle number loss; this is the critical parameter here. Such an approach has been previously taken by, e.g. (Grieshop et al., 2007) for in-chamber isothermal dilution experiments, where particle number loss to the

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walls is a significant concern, and by (Grieshop et al., 2009) for thermodenuder experiments. That being said, for the measured VUV mass spectra, it is important to account for the particle number loss if the observations are to be quantitatively compared with the size-based SMPS observations (note that this will have no influence on the comparison between normalized VUV-MS's collected at different temperatures). This was done in our analysis, but we failed to state this; that the overall peak thermogram was corrected for particle number loss is now stated.

R1.8: Fig. 3: Some of the peak thermograms in Fig. 3 show "fraction remaining" values above 1. Is this a consequence of the applied normalization procedure? Can it be explained by recondensation of some of the lubricating oil on the particles in the thermodenuder, either from the same experimental cycle or by contamination from former experimental cycles? Have any tests been performed to exclude contaminations due to re-evaporation of material that has condensed in the thermodenuder during former experiments?

Most of the traces for which fraction remaining values are above 1 correspond to some of the much smaller (i.e. lower intensity) peaks in the mass spectrum, which have lower signal to noise ratios making exact normalization difficult for these features. All measurements were done by running all experiments in "reverse", i.e. from high temperatures to low temperatures, thus minimizing or eliminating contaminates from previous experiments.

R1.9: Page 28441: taking the C*/MW relationship, the alpha and the observed MW do not match. Have you tried to fit the data with alpha that correspond better to the observed mass distribution?

This relationship is only valid for saturated hydrocarbons, not for compounds with oxygenated functional groups. For aP aerosol, we assumed a fixed value of 150 amu. This is now stated explicitly.

R1.10: Page 28444: Considering the MW of the alphaP aerosol it is highly unlikely that it persists as a glass up to 130C (see general comment).

See reply above.

R1.11: Page 28468, Fig. 5b: Hoffmann (1997) and Pathak (2006) are missing from the reference list. The y-axis title is confusing. It should be changed to "SOA mass fraction" as in Pathak (2007a).

These references have been fixed and the figure changed.

R1.12: Technical comments.

All technical comments have been corrected.

Referee #2

R2.1: Page 28435, line 4: Is this diesel lubricating oil, and is it the same type used by the CMU group to develop their basis set?

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Like CMU, we used SAE 10W-30 lubricating oil (LO) for our experiments. However, as noted in the comment by Grishop and Robinson, our methods of aerosol production were different. Whereas we used homogeneous nucleation via heating to produce particles, the CMU group used flash vaporization. This may have caused the LO aerosol in our experiments to have a somewhat different composition than in the CMU experiments. We now note this difference in LO aerosol generation method explicitly in Section 3.2 and briefly mention the implications of this for our study (namely, that if our LO aerosol is more volatile than the basis-set aerosol, the derived evaporation coefficients would be upper limits).

R2.2: Page 28436, line 11: Please provide a reference for the assumed alpha-pinene SOA density.

This has been done (Shilling et al., 2009)

R2.3: Page 28438, lines 1-4: It might be worthwhile adding a comment and reference regarding the carbon number distribution of diesel lubricating oil and comparing it to the observed mass spectrum. For example, there is a chromatogram in Sakurai et al., Atmos. Environ. 37, 1199-1210 (2003) for 15W40 diesel oil, or perhaps the authors know other references.

This is a useful suggestion and we thank the reviewer for pointing us to the chromatogram in Sakurai (2003). The largest set of peaks in the VUV-MS for LO aerosol are around 335 amu, which corresponds to a N_c ~ 23-24 carbon atoms.

Besides the Sakurai chromatogram, we have found that there are a number of gas chromatograms available for 10W-30 lubricating oil. For example, Lambe et al. (2009) present a chromatogram for a mixture of fuel and 10W-30 oil (Lambe et al., 2009). They find a peak in the chromatogram for the unresolved complex mixture (UCM) around 26 or so carbon atoms. Reardon et al. find that the UCM for 10W-30 peaks somewhere around 26-27 carbon atoms (Reardon et al., 2007). Grieshop et al. (2009) present GC results for both liquid and aerosol (from flash vaporization) 10W-30 LO, and found that the aerosol GC peaked a bit earlier than the liquid GC, suggesting that the aerosol was slightly more volatile than the source LO (Grieshop et al., 2009), although perhaps only by 1-2 carbon atoms. This is highly consistent with our observations (N_c ~ 23-24), with the VUV-MS indicating the homogeneous nucleation LO has 2-4 fewer carbons than the source LO (which we assume to have 26 or so carbons). Further, we note that fragmentation of molecules in the VUV-AMS is going to skew the observed distribution of peaks in the mass spectrum visually towards smaller carbon number compounds. This means that our observed distribution represents a likely lower limit on the typical N_c of compounds comprising our LO particles. This is now discussed in Section 3.1.

R2.4: Page 28438, line 27 through Page 28439, line 25: How does the mass spectrum obtained with VUV compare with those obtained by Murray Johnston and co-workers, who have published a number of papers on alpha-pinene + O3 SOA analyzed by electrospray MS. The comparison is probably worth noting, since both are presumably soft ionization methods.

The VUV-MS spectrum at the ALS compares favorably with the PIAMS spectra for α-pinene + O_3 aerosol obtained by the Murray group. We thank the reviewer for reminding us of the comparability of these two

measurements methods. We have added brief discussion of the PIAMS spectrum in relation to ours in section 3.1.

R2.5: Sections 3.1 and 3.5.1: Might some of the differences between the CMU dilution experiments indicating equilibrium partitioning, the Docherty et al. (2005) desorption experiments, and the results observed here be due to the differences in the timescales for evaporation, which are very different?

Yes, the different timescales may certainly play an important role. We have added mention of the in-chamber dilution experiments from CMU (Grieshop et al., 2007) and discuss further the importance that evaporation timescales may play in Section 3.5.1.

R2.6: Page 28442, line 25 through Page 28443, line 2: It seems like an alternative model that could explain the observations for alpha-pinene SOA is that the SOA is composed primarily of oligomers and that evaporation does not occur layer-by-layer but monomer-by-monomer as monomers with constant average composition dissociate from essentially non-volatile oligomers. This would not require any assumptions about the particle phase.

This is an interesting idea. In the literature there appears to be much debate over the exact abundance of oligomers in SOA of various types. Some methods seem to indicate very large contributions from oligomers whereas other methods suggest small contributions. The quantification of oligomers in particles is certainly still analytically challenging. Nonetheless, if we assume that the OA is primarily comprised of oligomers, then we think it is important to also ask the question, how would this influence the particle phase or traditional partitioning theory? Both models (oligomers vs. amorphous phase) require that something happens to the compounds after they condense to the particle phase that makes it such that the observable properties (at least in our experiments) are inconsistent with traditional partitioning theory. Furthermore, our results, along with those of Johnston and co-workers, suggest that this particle-phase conversion process can be fast.

In any case, we believe that the model suggested by the reviewer would look very similar to the model presented by us: namely that as compounds condense they are converted to a "non-volatile" and "non-absorbing" state and thus do not evaporate as expected. Numerically, such a model would be very similar to that presented by us, but we grant that conceptually these are somewhat different. We now mention the reviewers idea in Section 3.4, stating that "It is possible that the conversion to this non-absorbing phase involves the formation of oligomers." We have additionally added an entire paragraph at the end of this section that discusses this idea in some detail.

R2.7: Page 28444, lines 7-8: More appropriate diffusion coefficients for comparison than water at 150-160 K are probably values in glassy organic polymers, such as 4×10^{-18} m2 s-1 for iodohexane in polystyrene [Hui et al., J. Appl. Phys. 61, 5137-5149 (1987)] or 3×10^{-20} m2 s-1 for a small oligomer (640 g/mol) in polymethylmethacrylate [Bucknall et al. Chem. Eng. Sci. 56, 5473–5483 (2001)].

We thank the reviewer for pointing us to these references and agree that they will provide a more appropriate comparison. The manuscript has been changed accordingly.

R2.8: It would be useful to quote, with references, typical values of glass transition temperatures for organic polymers for comparison with the TD temperature range of these experiments. This will add support for the proposal that the alpha-pinene SOA is always in a glassy state in the TD.

We have revised the manuscript to include explicit discussion of T_g values for individual compounds, both the low MW species here as well as for longer polymeric compounds (see comment R1.3). We have also revised the manuscript to emphasize that, as the reviewer points out, high viscosity/slow diffusion is key and that specifically calling the particles "glassy" is an assumption.

Response to Grieshop and Robinson:

R3.1: Our aP aerosol dilution experiments with a unit-resolution AMS showed variation (though not necessarily reversible) in the relative contribution at various m/z during both formation and later evaporation of the aerosols by dilution (Grieshop et al. 2007). For example, the contribution at m/z 44 decreased during two stages of aerosol formation and increased during dilution, indicating a variation in particle composition with aerosol loading consistent with the partitioning of semivolatile products with different volatilities and levels of oxygenation (Figure 3 in Grieshop et al., 2007), similar to what has been observed in some TD studies.

We thank the commenters for reminding us of this important result. We now mention this explicitly in the text in the literature comparison section.

R3.2: Discussion in Section 3.5.3 contrasts evaporation coefficients (γ_e) determined using a model of particle evaporation in the TD to those implied by the slow evaporation observed in our chamber-dilution experiments with aP (Grieshop et al. 2007) and LO (Grieshop et al. 2009) aerosols. The results for aP particles seem broadly consistent, while those for LO are quite different. The slow evaporation of both aerosols in our experiments was a surprise for us and certainly could be consistent with glass-like aerosol. Loss of semivolatile vapors to the Teflon walls of the smog chamber (Loza et al. 2010; Matsunaga and Ziemann 2010) does complicate interpretation of the formation and evaporation of semivolatile organic aerosols. For example, a 'buffering' of vapor-phase concentrations in the chamber during dilution by slow release of vapors lost to the walls could retard the evaporation of particles in our experiments. However, one must also be concerned about condensed phase reactions at elevated temperatures inside a TD.

However, there are likely significant differences between the aerosols in these and our experiments that should be noted and complicate a direct comparison. For example, the LO aerosols were generated in different ways. In this study, they were produced for introduction into the TD by heating liquid oil at 80 to generate particles via homogeneous nucleation in air, followed by dilution to control aerosol concentrations. This approach will likely create aerosols that are comprised of the more volatile fraction of the LO. Although LO aerosol may completely evaporate inside a TD at 80 C the concentration of lube oil is very low. In an engine, LO does not evaporate at 80 C because concentrations are much higher. In contrast, our study was based on aerosols generated with used LO flash vaporized at 425 C directly into

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the chamber, also forming aerosol via homogenous nucleation. Figure S.1 in the Supplemental Information accompanying the paper showing the LO data (Grieshop et al. 2009) indicates that our LO aerosols were quite similar in composition to the source oil, though perhaps slightly biased towards higher volatility material. The LO thermogram in this manuscript shows an aerosol that is substantially more volatile than that in our work.

The authors make a good point that condensed phase reactions at high TD temperatures are a concern. We cannot fundamentally rule out the influence of such reactions, although we point out two observations which suggest that, for our experiments, such reactions are of minimal concern: (1) the aP spectrum does not significantly change with heating, suggesting minimal compositional changes over the temperature range considered here and (2) strong differences between the LO and aP systems are observed to occur at room temperature, simply from the presence of the charcoal in the TD.

Regarding the concerns that there are likely <u>significant</u> differences that complicate a direct comparison, we agree that some compositional differences may arise due to differences in aerosol generation method. However, as noted in our reply to Reviewer #2 (comment 3), the magnitude of these compositional differences may not be as large as the commenters imply. The commenters allow that their LO aerosol (from flash vaporization) is "perhaps slightly biased towards high volatility material". Given that our LO aerosol seems to have only 2-4 fewer carbon atoms than the source oil, and that the CMU LO aerosol is somewhat more volatile than the source oil (by ca. 1-2 carbons), this suggests that, although there may be a difference in the volatility of ours and their LO aerosol, this difference may be smaller than the commenters seem to imply.

Finally, we look towards the mass thermograms presented for lubricating oil by Grieshop et al. (2009). Like Grieshop et al., we find that the MFR for LO aerosol does not go to zero until ~70°C, suggesting reasonably similar volatility. We recognize that the experiments were conducted at very different mass loadings, which can complicate such direct comparison of mass thermograms. However, the Grieshop et al. mass thermogram was determined using a much smaller initial LO loading (70 $\mu g/m^3$), which should naturally be "less volatile" than the same aerosol type at a much higher mass loading (as in our experiments or in their isothermal dilution experiments). Certainly, visual comparison of mass thermograms collected under different conditions is challenging (and fraught with peril), but we believe that this qualitative comparison supports our above contention – namely that there may be differences in composition between our LO aerosol and theirs, but that such differences are not as significant as implied.

R3.3: P. 28438, L23-25 – This statement is unclear.

We have clarified.

R3.4: P. 28454, L15 – Grieshop is misspelled.

This has been fixed.

References:

Cappa, C. D.: A model of aerosol evaporation kinetics in a thermodenuder, Atmos. Meas. Technol., 3, 579-592, doi:10.5194/amt-3-579-2010, 2010.

Grieshop, A. P., Donahue, N. M., and Robinson, A. L.: Is the gas-particle partitioning in alpha-pinene secondary organic aerosol reversible?, Geophys. Res. Lett., 34, L14810, doi:10.1029/2007GL029987, 2007.

Grieshop, A. P., Miracolo, M. A., Donahue, N. M., and Robinson, A. L.: Constraining the Volatility Distribution and Gas-Particle Partitioning of Combustion Aerosols Using Isothermal Dilution and Thermodenuder Measurements, Environ. Sci. Technol., 43, 4750-4756, doi: 10.1021/es8032378, 2009.

Huffman, J. A., Docherty, K. S., Mohr, C., Cubison, M. J., Ulbrich, I. M., Ziemann, P. J., Onasch, T. B., and Jimenez, J. L.: Chemically-Resolved Volatility Measurements of Organic Aerosol from Different Sources, Environ. Sci. Technol., 43, 5351-5357, 2009.

Lambe, A. T., Miracolo, M. A., Hennigan, C. J., Robinson, A. L., and Donahue, N. M.: Effective Rate Constants and Uptake Coefficients for the Reactions of Organic Molecular Markers (n-Alkanes, Hopanes, and Steranes) in Motor Oil and Diesel Primary Organic Aerosols with Hydroxyl Radicals, Environ. Sci. Technol., 43, 8794-8800, doi: 10.1021/es901745h, 2009.

Reardon, M. R., Allen, L., Bender, E. C., and Boyle, K. M.: Comparison of Motor Oils Using High-Temperature Gas Chromatography-Mass Spectrometry, Journal of Forensic Sciences, 52, 656-663, doi: 10.1111/j.1556-4029.2007.00421.x, 2007.

Shilling, J. E., Chen, Q., King, S. M., Rosenoern, T., Kroll, J. H., Worsnop, D. R., DeCarlo, P. F., Aiken, A. C., Sueper, D., Jimenez, J. L., and Martin, S. T.: Loading-dependent elemental composition of alpha-pinene SOA particles, Atmos. Chem. Phys., 9, 771-782, doi:10.5194/acp-9-771-2009, 2009.

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