

## ANSWER TO REVIEWERS

**Urban aerosol in Cork City (Ireland) using aerosol mass spectrometry” by M. Dall’Osto et al.**

**Anonymous Referee #1**

**Received and published: 13 December 2012**

This paper describes two sets of complimentary aerosol mass spectrometry measurements during a three-week campaign in Cork, Ireland. Statistical analysis was used to separate the individual mass spectra identified by both techniques. The HR-ToF-AMS resolved five individual organic particle types and the ATOFMS statistical program resolved ten different types of both organic and inorganic aerosol particles, later simplified down to four broad aerosol particle types. The HR-ToF-AMS separate typical organic species: HOA, LV-OOA, and a cooking organic aerosol (COA). In addition the authors identified an additional organic aerosol type that was associated with domestic fuels, "peat and coal" OA(PCOA). The combined datasets provide interesting measurements at a coastal site in southern Ireland and the analysis of the two datasets are well done.

*We thank reviewer 1 for the appreciation of this manuscript*

However, more attention needs to be paid to the preparation of figures and consistency within the text. I consider that the material and discussion will suitable for publication in atmospheric chemistry and physics after the following corrections.

*We address major and minor comments below in italics.*

Comments:

1) A section of the discussion is dedicated to local ship emissions. In section 3.2 the authors mention that SO<sub>2</sub> emissions were monitored during the study and state that these would be discussed in more detail in section 4.2 (Page 29666 Line 3 to line 5). However, the discussion of SO<sub>2</sub> emissions is not included in section 4.2 or elsewhere. In addition SO<sub>2</sub> measurements are not included in any of the tables or figures.

*The SO<sub>2</sub> measurements are now included in Table 1 and briefly discussed in section 4.2 of the revised manuscript.*

a) Several studies (e.g Lack et al., 2009) have noted the increase in sulphate emissions associated with shipping emissions. The authors should add a sentence regarding the changes in inorganic particle concentrations measured by the HR-ToF-AMS during shipping episodes. Lack, D.A.et al. Particulate Emissions from Commercial Shipping: Chemical, Physical, and Optical Properties. Journal of Geophysical Research - Atmospheres, 2009.

*This comment is addressed in section 4.2.*

2) A cooking factor is identified. The authors suggest that using measurements of  $m/z$  55 and  $m/z$  57 are not sufficient to distinguish a cooking factor. The discussion of the cooking factor in section 4.4 could be substantially improved. Figure S8 is specifically referring to the COA but is not referenced in either of the sections discussing the COA. The author prepared this figure, which shows very nicely the different diurnal profiles using the HR-resolved peaks at  $m/z$  55(C<sub>3</sub>H<sub>3</sub>O vs C<sub>4</sub>H<sub>7</sub>) and  $m/z$  57(C<sub>3</sub>H<sub>5</sub>O vs C<sub>4</sub>H<sub>9</sub>), but did not include it in the discussion.

*We now refer to Figure S8 in the revised manuscript and include a discussion (also in section 3.4.2 COA) on the possible origin of the COA temporal trend.*

3) The author referenced the work of Mohr et al., 2012 (ACP) when discussing the COA. In the Mohr et al., manuscript it was demonstrated that using the ratio of UMR peaks at  $m/z$  55 to  $m/z$  57 allowed them to distinguish between HOA and COA. The authors should apply the method of Mohr et al to separate a COA and HOA factor. It would be interesting to see if the Mohr method is applicable to other datasets.

*We applied the method of Mohr et al (2012) and report the results in section 4.2.3.*

4) The authors note that the hour when the COA increased in concentration is later than the expected dinner time. Cork Harbour is situated about 2 miles east of the centre. Similar to the analysis by Mohr et al., the authors could discuss the changes in OA concentrations with wind direction and speed.

*We describe this in section 3.4.2 COA, and also added a discussion on the analysis of Mohr et al. (2012).*

5) The mass spectra presented in Figure 4 are of poor quality with axis and legends that are difficult to read. Since there are ten different types of MS to present the author should make them readable and if necessary separate them in two figures. This comment extends to the majority of other figures presented in the manuscript. Most figures have axis with font sizes too small. In addition boxes around the legends make the figures cluttered and difficult to read.

*We have improved the quality of all Figures in the revised manuscript.*

6) Table 1. shows gas- and particle-phase measurements during different meteorological periods of the campaign. For both meteorological periods, errors are included. The author should explain what these errors represent in the table caption. For the "sunset" data no errors are provided and AMS data show only percentages, which I presume are the fractional contribution of each component. The ATOFMS data has only the number of particles but neither fractional contribution nor errors are provided. The author should be consistent within a table and explain what is being presented.

*We have now included errors (one standard deviation, explained) in all the measurements reported in Table 1.*

7) Both instruments are described as providing size resolved aerosol composition. In section 3.3 the authors explain the different ATOFMS particle types and their corresponding Size distribution. However, for the HR-ToF-AMS there is no mention of the resolved size distribution. These distributions could be mentioned in section 3.4.1 and also again when comparing the differences in Period S and Period M.

*We thank reviewer 1 for this suggestion. We have added a new figure (S12) depicting the AMS size distribution for the periods ALL, Marine and Stagnant, as discussed in section 4.3.*

*In order to facilitate the quantification of the relative contribution of different domestic fuel sources to ambient PM1 levels a series of controlled experiments were undertaken to obtain mass spectra of peat and coal combustion. A controlled combustion experiment for each of the fuel types was performed, with each burned for approximately 40 min in an outdoor grate with fresh combustion particles being introduced into the HR-ToF-AMS. The grate was open to ambient air without temperature control (ambient conditions represented very clean air masses with Organics concentrations  $\sim 0.3 \mu\text{g m}^{-3}$ ,  $\text{NO}_3 \sim 0.02$ ,  $\text{SO}_4 \sim 0.8$  and  $\text{NH}_4 \sim 0.1 \mu\text{g m}^{-3}$ ). The coal used was smokeless coal which is a legal prerequisite for burning coal in Cork City as it is a designated smokeless fuel zone. Emissions were diluted to  $\sim 30 \mu\text{g m}^{-3}$  with filtered ambient air. Peat, which is used extensively in Ireland for domestic space heating, was obtained locally, concentrations were maintained  $\sim 100 \mu\text{g m}^{-3}$ . All experiments were repeated twice with similar results, therefore, the mass spectra presented in this study represents the  $m/z$  averages over both experiments.*

Minor Corrections:

Page 29658, Line 20: ..coal..

*Edited*

Page 29659, Line 16 to 23: On line 16, it is stated that the PM10 concentration was measured at eighteen monitoring stations in Ireland during the year 2009, and "that all locations were compliant with the standards introduced since 2005". However, on Line 24, the authors state that the EU limit of  $50 \mu\text{g m}^{-3}$  was "exceeded only six times" in Cork city. Then on page 29665, Line 16, it is mentioned that PM10 values were not exceeded in Cork city during the field study. Can you clarify if Cork city is within the eighteen monitoring stations and whether or not it exceeded the standards?

*In the air quality directive (2008/EC/50), the EU has set two limit values for particulate matter (PM10) for the protection of human health: the PM10 daily mean value may not exceed 50 micrograms per cubic metre ( $\mu\text{g}/\text{m}^3$ ) more than 35 times in a year and the PM10 annual mean value may not exceed 40 micrograms per cubic metre ( $\mu\text{g}/\text{m}^3$ ). In Ireland all locations were compliant with this. Although, the PM10 daily mean value of  $50 \mu\text{g}/\text{m}^3$  was exceeded on six occasions in 2009 (considerably less than the allowed number of 35), none of these exceedances occurred during the field campaign. The text has been changed accordingly to make this clear.*

Page 29660, Line 1: Please state why "...only about half of the particulate matter was analysed."

*This comment relates to the previous study of Hellebust et al. (2010) where the sources of PM were determined without detailed characterization of the component chemical species. The text has been modified for the sake of clarity.*

Page 29660, Line 3: add % for the long range transport.

*Edited*

Page 29661, Line 1: use "to" instead of "-" Here and elsewhere.

*Edited*

Page 29662, Line 20: Include text to say that the ammonium nitrate particles are used to determine the ionization efficiency of the HR-ToF-AMS.

*Edited*

Page 29662, Line 20: The authors state, that both ionization efficiency and time-offlight calibrations were performed during the study for the HR-ToF-AMS. Are these calibrations necessary for the ATOFMS and if so, were they performed?

*Edited - we performed a size calibration before the field study.*

Page 29663, Line 15: Define PMF. You should reference Ulbrich et al., 2009 or Lanz et al., 2007.

*Edited – a referenced has also been added*

Page 29663, Line 25: You could refer to table 1 here. Why are SO<sub>2</sub> measurements excluded from table 1 (and from further discussion).

*Edited - added*

Page 29664, Line 2: What are the inlet diameters? Was care taken to ensure isokinetic sampling for larger particle sizes?

*Edited - we used 1/4inch tubing assuring the PM mass sampled (roughly PM<sub>1</sub> for the AMS and PM<sub>1.5</sub> for the ATOFMS). Edited in the text.*

Page 29664, Line 19: Add a short sentence saying that back trajectories were calculated using the HYSPLIT model and then refer to section S1. Change the Draxler et al., 2003 reference to Draxler and Rolph 2003 (as in section S1).

*Edited*

Page 29665, Line 1: were chosen.

*Edited*

Page 29665, Line 16: Reword :...not exceeded in the city of Cork during the field study, ....

*Edited*

Page 29665, Line 18: Reword." ...twice in the city and once in the port area".

*Edited*

Page 29665, Line 19: ..During Period S...

*Edited*

Page 29665, Line 19: What does PMX represent?

*Edited - PM10 and PM 2.5*

Page 29665, Line 21: PM10 or PM2.5 or both?

*Edited - both*

Page 29665, Line 20: Reword " ...Period M., likely due to the ..."

*Edited*

Page 29665, Line 25: "Gaseous concentrations for NO and NO2 were..." Are these values representative of the entire campaign? What were the values for the EC/OC.

*Edited - added*

Page 29665, Line 23: Do you mean Figure 3? In section 3.3, the only mention of these dates (Feb 4, 9,11, and 18) are during the discussion for Ca-Dust particles. However you do not state that the Ca-Dust particle resulted from local emissions or that it is correlated to the increase in PM2.5.

*Edited - it is due to both Ca-Dust and EC-POS (see also Table 2 ATOFMS particle types, classified as "spikes" temporal trends).*

Page 29666, Line 3: There are no discussions of SO2 concentrations in section 4.2 or elsewhere.

*Edited – SO2 levels were often below the detection limit, but spikes were well defined and reported.*

Page 29666, Line 11: Do "ship emissions" represent one of the particle categories?

*Edited - we modified Table 2 and included a possible source attribution column in the text (beside the general name and cluster name)*

Page 29666, Line 11: According to table 2, it would be more correct to say that the inorganic particles represented less than 4%.

*Edited - 4%*

Page 29666, Line 15: "ATOFMS efficiency depends on particle type". More detail could be included on the matrix effects within each single particle and chemical ionization efficiencies of alkali metals.

*Edited – this is also discussed in section 4.4.*

Page 29667, Line 13: Change "mode" to "distribution".

*Edited*

Page 29668, Line 11: Be consistent with the date format throughout the manuscript; 4 February/ 4th (Page 29665, Line 24).

*Edited*

Page 29669, Line 13: reword: "..but its unique strength lies in the fact that it can monitor real-time variations in the single particle composition."

*Edited*

Page 29669, Line 16: Attribute

*Edited*

Page 29669, Line 21: remove "..unique as"

*Edited*

Page 29669, Line 7: remove "seems"

*Edited*

Page 29669, Line 16: The authors mention that it is difficult to assign "ATOFMS particle types to specific space heating sources" and then said "it was surprising" that other studies have already assigned different ATOFMS mass spectra to biomass burning related aerosols.

However, on Page 29670, Line 17, the authors associate two different particle types (OC-EC-CH and OC-EC-SUL) to domestic fuel combustion sources and to peat combustion. The authors should reword this section, showing that, in agreement with previous studies, they were able to assign/relate certain mass spectral signatures to domestic fuel sources.

*Edited*

Page 29670, Line 15: Do the authors mean aerosol particles rather than "processes"?

*Edited*

Page 29670, Line 23: Since Middlebrook et al., describes how the CE of the AMS changes as a function of the measured aerosol composition, I suggest that the authors explain why they use a composition independent CE of 0.5. e.g..Since ammonium nitrate concentrations always contribute less than 25% to the total aerosol mass a composition independent CE of 0.5 was applied to the data....

*In the supporting information we show that good correlations were found for all species (nitrate, sulphate, ammonium, organic carbon, chloride,  $R^2 > 0.7$  for all species) suggesting our CE is appropriate.*

Page 29671, Line 1: Non refractory should be hyphenated.

*Edited*

Page 29671, Line 2: "Figure 5 shows that 62% of the aerosol mass loading "

*Edited*

Page 29671, Line 5: Include information on the remaining 2.5%

*Edited*

Page 29671, Line 25: Change to NH<sub>4</sub>Cl

*Edited*

Page 29672, Line 5: reword "...resulted in a behaviour of the existing factors.." e.g. resulted in a decrease in the correlation of the factors with supplementary data (or something similar).

*Edited*

Page 29672, Line 24: In Figure 6 change legend from OOA to LV-OOA.

*Edited*

Page 29673, Line 13: This sentence is not very clear, do you mean "..Na-K-OC-NIT) that are always/often attributed to" or "..Na-K-OC-NIT) and can be attributed to secondary or aged..."

*Edited - markers for secondary and aged aerosol*

Page 29674, Line 3: Correlate

*Edited*

Page 29674, Line 27: Clusters

*Edited*

Page 29675, Line 18: lesser

*Edited - we modified the text.  $R^2$  can be quantified, lower*

Page 29675, Line 20: .similar to this factor, PCOA...

*Edited*

Page 29677, Line 11: ..also with detectable signals in cooking emissions.

*Edited*

Page 29677, Line 18: Why do you not mention Figure S8 in this discussion or in Sect.4

*Edited - we now refer to Figure S8.*

Page 29678, Line 12: Do you mean Figure 3 and 8?

*Edited - yes*

Page 29679, Line 14: The authors should discuss changes in the inorganic aerosol measured by the HR-ToF-AMS during the ship emissions periods. If SO<sub>2</sub> measurements are available they could also be discussed in relation to the ship emissions.

*Edited - we added a description of it in section 4.2.1*

Page 29680, Line 13: Can the authors include another sentence to explain the consequences of dioxin formation?

*Edited - human health*

Page 29680, Line 19:...) are peaks due to

*Edited*

Page 29680, Line 26: According to table S3, m/z values for C<sub>4</sub>H<sub>7</sub> and C<sub>4</sub>H<sub>9</sub> are equally associated with HOA, COA, PCOA, and BBOA.

*Edited - deleted*

Page 29681, Line 9: "...for the entire study"



*Edited - modified*

Page 29681, Line 23: You mention that there is "...a chemical (aging) and/or physical process (evaporation) affecting the life time of BBOA versus PCOA organic aerosols." You could include the variations in gas phase measurements (NO, NO<sub>2</sub>, and O<sub>3</sub> as evidence for chemical aging.

*Edited - more ozone in Marine P air masses.*

Page 29683, line 19: Please include more information on why the diurnal trend "was found to be surprising"

*Edited*

Page 29683, line 19: Correctly

*Edited*

Page 29683, Line 20: first

*Edited*

Page 29698, Figure 2: (c) ATOFMS main particle types,

*Edited*

Page 29702, Figure 6/7 : " The ion families of the different factors are shown in boxes ". There are many boxes in this figure. Could the authors reword this caption, e.g. m/z values are each colored by their corresponding ion family?

*Edited*

Page 29694, Table 1: "Averages for the entire field study", Also please include a description on the errors provided.

*Edited*

SI 3, Figure S2; Increase Font sizes in graphs. Remove boxes around legends.

*Edited*

Figure S8: which is captured by the PMF. Change C<sub>3</sub>H<sub>5</sub>O to (C<sub>3</sub>H<sub>5</sub>O)

*Edited*

**Urban aerosol in Cork City (Ireland) using aerosol mass spectrometry” by M. Dall’Osto et al.**

**Anonymous Referee #2**

**Received and published: 15 January 2013**

The manuscript presents the results obtained within a 3 weeks campaign held in Cork (Ireland) by 2 state-of-the art aerosol mass spectrometry approaches: AToFMS and HR-ToF-AMS. The discussion is supported by other results obtained by semicontinuous OC/EC field analyzer and offline measurements (one can regret the absence of SMPS). From the PMF analysis performed with AMS data authors choose a 5 factors solution with 3 now well-know factors HOA, LV-OOA, and BBOA, one still under discussion but in the way to be largely accepted (COA; Cooking OA) and one new factor PCOA for Peat and Coal Organic Aerosol. The discussion is conducted fairly and uncertainties are clearly stated and discussed. AToFMS spectra have been classified in 10 particle types including 5 organic-rich types, representing 93% of the total particles classified (ie : 1 200 000). As stated by the authors this approach is not quantitative but provides very relevant information on the single particles composition, while AMS provides bulk information. As for AMS results, the discussion on the AToFMS results is clear (not as clear as the AMS section) and uncertainties/limitations clearly stated and discussed. The high quality results obtained within this study and the discussion developed here makes this paper suitable for publication in ACP.

*We thank reviewer 2 for these comments*

However this paper can greatly be improved. Thus I recommend publication after the following points/recommendations have been clearly corrected/explained/improved.

*We addressed comments below in italics*

General recommendations/points

1-Even if the article has been slightly modified since its initial submission, my major issue is the lack of connections between the results obtained by the two main instruments used here. I still wonder why the authors have not try to perform multi regression analysis between AMS-PMF factors and the organic rich particles types? AMS-PMF is not an ultimate approach (as discussed by the authors) and almost nothing is known on the chemical nature of the various factors obtained by AMS-PMF and widely used since about 5 years. Such multi regression approach will have provide a lot of very interesting, and maybe capital, information to understand the chemical nature at the particle level of these bulk fractions and/or to highlight the difficulty to clearly discriminate the different factors (ie HOA vs COA?, PCOA vs BBOA?). This paper can be published without this analysis, but this lack is from a scientific point of view very frustrating.

*We agree that this type of analysis would be useful, but it is beyond the scope of this manuscript. Multi-regression analysis incorporating the AMS-PMF factors, ATOFMS data and other measurements is currently in progress and will be the subject of a separate future publication.*

In this case, insert table S5 in the main text and add some figures to support the discussion. I suggest to develop the comparison between AMS-PMF factors and ATOFMS particle types in the light of their size distributions.

*We agree that table S5 is important, but would rather leave it in the supporting information because we do not want to add confusion between the 4-factor and 5-factor solutions generated from PMF analysis. The comparisons and correlations between the AMS and the ATOFMS data are made at several points in the manuscript and are summarised in the abstract and in the conclusions section.*

2-Relations between figures and text have to be significantly improved to support the discussion. More generally the quality of the figures must be improved (see detailed comments below).

*We have improved the quality of the figures and have also made more referrals to them in the body of the manuscript.*

Specific but not minor comments :

1- page 29658, line 20 : “coal” instead of “cool”

*Edited*

2- line 23 : If Peat, coal and wood combustion contribute to 44% of OA, it doesn't mean that these sources contribute to 28 % of non refractory PM mass (except if you calculate the primary fraction of nitrate, sulfate, ammonium, originating from these sources ; the secondary fraction is another story).

*Edited - total mass detected*

3- page 29658, line 14-18 : The 50  $\mu\text{g}/\text{m}^3$  corresponds to a daily limit. It is not relevant to compare this value to an annual mean concentration. On the same way the limit of 25 $\mu\text{g}/\text{m}^3$  for PM<sub>2.5</sub> refers to an annual mean and should be compared with annual average and not with specific period of the year. I understand the motivation of the authors to compare this limit value to PM<sub>2.5</sub> concentration observed during winter, but clarify in the text.

*This part of the manuscript has been edited and clarified.*

4-page 29659, line 19 : Since you are measuring aerosol from different class of size “(ie PM<sub>2.5</sub>)” is not necessary and confusing.

*Edited - we clarified in the text the PM2.5 and the PM10 limits, and the need to better characterise the PM2.5 fraction.*

5- page 29660, line 1 : “half of the particulate matter was analysed” : not clear. Not apportioned? Not measured? If not measured it doesn't mean that the source contributions do not consider the mass of organic if the adjustment is performed on the PM mass. Clarify.

*This comment relates to the previous study of Hellebust et al. (2010) where the sources of PM were determined without detailed characterization of the component chemical species. The text has been modified for the sake of clarity.*

6- page 29661, line 4 : The Old Station Road is not reported in the map (figure 1)

*This monitoring station is included in the new map.*

7- page 29661 section 2.2 : Even if the results from off line techniques are not developed in the text (or too scarcely) and the methodology already described in Kourtchev et al., 2011, the authors have to be more precise in this section. Pallflex quartz fiber filter : I assume this description corresponds to Tissuquartz™ filters ;

*Edited: Pallflex Tissuquartz filters*

The filters were extracted : how? In which solvent?; I also assume that internal standard have been used for the quantification: which one? Added in which step of the extraction process?

*The text has been extended to cover the relevant details:*

*The filters were extracted and analyzed by GC/MS as described in Kourtchev et al. (2011). Briefly, a part of the quartz fiber filter, 6–12 cm<sup>2</sup> depending on the organic carbon (OC) loading, was spiked with 0.5 µg of the internal recovery standard methyl-β-D-xylanopyranoside (MXP) and left to dry for 30 min before being extracted three times with 20 mL of dichloromethane–methanol (80:20, v/v) under ultrasonic agitation for 30 min. The filtrates were combined, reduced to approximately 1 mL with rotary evaporation at 35 °C and filtered through a Teflon filter (0.45 µm). The filtrate was transferred to a 2 mL glass vial and evaporated to dryness under a gentle stream of nitrogen. The residue was derivatized by addition of 50 µL of N,O-bis(trimethylsilyl)trifluoroacetamide containing 1% trimethylchlorosilane (BSTFA+1% TMCS) and 30 µL pyridine, and heated at 70 °C for 1 h. After cooling to room temperature, an aliquot of 1 µL was analyzed by GC/MS in Electron Ionization (EI) mode.*

As levoglucosan have been measured a derivative must have been added : which one?

*Derivative? No, the trimethylsilyl ester derivative of levoglucosan was detected, not added.*

Out of the fifteen organic marker compounds in PM2.5 : What does it mean? In PM2.5 there are much more than fifteen compounds. ..I assume, the authors refer to the number of compounds targeted in their study, please clarify ; only levoglucosan,

mannosan, galactosan were detected above the dl : I am very surprised.. Mannosan and galac- tosan are “minor“ compounds (much less concentrated than levoglucosan – by a factor of about 10-), compounds such as fatty acids, sterols or linear acids should have been detected (especially if COA represents  $\square$ 20% of OA) . Where are the concentrations of levoglucosan, manosan and galactosan? Not reported in any tables (main text and SI) and in any figures. Please insert a table with the concentration of organic markers (for example in table 1). It could have be very interesting to look at the ratio Man/levo. Even if qualitative, this ratio can provide valuable information on the nature of the biofuel. (se for ex, Favez et al, ACP, 2010 or Schmidl et al, Atmos Env., 2008).

*Yes, ambient SOA contains thousands of different compounds covering a wide range of polarities and the aim of the current work was not to detect all possible species, but to identify and quantify markers for fungal spores, isoprene, monoterpene and domestic solid fuel burning, for which conversion factors are available enabling estimation of input from these sources (please see Kourtchev et al., 2011). The concentration of levoglucosan in winter samples reached up to  $1.3 \text{ ug/m}^3$ , which is a very high concentration. As the reviewer noted, despite the 10 fold difference in the mannosan, galactosan and levoglucosan concentrations, their contributions are very significant. Therefore, to avoid the overload of the GC column, only a very small portion of the filter was analysed using a very high injector split ratio. I suspect the concentration of the acids mentioned above by the reviewer was much lower than those of anhydrosugars at the current sampling site (please see a typical winter time GC/MS chromatogram for Cork ambient samples, Fig 1. Kourtchev et al., 2011). Therefore, the short and long chain fatty acids were not detected.*

*To clarify this issue, the text has been edited:*

*The employed GC/MS method was optimized for determination of polar organic compounds that are markers for fungal spores, isoprene,  $\alpha$ - $\beta$ -pinene oxidation products, biomass burning. During the winter period, only biomass burning compounds, i.e., levoglucosan, galactosan and mannosan were detected and quantified. The concentrations, time trends and contribution of these polar compounds to the OC are reported in Kourtchev et al., 2011.*

8-line 26 : OC/EC measurements : Did the authors use the EUSAAR or NIOSH or other protocol ? Please specify.

*The following text has been added:*

*The system uses a modified version of the National Institute for Occupational Safety and Health (NIOSH) 5040 thermal–optical protocol during analysis, to provide time-resolved OC/EC splits on a semi-real-time basis.*

9- page 29662, line 8: What is the resolution of the AToFMS.

*Edited*

10-Line 18 and 19 : prefer the notation  $m/iA, D^{\sim} m$  for the resolution

*Edited*

11- Is the AMS operating behind a dryer? What was the relative humidity at the inlet of the AMS?

*Edited - yes a dryer was deployed*

12- page 29663, line 13. validated by intercomparison . . . (see section 3.4.1). I can not consider that the 2 sentences in section 3.4.1 and figures SI.3 validate the constant ratio of 0.5 used here especially if no dryer have been installed upstream the AMS and considering the high RH observed during the study (figure S1). Please explain and clarify.

*Edited - we modified the text and addressed the CE issue in the revised manuscript.*

13-page 29664, section 2.5 : Please provide more details. Concentration? Dilution system? How the emissions where diluted? How many experiments? Temperature of the emissions? In the result section, the discussion and comparison with the PCOA factor must be developed more. The split of the PCOA factor and the mass spectra of peat and coal OA obtained within these dedicated experiments in two figures (6 and 7, respectively) makes the comparison very difficult for the reader.

*Edited*

14-Page 29665, line 19 : (figure 3) as figure 3 appears before figure 2 in the text modify the order of the figures.

*A reference to Figure 2 actually appeared before this point in the text.*

15-Line 19-21: Considering values reported in table 1, the differences between periods M and S are not statistically significant.

*Edited*

16-P 29666, line 1 : Please specify local or UT, here and in all the text and figs.

*Edited in section 2.1*

17-Line 3-5 : is there any relation with SO<sub>2</sub> events and PM concentration differences observed between port and city center (fig 2)?

*Edited - no could not find any association between SO<sub>2</sub> and PM differences*

18-Pages 29667-29668 : -Diurnal variations of the various particles types and especially the strong increases observed during the night are discussed in terms of partitioning of volatile species (mainly ammonium nitrate), PBL dynamic and sources. These are obviously the main reasons to explain such behaviors, but I will have preferred a more global discussion on this specific point. -Considering fig 2 a, min temp is about 1-4 C (nighttime) and max temp is about 6C (afternoon). Is this sufficient to increase significantly the partitioning of ammonium nitrate towards the particulate phase during nighttime?

*Edited - we expanded the section and include discussion of sources and PBL dynamics.*

-Figures presenting the size distributions of the different particles types (at least in SI) could greatly improve the visibility of this section.

*Edited - as suggested by reviewer 1, we report AMS size distributions for the detected species. Regarding the ATOFMS, unfortunately we were not able to deploy SMPS-APS systems to report scaled ATOFMS size distributions, and for that reason we only briefly describe them in this section*

- Ca-EC and EC-POS present different mass spectra but are attributed to the same source (ie. lubricating oil from vehicular emissions). Clarify/comment.

*Edited, and cited Spencer et al (2006) where these single particle mass spectra and the sources are presented and discussed.*

-As the figures 2a,b,c,.. have no y axis, it is impossible to compare the different factors in terms of abundance of a particular ion. Are these mass spectra represented as a fraction of total current ion intensity or absolute intensity?

*Edited all figures and made clearer*

-Be homogenous in the notation of the ions. For example, [C<sub>x</sub>H<sub>y</sub>-], line 11 and C<sub>3</sub>H<sub>+</sub> line 7. Choose a notation/nomenclature all along the text. Other example line 21 page 29668 [VO], [V] with no charge.. if you choose [xxx] (this is not a recommendation), the charge must be outside the square brackets.

*Edited – the notation [X]<sup>+</sup> or [X] has been used throughout.*

-P29667, line 9-11. the negative mass spectra are characteristic of primary hydrocarbons species, rather than secondary species as seen associated with the previous two particles types. It is difficult to compare as the previous secondary species were nitrate and sulfate and not organics.

*Edited*

19-p. 29669-2970. ATOFMS discussion. Why particles types are not compared with ancillary data such as levoglucosan or EC?

*Edited - we added a correlation between ATOFMS and external measurements such as levoglucosan and EC in this section.*

20-P. 29670, line 22-27. R2 indicates only if the choice of a constant CE is a relevant solution, but do not give any information on the choice of this constant value. The authors have to discuss the slope presented in fig S2. For ammonium and nitrate the slopes are greater than one while for OC, sulfates the slopes are lower than one. Can the authors discuss this point? In the lights of this discussion the conclusion regarding chloride could be less definitive.

*Edited - and discussed along with the recent extensive manuscript of Middlebrook et al. (2011).*

21-P29672 : The authors discuss the size distribution of AToFMS particle types. Why such information are not provided for AMS-PMF factors?

*Edited - it is not possible to obtain such information with the current version of the PMF analysis carried out.*

22-P29672. HOA. The authors do not discuss the correlations with EC (tab S5). These correlations are pretty unusual as EC is significantly more correlated to PCOA and BBOA than to HOA.

*Edited - the PCOA and BBOA contributed to the EC component. We edit this in the text, and also describe good correlation for Ca-EC (AToFMS marker for traffic) and gaseous measurements of NOx.*

23-Line 24. LVOOA in the text, but OOA in figures 2, 6, 8

*Edited*

24-P. 29673 line 3 : CO<sub>2</sub>+ instead of CO<sub>2</sub>. The same comment can be made in too many lines of this section and the following sections. Please correct all.

*Edited*

25-P29675 line 1 : K, R<sub>2</sub>=0.76 ; 0.5 in table S5

*Edited*

26-Line 3 : R<sub>2</sub>=0.76, table S5 ; 0.75 in table S5. Please check and correct all these values.

*Edited*

27-p 29679 line 10-15 : Did you observed any correlations with PAH (from AMS measurments)?

*The AToFMS did not detect any specific particle types associated with PAH so this type of comparison or correlation could not be done.*

28-P29682: line 28. The fact that no correlation exists between COA and any AToFMS particle types is very interesting, and meaningful. . . Why only one sentence on this subject?

*Edited - we expanded this section, and linked to a previous paper which deals with this topic in more detail (Dall'Osto and Harrison 2012).*

Table 1 : Standard deviations are reported for a, b and c but not for d, e and f.



*Edited - added*

Table 2 : total number of particles 1 335 994. In the text and abstract 1 200 000?

*Edited*

Table 3 : add charges. HxOy+ instead of HO.

*Edited all and other chemical formula*

Fig 1. Not very helpful for the reader. Is it possible to insert a map with a higher resolution and more details?

*Edited*

Fig. 2. Hours : local or UT?

*Edited*

Fig 3. Not very useful. In SI?

*Edited - moved*

Fig 4. Very difficult to read. Add units to the y axis.

*Edited - when considered it in one large figure.*

Fig 8. Not discussed in the text. . .

*Edited*

SI.1. An example of each air masse types could be useful for the reader

*Edited - added*

Table SI1. What is the meaning of “v”?

*Edited - days considered for marine and stagnant period. Addressed.*

Table S5: Why the 4 factors solution is presented ? (and not discussed in the text)

*Edited - the 4-factor solution is not discussed because it does not explain the dataset well. Hence the 5-factor solution was selected. We address this in the text.*