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Comment

Interactive comment on “Measurement of non-volatile particle number size distribution” by G. I. Gkatzelis et al.

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Received and published: 25 October 2015

(1) *This paper describes data collected through a thermodenuder (TD) operated at high temperature (400 C) during several laboratory and field measurements of aerosol size distribution, chemical speciation (with a HR-AMS) and black carbon/aerosol light absorption (with a MAAP). The results show that SOA particles formed in chamber experiments from single precursor compounds essentially completely evaporate during passage through the TD – evidenced by a complete loss of aerosol mass and number. On the other hand, ambient measurements, and measurements of oxidation of ambient aerosols, indicate that a substantial fraction of the particle number contains what are termed ‘non-volatile’ cores. The study quantifies the number fraction remaining*

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via the particle size distributions measured before and after heating, and uses these measurements to gain insight into the sources of ‘non-volatile’ cores.

This is an interesting set of studies, but I question whether what is presented is really a new experimental methodology, and thus whether AMT is the appropriate venue. Thermodenuders have been operated for decades, including at elevated temperatures (Clarke et al. 2007; Clarke 1991; Wehner et al. 2002), and number-weighted size distributions have been compared in many of these studies. At the most, the paper presents a slightly different way of presenting data collected using what is now a fairly standard technique. Therefore, my feeling is that this work does not belong in a journal the focus of which is new method and tool development because there is quite sparse information on the actual data analysis (e.g. PMF on denuded aerosol spectra) and many of the insights are very particular to the campaigns in which the measurements were collected.

We understand the dilemma of the referee given that our study includes both elements of method development and also its application and testing under ambient conditions. We think that AMT is the best choice for its publication because even if thermodenuders have been around for a long time there has been relatively little study of what they actually do under ambient conditions. Most of their testing has been in the laboratory with model aerosol (usually consisting of one component). We do propose the use of a thermodenuder under relatively extreme conditions compared to most other applications (e.g., much higher temperature and residence times) and show that these are sufficient to evaporate fresh secondary organic aerosol and particles originating from nucleation/growth events. On the other hand we show that the same conditions are not enough to evaporate all the organics under ambient conditions. We do believe that these are significant contributions to the development of methods for a journal like AMT. We do agree that some of the results of the application are specific to the campaigns but this is unavoidable when an experimental method is tested in the field. We have added additional information about the PMF on denuded aerosol spectra in the revised

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manuscript.

(2) *Apart from this issue, my main concerns pertain to issues with data analysis and presentation of results. Below I list several of these. One other general issue is that the tables and figures are excessive and not very 'information-dense' – there are 14 figures and many of them are essentially displays of raw data time series. I would suggest that the authors work to reduce the number and select figures that more strongly support the point of the paper. Figures 1 through 8 could easily be moved to a supplement.*

We have followed the referee's suggestion and moved Figures 1, 2 and 3 to the Supplement. We do consider figures that represent the results of our chamber experiments (Figures 4 through 10) an important aspect of this work, since these are rather unique to the best of their knowledge, and they could serve as a basis of laboratory intercomparisons of thermodenuders with more complex aerosols. We have combined though Figures 4-5, 6-7, and 8-10 into just three reducing the overall number of figures from 14 to 7.

(3) *It would be helpful to see a figure like Fig. 11 showing NFR vs BC mass fraction, rather than just BC mass.*

We have prepared the requested figure including the organic aerosol concentrations and mass fractions and added it to the Supplementary material of the paper (Figure S4). The use of the BC mass fraction instead of the BC concentration complicates things because of the existence of the nighttime periods with a lot of biomass burning organic aerosol and the rush hour morning periods with a lot of aerosol from traffic. During the traffic dominated periods there are relatively high BC mass fractions but relatively low NFRs because of the existence of small semivolatile particles in the traffic emissions. During the nighttime biomass burning periods the mass fraction of BC is lower because there are a lot of organic compounds emitted from this source. However, because most particles include an extremely low volatility core these low BC mass

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fractions correspond to higher NFRs. We have added the above discussion to the Supplementary material and kept the original figure with the BC mass concentration in the main text.

(4) *Figures showing size distributions should indicate the number of scans or time span shown, and should ideally include confidence intervals. Focusing the presentation of results would help make the paper more cohesive.*

We have added the information about the scans in the corresponding figure captions and also added the confidence intervals in the figures.

(5) *Title: The title is not representative, as a good amount of the discussion and supporting evidence comes from mass (and absorption) measurements. "Measurement of non-volatile sub-micron particle fraction" might be a more appropriate choice.*

Chamber experiments, done for the characterization of the instrument, focused only on the number concentration and size distribution of fresh SOA coming from classic biogenic and anthropogenic precursors (Figures 4 to 10). Furthermore, the results derived during the Athens campaign (Figures 11 to 14) were related to the NFR and size distributions of these particles. Although, during the Athens campaign we used the mass concentration for the characterization of non-volatile particles, the focus of this work is on their number concentration and size distribution. Therefore, we would prefer to keep the original title of the paper mentioning the particle number size distributions.

(6) *I also question the characterization of the material measured under these conditions as 'nonvolatile'. This is 'operationally defined' here based on the measurement parameters, but the potential impacts of changes in these measurements are not given. For example, TD residence time can have a controlling effect on particle evaporation (Saha et al. 2015; Saleh et al. 2011) and organics may form char or form oligomers at high temperatures (Denkenberger et al. 2007). 'Non-volatile' may be a short-form*

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name for what was measured, but these potentially influences on measurements are mostly not discussed.

This is a valid concern. We now clarify early on in the paper that we define as non-volatile the particles that do not evaporate completely under the conditions of our measurement. Based on our estimates the saturation concentration of the corresponding compounds at room temperature should be less than $10^{-5} \mu\text{g m}^{-3}$. According to the terminology proposed by Murphy et al. (2014) these compounds if organic should be categorized as extremely low volatility organic compounds (ELVOCs). If they are BC or other similar material they should be categorized as practically nonvolatile. After this clarification we do use the operationally defined term “non-volatile” in the rest of the paper.

We have tried to address the potential formation of char or oligomers in our laboratory experiments. We did not observe such artifacts for the systems that we studied. However, the situation could be different for the ambient measurements. The AMS data and the corresponding PMF analysis did not indicate any major issues. We also tried to use results of previous studies regarding the potential magnitude of such artifacts concluding that the corresponding uncertainty for our measurements is of the order of 10 percent or less. We do discuss these issues and the corresponding pitfalls in the revised paper.

(7) The use of the chamber-generated SOA evaporation to assess the method is interesting, but these aerosol are relatively homogenous and don't contain non-volatile cores, to which materials might, for example, adsorb. Chamber experiments incorporating nonvolatile seeds (e.g. fullerene soot, or even NaCl) would be more relevant to assessing the method.

In this work we focused on the generation of relatively homogeneous biogenic and anthropogenic nanoparticles from the ozonolysis of classic SOA precursors to characterize our system. Our major concern was the same as that of the referee in Com-

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ment 6 above; the formation of char or oligomers from these organics in the thermodenuder. There is also the issue of formation of extremely low volatility organic compounds (ELVOCs) in these particles which theoretically could remain in our system. The suggestion of the referee about investigating the role of a nonvolatile core and the corresponding adsorption is excellent and we plan to pursue it in future work.

(8) *P6357, L 15-17 – ‘Could have more significant health impacts’ – this is vague and not sufficiently justified. The latter part of this sentence is not clear why can’t the impacts be determined via mass measurements? That is what you purport to do with BC measurements – what additional information does this approach give you? If this statement is true, it could be true for both semi-volatile and non-volatile insoluble aerosols. Health effects of the semi-volatile fraction (substantially available in the ultrafine range) could be also complicated because of its dynamic nature and ability to partition into different phases.*

The toxicity of ultrafine particles (which represent usually a small fraction of the particle mass but most of the particle number concentration) is an issue of intensive research. We have added references to both a general overview of the issues involved (Fuzzi et al., 2015) and a more specialized paper in the medical literature (Terzano et al., 2010).

(9) *P6359, L24 – This design has a room temperature centerline RT of 15 seconds, which means particles in this study actually had a substantially shorter residence time (298K/673K *15 s). It is not relevant that the RT is longer than other designs if the aerosol system does not equilibrate – was it run at other residence times to assess whether the aerosol had equilibrated??*

We have now clarified this point (see also our response to Comment 4 of Referee 1) and given the average residence time in the heating and cooling sections at the corresponding temperatures in the revised paper. The equilibration time does depend on particle size. Our laboratory experiments discussed in the paper indicate that the

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residence time was sufficient for the complete evaporation of a variety low volatility organics in ultrafine particles which were the focus of this study.

(10) *P6360, L16 – This CPC doesn't have a 1 LPM flow mode. If the flow rate was modified somehow this should be clarified.*

We now clarify in the revised paper that we had modified the CPC with the addition of a clean air line with a HEPA filter thus operating at an effective sample flow rate of 1 LPM.

(11) *Eq. 1 – This represents transmission, not loss. Particle loss at higher TD temperature is an important, but uncertain step for interpreting TD data.*

We have corrected the typo and added the missing one and the minus sign in front of the fraction in Equation 1. We performed 9 different experiments to quantify the losses in our system at its high operating temperature resulting in a good characterization of the corresponding uncertainty (see error bars in original Figure 3 that has now been move to the Supplementary material).

(12) *Eq. 2 – Application of empirically estimated loss parameterization using a non-volatile tracer (e.g., Eq.2 in this study using NaCl) to a wide range of laboratory and atmospheric conditions is challenging should be critically evaluated. For example, evaluation of the non-volatile particle size distribution measurement with a direct measurement of lab-generated pure BC particle (e.g., fullerene soot) could be used to evaluate Eq. 2 with a more atmospherically prevalent species.*

NaCl has been used to determine the particle loss in several previous thermodenuder studies (Wehner et al., 2002, Huffman et al., 2008) and therefore we have relied on it due to its simplicity. Using soot particles would be more relevant however it would add complications to the experiments and its conclusions due to the shape issues. The

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shape of atmospheric BC particles does depend on their source, their atmospheric processing, and can also change during the measurement. Untreated fullerene soot, considered a good calibration standard for instruments like the SP2, can be quite different compared to ambient BC particles (Laborde et al., 2012) so while additional loss studies can be interesting, we are not sure that we will reduce the uncertainty regarding the losses of realistic ambient particles.

(13) *In addition, it is not clear how mass loss in the AMS was addressed. Was equation 2 applied? If so, how was this done?*

A time-dependent AMS collection efficiency during the campaign was calculated using the Kostenidou et al. (2007) algorithm combining the AMS and SMPS size distributions. The average collection efficiency was 0.85 ± 0.23 . For losses in the thermodenuder the AMS data were corrected using equation 2 which suggests approximately 50 percent losses for the corresponding mass concentration. This information has been added to the revised paper.

(14) *P6362, L6-9: No details are given on the operation or configuration of the AMS. Details on SMPS operation are repeated. I recommend that instrumentation description be combined into one section.*

We have followed the referee's suggestion adding information about the operation of the AMS and combining the instrumentation description into one section.

(15) *P6366, L9-L10: The MAAP does not directly measure aerosol mass, rather measures aerosol absorption at a specific wavelength and applies an assumed mass absorption cross-section (MAC) to estimate mass. This MAC can vary by a factor of 2-3 between locations. Therefore, reporting and using BC mass is not advised unless these values were compared with another, mass-based instrument. If mass data (e.g. from OCEC analysis) is not available, the impact of potential variation in the MAC*

should be assessed and discussed. Where BC is only used in a relative sense, this is less a concern, but where BC ‘mass’ is compared to e.g. AMS mass – this needs to be done with caution and uncertainties discussed.

We have rephrased this sentence clarifying that the MAAP was used to measure aerosol absorption at 670 nm and that the BC concentration was then estimated using an assumed mass absorption cross section. A reference for the corresponding uncertainties in the estimated absolute BC levels has been added. These BC concentrations are used in a relative sense in this paper and therefore the corresponding uncertainties in their absolute values do not affect the conclusions of our work.

(16) *P6367, L14-20 – The use of PMF on aerosol that has been heated to such an extent needs more explanation/discussion. The assumption here seems to be that the factors extracted from PMF (e.g. OOA, BBOA) are consistent at ambient temperature and 400 C. It seems questionable that all of the species that contribute to these factors evaporate at exactly the same rate, and also that some of these species wouldn't be modified by such vigorous heating. However, no assumptions are discussed and the only mention of the potential chemical transformation is organic pyrolysis and soot oxidation. Examining the spectra of the residual OA and the factors extracted using only denuded spectra and only ambient spectra is called for. The assumption of ‘constant’ OA factors has been made and assessed in previous AMS-TD studies (Huffman et al. 2009a; b), it needs to be re-examined here.*

This is a valid concern. We have performed the PMF analysis twice: once using only the ambient AMS measurements and the second time combining the ambient and thermodenuder measurements at all temperatures. The resulting factor spectra were all practically identical to each other (the angles between the corresponding vectors were less than 2 degrees), except for OOA, where for which theta angle was 6.3 degrees. However, even this discrepancy is easily within the uncertainty of the PMF analysis. So if there is chemical change during the processing of the organic aerosol

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by the thermodenuder it is minor. We have added a brief summary of the above in the revised paper and a reference to the Huffmann et al. (2009a, b) papers. These thermodenuder-AMS results are discussed in detailed in a different paper (Louvaris et al., in preparation) in which the volatility of the corresponding factors is estimated.

(17) *P6368, L15: what are detection limits?*

The corresponding detection limits (MFR 0.03 to 0.05) have been added to the revised paper.

(18) *P6368, L17-18: this statement calls for a reference to work that has shown this to be true.*

We have added a reference to the Florou et al. (in preparation) paper.

(19) *P6369, L1-3: This is an estimate of an error in total mass, but the method discussed here refers to aerosol number. A small amount of mass may correspond to an enormous number fraction of particles, especially in the ultrafine range. Extending this uncertainty estimate to number seems to be required if this justification is applied to develop this method. See also comment about use of AMS spectral information (and potentially aerosol-time-of-flight) to assess changes in organics with heating. AMS aerosol-TOF data could also be used to assess the fractal dimension of the aerosol under heated/unheated conditions to assess whether aerosol shape changes, which could potentially effect sizing in the SMPS.*

We do clarify that we assume that these artifacts are to a zeroth order approximation the same for all particle sizes. We have not seen any preference for such artifacts in the ultrafine particle range. However, we do state that this is an issue that clearly requires additional study.

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