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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 #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. 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.

Comments:

1) A section of the discussion is dedicated to local ship emissions. In section 3.2 the authors mention that SO_2 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_2 emissions is not included in section 4.2 or elsewhere. In addition SO_2 measurements are not included in any of the tables or figures.

1 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.

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_3H_3O vs C_4H_7) and m/z 57(C_3H_5O vs C_4H_9), but did not include it in the discussion.

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.

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.

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.

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.

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.

Minor Corrections:

Page 29658, Line 20: ..coal..

Page 29659, Line 16 to 23: On line 16, it is stated that the PM_10 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 µg m^{-3} was "exceeded only six times" in Cork city. Then on page 29665, Line 16, it is mentioned that PM_10 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?

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

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

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

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.

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

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

Page 29663, Line 25: You could refer to table 1 here. Why are SO_2 measurements excluded from table 1 (and from further discussion).

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

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).

Page 29665, Line 1: were chosen.

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

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

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

Page 29665, Line 19: What does PM_X represent?

Page 29665, Line 21: PM_10 or $PM_2.5$ or both?

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

Page 29665, Line 25: "Gaseous concentrations for NO and NO_2 were..." Are these values representative of the entire campaign? What were the values for the EC/OC.

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 $PM_2.5$.

Page 29666, Line 3: There are no discussions of SO_2 concentrations in section 4.2 or elsewhere.

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

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

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

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

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."

Page 29669, Line 16: Attribute

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

Page 29669, Line 7: remove "seems"

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.

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

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....

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

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

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

Page 29671, Line 25: Change to NH_4Cl

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).

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

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..."

Page 29674, Line 3: Correlate

Page 29674, Line 27: Clusters

Page 29675, Line 18: lesser

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

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

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

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

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_2 measurements are available they could also be discussed in relation to the ship emissions.

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

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

Page 29680, Line 26: According to table S3, m/z values for C_4H_7 and C_4H_9 are equally associated with HOA, COA, PCOA, and BBOA.

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

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_2, and O_3 as evidence for chemical aging.

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

Page 29683, line 19: Correctly

Page 29683, Line 20: first

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

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?

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

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

Figure S8: which is captured by the PMF. Change C3H50 to (C_3H_5O)

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