

Interactive comment on “Understanding of atmospheric aerosol particles with improved particle identification and quantification by single particle mass spectrometry” by Xiaoli Shen et al.

Anonymous Referee #2

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Shen et al describe single-particle mass spectrometry (SPMS) data analysis using LAAPTOF data from a summer 2016 field campaign in rural Germany. While the SPMS data itself appears sound, there are many major technical issues with their analyses, as well as their assertions of originality. Unfortunately, the authors appear to be unaware of the majority of the SPMS literature, which their work would highly benefit from. Please see below for description of major issues, with references to previous literature that I hope will be useful for the authors to place their current work in context and aid in their data analysis and interpretation. I encourage the authors to rethink the framing of their manuscript and, instead of focusing on data analysis methods, consider the science that can be learned from their data itself by examining particle composition

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as a function of time and meteorological conditions, for example.

Method development to obtain mass concentrations from SPMS data was previously shown through method development papers by Allen et al. (2000, Environ. Sci. Technol., “Particle detection efficiencies of aerosol time of flight mass spectrometers under ambient sampling conditions”), Fergenson et al. (2001, Analytical Chemistry, “Quantification of ATOFMS data by multivariate methods”), Wenzel et al. (2003, J. Geophys. Res., “Aerosol time-of-flight mass spectrometry during the Atlanta Supersite Experiment: 2. Scaling procedures”), Zhao et al. (2005, Analytica Chimica Acta, “Predicting bulk ambient aerosol compositions from ATOFMS data with ART-2a and multivariate analysis”), Allen et al. (2006, Aerosol Sci. Technol., “Instrument busy time and mass measurement using aerosol time-of-flight mass spectrometry”), Bein et al. (2006, Atmos. Environ., “Identification of sources of atmospheric PM at the Pittsburgh Supersite – Part II: Quantitative comparisons of single-particle, particle number, and particle mass measurements”), and Qin et al. (2006, Analytical Chemistry, “Comparison of two methods for obtaining quantitative mass concentrations from aerosol time-of-flight mass spectrometry measurements”). The authors “new” method is very similar to the work discussed these older papers, yet these papers are not even cited in the current paper. Many subsequent SPMS papers have used these approaches to provide chemically-resolved mass concentrations: Bhave et al. (2001, Environ. Sci. Technol.), Ault et al. (2009, Environ. Sci. Technol.), Qin et al. (2012, Atmos. Environ.), Healy et al. (2012, Atmos. Chem. Phys.), Healy et al. (2013, Atmos. Chem. Phys.), Gunsch et al. (2018, Atmos. Chem. Phys.), and May et al. (2018, Environ. Sci. Technol. Lett.). I highly suggest that the authors review these previous papers to decide how to move forward with their own work, placing it into the context of previous studies.

The authors assert in the abstract (Page 1, Lines 30-31) that “[their] approach allows for the first time to assign the non-refractory compounds measured by AMS to different particle classes.” Similarly, in the conclusions section, it is stated “our study...opens a new way for quantitative information of single particle data, and together with the

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complimentary results from bulk measurements by AMS we have shown how a better understanding of the internal and external mixing state of ambient aerosol particles can be achieved.” These statements are not accurate, as many SPMS analyses have incorporated bulk aerosol composition data (both off-line impactor and online AMS): Bhave et al (2002, Environ. Sci. Technol.), Middlebrook et al. (2003, J. Geophys. Res.), Spencer & Prather (2006, Aerosol Sci. Technol.), Ferge et al. (2006, Environ. Sci. Technol.), Drewnick et al. (2008, Atmos. Environ.), Dall’Osto et al (2009, Atmos. Chem. Phys.), Pratt et al. (2010, J. Atmos. Sci.), Pratt et al. (2010, J. Geophys. Res.), Pratt et al. (2011, Atmos. Chem. Phys.), Decesari et al. (2011, J. Geophys. Res.), Dall’Osto & Harrison (2012, Atmos. Chem. Phys.), Dall’Osto et al. (2012, Aerosol Sci. Technol.), Dall’Osto et al. (2012, J. Geophys. Res.), Dall’Osto et al. (2013, Atmos. Chem. Phys.), Healy et al. (2013, Atmos. Chem. Phys.), Decesari et al. (2014, Atmos. Chem. Phys.), Gansch et al. (2018, Atmos. Chem. Phys.), and others. In fact the title of Healy et al. (2013, Atmos. Chem. Phys.) is “Quantitative determination of carbonaceous particle mixing state in Paris using single-particle mass spectrometer and aerosol mass spectrometer measurements”. Again, these papers are not cited in the current work and should be considered in their data interpretation and discussion.

Figure 1, which shows the overall detection efficiencies for various particle types, as determined in the laboratory, is useful. However, apparently these data are all already published in Shen et al. (2018, Atmos. Meas. Technol.), unfortunately limiting the originality here. It would be great if additional particle type proxies, based on those observed in the field could be added (e.g. soot, biomass burning). Considering these data and Figure 2 (dominance of soot from 0.2-0.4 μm), I encourage the authors to characterize their detection efficiency of soot particles in the laboratory. Also, the authors apply this laboratory-derived ODE to their field data, but it is not discussed whether the ODE was verified in the field, or how reproducible it is in the field. Furthermore, the authors note that using the mean ODE introduces significant uncertainty; this is also why the previously published methods (e.g. Qin et al 2006) determine the detection efficiencies in the field with time. Also, in presenting this curve to LAAPTOF users, it

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is important to note that this curve should not be extrapolated to other LAAPTOF or SPMS instruments without a standard to check against (e.g. PSLs). The authors simply note that “alignment and variance in particle-laser interaction lead to uncertainty in ODE” (Page 5, Lines 33-34). This paragraph suggests that this variance is included in the 540% ODE spread for various lab-generated aerosols; however, it should be noted that the ODE dependence on sizing laser and desorption/ionization laser powers and alignments will change with time, especially when the instrument is moved. This is why the previously published methods noted above (e.g. Qin et al. 2006) characterize detection efficiencies in the field. For example, Jeong et al. (2011, Atmos. Chem. Phys.) and Wenzel et al. (2003) show how the hit fraction of particles can change with time during and between field campaigns; this is taken into account in the Wenzel et al. (2003) and Qin et al (2006) method. Also, for consideration of “variance in particle-laser interaction” (Page 5, Line 34) the authors may be interested to review Wenzel & Prather (2004, Rapid. Commun. Mass Spec., “Improvements in ion signal reproducibility obtained using a homogeneous laser beam for on-line laser desorption/ionization of single particles”).

Page 5, Lines 3-28: If the authors have chemically-resolved ODEs, why did then choose to apply a mean ODE to all data? If the ODEs are stable relative to a standard (e.g. PSLs), it seems like a strength of the current work that chemically-resolved ODEs, for each particle type, could be applied in the calculation of mass concentrations.

The authors make many subjective statements that can be refuted by previously published literature, such as those mentioned above (and others not listed here). I caution the authors from making such statements. For example, “SPMS is a useful, albeit not fully quantitative tool” (Page 1, Line 14) and “SPMS data analysis has been proven difficult under real world conditions” (Page 2, Lines 2-3).

The authors state that “mass spectroscopic signatures do not necessarily reflect the primary composition of the particles” (page 2, lines 7-8). However, many previous pa-

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pers (e.g., Bhave et al. 2001, Environ. Sci. Technol., Reinard et al., 2007, Atmos. Environ., Toner et al. 2008, Atmos. Environ., Pratt & Prather 2009, Environ. Sci. Technol., Healy et al. 2010, Atmos. Chem. Phys., and others) have examined the SPMS source signatures of primary particles and apportioned ambient particles according to these signatures, which is arguably one of the strengths of SPMS.

Page 3, Line 36-37: The authors state that the LAAPTOF has a size range of 70 to 2500 nm; however, Figure 1 shows that the detection efficiencies of particles <400 nm and >1200 nm is extremely low (<1%), making this earlier statement seem misleading.

Section 2.2: The authors apply particle densities to each particle class and assume that all particles are spherical. Instead the authors could consider applying measured individual particle effective densities (reducing assumptions) (e.g. Zelenyuk et al. 2008, Analytical Chem., Spencer et al. 2007, Environ. Sci. Technol., Zhang et al. 2016, Atmos. Chem. Phys.), as has been done in other SPMS studies converting to mass concentrations (e.g. Qin et al. (2012, Atmos. Environ.), Gunsch et al. (2018, Atmos. Chem. Phys.), and May et al. (2018, Environ. Sci. Technol. Lett.).

Section 3.1: This section does not provide any new information in terms of methods/technology; this is simply a description of mass spectra particle types observed during the field study. I also have several concerns about particle type identification, mostly with the respect to the attribution of nearly all particles as “dust-like”, which does not have support by the m/z marker ions shown and described, as I note below. In fact, mass spectral markers supporting dust are only shown (in Fig 2) and discussed here for Class 1 (5%, by number) and Class 7 (4.6%, by number), leaving >90% of the particle as non-dust particles. Also, it would be useful to move Figure 4 and its discussion to this section, as that figure is useful and aids with particle type classification.

Particle Class 4: The authors call these “Secondary inorganic and amine like particles” and discuss secondary markers on lines 24-25 (page 6) and larger size (0.5-1 μm) (line 27). Yet, the next sentences (lines 26-27) states “class 4 is relatively “clean” with

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the fewest peaks, indicating that the particles might be relatively fresh.” There is no mass spectral support for these as freshly emitted particles; in fact the authors say “secondary” in the naming of the particle class. This discrepancy must be fixed.

Particle Class 5: The authors call these “Potassium rich and aromatics coated dust-like particles”, with m/z 39 (K+), aromatic marker peaks, and m/z 213 (K₃SO₄+). The authors note that these “particles might originate from biomass burning”. No mass spectral support is provided for identification as dust. Based on other SPMS literature of biomass burning studies, I believe this particle class should be labeled as “Biomass Burning”.

Particle Class 6: The authors call these “Organosulfate coated dust-like particles”, with organosulfate marker ions. Again, no mass spectral marker ions are discussed to support identification as dust. Also, these particles seem very similar to Class 5 (with large K+, m/z 213, etc); could they correspond to more aged biomass burning particles?

Page 5, Line 41: m/z 24 (C₂-) is attributed here to organics, which is possible for 193 nm at high laser pulse energy (e.g., Zelenyuk et al. 2009, Int. J. Mass Spec.); however, it is also a common elemental carbon marker peak (e.g., Zelenyuk et al. 2017, Int. J. Engine Res., Spencer et al. 2006, Aerosol Sci. Technol.).

Page 6, Lines 6-8: I am quite confused by this statement. Does this mean that fuzzy classification does not separate individual mass spectra into individual clusters? Or, if this isn't the case, why are the authors using “similarity” to estimate the number fraction of particles in each group? Why not simply count the number of mass spectra in a given group and then divide by the total number of particles sampled? Please clarify. Neutral networking algorithms used previously in SPMS (e.g. Rebotier & Prather 2007, Analytical Chimica Acta) separate individual mass spectra (corresponding to individual particles) into separate clusters such that it is simple to calculate number fractions.

Figure 2: I suggest raising the cut-off intensity for the mass spectra peak areas, as

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there is significant noise shown in all mass spectra currently. Some labeled peaks also do not appear to be above the limits of detection; please check. Also, it would be useful to add the particle type names, in addition to the numbers, to the labeling of the mass spectra. Please also clarify what is meant by “background fragments that exist for every particle class”; do the authors mean common ions, or do they mean that there is a chemical background somehow in the mass spectrometer?

Figure 3: Given the large number fraction of EC particles (class 2) in Figure 2, why is this not reflected in Figure 3, especially since the particle number concentration mode should be at less than 0.2 μm ? I’m concerned that there could be a problem here in the application of the ODE to the “corrected number fractions” shown here. Also, since the authors have taken the time to convert to number and mass concentrations, it would be useful to show to chemically-resolved number and mass concentration time series plots. It would also be useful here and throughout to refer to particle classes chemically (e.g. dust, EC, biomass burning, organic carbon-sulfate) rather than numbers that require the reader to refer regularly back to Section 3.1.

Page 7, Lines 26-27: The authors state here “. . .there is no well-defined relationship between spectral signal and quantity.” I disagree with this statement, as many SPMS (and LDI generally) papers have investigated this relationship, which is governed by ionization energies of species. Based on the statements on Page 2, Lines 20-26, I’m concerned that the authors may have some confusion about LDI, which is known to primarily result in neutral (rather than ion) formation. I encourage the authors to read textbook or review literature on MALDI and LDI (e.g., Zenobi & Knochenmuss 1998, *Mass Spec. Rev.*, “Ion Formation in MALDI Mass Spectrometry”). For example, in the positive ions, typically the largest ions correspond to those with the lowest ionization energies (of those in the sample). SPMS data analysis methods to account for LDI matrix effects are discussed by Hatch et al (2014, *Aerosol Sci. Technol.*). The authors do mention in the introduction that SPMS relative sensitivity factors that account for differences in ionization energies are discussed by Gross et al. (2000, *Analytical Chem.*).

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Woods et al. (2001, *Analytical Chem.*, “Quantitative detection of aromatic compounds in single aerosol particle mass spectrometry”) is another reference. Thomson et al. (1997, *Aerosol Sci. Technol.*, “Thresholds for laser-induced ion formation from aerosols in a vacuum using ultraviolet and vacuum-ultraviolet laser wavelengths”), Thomson & Murphy (1993, *Applied Optics*, “Laser-induced ion formation thresholds of aerosol particles in a vacuum”), and Reinard & Johnson (2007, *J. Am. Soc. Mass Spec.*) will likely also be useful to the authors. Other papers discussing relationships between species quantities and SPMS ion signals are provided above in the comments about SMPS quantification and comparisons with bulk measurements.

Sections 3.2 & 3.3: My comments about this section are primarily summarized above in my notes about previous work producing mass concentrations from SPMS data. I want to add here two additional comments. 1) Given the differences in typical detection efficiencies between the LAAPTOF and AMS, one would not expect good correlations without examining only the size range of overlap, which I would encourage the authors to do. Figure 5 should be revised accordingly. I also encourage the authors to look at previous SPMS-AMS comparisons (see comments above) for greater interpretation of their results and also for additional ways to conduct this analysis that have previously been successful. For individual ions (Page 8, Lines 22-34), I suggest the authors look at Hatch et al. (2014, *Aerosol Sci. Technol.*) and Healy et al (2013, *Atmos. Chem. Phys.*, “Quantitative determination of carbonaceous particle mixing state in Paris using single-particle mass spectrometer and aerosol mass spectrometer measurements”). 2) The authors note that sulfate salts may have been missed during P3. As such I suggest the authors consider the work of Wenzel et al. (2003, *J. Geophys. Res.*), who developed a method to identify and quantify “missed” particles, consistent with pure ammonium sulfate.

Figures 6-8: Due to matrix effects in LDI, peak areas of a given species will depend on the full matrix of a particle, such that an ammonium peak area for a given quantity would be expected to be different on a dust particle vs an organic carbon particle. As

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such, it is not advised to compare peak areas across all particle types together. Please see Hatch et al. (2014, *Aerosol Sci. Technol.*). Also see Healy et al. (2013, *Atmos. Chem. Phys.*) for suggestions of how to compare SPMS and AMS data, as they found agreement when the data are handled properly. Bhave et al. (2002, *Environ. Sci. Technol.*) may also be useful, as they compared ammonium and nitrate SPMS data to bulk filter data. For organics in particular, the authors may consider Spencer & Prather 2006 (*Aerosol. Sci. Technol.*, “Using ATOFMS to determine OC/EC mass fractions in particles”) and Ferge et al. (2006, *Environ. Sci. Technol.*).

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