**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Urban organic aerosols measured by single particle mass spectrometry in the megacity of London" *by* M. Dall'Osto and R. M. Harrison

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General Comments: In their manuscript DallOsto and Harrison describe the analysis of a sub-set of particle types measured in central London during the REPARTEE-I experiment using a single particle aerosol mass spectrometer (ATOFMS). During the REPARTEE-I experiment various aerosol properties were measured in central London in the Regent's Park using – among others – two aerosol mass spectrometers. After the same authors have presented nitrate-containing particles and secondary aerosol par-

ticles measured during this field campaign with the ATOFMS in previous manuscripts, this manuscript focuses on presumably locally generated particle types from the same data sets. In addition to a description of the typical mass spectra of the selected aerosol particle types the attempt is made to identify the sources or source processes and to determine the nature of these particles. The manuscript is well written and the impression that the work was performed very thoroughly and self-critically is given. The individual mass spectra are extensively described and every effort was made to identify the nature of the particle types. In addition the limitations of the measurements and the associated analysis are clearly named, which supports the credibility of the analysis significantly.

"We thank the reviewer for the appreciation of the paper."

However, after reading both, the abstract as well as the whole manuscript the impression is left that a significant fraction of the source identification of the particle types and of the comparison of ATOFMS with AMS data is based on speculation and that no real conclusion about these sources can be made. Besides the Ca-EC particle type none of the particle types described here seems to be really identified and can be associated with any source with reasonable certainty. This becomes also clear when reading the conclusions of the manuscript, which mainly state that none of the instruments alone (AMS and ATOFMS) provide sufficient information for a reasonable explanation of the particle types, but also the combination of both does not really allow a reasonable identification of the nature and sources of the particles.

"Jimenez and DeCarlo (2008) commented (http://www.atmos-chem-phys-discuss.net/7/6413/2007/acpd-7-6413-2007-discussion.html) upon an ACPD paper (Moffet, R. C. et al, ACPD, 7, 6413-645, 2007) about measurement of ambient aerosols in northern Mexico City by single particle mass spectrometry. These comments provoked intense discussions between the ATOFMS and the AMS communities. Several issues were discussed, and the reviewer concluded that "Many instruments including the ATOFMS and the AMS are providing a wealth of data from which sometimes

diverging conclusions are drawn". We believe it is important not to speculate excessively on ATOFMS sources and imperative to compare the results obtained with other instruments during the same campaign. We are therefore cautious in assigning an identity/source to given ATOFMS particle types.

It is worth remembering that other papers published in this journal show that the ATOFMS is consistent with measurements by AMS when considering OC, nitrate sulphate and ammonium (see for example recent paper of Jeong et al. Quantification of aerosol chemical composition using continuous single particle measurements, ACPD, 11, 1219-1264). As stated by both reviewers, papers describing comparison between the ATOFMS and the AMS are important ones. We therefore reject the opinion that the combination of both does not really allow a reasonable identification of the nature and sources of the particles.

Our paper focuses on organic particle types and not only on total OC and inorganic species and we unfortunately find a very complex ensemble of different organic particle types, yet to be fully elucidated.

AMS broadly has seen two main factors over the last decade (Canagaratna et al 2007) but in the last two years application of PMF to AMS data has been showing a number of different factors (Ulbrich et al 2008). Allan et al (2010) show four factors, one of which (COA, primary cooking organic aerosol) is new and interesting. We tried hard to find correlations and to better describe this important cooking organic aerosol source by analyzing the ATOFMS datasets in depth in order to support the COA source and we report our findings."

It is unfortunate that already two papers have been published with the other fractions of the results of these measurements with this instrument. Otherwise the information within this paper could have well been added as a short paragraph to one of these papers to round up the information there. However, I do not think that the results presented here provide sufficient information to justify a whole paper.

"Many ATOFMS papers contain similar amounts of information, due to the characteristics of the measuring device, such that sometimes it is difficult to comprehend the data as a whole. We strongly believe there are different levels of analysis, and diverse conclusions can be drawn from analyzing of the order of 100,000 single particle mass spectra collected over fortnight periods. This analysis is largely unconnected with the chemical and physical properties we discussed in Dall'Osto et al (2009a) concerning a fog event and in the different types of nitrate containing particles (and relative physical properties) presented in Dall'Osto et al (2009b)."

Specific Comments: Abstract, Line 11: "... probably from condensation of semi-volatile species ...": While this seems reasonable I wonder how you can be sure that these species are local in origin?

"We consistently saw these particle types independent of air mass origin, pointing to a local origin. We have now modified the text to "postulated to be due to locally generated aerosol"."

Abstract, Line 19: Do the particle types really correlate with the HOA fraction or with the absolute concentration of the HOA?

"Absolute concentration of the HOA."

P3L3: "Primary particles" are not defined as only particles from combustion sources. There are many other sources for primary particles (e.g. mineral dust, sea salt, pollens, plant debris, ...)

"Modified, primary urban organic particles."

P3L10-12: Give a reference for this information.

"Hallquist et al. 2009."

P3L7-P5L7: There is an extensive description of secondary organic aerosol formation in this introduction. It is not really clear how this is related to the present manuscript,

which does not focus on SOA.

"We have modified the introduction in the paper."

P5L13: The description of the AMS used in this study is contradictory: Either it was a high-resolution ToF-AMS, then its name is HR-ToF-AMS or W-ToF-AMS, or it was a compact ToF-AMS, then its name is C-ToF-AMS.

"C-ToF-AMS."

P5L17: The claim that the AMS measures quantitatively 'precise' mass concentrations seems a bit exaggerated. Typically AMS precision is not better than 25-30%, especially when methods like PMF are used. I suggest deleting the word 'precise'.

"Agreed, and amended."

P6L3-4: "In summary, three contributions were identified in REPARTEE I: . . ." – contributions to what? Write briefly how they were identified.

"Agreed and amended."

P6L7-18: This paragraph sounds a bit like cutting the whole ATOFMS data set into pieces for several papers. Make clear what the reasons for the presentation of individual subsets of data from the same instrument measured in the same field campaign in different manuscripts are.

"Agreed and amended."

P7L2: The measurement site was on an area reserved for parking. Was there local traffic which could have contaminated the measurements?

"No, there were no cars or parking next to the measurement site."

P7L20-22: Here it is claimed that the ATOFMS can provide quantitative information on particle number as a function of composition. It is not stated what kind of information this is (e.g. number concentration of such particles) and how it is related to real-world

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quantities. In addition according to DallOsto et al. 2006 (also stated further below) no quantitative information on particle concentrations can be provided by the ATOFMS since detection or analysis efficiencies depend on the particle type and composition. P8L9: "In addition to the mass spectrometers . . ." – Only the ATOFMS was briefly described.

"Agreed and amended."

P8L10: The instruments described in this section do not measure physical but mainly chemical characteristics of the particles.

"Agreed and amended."

P9L11: Here it is stated that 'extensive calibrations' are needed to provide quantitative information on concentrations of particle types. Have these calibrations been performed?

"Whilst some semi-quantitative ATOFMS measurements have been reported (i.e. Qin et al., 2006) in the literature, no attempt was herein tried to scale ATOFMS measurements with other instruments. We obtained scaling factors as described in Dall'Osto et al (2006) but we only used them for reporting scaled aerosol size distributions."

P9L14-18: This section again sounds like the data set was cut in slices to be presented in different papers. Provide reasons for this division of the data.

"We have added in the introduction the reason for "slicing" the data into different papers. There are different levels of analysis in complex instruments such as the ATOFMS and the AMS. Previous papers have focused on a fog event, and upon nitrate particles. A single paper would be very long and lack clarity."

P10L2: This seems like a very small diurnal variation of temperature and humidity.

"This is what we observed."

P10L11-P11L4: Partially the description of the mass spectra (area matrices) is con-

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fusing. The shown AMs do not seem to reflect well what is described in these two paragraphs. For example in Ca-EC the EC intensity is much less than that of nitrate-lated peaks, but EC is seen as a major component while nitrate is not. Sulfate has similar intensity as EC, but is seen as negligible. Cluster OC is claimed to be internally mixed with sulfate contrary to Ca-EC, however, in the latter the m/z 48 signal (SO)is more intense than in the OC cluster. What is the origin of signals at m/z 37, 39, 41, 55 which are more intense than several others which are mentioned? Also in the AM of cluster Na-EC-OC several peaks (e.g. 48, 97, sulfate, 46, 62, nitrate, 39, 41, potassium?) are not mentioned in the description at all.

"We have changed some text in the manuscript to accommodate these points. We also accept the comment that the cluster ATOFMS Ca-EC should be called Ca-EC-NIT (Calcium-elemental carbon-nitrate) as the nitrate signal is as strong as the EC ones. However, since there are already a number of publications (Dall'Osto et al. 2009a,b) and other ATOFMS studies (Drewnick et al. 2005, Toner et al. 2007) calling this particle type Ca-EC and attributing it to primary traffic (lubricating oil) we leave the name Ca-EC. We state there is a higher amount of nitrate in this particle type relative to the previous studies."

P11L9-17: What is the point of showing this spectrum of a single particle? Is this spectrum typical for SOA-PAH? Then it should be reflected by the AM. If it is extraordinary, what is the point of showing it? The interpretation of this spectrum seems also a bit arbitrary. While some of the peaks are interpreted extensively using McLafferty (who describes electron impact mass spectra) others with similar intensity are simply neglected.

"The objective of clustering methods is to reduce the complexity of a large dataset by merging similar entities into groups. In this case, the clustering method (ART2a) and the operator reduce the degrees of freedom by orders of magnitude. Specifically, about 150,000 single particle mass spectra were reduced to 15 particle types. This undoubtedly reduces the amount of information contained in the area matrices. Many scientists

involved in mass spectrometry want to be able to look at real mass spectra, and not the cluster obtained by algorithms which inevitably modify (average) some features. Given the fact that we believe the particle type SOA-PAH has never been reported previously and presents some unique features (for instance the series m/z -107, -121, -137), we believe it important to report a mass spectrum typical of this particle type. We can only interpret peaks that are likely to be associated with fragmentation patterns (some of which are described by McLafferty) and we cannot interpret others."

P11L19: Similar here: m/z -73 is not dominant as claimed in the text. The signals at m/z -33, -49, -57, -80, -81 and -97 are larger than that at -73.

"The species responsible for m/z -33 is unknown, and signals at -80, -81 and -97are due to inorganic sulphate. We have modified the text accordingly."

P12L1: There is no "complete absence" of nitrate-related peaks as claimed. Signals at m/z -46 and -62 are clearly visible.

"Agreed and amended."

P12L24: Why are the size distributions of Ca-EC and OC indicative of a primary origin of these particles? How would be a secondary origin of these particles be in contradiction to those size distributions?

"Amended. Previous ATOFMS findings point to primary combustion particles peaking at the smallest detectable ATOFMS particle diameter, whilst more aged secondary organic components (i.e. long range transport organic aerosol) are more commonly distributed in the accumulation mode at around 500nm (Sullivan and Prather, 2005)."

P13L1-2: Is there any interpretation for the second smaller mode in the size distribution of Na-EC-OC in the coarser region? In addition also for Ca-EC and OC hints of such a mode can be seen in the size distributions. Generally I doubt that these features in the size distribution are very significant. Taking into account the percentage of Na-EC-OC (1,7%) and the total number of particles analyzed (153595) only 2611 particles belong

to the Na-EC-OC cluster. With the given range of the concentration of particles in Figure 3 it can be calculated that within this additional mode between 1 and 5 particles have been measured in the individual size bins. Add error bars to the size distributions to show whether such features are significant.

"The second mode of the Na-EC-OC particle type is not important for the discussion of the paper and the comment has been removed. This smaller mode in the region >1μm is likely to be due to some dust particles characterized by the same mass spectra and included in this particle type."

P13Chapter3.2.1: Since all four particle types together make up less than 12% of the total, correlations between bulk or ensemble measurements and time series of these types of particles can easily be by chance, especially when the correlation coefficients are so low.

"It is correct that the four particle types do not represent the total number of particles detected. It is worth remembering that the ATOFMS detects both organic and inorganic species, refractory and non-refractory species including metals. In order to compare the organic matrix of the AMS dataset, we had to look at organic rich particle types. A correlation between AMS factors (HOA, OOA, COA) and inorganic ATOFMS particle types (NaCl, Fe), non refractory material (EC) and nitrate particles was not found, giving confidence that correlations which are found may be meaningful."

P13L20: Average diurnal profiles are not necessarily very meaningful. They can easily be strongly biased by few extreme values accidentally occurring during a certain time of a day. Add either median and percentiles or error bars.

"Figure 5 was amended to exclude any unrepresentative extreme values occurring during a certain time of a day."

P15: How are all the uncertainties in this chapter calculated? How much of it is due to counting statistics? Within the uncertainties almost none of the differences are signifi-

cant. How significant are these differences?

"The text has been amended to address this point. While cluster Ca-EC and cluster SOA-PAH were found to be two independent groups significantly different from one another (t-test, 95% confidence), cluster OC (12$\pm$17, 9$\pm$7) and cluster Na-EC-OC (4$\pm$3, 4$\pm$5) did not show any statistically significant WD-WE oscillation. Factor COA did not show statistically significant variation, (1.4$\pm$1.1 μg m-3 and 1.2$\pm$0.9 μg m-3, for WD and WE, respectively). However, given the fact that AMS factor COA presents two peaks at about 12:00 and 20:00, further separation was required. Factor COA was divided into WD-WE periods, further split between day time (09:00-18:00) and evening time (18:00-24:00). COA-day was found to be about 25% higher during weekdays (1.03$\pm$0.78 μg m-3) relative to weekend (0.76$\pm$0.41 μg m-3), statistically different (t-test, 95%)."

P16L6: The previous association of cluster Ca-EC with primary traffic-related combustion particles 'is in agreement' with the assumption that those particles here are also from such sources, however, it does not 'confirm' this.

"Agreed and amended."

P16L6-13: Is it realistic that such different processes or sources generate the same type of particles? The explanation here sounds a bit like the desperate search for an explanation rather than that these measurements provide real insights into the processes occurring. Why is the small diameter of the particles an indication for organics condensing onto existing sulfate-rich particles? Also the following paragraphs – until the end of 4.1 – do not really provide a clear idea about the sources or nature of the particle types. All the attempts to explain them seem to be pretty speculative with some of the speculations being contradictory. Bottom line of this chapter is more or less that the sources and the nature of these particle types are not known – besides those for Ca-EC. For SOA-PAH the discussion even suggests that this particle type consists of different particle types mixed together in the analysis.

"Source apportionment of organic aerosols, especially with instruments such as the ATOFMS, can generate a large amount of speculation in the interpretation. We believe we have a particle type attributed to a primary traffic source (Ca-EC), an interesting new particle type generated by secondary organic aerosol production from traffic-related VOC (SOA-PAH). We have two other broad general particle types: Na-EC-OC and OC. The former, enhanced during evening times, is attributed to condensation of semi-volatile species on the background aerosols. The latter is a broad group of OC containing particles and unfortunately is likely to be a mixture of OC morning and evening sources. This is what we have stated and we do not believe we are extrapolating beyond what the data show."

P19L17-19: The description of OOA that is provided here seems more like a description which is typically given for OOA-I and OOA-II. Is this meant here?

"Given the fact that OOA-I and OOA-II is an old misleading terminology, we did not include it in the text. We report the first important paper describing the PMF application on AMS organic matrices and we then move onto the interesting factor reported by Allan et al. (2010)."

P20L1-4: ". . . as the qualitative temporal information of the ATOFMS particle number concentration of single particle mass spectral type does not allow a meaningful correlation with quantitative aerosol mass loading concentrations of organic components provided by the AMS." If this does not allow a meaningful correlation, what is the point of doing it nevertheless?

"We showed for example that nitrate containing particles sampled with the ATOFMS correlated very well with nitrate AMS mass loadings (R2=0.75). Whilst the ATOFMS is a semi-quantitative instrument for both refractory and non-refractory components, the AMS provides quantitative mass loadings of the non-refractory components. We do try to correlate the ATOFMS and the AMS keeping in mind the limitations of it. We would like to stress that other studies (Open Ocean measurements of marine organic

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aerosols by using on line particle mass spectrometry, Dall'Osto et al. 2011 – submitted to JGR-Atmospheres) shows correlation between three ATOFMS clusters and 3 AMS PMF factors of R2 higher than 0.7. Hence high correlations can be observed in favourable cases."

P20L11-13: This statement suggests that there is no real 'hard' reason for the 4-factor solution in the AMS PMF analysis.

"Correct, but it also means that there is some variance not explained in the 3-factor solution."

P20L14-P21L3: The conclusion of this paragraph is not very clear to me. There seems still no real explanation about the origin and nature of SOA-PAH.

"The fourth class (SOA-PAH) exhibited maximum frequency during the warmest part of the day, and a number of factors point towards secondary aerosol production from traffic related volatile aromatic compounds. We changed the text and made it clearer."

P21L4-16: The discussion about the m/z 55 particles is a bit confusing. It suggests that this type is the sum of OC, Na-EC-OC and SOA-PAH types. However, it is not clear, whether this is really the case. Write clearly what is the case."

"We have changed the text and made it clearer."

Conclusion: This work shows that not only AMS or ATOFMS alone are not able to give a comprehensive insight into aerosol composition and sources, but also the combination did not provide this insight – contrary to what is stated here.

"We hope that we have addressed all the comments of reviewer 1 and thank him/her for improving the quality of this manuscript."

Anonymous Referee #2 Received and published: 14 April 2011

This is an interesting paper representing a well executed study. However, there are weaknesses in the data analysis and interpretation and as a result the overall signifi-

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cance of the findings in unclear. The association of the Ca-EC particle type with vehicle emissions is well supported and consistent with work reported by others.

We thank the reviewer for the appreciation of the paper.

Other findings, such as the preferential deposition of amines onto less acidic particles go counter to current thinking on this subject; this brings into question the use of m/z 81 as an indicator of particle acidity.

Figure 6 suggests that more acidic particles enhance secondary organic aerosol production (positive values). We interpret the higher amount of organo-nitrogen peaks in the less acidic particles as one of the possible reasons for the reduced acidity. In other words, the organo-nitrogen species are the species responsible for the reduced acidity of this particle type.

It is not clear why the AMS factors were only compared to the four ATOFMS particle types described in this paper, rather than the entire set of 15.

This study did not aim to look at general organic and inorganic components, but aims to present specific organic particle types occurring during this study. The behaviour of other particle types such as nitrate has been reported in other papers.

The comparison of m/z 55 time series from the ATOFMS and AMS requires substantial clarification or should be removed. Many of the issues raised below can presumably be addressed through revisions and perhaps some additional analysis. The conclusion section requires revisions so as to focus on what was determined through this study.

We have made substantial changes to provide clarification of this section.

Detailed Comments

Abstract P2-L5: weren't all particles that were classified accompanied by the AMS measurements?

Changed in the text. Some of the particle types were inorganic or refractory in nature

(EC, NaCl, nitrate, Fe) and therefore could not be compared with the AMS as it is unable to measure these. P2-L7 We do not know that these four types are due to local particles. Perhaps you could revise to" postulated to be due to locally generated aerosol"

Agreed and amended.

P2-L10-15 This is a difficult sentence that should be revised.

Agreed and amended.

P2 L18 Secondary aerosol production

Agreed and amended.

Introduction P3-L10 Define VOC (not just in abstract)

Agreed and amended.

P6-L9 The Harrison 2010 reference is missing

Amended.

P6-L10 Introducing the summary table (Table 1) of the campaign at this point would help. If 15 particle types were classified, and only 4 are reported here, then what is the significance of the others? What were the key findings for the others? The summary table should be used to help clarity the objective of this work within the context of the previous papers. The acronyms used in Table 1 should also be defined, perhaps in the figure caption

Agreed. Both Table 1 and the text have been changed.

Experimental P8-L2-6 Aside from allowing for the detection of high molecular weight species, what are the potential consequences of this for particle classification and identification? Was the use of this low energy a deliberate choice or the result of an aging flash-lamp? Elaborate on the reasons for this choice as it is not common practice and

it likely influenced your spectra.

The reason for selecting lower laser fluence was to reduce the fragmentation of organic compounds, enhancing the detection of high molecular weight species as molecular ions (Silva and Prather, 2000). As a result, a wider variety of particle mass spectra are generated and those can great a better understanding of the different sources and processes occurring in the urban atmosphere.

P9-L2 What were the criteria for similarity? It is not elaborated on in detail in Dall'Osto and Harrison, 2006.

This is a standard procedure used. Some of the clusters obtained by ART2a were similar (little differences in the mass spectra for example) and therefore manually merged. The following criteria apply in order to be merged together: they had to present similar temporal trends, size distributions and similar mass spectra in order to be merged.

P9-L8 Sampling artifact may not be the correct terminology here. You are probably referring to transmission efficiency biases here.

Agreed and amended.

P9-L11 Replace "techniques" with measurements or instruments?

Agreed and amended.

Results P9-L13 You should adhere to one term for particle types or clusters, or distinguish them if there is a difference for this study. It appears as though they are used interchangeably.

Agreed and amended.

P9-L13 If 12 particle types were organic in nature, then shouldn't you consider the entirety of these for comparison with the AMS organic PMF factors? The 4 you have chosen represent a very small number concentration of all particles measured by ATOFMS, even for the organic particle types. Referring to the table containing a summary of all

the particle types from REPARTEE-1 would be useful here.

Agreed and amended.

P10-L11 The spectrum for Ca-EC only has very minor peaks at -36, -48 and -60. Why is EC being emphasized over OC as being characteristic of this particle type? State your naming criteria. The OC peaks (27, 43) seem to be more prevalent. Perhaps showing these spectra on a log scale would better illustrate the extent to which EC was present. Also peaks at 36.48 and 60 can arise from the fragmentation of organic compounds. Using a log scale might better indicate if higher mass peaks (72, 84 etc) were also present.

Explained in the text.

P10-L15 Is this low sulfur diesel fuel or gasoline?

It is both.

P11-L13 Many of the listed peaks are not visible in these figures. Using a log scale might help

We prefer to use the common practice of the last 15 years in publications of ATOFMS data which does not employ log scales. If some minor peaks are unique and important, they are usually described in the text.

P11-L20. The peaks listed are indicative of sulphate which may or may not be fully neutralized. They do not necessarily indicate acidic particles or compounds. m/z -195 is more commonly used as a marker of acidity (i.e., m/z -81 is very often present, while m/z -195 is much less often observed). From these mass spectra, m/z -195 is absent, or very low. Is there other evidence to suggest that these particles are acidic?

M/z 81 ([HSO3]-) is an ATOFMS marker for particle acidity (Whiteaker et al. 2003, Pratt et al. 2009). We tried to query the datasets of m/z -195 but not enough particles were found with this peak due to its much lower intensity relative to m/z -81.

P12-L12 Qin et al. (2006) reported a scaling method using APS and MOUDI. The authors should discuss the scaling method using both DMPS and APS data in more detail.

OK changed in the text.

P12- L28 These fragments may have been produced as a result of the decreased laser power used during this campaign.

We do not know if these fragments could be produced also at higher laser powers.

P12:L15 Fig. 3 shows only up to just above 1um. P12-L21 How do these size distributions show a primary source? This appears to be an overstatement. Perhaps replace indicative by suggestive?

Agreed and amended.

P12-L23 350 nm is not coarse Perhaps "larger" would avoid confusion

Agreed and amended.

P12-L26: The meaning of this statement is not clear as these are complex particles. The core may or may not have been primary. By definition the SOA coating is not primary. However, presumably the PAH compounds that deposited on the particles were primary with some degree of secondary processing.

Agreed.

P13-L9 10th-11th (?)

Amended.

P13-L11 Consistent terminology will help readers. The AMS components are not clusters. Are the PMF factors, components, factors or something else?

OK. Changed to AMS PMF factors.

P13-L25 How did you determine this? Include the Pearson R correlation coefficient and indicate if it was statistically significant, and what do you define as a "strong correlation"?

OK, changed.

P14-L24 What are the +- here? Is it still mean +- 1 standard deviation?

Yes, changed.

Discussion

P16-L5 The meaning of "confirms its primary origin" is unclear and possibly an overstatement. Is the suggestion that this study confirms that at this site these particles only come from vehicles or mostly (primary) come from vehicles. Presumably the meaning in not intended to be broader and applicable to all sites. While the weight of evidence certainly points to vehicle emissions, it is not clear if this has been demonstrated conclusively, if this is the intended meaning of "confirm" Thus do your results really "confirm" that it's vehicular emissions? You might summarize here why your results suggest vehicular emissions (i.e., reiterate that it "correlates strongly" with vehicular emissions tracers). Further, is it fair to compare these mass spectra to others that were generated using higher laser intensity? If so, justify why? If caution should be exercised when interpreting these mass spectra (and there should be), explain what parts of the interpretation should be performed more carefully. Some fragments will likely always appear (i.e., m/z +27/43), but others may never be observed under traditional ATOFMS operating conditions.

From our experience with ATOFMS data, we usually see two main differences when using different laser fluences. When using high laser fluence, we mainly detect more inorganic species such as NaCl and dust particles. Organic particles usually contain less intense peaks at high m/z but similar features in the mass spectra. When using lower laser fluence, we tend to see less inorganic particle types, and the mass spectra

of organic rich particles contain more information. However, broadly spectra are not much different between higher and lower laser fluences (if using 1.2-1.4 and 0.7-0.9 mJ per pulse). If using really low laser fluence (0.2-0.3mJ) then the mass spectra looks different.

Pg 16 –L10 Does the sulfate or evening peak (or both) suggest an additional source in the evening? This is a bit confusing.

OK, revised.

P16L12 Onto sulfate rich particles only in the morning? Clarify why you believe that particles are sulfate rich in the morning. For example, is the sulfate signal higher in this cluster in the morning?

OK, revised.

P16 –L15 As shown in Fig3, the second mode of the cluster is 0.9 um. Is there any possibility that these larger particles are from misclassification of aged sea salt particles ($NaNO_3$ or Na_2SO_4)? It also would be useful to provide back-trajectory analysis to identify source regions for the Na-EC-OC cluster.

Yes, it could be that some dust particles with similar mass spectra enter into this classification. The larger mode nevertheless is not statistically different from the other distributions and represents less than 10% of the particles belonging to cluster Na-EC-OC.

P17-L15 Refine the wording here (e.g. indicates and anthropogenic source). If there were multiple VOC sources contributing to this particle type, then this trend does not necessarily exclude a biogenic source. It could possibly be biogenic with another week-day influenced source added to it.

Agreed and amended.

P17-L16 Again, you should justify that what you've measured can indeed be compared

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to previous measurements.

Agreed and amended.

P19-L2 Can additional evidence be provided of particle acidity? The use of -81 peak alone is debatable. Does your observation hold true when you consider m/z -195 as a marker for acidity instead? The suggestion that amines are more prevalent on less acidic particles goes counter to most of the existing lab and field data or current understanding based on thermochemical modeling. Further in what sense are these organo-nitrogen peaks secondary? They could be primary amines. Perhaps what you mean to say is that they promote uptake of gaseous amine precursor compounds. However, this uptake has previously been found to be promoted on acidic particles.

Agreed and amended. We interpret the higher amount of organo-nitrogen peaks in the less acidic particles as the reason for the reduced acidity. In other words, the organo-nitrogen species are the species responsible for the reduced acidity of this particle type.

P20-L1: Were the AMS factors only compared with these four particle types or all 15? If it was only these four, why? If it was all 15 then these findings should be summarized.

This has been explained above and changed in the text. It is worthwhile to remember that the ATOFMS detects both organic and inorganic species, refractory and non- refractory and also metals. In order to compare the organic matrix of the AMS dataset, we had to look at organic rich particle types. A correlation between AMS factors (HOA, OOA, COA) and inorganic ATOFMS particle types (NaCl, Fe), non-refractory material (EC) and nitrate particles was not found.

P20- L10-14 This statement doesn't make sense when following the previous statement. Four factors were not chosen because it resulted in factor splitting. You need to develop this thought further.

Agreed and amended.

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P20-L21 What do you mean by "atmospheric chemistry" here? Do you mean oxidation of VOC precursor gases from sources other than food cooking?

Amended to clarify.

P20-L25 Why do you focus on m/z 55 for both of these very different instruments? How can you be sure that this one ion fragment resulted from the fragmentation of the same type of compound. These two instruments rely on very different ionization principles, which inherently result in very different fragmentation patterns. More evidence is required to say that m/z 55 represents the same "parent compound". Were the 11500 particles with M/z drawn from the whole populations of 150,000 or only the four clusters discussed in this paper? If it is from the 150,000 then it is interesting that this 55 peak was only evident in three of the clusters, those discussed in this paper. If the 11,500 spectra were drawn only from the particles discussed in this paper than the meaning of this analysis is unclear. Since the basis for performing this comparison and the findings are very unclear I recommend deleting this section. This section has been completely revised.

Conclusions Pg 22 L1-5 While these statements may be true, it's not clear how these conclusions arise from data presented hear P20-L16. Didn't you compare a lab and ambient spectra to "confirm: that the Ca-EC particles came from vehicles?

Yes, the study of Toner et al (2006) (added to text) shows that the Ca-EC particle type is associated with lubricating oil

Figures and Tables Table 1 define the acronyms, perhaps in the figure caption Table 2: Are any of these r2 values statistically significant? Fig 4 caption: replace profiles with factors Fig 3-5: use same color scheme and markers for the four ATOFMS clusters Fig 6: Why are these axes in red? If these difference calculations were performed with absolute peak area as the unit, then why are the differences E-02? They should be much larger. Are these a fractional difference? The meaning of "and little content" in the caption is unclear

This has been amended to clarify and correct the text.

Interactive comment on "Urban organic aerosols measured by single particle mass spectrometry in the megacity of London" by M. Dall'Osto and R. M. Harrison

j. Ma jxmachina@gmail.com Received and published: 30 March 2011

This is well-written paper and provides an extensive analysis of the particle types observed by ATOFMS, and also a correlation with AMS analysis, which will be valuable for many researchers. I have a couple of questions, not sure if they are valuable

We thank the Dr J. Ma for the appreciation of the paper.

(1)Why the particular four particle types are selected (they together account less than 12% of the total), not other types in this paper?

See reply to other reviewers.

(2)Introduction: are primary particles from combustion sources only? Sea spay? Windblown dust?

See reply to other reviewers.

(3)Introduction: 5045, line 13-15. Is there any reference supporting this statement? (perhaps, Zhang et al., GRL, 2007, 34, L13801?)

Yes, now included.

(4)P5047, Line 13. Is it a HR-ToF-AMS? then the corresponding citation should be "DeCarlo et al, Anal. Chem. 2006, 78, 8281-8289"

Yes, corrected.

(5)5052, Line 10: i wonder why Ca-EC is not called Ca-EC-OC (it has signatures of both OC and EC), or why Na-EC-OC is not called Na-EC?

The naming of ATOFMS particle types is an indication of features of the mass spectra.

We agree that cluster Ca-EC has both OC and EC and also nitrate, but given the fact we see it in a previous field study and we attribute it to traffic sources, we prefer for consistency to use the name usually adopted in other papers.

(6)5054, line 15: Why only 100nm intervals are used, when 10nm resolution is available? does this treatment lose or not lose some information (the size distribution plots seem like lose some details in my opinion)?

We do not need information at the 10nm level and we provide broader simpler size distributions.

(7)5061, Line 5-10: Since i am involving in a project about nucleation studies including effects of amines. I am quite strange about the statement "when the sulphuric acid content is very low, clear organo-nitrogen peaks (likely to be amines) can be seen in less acidic particles". Since amines are basic compounds, and very recent studies (See Ge et al., Atmos. Environ., 2011, 524-546 and 561-577) proves that most of them are stronger than ammonia to react with acids. It seems like that amines are more probably present in more acidic particles, not less acidic ones.

See responses to other reviewers.

(8)The work aims to raise the combination of AMS and ATOFMS can give more insights into the composition and sources, while for me, the correlation between ATOFMS and AMS shown in table 2 seems like not convincing. Does $R^2=0.65$ and 0.50 really mean a high correlation?

We can only report what we found, and it is unfortunate the correlations are not larger.

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/11/C3670/2011/acpd-11-C3670-2011-supplement.pdf