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Interactive comment on “Quantitative determination of carbonaceous particle mixing state in Paris using single particle mass spectrometer and aerosol mass spectrometer measurements” by R. M. Healy et al.

Anonymous Referee #3

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Healy et al. describe ambient aerosol measurements in Paris during the MEGAPOLI campaign. They focus on single-particle measurements using an ATOFMS, and rely heavily on an attempt to mass quantify the single-particle MS data by comparing ATOFMS measurements to co-located aerosol mass measurements from a variety of instruments. It is not clear if the focus of the paper is to describe this new method (as the title suggests), or to learn something about the sources of particles in Paris (as the Results and Conclusions suggest). While both aspects of the paper are interesting and have their merits, neither one is developed in enough detail to truly understand and

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discuss that topic. The authors should try to improve upon this lack of focus and clarity when they revise the paper. Perhaps more of the method details could be added to the Supporting Information. The authors should also make it very clear that the mass calibration method that they rely heavily on for much of the results presented here is based on many key assumptions and is not terribly accurate or robust. This compromises most of the aerosol mass data discussed here, but it is presented as though the ATOFMS reliably determined the mass of various aerosol components. I do think this manuscript is an interesting and valuable contribution to the literature. It should be suitable for publication in ACP, but could definitely be improved in revision.

My major concerns are i) the relative sensitivity factor developed here for the ATOFMS, while interesting and valuable, has a significant uncertainty behind it; and ii) that there is too much focus on aerosol mass measurements, and these rely on the use of this RSF.

I was surprised that the authors barely present any ATOFMS data in a single-particle or number metric, but instead jump to an aerosol mass metric for almost all of the results. Figures 3 through 12 are all aerosol mass based. While there is certainly value in converting from particle number to mass, this introduces many important assumptions and uncertainties. It also does not utilize the unique single-particle measurement ability of the ATOFMS. Understanding the source contributions to particle number is very important for constraining the contribution of different sources/processes to CCN budgets, for example. The authors should present more of their results in a single-particle or particle number metric, before jumping to particle mass (which requires the use of conversion factors with their inherent uncertainties). For example, at the least the temporal variation in the contributions to total particle numbers by particle class should be presented. This will also help to show what the contribution of the carbonaceous particles focused on here to the total particles sampled was. It would also be useful to show the breakdown of particle class by number versus particle size (i.e. Fig. 7 but in a particle number metric).

More discussion of how an attempt to convert the ATOFMS single-particle number data to mass concentrations through comparison to co-located aerosol mass instruments must be presented. This is certainly an interesting and worthwhile effort, but it is fraught with difficulties and uncertainties. While some of these are discussed in the Methods section, once we move to the Results the ATOFMS-derived mass concentrations are presented as a well-known quantity. This is just not accurate. I am particularly concerned that only one relative sensitivity factor was derived for the entire campaign, using the average mass spectrum from 1.5 million individual carbonaceous particles. Most likely the laser ionization process is quite dependent on the particle matrix itself, thus precluding the use of one RSF for all the particles, as was used here.

The log-normal size distributions presented in Fig. 2 are not that informative. The actual ATOFMS size distributions for the various particle classes should be presented. The raw data could be presented as particle class fractions of total particle counts versus size, and then the size distributions from the scaled particle number data could also be presented. If AMS PToF data was collected, it would be really useful to compare the sizes of ATOFMS particle classes with those of AMS factors, to better help interpret the sources of the aerosol using the two methods.

Table 1 has interesting information regarding the mass contributions of various components to each particle class (but it must be stressed that these are only estimates), but is not presented effectively as a table. Perhaps a color stack could be shown for each of the spectra in Figure 1 corresponding to the estimated component mass fractions?

The estimated mass fractions also introduce some issues with how the particle classes are labeled. For example, K-OA-SO_x is labeled as containing K, yet in Table 1 has < 0.01% of K by mass fraction. Other particle classes that also have < 0.01% K are not labeled with “K”. While the K peak is clear in the mass spectrum of the K-OA-SO_x class, its assignment is not supported by the component mass estimates. Similarly, K-OC-SO_x has almost as much NO_x mass fraction as the EC-OA-NO_x, yet it is not given the “NO_x” label.

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Is the lack of a EC-SO_x particle class (without significant OA) surprising and telling? Does it suggest that EC is aged by the simultaneous condensation/uptake of both OA and sulfates, and that you don't get a lot of sulfate uptake without also OA uptake?

Were any marine particles detected during the marine air masses?

The comparison between (somewhat arbitrarily) selected ATOFMS particle class estimated mass and AMS factor mass is interesting but rather simplistic. A more complex multivariate analysis seems required here to better deal with the fact that different AMS factors could be dispersed amongst numerous ATOFMS particle classes.

The use of the measurements to determine the contributions of local versus transported particles is the most compelling aspect of this work. I think this could be highlighted better. As the Results section is rather long, perhaps a Summary should be added so the various findings can be summarized more clearly. Or the Conclusions could be extended some.

Page 10350, line 9: It is not made clear why quantitative measurements from SPMS remain "challenging". Please clarify. The roles that laser shot-to-shot variation and different ionization/fragmentation responses for different particle types (matrix effects) play in confounding this should also be discussed here.

Section 2.1: Effectively sampling and detecting particles across such a wide range of sizes from 100-3000 nm as stated here is difficult to achieve. The size distribution of the actual raw measured particles counts (by particle class) versus size should be presented so it is clear what size range was actually measured effectively with the lens inlet. Also, referencing [Su et al., 2004] seems appropriate here. Please also state the LDI laser power used in this study.

The collection efficiency of the AMS is a key factor that will also bias the estimated mass concentrations from the ATOFMS data. How much did the derived CE value vary during the study?

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Was the aerosol sampled by the ATOFMS also sampled after a cyclone or other sampler, as the AMS was? Was the aerosol dried or otherwise conditioned? The fact that the ATOFMS sampled from a different inlet than the other instruments that are used to estimate mass concentrations for the ATOFMS is concerning.

Section 2.2. The K-means clustering algorithm should be briefly explained, so it is clear to non-experts. Is it exclusive or non-exclusive clustering?

What fraction did the ten carbonaceous particle classes analyzed here represent out of the total good particle spectra sampled? What was the contribution from uni-polar spectra?

What size range did the TDPMS measure over? Earlier it was stated that the ATOFMS sampled particles from 100-3000 nm, yet the TDPMS cannot measure supermicron sizes. So what size range was the ATOFMS data scaled?

The choice of particle density could be better selected based on the measured particle class composition, rather than using one value for all particle types [Qin et al., 2006].

Were any (ultra)fine metal particles detected?

Section 3.1.1: Please justify the assignment of the CN⁻ ion at m/z -26 as organic nitrogen.

Section 3.1.4: Please justify why C3⁺ (m/z 36) is assigned as organic carbon. This is an elemental carbon fragment, though it can be produced from fragmentation of OC (as is discussed on page 10364). The OA-NO_x particle spectrum does not seem to have any prominent OC fragments, just m/z 12 and 36, corresponding to C1 and C3. This could be EC-NO_x. It is hard to say as the spectra of the EC particle classes are not shown. m/z 12 is mislabeled as C2 in Fig. 1 (also for OA-SO_x).

The average spectra of all the 10 carbonaceous classes studied here should be presented in Fig. 1. The EC classes are missing.

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Section 3.2: How does OA/EC vary with particle size, and does this tell you anything about the aging/growth of EC?

Section 3.3: Choosing which ATOFMS particle classes might best match AMS factors seems rather arbitrary and simplistic. One might expect the OA in the EC-OA-SOX class to be more like OOA than HOA as this particle class is aged EC.

ATOFMS EC particle class mass estimates are compared to AMS OA factors, yet the fact that the AMS does not measure EC is not mentioned here. This should be discussed. Does it explain some of the differences between ATOFMS and AMS aerosol mass?

Page 10367, line 13: What is the mode size of the AMS COA factor? Does it support your assertion that these particles were too small for the ATOFMS to detect? While it is true that fatty acids and other likely components of COA do not ionize readily with the 266 nm LDI laser, if these components are mixed with other particle types, the COA components could be detected.

Section 3.4. This is the strongest and most interesting section. While it is not the focus of this paper, it would be useful to also discuss how the AMS factors split between local and transported. Does this agree with the ATOFMS data? Can it help to better interpret the ATOFMS particle classes and AMS factors?

Page 10365, line 19: “lower sizing limit of the 20 ATOFMS (150nm)”. The ATOFMS has a larger particle size detection limit than the AMS.

References

Qin, X. Y., P. V Bhave, and K. A. Prather (2006), Comparison of two methods for obtaining quantitative mass concentrations from aerosol time-of-flight mass spectrometry measurements, *Analytical Chemistry*, 78(17), 6169–6178.

Su, Y. X., M. F. Sipin, H. Furutani, and K. A. Prather (2004), Development and characterization of an aerosol time-of-flight mass spectrometer with increased detection

efficiency, *Analytical Chemistry*, 76(3), 712–719.

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