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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Source apportionment of $PM_{2.5}$ in Cork Harbour, Ireland using a combination of single particle mass spectrometry and quantitative semi-continuous measurements" *by* R. M. Healy et al.

Anonymous Referee #1

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General comments:

Local and regional aerosol sources impacting Cork Harbour, Ireland over 3 weeks in August 2008 were identified using positive matrix factorization applied to several aerosol measurements, including aerosol time-of-flight mass spectrometry (ATOFMS). The majority of the manuscript discusses in detail the mass spectral signatures of the observed particles. As written, the manuscript does not contribute significantly to the overall understanding of aerosol sources, and although the manuscript focuses significantly on the analysis approach, it is not novel. A more thorough literature search

should be conducted and integrated, considering other studies of long-range aerosol transport to Ireland, as well as previous single-particle mass spectrometry studies. The conclusions are not well supported or discussed in terms of the overall applicability of the results or method to future work. This manuscript is not currently recommended for publication in ACP; rather, following significant revisions, it is recommended that the manuscript be resubmitted to a different journal, such as Atmospheric Environment, in line with previous publication of similar studies.

Specific comments:

Abstract: The first half of the abstract reads similarly to a methods section with the second half of the section stating some results. However, it is unclear what has been added to the scientific understanding of aerosol source apportionment. Further, it is not appropriate to include such information as the number of ATOFMS mass spectra generated here. The abstract should be reorganized to primarily be a discussion of the main results of the work.

Introduction, Paragraph 2: This summary of the use of single-particle mass spectrometry for source characterization is highly incomplete; several studies using single-particle mass spectrometry have focused on source characterization of ambient aerosol [eg. Bein et al., 2007, Pekney et al., 2006, Reinard et al., 2007]. In addition, there is no reference here to previous studies of ship emissions, which seems particularly pertinent for this work [Ault et al., 2010, Ault et al., 2009, Healy et al., 2009]. A more thorough literature search should be completed and integrated into the introduction.

Introduction, Last Paragraph: While it is useful that ATOFMS mass spectral signatures were obtained for coal, peat, and wood combustion, ATOFMS source signatures have been measured previously for coal and wood combustion [Gard et al., 1997, Liu et al., 2003, Silva et al., 1999].

Section 3.2.1: Previous measurements of the ATOFMS source signature of coal combustion [Liu et al., 2003] should be compared to these results.

Figures 4 & 5: Due to the large temporal variability of the “coal-amm-nit” and “peat-nit” particle classes (Figure 5), it seems deceiving to report average diurnal trends in Figure 4. Please address this. Also, why are the other particle types shown in Figure 4 not shown in Figure 5?

Page 1048, lines 7-10: Why is adsorption, condensation, or hydrolysis expected to the dominant processes? Please support this further. Previous studies have shown conversion from KCl to K2SO4 and KNO3 during biomass burning plume aging, for example [Gaudichet et al., 1995, Li et al., 2003, Yokelson et al., 2009].

Page 1049, lines 3-4: It seems important to note that Figure 4 shows the “non-nitrated”, fresh subclasses to peak at night, as well. This point should be considered in the discussion of the nitrate formation, particularly since aged sea salt had a similar temporal pattern compared to fresh sea salt (page 1050, lines 13-15).

Section 3.2.3: Comparison with Ault et al. [2010, 2009] should also be made for the source signature of the ship emissions.

Sections 3.2.4 and 3.2.5: It is suggested to discuss more clearly the chemical and size differences between the EC particle types. These sections should be reorganized to make these differences clearer and to incorporate discussion of additional comparisons with previous ATOFMS source studies of vehicle emissions [Shields et al., 2007, Silva and Prather, 1997, Sodeman et al., 2005, Suess and Prather, 2002, Toner et al., 2008, Toner et al., 2006]. Comparison with Vogt et al. [2003] may also be appropriate.

Page 1052, last paragraph: While it is noted in Figure 8 that m/z -95 may be attributed to methanesulfonate, this is not discussed throughly and should be, particularly given the marine origin of the air mass. Without the presence of m/z -79 or m/z -63 (confirming the presence of phosphate), it is speculative to call these particles “EC-phos-aged”.

Page 1053, lines 25-28: What is the likelihood of vehicle exhaust particles surviving transport to the surface in Ireland from North America following 5 days of transport?

Based on the temporal trend in Figure 9, it would seem as though there was a local background of these particles as well.

Page 1056, lines 20-21: What is the significance of an error of “100”? What does this mean and how specifically was it chosen?

Page 1057, lines 1-10: How does this solution compare with previous PMF studies? In particular, comparison with other single-particle mass spectrometry studies utilizing PMF, including Owega et al. [2004] and Pekney et al. [2006], should be incorporated in this manuscript with more detailed discussion of the source results.

Page 1058, lines 1-2: What chemical species is proposed that would not be detected? Biological material has been previously detected by single-particle mass spectrometry using 266 nm radiation for laser desorption/ionization [Gaston et al., 2010, Pratt et al., 2009, Russell, 2009].

Page 1058, lines 2-7: This comparison of previous results by Hellebust et al. should be expanded in this manuscript given the similarity of the studies.

Page 1060, lines 22-24: The reasoning for biogenic SOA and crustal dust as missing ATOFMS particle types is not well supported and should be discussed further. The authors are directed to previous cases of missing particles (likely pure ammonium sulfate), where light absorption and scattering were utilized to identify these particles that were not chemically analyzed [Spencer et al., 2008, Wenzel et al., 2003]. This conclusion should be examined further and reconsidered.

Technical corrections:

Page 1036, lines 2-5: This sentence is misleading as it implies that the ATOFMS was used for quantitative measurements. Please rephrase to make the product(s) of the ATOFMS measurements clearer.

Page 1036, lines 10-11: Canada is considered to be part of North America. Please fix this phrasing. Also, note this mistake on page 1044 (line 4), page 1053 (lines 13-14),

page 1053 (lines 13-14 and 26), page 1058 (line 17), and page 1060 (line 20).

Page 1036, lines 16 & 17: Please clarify what is meant by “shipping traffic” and “shipping”.

Page 1037, lines 12-15: The Reinard et al. paper used the RSMS-3, not ATOFMS.

Page 1037, lines 15-16: Why are vehicle emissions and biomass burning considered here to be “diffuse sources”? Several single-particle mass spectrometry studies have focused on vehicle emissions

Page 1038, lines 3-4: The PIAMS is not a single-particle mass spectrometer in the study by Dreyfus et al. as stated here.

Page 1039, line 15: Fix typo “collinear”.

Page 1044, lines 2-5: What method was utilized to obtain the air mass origins?

Page 1046, line 29: If this paragraph is now discussing ambient data, please make this clearer.

Page 1048, lines 16-17: Please describe this temporal feature with more detail to make the discussion clearer.

Page 1055, lines 6-9 and Figure 11B: In Ault et al. [2009] and other ATOFMS papers [eg. Moffet and Prather, 2009], this mass spectral signature is labeled “ECOC” as OC does not appear as the primary signature.

Page 1055, lines 12-13: What source was previously assigned by Dall’Osto and Harrison in that study?

Page 1057, lines 17-20: Can this result also be attributed to the assignment of an incorrect source or multiple sources producing similar chemical fingerprints? What is meant by “incorrect classification. . .during clustering”?

Page 1058, line 14: What is the reference for the previous Cork Harbour study?

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