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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterization of urban aerosol in Cork City (Ireland) using aerosol mass spectrometry" *by* M. Dall'Osto et al.

Anonymous Referee #2

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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 semi-continuous 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 composi-

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Discussion Paper

tion, 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.

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

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. 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.

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).

Specific but not minor comments :

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

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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 refratory PM mass (except if you calculate the primary fraction of nitrate, sulfate, ammonium, originating from these sources ; the secondary fraction is another story).

3- page 29658, line 14-18 : The 50 μg/m3 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 25μg/m3 for PM2.5 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 PM2.5 concentration observed during winter, but clarify in the text.

4-page 29659, line 19 : Since you are measuring aerosol from different class of size "(ie PM2.5)" is not necessary and confusing. 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.

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

7- page 29661 section 2.2 : Even is 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 TissuquatrzTM 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? As levoglucosan have been measured a derivative must have been added : which one? 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-

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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 ∼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).

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

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

10-Line 18 and 19 : prefer the notation m/ïĄĎm for the resolution

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

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.

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.

14-Page 29665, line 19 : (figure 3) as figure 3 appears before figure 2 in the text,

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modify the order of the figures.

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

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

17-Line 3-5 : is there any relation with SO2 events and PM concentration differences observed between port and city center (fig 2)?

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 6°C (afternoon). Is this ïĄĎT sufficient to increase significantly the partitioning of ammonium nitrate towards the particulate phase during nighttime?

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

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

-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?

-Be homogenous in the notation of the ions. For example, [CxHy-], line 11 and C3H+ 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.

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-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.

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

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.

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

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.

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

24-P. 29673 line 3 : CO2+ instead of CO2. The same comment can be made in too many lines of this section and the following sections. Please correct all.

25-P29675 line 1 : K, R2=076 ; 0.5 in table S5

26-Line 3 : R2=0.76, table S5 ; 0.75 in table S5. Please check and correct all these values.

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

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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?

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

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

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

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

Fig. 2. Hours : local or UT?

Fig 3. Not very useful. In SI?

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

Fig 8. Not discussed in the text...

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

Table SI1. What is the meaning of "v"?

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

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 29657, 2012.