The authors would like to thank the reviewers for these very useful comments. Individual responses are provided to each comment below, and appropriate changes have been made to the revised manuscript, figures and supplement where necessary.

Reviewer #1

General comments:

The results are surprisingly good, in that the single particle mass spectrometry data, often presented as non- or only semi-quantitative, proves to be comparable to that of the AMS, which is often portrayed as fully quantitative, while providing more subtlety in the analysis. The paper is strong and should be published, but in its current form, the paper is too long and I believe that the balance is not correct, between descriptive results and method evaluation.

This comment is addressed in the next response

Specific comments:

1. I believe that a shortcoming of this paper is that it is presented as an exhaustive report rather than as a presentation of a scientific story. It could be dramatically improved if the authors were to tailor it to one of the two major themes which are present in the research: 1) the result that is relevant to the air quality in Paris, that most PM1 sampled there is transported to the city, or 2) the result that is relevant to the quantitative analysis of atmospheric aerosol data using mass spectrometry. Right now, it seems that both themes are emphasized, which has the effect that neither one stands out.

The lack of emphasis on the quantification approach was also raised by Reviewer 2. In order to address the balance issue, we have decided to focus the narrative more on the quantification aspect. The relative importance of transported particulate matter in Paris has been noted in several recent publications (Crippa et al., 2013a; Freutel et al., 2013; Sciare et al., 2010), and thus the focus has been shifted to the quantification results in the revised manuscript. The Results and Discussion section now begins with a description of the quantification results, and an additional figure has been added to the manuscript comparing ATOFMS and HR-ToF-AMS mass-size distributions for each species. In an effort to reduce the overall length of the revised manuscript, the detailed description of each single particle class has been moved to the Supplement (Section S4) to improve flow. The description of transported particulate matter has also been reduced in length and Figure 10 has been moved to the Supplement.

2. The paper should include some general statements about which instruments need to be co-located to do an analysis such as the one presented, and to discuss the aspects of the method that can be replicated or exported to other studies.

The same approach is expected to be applicable to other studies even in the absence of on-line speciation instrumentation. A single relative sensitivity factor (RSF) was calculated for each species based on the average mass concentration for that species detected over the entire measurement period. Thus, off-line chemical analysis of filters would suffice. While hourly data for each species were useful to validate the approach, high temporal resolution is not required to calculate relative sensitivity factors. However, particle number-size distributions from a co-located particle sizing instrument, the TDMPS in this case, are required to scale the ATOFMS size distributions. The following lines have been added to the Conclusions section:

“The results indicate that quantitative mixing state information for multiple chemical species can be estimated simultaneously using this approach. This method could also be applied in future studies using lower temporal resolution off-line speciation data, although scaling for size-resolved particle detection efficiency would require a co-located particle sizing instrument.”

3. A discussion of how generally applicable the authors think these results are, would be welcome; do they think these good correlations between ATOFMS and AMS data will be observed everywhere, or are there special conditions in Paris which facilitated them?

There are no specific conditions under which such good agreement should be expected, although the relatively low contributions of crustal material and metallic particles did facilitate the focus on carbonaceous particle quantification in this work. Other locations, impacted by high mass loadings of sea salt or road dust, would be characterised by less homogeneous particle density, complicating the scaling procedure used here. Others have overcome this problem by assigning separate density values to different particle classes or size ranges prior to scaling (Qin et al., 2006; Qin et al., 2012). The following line has been added to Section 2.2 of the revised manuscript:

“The selection of a single density value will be less appropriate for locations impacted by significant metallic or crustal particle mass concentrations.”

4. In general, I feel that the method developed should be presented within the results section of the paper, as it is a new application of a data analysis method. It requires significant discussion, and seems out of place in methodology.

Further detail has been added to this section in response to subsequent comments, however it is the authors' opinion that the Results and Discussion section should remain focused on the output of this methodology rather than the step by step procedures in order to maintain flow. Additions to this section have been made in response to Reviewer 2, however.

5. p. 10350, line 26: It is not clear if the particles sampled by the ATOFMS were dried as were the particles sampled by the other instruments. This should be mentioned here and, if they weren't, the implications of this should be discussed in the results.

Particles were not dried prior to detection in this case. The positive and negative ion mass spectra for all ten carbonaceous particle classes were found to be homogeneous, however, with minimal contributions from spectra exhibiting supressed negative ion signals. Although particle phase water has been demonstrated to affect negative ion formation previously (Neubauer et al., 1998), negative ions were consistently observed in this case, even during the fog event on 18/01/2010. A significant reduction in particle water content has previously been associated with using aerodynamic lens inlet systems (Zelenyuk et al., 2006). It is possible that the relatively high detection efficiency for negative ions observed here is associated with using an aerodynamic lens inlet instead of a nozzle inlet for particle transmission to the sizing region. The following lines have been added to Section 2.1:

"Particles were not dried prior to detection. However, dual ion mass spectra were successfully collected in almost all cases, indicating that negative ion suppression associated with high particle water content was not an issue (Neubauer et al., 1998). This could be due to evaporation of particle phase water during transmission through the aerodynamic lens (Zelenyuk et al., 2006; Hatch et al., 2011)."

6. p. 10352, lines 10 – 12: This statement suggests that there were no metal/inorganic particle types that made up significant classes. This result should be compared to other urban areas that have been studied. Is this typical or novel for Paris during this measurement?

The dominance of carbonaceous particles and secondary inorganic ions in Paris aerosol is typical and has been demonstrated previously (Sciare et al., 2010; Bressi et al., 2012). Organic and elemental carbon, ammonium, sulphate and nitrate were estimated to account for approximately 92% of the $PM_{2.5}$ mass in Paris. While sea salt, dust and metal-containing particle classes were identified in the ATOFMS dataset, their number contribution was minor (as discussed below in response to Reviewer 3, comments 9 & 20). Off-line analysis estimates an annual average sea salt contribution to $PM_{2.5}$ in Paris of approximately 3% by mass (Bressi et al., 2012). Here we have focused on PM_1 composition, and thus the relative contribution of sea salt and dust is expected to be even lower. The influence of particles with different densities is discussed in response to Comment 3.

7. *p. 10353, lines 14 – 19: The authors should also use naturally occurring isotope patterns as evidence for the fact that isobaric interferences are not likely a problem, when possible.*

The only potential interference from a quantitative perspective is the erroneous assignment of signal from organic carbon at *m/z* 39 to potassium. Examination of the ratio of *m/z* 39 to *m/z* 41 was explored for each ATOFMS particle class, and is approximately 13.3 for potassium. The ratios observed were: 12.9, 12.4, 10.6, 9.3, 9.1 and 7.0 for OA-TMA, K-OA, K-OA-NOx, K-OA-SOx, OA-NOx and OA-SOx respectively. The average absolute intensity at *m/z* 39 (arb. units) for each class decreased in the following order: 750, 430, 410, 220, 160 and

160 for K-OA, K-OA-NOx, K-OA-SOx, OA-TMA, OA-NOx and OA-SOx, respectively. The results indicate that for the classes associated with the highest potassium content, the isotopic ratio is closer to that expected for potassium, while those with lower potassium content are subject to more interference from organic carbon at *m/z* 39. Unfortunately this is unavoidable for unit mass resolution data. However, 83% of the potassium mass concentration is derived from the three ATOFMS classes with the highest signals at *m/z* 39 (Supplement, Figure S7). These classes are less influenced by any interference from organic carbon, and therefore the correlation between ATOFMS-derived and PILS potassium mass concentration remains very encouraging (R^2 = 0.78, slope = 0.76).

8. p. 10354, line 2: Was the relative peak area really obtained by normalizing each peak to the sum of all ions in both the positive and negative spectra? Most examples in the literature show normalization to total peak area of the same polarity of the ion under investigation.

Separate normalization is often used for dual ion mass spectral analysis. In this case, no significant improvement in mass reconstruction was observed when separate normalization was performed on negative ion and positive ion mass spectra instead of normalization of the combined dual ion spectrum. For comparison, the correlations observed for ATOFMS derived mass concentrations for each species and those measured with co-located instruments using separate and combined normalization are as follows:

Normalization	SO_4	NO_3	NH_4	OA	EC	K
Combined	0.78	0.67	0.78	0.75	0.72	0.78
Separate	0.78	0.68	0.79	0.77	0.72	0.78

The following line has been added to Section 2.2:

"Separate normalization for positive and negative ion mass spectra was also explored but did not lead to significantly different results."

9. p. 10355, line 1: There needs to be a description of how the mass concentration of ATOFMS classes is obtained.

An extended description of this procedure has now been added to the revised manuscript (Section 2.2) as follows:

"Approximately 1.75 million dual ion single particle mass spectra were collected during the MEGAPOLI winter campaign. The total hourly particle counts from the ATOFMS were divided into eight size bins in the size range 150-1067 nm (d_{va}) and then scaled using coincident hourly averaged TDMPS number-size distribution data assuming a single density value of 1.5 g cm^{-3} for all particles as described previously (Healy et al., 2012). Thus, size-dependent detection efficiency issues were accounted for. The selection of a single density value will be less appropriate for locations impacted by significant metallic or crustal particle mass concentrations.

Mass spectra were imported into ENCHILADA, a freeware data analysis software package (Gross et al., 2010), normalised based on peak area, and clustered using the *K*-means algorithm. Application of the *K*-means algorithm involves exclusive clustering of single particle mass spectra into a user-defined number of clusters (*K*) based on their spectral similarity (square of Euclidean distance) (Anderson et al., 2005). A refined centroid approach was employed here where 50 subsets of the dataset were first clustered separately in order to find optimal starting centroids or "seeds" for clustering the entire dataset. Once these centroids are chosen, several passes of the dataset are performed until two successive iterations produce identical cluster assignments. The user defined *K* value is then increased until further increases do not significantly affect the average distance of each particle from its assigned centroid in Euclidean space. In this work a *K* value of 80 was chosen because further increases in *K* did not appreciably reduce distance and resulted in clusters containing 1 particle. These eighty clusters were examined for homogeneity and manually regrouped into fifteen final classes as described previously (Healy et al., 2012). Ten carbonaceous classes were identified, comprising approximately 1.50 million spectra. The remaining mass spectra were either miscalibrated, dominated by noise, or belonged to classes with minimal contributions to the total particle number detected (< 2%). The number fraction of each particle class in each size bin was then calculated for each hour of the campaign, assuming equal detection efficiency and spherical shape. This procedure provided size-resolved particle number concentrations for each ATOFMS class for each hour of the campaign. Number concentrations were then converted to size-resolved mass concentrations using the single density value of 1.5 g cm^{-3}."

10. p. 10356, line 14: The number and duration of the back trajectories is ambiguously described: is it 72 hour back trajectories or 70 2-hour back trajectories?

This should be "72 hour back trajectories", and is now amended in the revised manuscript.

11. Section 3.1: This section should be shortened significantly (50 % or so). Much of the general description of the various classes can be provided in a table, or the text can be moved to the Supplementary section. The information that should be retained in the text of the main manuscript is the interpretation of the clusters. For the example of the K-OA cluster, *this would be p. 10358, lines 13 – the end of the paragraph (starting with "The strong diurnal…").*

In an effort to focus the narrative, this section has been reduced in length significantly. Furthermore, the Results and Discussion section now begins with the quantitative results instead, in order to emphasise that aspect of the study. The detailed description of each single particle class, and Figures 2, 3 and 4, have now been moved to the Supplement to improve flow. The Results and Discussion have also been reorganised into the following shorter subsections in the revised manuscript:

"3.1 ATOFMS quantification results

3.2 Carbonaceous ATOFMS classes

3.3 Quantitative mixing state of carbonaceous particles

3.4 Comparison of ATOFMS and HR-ToF-AMS organic aerosol apportionment

3.5 Local and regional/continental scale source apportionment"

This new layout emphasises the quantitative aspect (2500 words, 4 sections), while the discussion of local and regional emissions is much shorter (700 words, 1 section).

12. Section 3.2 is written from the perspective that the ATOFMS is the only instrument contributing to uncertainty. The uncertainties and assumptions inherent in the other instruments' quantitative results should be mentioned and discussed.

The uncertainty associated with the other instruments has now been included. The uncertainty associated with the OCEC analyser is already discussed in the manuscript (Section 2.1). The uncertainty of the PILS mass concentration measurements is 10%. The uncertainty associated with HR-ToF-AMS mass concentration measurements is 30%. These details have now been added to the revised manuscript as follows:

"A collection efficiency of 0.4 was calculated for the HR-ToF-AMS based on comparison with concurrent independent measurements (Crippa et al., 2013a). The uncertainty associated with mass concentration measurements for this instrument is 30% (Bahreini et al., 2009). The instruments were connected to a sampling system consisting of a PM_{10} inlet located approximately 6 m above ground level directly followed by an automatic aerosol diffusion dryer system, maintaining relative humidity in the sampling line below 30% (Tuch et al., 2009).

Elemental carbon (EC) and organic carbon (OC) in $PM_{2.5}$, sampled on the roof of the LHVP building (14 m above ground level), were analysed using an OCEC field instrument (Sunset Laboratory, Forest Grove, OR) (Bae et al., 2004) The OCEC analyser was operated at 8 L min^{-1} and provided semi-continuous hourly concentrations of OC and EC. A denuder was placed upstream in order to minimise VOC adsorption artefacts. Measurement uncertainty for this instrument is poorly described in the literature and thus an estimate of 20% is assumed here (Peltier et al., 2007; Sciare et al., 2011). A particle-into-liquid sampler, coupled to two ion chromatographs (PILS-IC) also sampled $PM_{2.5}$ from the roof of the same building, and was used to determine mass concentrations of inorganic ions including sodium and potassium. The instrument is described in detail elsewhere, and an uncertainty of 10% is associated with mass concentration measurements (Sciare et al., 2011)."

13. Section 3.3 is, it seems to me, the heart of the paper, but it is buried a bit too deep and is too wordy. This goes back to my Specific Comment #1 – this should be elevated to the main story, or it should be relegated to Supplementary with the Paris story being the central theme *of the paper. A significant editing of the text, and relegating some of the details to Supplementary Information, would strengthen this section significantly.*

As discussed earlier the emphasis is now focused on the quantitative aspects, including this section. Significant edits have been made to reduce the length of the Results and Discussion, however the authors feel that it is necessary to retain detail in this particular section, because the comparison of single particle and aerosol mass spectrometer organic aerosol apportionment is novel. However, some sentences have been removed in the revised manuscript to reduce length and improve flow.

14. Figure 5, K timeline: is the explanation for the big discrepancy between the PILS and the ATOFMS at the peak concentration that the ATOFMS peak area was saturated or mis-calibrated? Either of these could be occurring if the K levels in particles are especially high. This could easily be found by looking at the spectra during this time period.

Examination of the raw mass spectral data for this period did not uncover any significant differences in potassium intensity or saturation relative to the rest of the dataset. However, this period was characterised by the highest PM_1 mass concentrations detected during the campaign (approximately 50 µg m^{-3}, Fig. S1). The scaling factors required to reconcile the ATOFMS and TDMPS particle counts were considerably higher during this period. This is most likely due to increased instrument busy time and/or particle coincidence in the sizing region associated with high particle number concentrations (Allen et al., 2006; Su et al., 2004). Higher scaling factors will introduce more error, and this is apparent in the simultaneous underestimation of sulphate and overestimation of organic aerosol relative to the other instruments for this period. This would explain the divergence between the ATOFMS-derived and PILS-IC potassium mass concentrations on 27/01/2010.

15. Figure 10, temporal trends of local and regional/continental sources: This figure would be enhanced by the addition of a third pane, showing the total.

This panel has been added, however this figure has now been moved to the Supplement to decrease the length of this section.

16. Figure 11, average composition of local versus regional/continental sources: The language in the caption ("local" and "regional/continental") is not consistent with the labels in the figure ("local" and "transported"). They should be the same.

This has been amended in the revised manuscript.

17. Figure 12, estimated relative mass concentrations of local and regional/continental emissions: This caption should state that this figure is based on ATOFMS data.

In the revised manuscript this caption now reads:

"ATOFMS-derived relative mass contributions (%) of local and transported emissions to each chemical species and reconstructed PM mass in the size range investigated."

18. Supplementary Information, Figure S3: It appears that the ATOFMS data is scaled significantly based on particle number. However, the ATOFMS is sampling through an aerodynamic lens, so this is surprising. Was the instrument not working well during the data collection?

At the lowest particle sizes, particle detection efficiency is also affected by the limited amount of light scattered and detected at the PMTs in the sizing region. Thus, the highest scaling factors are required for this size range (150-191 nm, d_{va}). The size-resolved scaling factors used here were on the same order of magnitude as those reported in the literature previously, and are discussed in detail in Healy et al. (2012) as follows:

"The scaling factors employed here were observed to be strongly dependent upon particle size, but the magnitude of the factors is similar to that observed in previous studies involving the use of laser particle counters, aerodynamic particle sizers and scanning mobility particle sizers to scale ATOFMS particle number concentrations (Wenzel et al., 2003; Qin et al., 2006; Pratt et al., 2009b). The size bin width was generated by merging adjacent pairs of TDMPS size bins because the original size bins were found to be too narrow, resulting in low ATOFMS hourly counts in some bins during certain periods of the measurement campaign. The uncertainty associated with the TDMPS particle number concentrations in the size range used here (100-712 nm, mobility diameter) is estimated to be < 2% (Birmili et al., 1999). The bins used are wider than those used previously by Pratt et al (2009) but narrower than those used by Wenzel et al (2003) and Qin et al (2006). The bin width was not increased any further because, although this would reduce the magnitude of the scaling factors required, information on the size-dependence of the elemental carbon particles associated with different sources would be lost."

Technical corrections:

1. p. 10348, line 5: would read better as "Particulate matter is known to impact air quality…"

This amendment has been included.

2. p. 10348, line 13: remove "upon" to make it read better.

This has been removed.

3. p. 10352, line 26 and p. 10353, line 4: The approach taken in this paper is described in the first instance as "an adaptation" and in the second instance as a "different approach"– these should be made consistent.

"is an adaptation" has been replaced with "shares some similarities with"

4. p. 10363, line 6: "...are estimated to be composed of 62% EC: : :" needs to specify whether this is by mass, by number, or something else.

This percentage is now defined as "by mass"

5. p. 10364, lines 14 and 16: these two lines refer, respectively, to EC cores and BC cores. These should be consistent, or the distinction the authors are making should be clarified.

The EC term is more appropriate for single particle mass spectrometer data because elemental carbon is detected chemically, while BC is detected optically by the single particle soot photometer instrument. The distinction has been included in the revised manuscript as follows:

"…it is unrealistic that all carbonaceous particles should contain a primary EC core. Optical SP2 measurements of BC taken at a separate site for the same period determined that 95% of particles associated with continental transport did not contain a detectable BC core (Laborde et al., 2012). Assuming that EC and BC can be considered as comparable, it is possible that a fraction of the mass apportioned to EC using the ATOFMS quantification approach may arise from fragmentation of organic molecular ions to form $[C_n]^+$ and $[C_n]^-$ fragment ions in the mass spectrometer."

6. p. 10365, lines 19 – 20: the phrase "which is higher than that of the HR-ToF-AMS." Needs to be added after "...ATOFMS (150 nm)" to clarify the meaning.

This sentence has been reworded for clarification.

Reviewer #2

General comments:

Specifically, I wonder if the method of obtaining relative sensitivity factors for the different particle types, presumably by comparison to co-located instrumentation, would inherently bias the ATOFMS data to agree with these same co-located instruments. I recommend that the authors address this comment possibly through a more in-depth discussion of procedures used to obtain mass concentrations.

Although the particle number size distributions from the ATOFMS were scaled to the TDMPS data every hour, hourly scaling was not performed for each chemical species. Hourly scaling of each species would lead to excellent agreement between the ATOFMS and the co-located instruments, but precludes the assessment of whether the method can predict temporal changes in mass concentration. Instead, average ATOFMS mass spectral ion intensities for the whole measurement period (a single value) were compared to average mass concentrations obtained from the co-located instruments over the same period (also a single value) to obtain a single relative sensitivity factor (RSF) for each chemical species. The aim was to investigate whether using a single RSF value for each species in the ATOFMS mass spectral dataset would then enable accurate prediction of the variability of the mass concentrations reported by the other instruments for the whole campaign. Thus, no temporally resolved data from the co-located instruments were used in the scaling procedure.

This direct comparison will certainly bias the slope to be reasonably close to 1 when comparing ATOFMS data with the other instruments, and this was intended. However, accurate prediction of the variability of each chemical species will only be possible if similar variability is observed in the intensity of the marker ions chosen for that species in the ATOFMS dataset. The reasonably high correlations observed between temporal trends (now Fig. 2 in the revised manuscript) indicate that ATOFMS mass spectra can be used to predict the variability of elemental carbon, organic aerosol, sulphate, nitrate, ammonium, and potassium simultaneously.

To test this hypothesis, 7 day subsets of the ATOFMS dataset were also used to ‘predict’ the variability of these species for the remainder of the campaign. Corresponding 7 day average mass concentrations from each co-located instrument were used to generate RSF values for this test. Correlations between the ‘predicted’ mass concentrations from the ATOFMS and the co-located instruments were relatively unaffected when using these subsets instead of the entire dataset, indicating that the ATOFMS mass spectral data can predict the variability of these species. However, the slopes did change due to the different RSF values obtained for each 7 day period.

An expanded discussion of the procedure used to generate mass concentrations for each carbonaceous particle class has now been added in response to Reviewer 1. Further detail regarding the relative sensitivity factors used has also been included in the revised manuscript as follows:

“The ATOFMS relative peak area (RPA), defined here as the peak area of each *m/z* divided by the total dual ion mass spectral peak area, for the marker ions in the number-weighted average mass spectrum were compared directly to the average mass concentrations of each chemical species determined by concurrent OCEC field instrument, HR-ToF-AMS and PILS-IC measurements. RPA was chosen for quantification because it is less sensitive to the variability in ion intensity associated with particle-laser interactions when compared to absolute peak area (Gross et al., 2000). Comparison between the ATOFMS RPA values and mass concentration data from the other instruments enabled the determination of arbitrary relative sensitivity factors (RSFs) for each species. The ATOFMS is subject to different sensitivities for chemical species due to differences in their ionization energies. For example, laboratory studies have previously demonstrated that the ATOFMS RSFs for ammonium and sodium differ by two orders of magnitude (Gross et al., 2000). Matrix effects associated with different internal mixing states may also significantly influence the relative sensitivities observed (Reilly et al., 2000; Reinard and Johnston, 2008; Pratt and Prather, 2009). RSF values determined for each chemical species are included in the Supplement.”

A new section (S2) has also been added to the Supplement as follows:

“S2: Relative sensitivity factors

A single relative sensitivity factor (RSF) for each chemical species was determined by dividing its average mass concentration (for the entire four week period) by the summed relative peak area of the marker ions for that species observed in the average ATOFMS mass spectrum of the whole dataset (Fig. S2). Thus, the relative sensitivity of the ATOFMS for each species by mass was obtained.

The resulting relative sensitivity factors are shown in Table S1. The units are arbitrary, and all values are given relative to potassium. Smaller values indicate that the ATOFMS has higher sensitivity for those species. It is also important to note that the RSF value for elemental carbon (EC) and organic aerosol (OA) will change depending on the number of marker ions chosen for the calculation.

Table S1: Relative sensitivity factor (RSF) values for each chemical species used for estimating mass concentrations. ”

Species	K	EC	SO_4	NO_3	OA	NH_4
RSF	1	29	54	58	284	456

Specific comments:

1. Page 10350, Line 26: What diameter of tubing was used for sampling?

Stainless steel tubing (1/4” o.d.) was used for the ATOFMS sampling line. This detail has been added to the manuscript.

2. Were all acquired spectra dual polarity? Particulate water can suppress negative ion formation [Neubauer et al., 1998] Were particles dried before being sampled by the ATOFMS as well?

This comment has been addressed in response to Reviewer 1 (comment 5).

3. Please explain in more detail how you determined RSFs for the different chemical species. I'm assuming you compared the RPA to the mass concentration from the different instruments. Wouldn't this bias your correlations since you are scaling ATOFMS peak areas to the very same instruments that you are showing correlations for?

This comment is addressed in response to the general comment above.

4. Page 10355, Line 12: What is the significance of the changing slopes? Might this suggest that in addition to hourly scaling factors, hourly average mass spectra with an appropriate slope be used to scale data to mass concentrations?

The change in slope is associated with changes in the relative sensitivity factors calculated for the different ATOFMS subsets. As discussed in response to the general comment, using hourly scaling factors for concurrent measurements of each chemical species would lead to excellent agreement, but this was not our intent. The hypothesis tested was whether the ATOFMS data could predict the variability of each chemical species in the absence of simultaneous hourly measurements provided by the other instruments. Smaller, seven day subsets were chosen to test this hypothesis. The results suggest that the variability is predicted well despite the subset chosen, however the magnitude of the ATOFMS-derived mass concentrations obtained do diverge to varying extents from the values measured by the other instruments depending on which subset is used. A discussion of this phenomenon is provided in the revised Supplement.

5. Page 10355, Lines 25-27: It is surprising that marine air masses dominated the meteorology for so long yet little sea salt was observed. Perhaps much of the sea salt was aged into sodium nitrate particles, could this be confirmed by PILS? You attempted to quantify NaCl, but I'm not convinced you are apportioning the nitrate properly since much of the nitrate mass might be associated with sea spray particles that have reacted with nitrogen oxides (see [Gard et al., 1998; Gaston et al., 2011])

The relatively low contribution of sea salt to $PM_{2.5}$ mass concentration is discussed in response to Reviewer 1 (comment 3). There was evidence of both chloride and nitrate in the ATOFMS sea salt mass spectra, indicating that at least some displacement of chloride with nitrate had occurred during transport. However, the average mass concentration of sodium determined by the PILS-IC instrument for $PM_{2.5}$ for the sampling period was 0.14 µg m^{-3}. If sea salt chloride was completely displaced by nitrate, this would only account for approximately 8% of the nitrate mass concentration measured at the site. Also, because the ATOFMS analysis is focused on PM_1 and not $PM_{2.5}$, the relative contribution of sea salt nitrate is expected to be even lower.

6. Page 10357, Line 19: Why is the accumulation of ammonium nitrate assumed for the detection of the EC-OA-NOx particle type? Why not the accumulation of photochemically produced nitrate?

The presence of a signal at *m/z* 18 for ammonium does indicate that at least some nitrate may be present in the form of ammonium nitrate, however photochemically produced nitrate may also contribute. This sentence has been reworded in the revised manuscript as follows:

"EC-OA-NOx particles were tentatively identified as EC-OA particles that had accumulated nitrate and secondary organic aerosol (SOA), but exhibited a much larger mass-size mode to the other three classes and were associated predominantly with continental transport events."

7. Page 10357, Line 21: Your finding that EC-OA-NOx particles are larger than EC-OA-SOx and EC-OA particles is consistent with [Moffet and Prather, 2009]. This should be noted.

The following sentence has been added to the revised manuscript:

"The observation of larger, coated EC particles is consistent with previous urban ATOFMS studies (Moffet et al., 2008a; Moffet and Prather, 2009)."

8. Page 10357, Line 21: Please state the size modes for each soot type.

The mass-size modes for these particle classes were discussed in detail in Healy et al (2012). However for comparison, the number-size modes have now been added to the revised Supplement and are included in Fig. S6. The average number-size modes for EC-OA, K-EC, EC-OA-SOx and EC-OA-NOx are 158, 210, 195 and 205 nm, respectively (aerodynamic diameter). These details are now included in the revised Supplement. Although EC-OA-NOx particles exhibited a second, larger mass-size mode (Healy et al., 2012), the contribution to particle number at sizes greater than 400 nm is quite low. Thus, a unimodal lognormal fit has been used to represent the number-size distribution for EC-OA-NOx particles in the revised Supplement.

9. Page 10358, Line 5: These trends should be commented on more in each particle class section so the reader doesn't have to refer back to the figures each time.

This section and associated figures have now been moved to the Supplement as discussed in response to Reviewer 1.

10. Page 10358, Line 12: Your spectra for fresh biomass burning aerosol, including the large CN and NO2 peaks, agrees with spectra obtained from smoke plumes by [Pratt et al., 2011]. This paper also shows spectra indicative of aging plumes, please compare.

The following lines have been added to the revised Supplement to describe the comparison:

"The strong diurnal behaviour and relatively small number size mode (280 nm) suggests that these particles are fresh (Figs. 2 and 3), while the relatively high potassium content indicates that local biomass burning represents the most likely source (Silva et al., 1999; Bente et al., 2008; Healy et al., 2010; McGuire et al., 2011; Harrison et al., 2012; Pagels et al., 2013). Similar mass spectra have also been observed for particles detected in a fresh prescribed biomass burning plume in Wyoming, although additional peaks were observed for potassium chloride and potassium sulphate in that case (Pratt et al., 2011)."

11. Page 10359, Line 20: Is there more diesel combustion in these regions that would contribution more sulfate?

Higher sulphate mass concentrations are often observed in Paris during periods when air masses originate in Northern or Northeastern Europe. Power generation and industrial combustion are the major contributors to SO_2 and particulate sulphate rather than diesel combustion in those regions (Pay et al., 2012).

12. Page 10359, Line 24: Suggest citing papers that show enhanced sulphate formation due to aqueous phase processing/during elevated RH conditions as this is a well documented process.

The following details have now been added to the revised Supplement:

"Interestingly however, elevated mass concentrations (>5 µg m^{-3}) of K-OA-SOx particles are also observed during a low wind speed fog event on 18/01/2010 (Fig. 4). The latter observation indicates that oxidation of SO_2 to form particle phase sulphate can occur on biomass burning particles at a local scale in Paris during fog events. The enhanced formation of particulate sulphate under high relative humidity is in agreement with previous field and laboratory studies (Pandis et al., 1992; Laj et al., 1997)."

13. Page 10360, Line 5-7: This particle type could also be K-OA-NOx particles with a thick organic coating that masks the K. How does the size mode compare to K-OA-NOx? If it is larger, then the additional coating would make sense as a source for this particle type.

The number-size mode for OA-NOx particles is indeed larger than that observed for K-OA-NOx particles (420 and 325 nm, respectively). The suppression of ATOFMS mass spectral signals for core particle species associated with the presence of thick secondary coatings has been demonstrated previously using a thermodenuder (Pratt and Prather, 2009). In that case, the number of particles classified as metal-rich increased by a factor of six when coatings were evaporated, indicating suppression of metal signals by internally mixed secondary species. These metals included zinc, barium and tin. However, the ATOFMS is particularly sensitive to potassium (Gross et al., 2000), and in Pratt and Prather (2009) the intensity of the potassium signal observed for both coated and uncoated biomass burning particles dominated the positive ion mass spectrum. Furthermore, the average mass spectrum for OA-NOx particles demonstrates that signals for ammonium (*m/z* 18) are high relative to *m/z* 39. This suggests that if suppression of potassium is occurring, that this suppression is selective for potassium and not ammonium, which is unlikely. While suppression of positive ion signals is difficult to rule out completely, the high sensitivity of the ATOFMS for potassium suggests that OA-NOx particles are more likely to be associated with fossil fuel combustion or secondary organic aerosol formation than biomass burning.

14. Page 10360, Line 17: Do you see oxalic acid (m/z -89) and/or HMS (m/z -111)? This would suggest the prevalence of aqueous phase processing.

Although deprotonated oxalic acid ion *(m/z* -89) intensity was not observed to increase during the fog event on 18/01/2010, hydroxymethanesulphonate (HMS) levels did increase significantly (*m/z* -111). This phenomenon was discussed in depth in Healy et al. (2012). Briefly, difference mass spectra of particles that grew to larger sizes on that day were characterised by enhanced signals for HMS, confirming that they had undergone aqueous phase processing prior to detection. The relevant difference mass spectrum is available in the Supplement of Healy et al. (2012):

http://www.atmos-chem-phys.net/12/1681/2012/acp-12-1681-2012-supplement.pdf

A similar HMS enhancement was also observed when comparing OA-SOx particles detected on a day with and without fog (17/01/2010 and 18/01/2010, respectively).

15. Page 10360, Line 24: Were any ions indicative of organosulfates present (see [Hatch et al., 2011])?

No significant peak was observed for the ion previously associated with the isoprene epoxydiol-derived organosulphate (IEPOX) at m/z -215 (Hatch et al., 2011). On average, the peak area at m/z -215 contributed less than 0.002% to the total mass spectral peak area for the Paris dataset. Correlations between this marker ion and other relevant organosulphate marker ions (m/z -139, -153, -155 and -199) were also very low (R^2 = 0.04, 0.01, 0.06 and 0.38) relative to the agreement observed for the ANARChE and AMIGAS campaigns (Hatch et al., 2011). This disagreement indicates that the variability observed for these ions is most likely associated with species other than organosulphates. The Paris dataset was also collected in the winter, when the influence of biogenic volatile organic compounds and their related oxidation products is expected to be minimal.

16. Page 10361, Line 17: What about the formation of iminium salts from TMA and either nitrate or sulfate (see [Pratt et al., 2009])?

Iminium salts are the expected products of the heterogeneous reactions discussed in the manuscript, however this point has now been clarified in the revised Supplement as follows:

"These particles are tentatively assigned as internal mixtures of SOA, ammonium nitrate and sulphate that have undergone heterogeneous reaction with gas phase TMA to form iminium salts during transport over agricultural areas before arrival in Paris (Pratt et al., 2009a)."

17. Page 10362, Line 18: Consider making Figure S5 a main figure.

This figure is now included in the main body of the revised manuscript (Fig. 3), in line with the increased emphasis on the size-resolved quantitative discussion.

18. Page 10364, Line 7: Also the instrumentation was different for these ratios in the Crippa paper. How would this bias the ratio?

Although BC was quantified using an aethalometer in Crippa et al. (2012), and EC is measured here using the thermal/optical approach, the mass concentrations reported by these two instruments agreed very well for the duration of the campaign (R^2 = 0.86, slope = 0.94) (Healy et al., 2012). Therefore it is likely that the bias in the ratio of OA/EC is introduced by differences in the apportionment of organic aerosol using the ATOFMS and AMS datasets, as discussed in the manuscript.

19. Section 3.3: It is interesting that your agreement with the AMS factors improves when fresh and aged particle types are combined. Could your study contribute to improvements in PMF analysis to help AMS data further distinguish particles based on their age?

The diversity of particle composition is described more explicitly using the ATOFMS dataset because useful tracers other than organic aerosol fragment ions are included in the analysis. For example, the association of OOA-containing particles with five mixing states was possible because of the inherent capability to measure elemental carbon, potassium, sulphate, nitrate, ammonium and trimethylaminium in the same single particle mass spectra as organic aerosol. This offers an advantage over using organic aerosol fragment ions exclusively in AMS PMF analyses. While particle age is more difficult to assess using single particle mass spectral data, relative increases in inorganic ion concentrations do add a very useful dimension, and may help to improve current analysis approaches. Recent efforts to include inorganic ions together with organic fragment ions in PMF analysis of AMS mass spectral datasets have also resulted in further refinement of the apportionment procedure, for example (Chang et al., 2011; Crippa et al., 2013b).

20. Page 10365, Line 20: I thought most AMS's have a lower size limit than this. State in the experimental what the size limits are of the AMS.

This sentence refers to the lower sizing limit of the ATOFMS instrument and not the AMS. The ATOFMS limit is due to inefficient scattering of 532 nm light by particles of 150 nm or less in diameter. The aerodynamic lens transmits particles in the size range 100-3000 nm, but only those larger than 150 nm were sized efficiently. The HR-ToF-AMS lower sizing limit is approximately 40 nm. To avoid confusion, this sentence has been reworded as follows:

"However, the ATOFMS mass concentrations are biased low relative to the HR-ToF-AMS HOA mass concentrations. This may be partly due to differences in the lower sizing limit of the ATOFMS (150 nm) and HR-ToF-AMS (40 nm)"

21. Page 10366, Line 20: How did m/z 43 compare to OOA? See [Qin et al., 2012] who showed that SOA is well tracked by this ion marker.

The relationship between hourly scaled intensity for *m/z* 43 in the ATOFMS dataset and hourly OOA mass concentrations did agree well here ($R^2 = 0.71$), providing further support that this ion is a useful tracer for secondary organic aerosol. The following lines have been added to the revised manuscript.

"The scaled ion intensity at *m/z* 43, a tracer ion for SOA in ATOFMS datasets (Qin et al., 2012), also agreed well with OOA mass concentrations (R^2 = 0.71). The mixing state of SOA in Paris can therefore be inferred to be relatively heterogeneous, distributed among five different particle classes during the measurement period."

22. Page 10367, Line 4: Is it possible that the AMS cannot vaporize some of the OOA and is missing a portion of the organics?

While there is a possibility that some highly oxidized organic aerosol might be thermally stable at 600 °C, the simultaneous underestimation of other OA factors using the ATOFMS approach suggests that differences in the apportionment procedures lead to these differences in mass concentration.

23. Page 10367, Lines 7-9: I suggest showing a temporal of COA. Could you try searching for markers for nonanal (see [Silva and Prather, 2000]), a tracer for meat cooking? What about searching for m/z 57 vs 59, the same ion used by the AMS for meat cooking?

The most relevant marker ion identified for a nonanal standard by Silva and Prather was the deprotonated molecular ion at *m/z* -141. Poor agreement was observed between the temporal trend for this ion in the ATOFMS dataset and the AMS COA factor in this work (R^2 = 0.03). Poor agreement was also observed for *m/z* 55, 57, 59 with COA (R^2 = 0.03, 0.05 and 0.002 respectively). The signal at *m/z* 59 is predominantly associated with trimethylaminium for the Paris dataset and therefore the correlation between *m/z* 59 and 57 is also relatively low (0.31).

Notably, nonanal was the only long chain aliphatic standard for which mass spectra could be obtained using the ATOFMS by Silva and Prather (2000). Other long chain aliphatic standards did not absorb efficiently at 266 nm, and were thus not ionized by the ATOFMS desorption/ionization laser. It appears that ambient cooking organic aerosol, at least when externally mixed, remains undetected by the ATOFMS. In the absence of any agreement between the two instruments for COA, this temporal trend was omitted from the manuscript, however further description of this factor is provided in Crippa et al (2013a).

Minor Comments:

24. Page 10348, Line 5: Change from "impact significantly upon" to "significantly impact"

This change has been made to the revised manuscript.

25. Page 10348, Line 26: What is your distinction between EC and BC?

Elemental carbon was determined chemically using a thermal/optical instrument and the ATOFMS while black carbon was determined optically using aethalometer, multi-angle absorption photometer and single particle soot photometer measurements. Thus, for clarity both terms are included in the introduction.

26. Page 10349, Lines 3-4: Change "predominant" to "dominant"

This change has been made to the revised manuscript.

27. Page 10349, Lines 3-4: Any estimates for how much vehicular emissions contribute vs biomass burning?

The following details have been added to the revised manuscript:

"Fossil fuel combustion associated mostly with local vehicular traffic was found to be the dominant source of EC and BC (88% and 85%, respectively), with the remainder attributed to domestic biomass combustion (Healy et al., 2012)."

28. Page 10350, Lines 5-7: How does the addition of a light scattering module help improve quantification?

The light scattering module only assists quantification for single particles. Aerosol mass spectrometers are routinely operated in bulk mode to quantitatively determine non-refractory aerosol composition, and are not subject to the same matrix effects observed for the ATOFMS (although particle bounce is an issue). Attempts to quantify these non-refractory species at the single particle level using AMS instruments remain sparse, however. The addition of the light scattering module to the AMS enables the collection of mass spectra for single particles of known diameter. Quantification of organic aerosol, nitrate, ammonium, sulfate and chloride at the single particle level can then be attempted (Cross et al., 2009).

29. Page 10350, Line 22: Add reference for the aerodynamic lens ATOFMS [Su et al., 2004]

This reference has been added to the revised manuscript.

Reviewer #3

1. 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 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 focus of the paper is an issue also raised by Reviewer 1. The emphasis has now been shifted significantly to the quantification approach in the revised manuscript. These changes are discussed in detail in response to Reviewer 1.

2. 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.

The quantification approach employed here does lead to good mass concentration estimates despite the inherent limitations in the conversion from particle number detected by the ATOFMS to mass concentration for each chemical species. Composition-dependent matrix effects, variability in laser output energy, inhomogeneous particle density and size-dependent detection efficiency issues are all expected to contribute to the error associated with estimating mass concentration values. The discussion of error associated with employing relative sensitivity factors has been discussed in detail earlier in response to Reviewers 1 and 2. A new section (S2) has also been included in the revised Supplement, describing the approach in further detail.

3. 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).

While the hypothesis tested in the manuscript was whether the ATOFMS could provide quantitative estimates for mass concentrations of elemental carbon, organic aerosol and inorganic ions using single particle data, the authors agree that including the number based results is quite useful for comparison with other single particle studies. The relative raw and scaled single particle number contributions are now included in the revised Supplement. A breakdown of the relative contribution of each particle class to total particle number with respect to time and size has now also been included in the revised Supplement (Figs. S4 & S5). A breakdown of the relative contribution of each particle class to unscaled number concentration, scaled number concentration and scaled estimated mass concentration is also included (Fig. S3).

4. 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.

There are certainly difficulties associated with attempting to convert raw particle number concentrations detected by the ATOFMS to volume and mass concentrations, and with attempting to quantify the mass fraction of chemical species present at the single particle level. Many of the potential sources of error are discussed previously in response to Reviewers 1 and 2. All particles are assumed to be detected with equal efficiency in each size bin. Particle density is assumed to be homogeneous and equal for all particle classes, and a spherical particle shape is assumed when converting aerodynamic diameter to corresponding mobility diameter and estimating volume. Shot-to-shot variability in laser power density and composition-dependent matrix effects are also expected to introduce error in the mass fraction estimates. The potential error associated with assuming a single particle density for all classes is also discussed earlier in response to Reviewers' comments.

The issues associated with using a single RSF value were also raised by Reviewer 2 (general comment). A detailed response is provided earlier. Briefly, the correlations observed using a single RSF value were better than expected considering the potential matrix effects, and reproduce the variability of elemental carbon, organic aerosol and inorganic ion mass concentration measurements reasonably well. The relatively high number fraction of carbonaceous particles (96%) and the relatively stable bulk aerosol density measured during the campaign (1.49 ± 0.07 g cm^{-3}) (1σ) both contribute to the agreement observed. The use of RSF values weighted by scaled particle number and mass contributions for each class were also explored as discussed earlier. Seven day subsets of the dataset were finally used to derive RSF values that could be used to predict the variability of each species for the remainder of the dataset. An expanded discussion of these procedures has now been included as Section 2 of the Supplement.

5. 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.*

A new figure (S5) has been included in the revised Supplement providing a breakdown of the raw relative number contribution of each particle class in each size bin used. The log-normal size distributions of all 10 classes are also now included in Fig. S6. Size-resolved information is unfortunately not associated with the HR-ToF-AMS OA PMF factors. However examination of PToF data for marker ions associated with each factor represents a very rough means by which to estimate their associated size dependence. The AMS ions *m/z* 44, 73 and 57 were selected as representative marker ions for OOA, BBOA and HOA, respectively. The mode diameter associated with each of these ions agreed reasonably well with the mass-size mode of the ATOFMS-derived OA associated with the same sources. Briefly, ATOFMS mass size modes for OA associated with SOA (OOA), biomass burning (BBOA) and traffic (HOA) were observed at 577, 353, and 216 nm, respectively. Mode diameters for AMS ions associated with OOA, BBOA and HOA were observed at 501, 380 and 380 nm, respectively. Thus both approaches agree within 15% for OOA and BBOA, but poor agreement is observed for traffic-related HOA. However, cooking organic aerosol (COA) and HOA mass spectra share marker ions, and thus some contribution from COA at *m/z* 57 is expected, potentially shifting the apparent size-dependence of HOA to larger diameters. Due to potential contributions from multiple factors, AMS ion size dependence has thus not been included in detail in the revised manuscript, although potential COA size dependence is discussed briefly in response to Reviewer 3 (comment 27).

6. 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?

A stronger emphasis has now been placed on the mass concentrations being described as estimates throughout the revised manuscript. Although colorstack plots are often very useful for assessing particle class homogeneity, the authors believe that Fig. 8 (now Fig. 6 in the revised manuscript), which accompanies Table 1 is the simplest visual representation of the breakdown of mass contributions for each chemical species in each particle class.

7. The estimated mass fractions also introduce some issues with how the particle classes are labeled. For example, K-OA-SOx 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-SOx class, its assignment is not supported by the component mass estimates. Similarly, K-OC-SOx has almost as much NOx mass fraction as the EC-OA-NOx, yet it is not given the "NOx" label.

This is an interesting point, and naming conventions for ATOFMS particle classes do vary across the literature. The potassium content is expressed here as a mass fraction, therefore for larger, more aged biomass particles (K-OA-SOx and K-OA-NOx) the relative content is much lower than for smaller, fresh biomass combustion particles (K-EC, K-OA). While the potassium mass content is relatively low for the K-OA-NOx and K-OA-SOx classes (0.5% and 0.3%, respectively), it is higher than that observed for the classes assigned to fossil fuel combustion (0.05-0.1%). Two decimal places were chosen to avoid clutter in the table. The naming approach is based on the relative peak intensity of marker ions, with positive ion mass spectral peaks, which are typically associated with primary or core composition, followed by negative ion mass spectral peaks that are usually associated with secondary composition. For K-EC, K-OA, K-OA-NOx and K-OA-SOx, potassium at *m/z* 39 is clearly the base peak in the positive ion mass spectra. For the remaining classes, either elemental or organic carbon fragment ions are more prevalent. The exception is OA-TMA, where *m/z* 59 $[N(CH_3)_3]^+$ is the most intense peak in the positive ion mass spectra, although this is expected to be a secondary component and so is placed at the end of the name. Although *m/z* 36 is assigned as elemental carbon, and is the base peak for OA-SO_x and OA-NO_x, these classes are instead prefixed with "OA" to highlight their higher estimated OA mass content relative to the "EC" prefixed classes.

Although K-OA-SOx does also contain a significant nitrate mass fraction, longer particle class names were avoided for brevity. OA-TMA could alternatively be named TMA-OA-NOx-SOx to include all relevant species, for example, however the name is unwieldy. The average mass spectra and the estimated mass fraction values are included as figures and therefore the relative estimated contributions of each species are available to the reader.

8. Is the lack of a EC-SOx 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?

The best example of the atmospheric processing of EC-OA-SOx particles was observed during a fog event on 18/01/2010. During this period, larger diameter EC-OA-SOx particles were observed. This phenomenon is discussed in detail in a previous article (Healy et al., 2012), specifically in the Supplement. Difference spectra for larger (>400 nm) vs smaller (<400 nm) EC-OA-SOx particles indicated that the larger particles were enhanced in sulphate, nitrate, hydroxymethanesulphonate and OA. Thus, simultaneous local uptake of all of these species was observed under these conditions. It is also interesting that there is an absence of any EC-rich particle class without significant OA content. Even particles associated with fresh vehicle exhaust (EC-OA) are estimated to contain approximately 30% OA.

9. Were any marine particles detected during the marine air masses?

A contribution from sea salt particles was observed during the marine periods. Although this particle class was omitted from the mass concentration procedure described in the manuscript due to the focus on carbonaceous particle classes, the raw counts and size distribution are now included in the Supplement for comparison to demonstrate the relative contribution of sea salt (Figs. S4 and S5)

10. 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 higher number of ATOFMS carbonaceous particle classes relative to the AMS factors did lead to the merging of the OA content of multiple ATOFMS classes to enable a direct comparison. However, the process was not arbitrary, although some relationships were more immediately apparent than others. For example, the diurnal trends of the BBOA and the K-EC and K-OA classes all point to a common local domestic wood burning source and thus the OA content of K-EC and K-OA were simply merged for this comparison.

The OA content of the EC-OA class was first compared directly with the AMS HOA factor because the diurnal behaviour of both suggested fresh vehicle emissions. However, the correlation improved significantly when the OA content of EC-OA-SOx particles was included. This finding indicates that the HOA detected by the AMS is associated with two particle mixing states.

The OOA_2-BBOA AMS factor represents aged biomass burning organic aerosol (Crippa et al., 2013a), and so was compared with the estimated organic fraction of K-OA-NOx particle class, which also contains elevated potassium, OA and nitrate. This composition is consistent with aged biomass burning aerosol. Both time series exhibited elevated mass concentrations during regional stagnation events that were not influenced by sulphate emissions in Eastern/Northeastern Europe.

Finally, particle classes that were associated with continental transport events were found to be best correlated with the AMS OOA factor, representative of secondary organic aerosol (SOA). Thus the OA content from these classes was combined for the comparison. While this does provide an interesting perspective on potential SOA mixing state, it is admittedly difficult to confirm whether OOA is truly internally mixed in all five of those particle classes. Although PMF analysis of ATOFMS mass spectral datasets has proven to be effective (Zauscher et al., 2013), it is beyond the scope of this study. PMF does represent a potential means by which the variability of each AMS factor might be distributed among the various ATOFMS particle classes in a less exclusive manner to that reported here. However, both approaches still rely on temporal coincidence. The five ATOFMS particle classes associated with continental air mass periods are expected to mostly be associated with the same factor in a PMF solution because they track each other temporally.

11. 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.

The overall structure of the manuscript has now been revised significantly in response to the Reviewers' suggestions, to reduce length, improve flow and to focus on the quantitative estimates provided by the ATOFMS in more detail. The separation of the local and transported influence upon air quality in Paris has been discussed in several recent articles (Crippa et al., 2013a; Sciare et al., 2010; Freutel et al., 2013), as discussed in response to earlier comments. However, the application of the ATOFMS to estimate these contributions is quite successful when compared to other approaches, and thus this section has been retained in the revised manuscript, but shortened in length. Several figures have also been moved to the Supplement as described earlier. The Conclusions section is now divided into three distinct subsections, and written in the style of a summary to better highlight the major findings.

12. 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.

The revised Introduction has now been expanded to as follows:

"Composition-dependent ionization efficiency issues and size-dependent particle detection efficiency are the predominant confounding factors (Allen et al., 2000; Reilly et al., 2000;

Kane and Johnston, 2000; Wenzel et al., 2003). Matrix effects result in different sensitivities for chemical species depending upon what other constituents are present in the same particle (Neubauer et al., 1996; Liu et al., 2000). Shot-to-shot variability in desorption/ionization laser power density can also lead to variations in resultant mass spectral peak height and area (Reinard and Johnston, 2008), although this phenomenon can be countered to some extent by using relative peak area for quantification instead (Gross et al., 2000). Sizing efficiency scaling curves can be generated using co-located particle sizing instruments (Allen et al., 2000; Qin et al., 2006; Reinard et al., 2007; Pratt and Prather, 2009), and significant advances have also been made in the quantification of specific chemical species in single particles based on their respective mass spectral ion intensities (Fergenson et al., 2001; Hinz et al., 2005; Ferge et al., 2006; Spencer and Prather, 2006; Zelenyuk et al., 2008; Pratt et al., 2009a; Froyd et al., 2010; Jeong et al., 2011)."

13. 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 size range 100-3000 nm refers to the lower and upper limits for which the aerodynamic lens can transmit particles to the sizing region. Due to limited light scattering for smaller particles and the upper sizing limit of the TDMPS instrument used for scaling particle number concentrations, only the size range 150-1067 nm was investigated here. A new figure has been added to the Supplement displaying the relative raw counts in each size bin detected by the ATOFMS for each particle class (Fig. S5). The Su reference has now also been added. The LDI power output ranged from 1.1-1.3 mJ per pulse. The following details have been added to the revised manuscript:

"An ATOFMS (Gard et al., 1997) (TSI model 3800) fitted with an aerodynamic lens (TSI model AFL100) (Su et al., 2004) was used to measure the size-resolved chemical composition of single particles in the size range 150-1067 nm (vacuum aerodynamic diameter, d_{va})."

"Particles are subsequently desorbed/ionized using a Nd:YAG laser (266 nm, operated here at 1.1-1.3 mJ/pulse), and the resultant positive and negative ions are detected using a bipolar time-of-flight mass spectrometer."

14. 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?

A single collection efficiency value of 0.4 associated predominantly with particle bounce was employed through comparison with co-located instruments and is described in Crippa et al. (2013a). Briefly, HR-ToF-AMS mass concentrations for OA and inorganic ions were compared with TEOM, MAAP, SMPS and off-line PILS-IC measurements to determine an average CE value. The variability of the inorganic ions determined by the PILS-IC instrument were reproduced well by the HR-ToF-AMS as described in detail in Crippa et al (Supplement section SI-2). The AMS data were chosen for comparison with the ATOFMS reconstructed mass estimates because size-resolved mass concentrations were available, and the OA apportionment approaches could be compared.

15. 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.

A cyclone was not employed at the ATOFMS sampling line inlet, nor was the aerosol dried. Although a separate inlet was employed for the ATOFMS, it was located adjacent to the inlet used for the HR-ToF-AMS and TDMPS, but at a lower height (6 m and 4 m, respectively). It is assumed here that particle composition and concentration is equal for all instruments. A discussion of the potential impact of the absence of a particle drier is discussed in detail in response to previous comments (Reviewer 1, comment 5). Other instruments, such as the PILS-IC and TEOM were located on the roof of the nearby LHVP building (Healy et al., 2012). Instrument inlets were located as close together as possible to minimise differences in aerosol composition. However, the site was predominantly impacted by urban background and regional air pollution, and thus composition is expected to be relatively homogeneous across the entire sampling site.

16. 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?

The *K*-means algorithm does involve exclusive clustering. The following detailed description of the approach has now been added to the revised manuscript:

“Mass spectra were imported into ENCHILADA, a freeware data analysis software package (Gross et al., 2010), normalised based on peak area, and clustered using the *K*-means algorithm. Application of the *K*-means algorithm involves exclusive clustering of single particle mass spectra into a user-defined number of clusters (*K*) based on their spectral similarity (square of Euclidean distance) (Anderson et al., 2005). A refined centroid approach was employed here where 50 subsets of the dataset were first clustered separately in order to find optimal starting centroids or “seeds” for clustering the entire dataset. Once these centroids are chosen, several passes of the entire dataset are performed until two successive iterations produce identical cluster assignments. The user defined *K* value is then increased in steps until further increases do not significantly affect the average distance of each particle from its assigned centroid in Euclidean space. In this work, a *K* value of 80 was chosen because further increases in *K* did not appreciably reduce distance and resulted in clusters containing 1 particle. These eighty clusters were examined for homogeneity and manually recombined into final classes as described previously (Healy et al., 2012).”

17. 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?

The ten classes discussed here represented 96% and 85% of the good quality mass spectra and total mass spectra collected, respectively. The contribution from sea salt and dust was relatively low, as shown in Fig S4. The contribution from uni-polar spectra was also very low, even under high humidity conditions, as discussed in response to Reviewer 1 (comment 5).

18. 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?

Only the ATOFMS counts in the size range 150-1067 nm (d_{va}) were scaled, assuming a density of 1.5 g cm^{-3} for all particles. This corresponds to a TDMPS size range of 100-712 nm (d_m). The entire size range measured by the TDMPS was 3-712 nm (d_m), but the lower sizing limit of the ATOFMS was 150 nm (d_{va}), precluding scaling of smaller particles. The following details from Healy et al (2012) are also provided in response to Reviewer 1:

"The scaling factors employed here were observed to be strongly dependent upon particle size, but the magnitude of the factors is similar to that observed in previous studies involving the use of laser particle counters, aerodynamic particle sizers and scanning mobility particle sizers to scale ATOFMS particle number concentrations (Wenzel et al., 2003; Qin et al., 2006; Pratt et al., 2009b). The size bin width was generated by merging adjacent pairs of TDMPS size bins because the original size bins were found to be too narrow, resulting in low ATOFMS hourly counts in some bins during certain periods of the measurement campaign. The uncertainty associated with the TDMPS particle number concentrations in the size range used here (100-712 nm, mobility diameter) is estimated to be < 2% (Birmili et al., 1999). The bins used are wider than those used previously by Pratt et al (2009) but narrower than those used by Wenzel et al (2003) and Qin et al (2006). The bin width was not increased any further because, although this would reduce the magnitude of the scaling factors required, information on the size-dependence of the elemental carbon particles associated with different sources would be lost."

Section 2.2 of the revised manuscript also includes a brief description of the procedure:

"Approximately 1.75 million dual ion single particle mass spectra were collected during the MEGAPOLI winter campaign. The total hourly particle counts from the ATOFMS were divided into eight size bins in the size range 150-1067 nm (d_{va}) and then scaled using coincident hourly averaged TDMPS number-size distribution data assuming a single density value of 1.5 g cm^{-3} for all particles as described previously (Healy et al., 2012). Thus, size-dependent detection efficiency issues were accounted for. The selection of a single density value will be less appropriate for locations impacted by significant metallic or crustal particle mass concentrations."

19. 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].

Applications of different particle density values for different particle classes, in particular for supermicron sizes is often a necessary procedure for scaling particle counts. However, the focus on submicron internally mixed carbonaceous particles, the minor contribution from crustal material, and the stability of the of the bulk aerosol density during the campaign (1.49 ± 0.07 g cm^{-3}) (1σ) (Healy et al., 2012), led to the decision to use a single density value of 1.5 g cm^{-3} in this work. A discussion of particle density is also provided in response to Reviewer 1 as follows:

The relatively low contributions of crustal material and metallic particles did facilitate the focus on carbonaceous particle quantification in this work. Other locations, impacted by high mass loadings of sea salt or road dust, would be characterised by inhomogeneous particle density, complicating the scaling procedure used here. Others have overcome this problem by assigning separate density values to different particle classes or size ranges prior to scaling

(Qin et al., 2006; Qin et al., 2012). The following line has been added to Section 2.2 of the revised manuscript:

“The selection of a single density value will be less appropriate for locations impacted by significant metallic or crustal particle mass concentrations.”

20. Were any (ultra)fine metal particles detected?

A minor contribution from metal-rich particles was observed (1.5% of the ATOFMS dataset by unscaled number). These include vanadium and iron containing particles most likely associated with oil combustion (Ault et al., 2010; Healy et al., 2009), and zinc/lead/chloride particles potentially arising from fugitive waste incinerator emissions (Moffet et al., 2008b). Due to their relatively minor contribution, these classes are not discussed in detail in the manuscript. However, their temporality and size dependence is now included in the revised Supplement for comparison with other ATOFMS studies (Figs. S4 and S5).

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

This fragment ion cannot be confirmed as organic nitrogen, and could instead be formed during the desorption/ionization process as an adduct ion (Silva et al., 1999). Thus the sentence has been reworded as follows:

“An intense base peak for potassium $[K]^+$ dominates the positive ion mass spectrum for K-OA particles while a strong signal is also observed for the $[CN]^-$ adduct ion (Fig. 5). The relative intensities for internally mixed nitrate $[NO_3]^-$ and sulphate $[HSO_4]^-$ are lower than those observed for the other OA classes. The strong diurnal behaviour and relatively small number size mode (280 nm) suggests that these particles are fresh (Figs. S6 and S7), while the relatively high potassium content indicates that local biomass burning represents the most likely source (Silva et al., 1999; Bente et al., 2008; Healy et al., 2010; McGuire et al., 2011; Harrison et al., 2012; Pagels et al., 2013). Similar mass spectra have also been observed for particles detected in a fresh prescribed biomass burning plume in Wyoming, although additional peaks were observed for potassium chloride and potassium sulphate in that case (Pratt et al., 2011)."

22. 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-NOx 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-NOx. 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-SOx).

The C_3^+ ion is assigned as elemental carbon throughout, and used (along with the other C_n ions) for the estimated quantification of elemental carbon. However, it is quite unlikely that all particles that contain a signal at *m/z* 36 also contain elemental carbon. Additional contribution at *m/z* 36 from fragmented organic carbon ions may contribute to the signal as discussed in the manuscript, and this is supported by simultaneous single particle soot photometer measurements (Laborde et al., 2012). Thus OA-NOx and OA-SOx are labelled according to their higher estimated OA mass fractions, as discussed earlier. OA-NOx particles are also significantly larger than EC-OA-NOx particles (number size modes of 420 and 205 nm, respectively), supporting a much higher OA mass content for the former. Although the naming conventions are subjective, the average mass spectra and estimated relative mass contributions are included in the manuscript as figures. The mislabelled C_2^+ fragment ions have also been corrected in the revised manuscript.

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

This figure has been edited to include all 10 classes in the revised manuscript.

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

The ratio of OA/EC increases with aerodynamic diameter, as shown in Fig. 7 (now Fig. 4 in the revised manuscript). At the smallest sizes detected (150-191 nm), the OA/EC ratio is estimated to be 0.56, but increases with increasing diameter, with a ratio of 3.66 determined for the largest particles (835-1067 nm). This finding suggests comparatively small coating thickness for smaller, freshly emitted combustion particles, and much thicker secondary coatings for larger, more aged combustion particles. EC-OA-NOx and EC-OA-SOx particles exhibit OA/EC ratios of 0.92 and 1.56, while EC-OA and K-EC particles exhibit much lower values of 0.44 and 0.38 respectively. The higher OA/EC rations for EC-OA-SOx and EC-OA-NOx particles, coupled with their larger size-number modes, indicates that these classes represent aged EC particles that have accumulated OA and inorganic ions through atmospheric processing.

25. 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.

The fact that the OA mass content of more than one ATOFMS particle class was required to be summed to achieve good agreement with the AMS factors is not very surprising. Firstly, there are more ATOFMS carbonaceous particle classes (10) than AMS OA factors (5), and secondly ATOFMS classes are separated based on their EC, OA and inorganic ion content while AMS OA factors are separated based on the temporality of OA ions exclusively. Although the approach here is simplistic, it is useful to treat the ATOFMS dataset as a set of 10 discrete mixing states for the purpose of estimating mass concentrations for each chemical species. This approach results in OA mass concentration estimates that track the variability of simultaneous quantitative measurements well ($R^2 = 0.75$ for ATOFMS OA vs AMS OA). Deciding which ATOFMS classes were combined was based on temporality, dependence upon time of day, dependence upon wind direction and air mass origin and chemical mixing state. A description of the approach is provided earlier in response to Reviewer 3 (comment 10).

26. 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?

The fact that the HR-ToF-AMS does not measure refractory species including EC should not be an issue here, because the comparison is between the OA mass content of the ATOFMS classes and the AMS OA factors. The mass contribution of EC and inorganic ions to each

ATOFMS class has thus been excluded for this comparison. To the authors' knowledge, this is the first time such a comparison has been attempted for OA.

27. 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.

Although the AMS PMF factors do not contain size dependence information, the size dependence of tracer ions associated with each factor can be examined. However, this approach is not ideal, as stated earlier. The mode diameter observed for *m/z* 41 peak intensity, a tracer ion associated with cooking organic aerosol, is approximately 400 nm (d_{va}). This lies well within the operational size range of the ATOFMS, suggesting that it is the chemical composition of COA, and not its mode diameter, that precludes its detection by ATOFMS. If, as Reviewer 3 suggests, COA were internally mixed within a suitable matrix that absorbs effectively at 266 nm, then the OA could potentially be detected very effectively. The absence of such a particle class suggests that COA at the measurement location is mostly externally mixed, and thus remains undetected. A more detailed description of attempts to identify COA in the ATOFMS dataset is provided in response to Reviewer 2 (comment 23). The revised manuscript has been edited to reflect the likely size-dependence of COA:

"It appears that the ATOFMS does not detect primary OA associated with urban cooking activities efficiently. It is unlikely that COA lies outside the size range of the ATOFMS, because the mode diameter for *m/z* 41, a tracer ion associated with COA, in the HR-ToF-AMS dataset was observed to be approximately 400 nm (d_a). Thus it is possible that cooking particles are sized correctly but not desorbed/ionized efficiently by the UV laser. Charbroiling and oil frying aerosol has been previously determined to contain saturated alkanes, alkenes, cycloalkanes, fatty acids, and no detectable EC (Schauer et al., 1999; Mohr et al., 2009; Allan et al., 2010). Low EC content, and potentially low polycyclic aromatic hydrocarbon content, for cooking aerosol relative to the other carbonaceous particle mixing states could result in low absorption efficiency at 266 nm, and may explain its absence in the ATOFMS mass spectral dataset."

28. 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?

The mass concentration estimation approach did prove very useful for the apportionment of each chemical species, OA and $PM_{0.15-1}$ to local and transported sources. This adds an extra dimension to the OA apportionment provided by the AMS PMF analysis, by allowing simultaneous apportionment of the other significant chemical species and PM mass concentrations. The estimated local contribution to OA based on the AMS PMF factors, if COA (undetected by the ATOFMS) is excluded, is 33%. This relatively low contribution is in broad agreement with the ATOFMS local OA apportionment (24%). If HOA and BBOA are treated as local OA and BBOA2_OOA and OOA are treated as transported OA, very similar local and regional temporality is observed for the AMS and ATOFMS apportionment approaches. For comparison, the relative contribution of local and transported AMS OA factors is now included in the Supplement, together with the local and transported ATOFMS OA contributions (Fig S12). Similar conclusions can be drawn regarding the importance of local vs regional contributions using either dataset, however this section has not been extended as discussed in response to Reviewer 1 (comment 1).

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

This detail has been corrected in the revised manuscript.

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