

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.

R. M. Healy et al.

robert.healy@ucc.ie

Received and published: 21 April 2010

The authors would like to thank the reviewers for their analysis and useful comments. Each general and specific comment has been addressed in detail below, and appropriate additions and changes to the manuscript have been made where necessary.

Reviewer 1 General Comment:

Local and regional aerosol sources impacting Cork Harbour, Ireland over 3 weeks in August 2008 were identified using positive matrix factorization applied to several

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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.

Response:

The authors believe that this work does make a significant contribution to our understanding of aerosol sources, particularly in a harbour location. The research is novel in its demonstration of the benefits of combining positive matrix factorisation (PMF) and single particle mass spectrometry data as a tool for source apportionment of PM_{2.5} mass concentration and particle number concentration, and more importantly in outlining how each technique improves the accuracy and validity of the other. As suggested by the reviewer the manuscript (the Introduction and Results and Discussion sections in particular), has been reorganised and expanded as outlined below to emphasise the importance and novelty of these findings and also to demonstrate the specific contribution of the work to the research area. The authors believe that, in agreement with Reviewer 2, this manuscript is of interest to readers of Atmospheric Chemistry and Physics (ACP) and that, in particular, the following points are of value to the scientific community:

1: Although PMF of ATOFMS mass spectral data has been used to apportion PM_{2.5} mass previously (Eatough et al., 2008), no standard spectra were used to confidently confirm specific sources, as is the case in this manuscript not only for domestic combustion sources but also for shipping exhaust. Shipping and oil refining emissions could not be separated in the case of Eatough et al. (2008), however in our case the

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confirmation of shipping plumes using corresponding berthing logs have enabled the inclusion of a shipping factor that is not influenced by any other combustion processes, or indeed any regional shipping activity. The identification of locally emitted ship exhaust particles in Cork Harbour is covered in more detail in a previous article (Healy et al., 2009), however much additional information has been added to the Results and Discussion section as outlined below in the response to specific comments. The exclusive contribution of the ATOFMS shipping particle class to the Shipping factor (100%, Table 2) demonstrates the value of collecting “standard” spectra for source apportionment where possible, as confident assignment of spectra to specific sources leads to a more accurate result. Furthermore, while PM_{2.5} mass was apportioned in the case of Eatough et al. (2008), particle number concentration was not. This has allowed the relative impact of vehicular and shipping traffic on submicron particle number concentration in an urban port environment to be estimated in our work. This quantitative estimation arises from the combination of the ATOFMS single particle identification and PMF techniques and cannot be determined using one or the other alone. The estimated shipping traffic contribution of 18% to ambient particle number (20-600 nm, mobility diameter), only a factor of 2 lower than the contribution from vehicular traffic, has important implications for air quality in port environments. Now that this source has been isolated, characterised and apportioned effectively in a relatively small urban port environment, the methodology described can be used in larger, more complex port environments worldwide. It is important to note here that while vehicular emissions are highly regulated, emissions arising from the combustion of residual fuel oil by ocean-going vessels are not (Fridell et al., 2008). The effect of regionally transported shipping emissions on air quality and health in coastal areas has come to the fore recently, with an estimated 60 000 deaths per annum attributed to this source, a number expected to rise over the next decade with an increase in global shipping activity (Corbett et al., 2007). Ship exhaust particles contain species with known toxicological effects such as polycyclic aromatic hydrocarbons, vanadium and nickel (Lippmann et al., 2006; Peltier et al., 2008; Murphy et al., 2009; Healy et al., 2009). A recent mod-

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elling study estimates that ship emissions could soon become one of the major sources of air pollution in Southern California, with some regions subject to a threefold increase in contribution to ambient PM_{2.5} mass concentrations from this source between 2002 and 2020 (Vutukuru and Dabdub, 2008). However, in-port ship emissions also need to be considered, in particular for cities with substantial shipping activity (Symeonidis et al., 2004; Ault et al., 2009; Tzannatos, 2009; Viana et al., 2009; Pey et al., 2009; Pey et al., 2010). Freshly emitted ship exhaust particle numbers reside predominantly in the ultrafine mode (Fridell et al., 2008; Healy et al., 2009; Ault et al., 2010), and epidemiological research suggests that fine or ultrafine particle number concentrations may represent a more accurate metric than PM_{2.5} mass concentrations when estimating the health impacts of anthropogenic particulate sources (Ibald-Mulli et al., 2002; Kreyling et al., 2006; Hoek et al., 2010). Thus particle number concentrations may be just as important to quantify and apportion as PM_{2.5} mass concentrations in future studies. Several articles focused on estimating the regional and global impact of emissions from shipping have been published recently in ACP (Eyring et al., 2007; Petzold et al., 2008; Jalkanen et al., 2009; Marmer et al., 2009), highlighting the need for corresponding source apportionment of particulate matter in locations impacted by this source. The authors believe that our findings regarding the relative contribution of ship exhaust particles of unregulated composition to air quality in a port environment, and the methodology required to calculate this contribution are expected to be of interest to other researchers, in particular considering the growth of shipping activity worldwide, and the expected resultant effect on human health (Winebrake et al., 2009; Dalsøren et al., 2010). The authors concede that this point may not have been made strongly enough in the original ACPD manuscript. The Introduction and Results and Discussion sections have been expanded to incorporate additional detail and discussion as outlined below.

2: The collection of reliable “standard” single particle mass spectra for domestic coal burning, peat burning and wood burning processes in order to satisfactorily identify these combustion particles in ambient air is important. Although ambient single par-

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ticles have been attributed to coal-fired power generation and domestic coal burning sources in the US and Poland respectively (Liu et al., 2003; Pekney et al., 2006a; Bein et al., 2006; Bein et al., 2007; Mira-Salama et al., 2008), the generation of locally sourced coal, peat and wood combustion particles using a domestic system allows for the comprehensive identification of similar domestic combustion particles in the ambient dataset using not only the presence or absence of individual ions in the mass spectra, but also the relative intensity of the ions present. This is particularly necessary when separating the coal and peat combustion particle classes, for example (Figures 1 and 2). Interestingly, the domestic coal burning mass spectra obtained in this work are quite different to those apportioned to coal burning in previous single particle studies, as outlined in the detailed response to specific comments below, and the authors believe that the domestic combustion mass spectra included (Figures 1-3) will be useful for other researchers in the analysis of single particle mass spectrometry data collected in future field studies. Although wood or biomass burning single particle mass spectra have been identified in several previous studies (Silva et al., 1999; Moffet et al., 2008; Guazzotti et al., 2003), this is the first reported identification of single particles formed through the combustion of peat. Peat is widely used as a domestic fuel not only in Ireland, but also in parts of Northern Europe (Orru et al., 2009). The peat burning single particle mass spectra collected during the combustion experiment match extremely well with those identified in the ambient dataset (Figure 2). The authors believe that the collection of standard combustion spectra and the subsequent confident assignment of ambient single particles to definitive sources are much more useful than listing single particle mass spectra as “sodium-containing” or “potassium-containing”, for example, along with possible sources. A recent article published in ACP involves the description of the different single particle classes observed at an urban site in Mexico City using ATOFMS and includes possible sources (Moffet et al., 2008). Dependence on meteorology was included but the article does not include any estimation of the contribution of each suggested source to ambient PM_{2.5} or particle number concentration. PMF of temporal trends of various single particle classes generated using laser ablation mass

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spectrometry (LAMS) has been performed previously to identify sources of particulate matter in Toronto, Canada, however no corresponding PM_{2.5} mass concentration, particle number concentration, or semi-continuous quantitative data was included or apportioned in that case (Owega et al., 2004). Single particle mass spectra have also been previously used to help validate the source apportionment of PM_{2.5} using off-line ICP-MS data in Pittsburgh, Pennsylvania, however the single particle mass spectral data was not included in the PMF analysis (Pekney et al., 2006a). Two articles involving PMF of aerosol mass spectrometry (AMS) particle ensemble data in order to apportion organic aerosol have been published in ACP recently, but without knowledge of single particle mixing states (Ulbrich et al., 2009; Aiken et al., 2009). The authors therefore believe that the demonstration of the synergy of single particle mass spectral classification and PMF to confidently apportion PM_{2.5} mass concentration and particle number concentration, using “standard” spectra for confirmation where possible, is a novel component of this work. Further detail is provided in the answers to specific comments below.

3: The possibility of intercontinental transport of North American anthropogenic particles to Cork Harbour is also interesting, considering that deposition processes are expected to minimise transport over such long distances. Cork Harbour represents a unique in-port site due to its position at the extreme west of Europe. The prevailing winds are south-westerly and the site is mainly influenced by clean marine air masses (Yin et al., 2005; Ceburnis et al., 2006; Healy et al., 2009). Thus, particles arising from anthropogenic activity are predominantly primary and emitted locally, as demonstrated in the manuscript. The anthropogenic ATOFMS particle classes identified herein exhibit a very strong dependence upon time of day (Figs. 4 & 7), supporting their assignment to local sources. However, the temporality of one carbonaceous single particle class, the EC-phos-aged class (now renamed as EC-MSA), is dramatically different, exhibiting a dependence upon air mass origin rather than time of day (Figure 10). These findings lead the authors to conclude that these particles have a sustained source to the west of the coast of Ireland that cannot be attributed to shipping because ship ex-

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haust particles can be identified and separated from other sources as described in the manuscript. Thus, the EC-MSA particles are either emitted from the Atlantic Ocean or further afield. The presence of internally mixed methanesulfonic acid (MSA), a species arising from phytoplankton emissions of dimethyl sulfide that has been recently detected in a range of anthropogenic single particle classes in California, strongly supports the theory of transport over an ocean surface (Gaston et al., 2010). While the source assignment here is indeed speculative, and the accuracy of the HYSPLIT back trajectories decreases with increasing temporal projection, the presence of elemental carbon fragments in particular suggests a combustion origin (Figure 8). Transport of North American black carbon and forest fire particles to Ireland and Western Europe respectively, and transport of Saharan dust particles to North America have been previously reported (Jennings et al., 1996; Forster et al., 2001; Singh et al., 2006; Owega et al., 2004). Thus North American anthropogenic activity may represent a source of submicron particles arriving in Cork Harbour, albeit extremely minor compared to the various other sources identified. A detailed discussion of this source assignment, including appropriate references to previous articles in this field, is given in the reply to specific comments below.

Reviewer 1 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.

Response:

This is a valid point. The following sentences have now been removed from the abstract: "Over 550,000 ATOFMS particle mass spectra were generated and classified

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using the K-means algorithm. The vast majority of particles ionised by the ATOFMS were attributed to local sources, although one class of carbonaceous particles detected is attributed to North American or Canadian anthropogenic sources." The following text has been added to the abstract: "The synergy of the single particle classification procedure and positive matrix factorisation allowed for the identification of six factors, corresponding to vehicular traffic, marine, long-range transport, power generation, domestic solid fuel combustion and shipping traffic." "The positive matrix factorisation procedure enabled a more refined interpretation of the single particle results, in particular for the separation of domestic and power generation coal combustion, while the single particle data enabled the identification of additional factors not possible with typical semi-continuous measurements, including local shipping traffic. One class of single particles exhibiting mass spectral signatures for elemental carbon, sulfate, methanesulfonate and oxalate is associated with possible intercontinental transport of anthropogenic particles from North America, although this represents an extremely minor source compared to local primary sources."

Comment:

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].

Response:

This section was originally kept to a minimal length considering the overall size of the manuscript but has now been expanded to include two of the references mentioned by the reviewer. A reference to the article of Reinard et al. (2007) was already included in the original manuscript. The following lines in the Introduction, Paragraph 2 have been amended as follows: "Aerosol time-of-flight mass spectrometry (ATOFMS) and other single particle mass spectrometry techniques have been employed in several

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field studies to identify point sources of PM_{2.5} including steel manufacturing, smelting, refining and power generation facilities (Reinard et al., 2007; Snyder et al., 2009; Liu et al., 2003; Bein et al., 2007; Pekney et al., 2006a; Bein et al., 2006).” Further lines have also been added to the Introduction, Paragraph 3 as follows: “A detailed campaign performed in Pittsburgh, Pennsylvania, focused on the identification of sources of particulate matter using a single particle mass spectrometer and off-line analysis of high-volume and micro-orifice uniform-deposit impactor (MOUDI) samples of PM using inductively coupled plasma-mass spectrometry (ICP-MS) (Pekney et al., 2006a; Bein et al., 2006; Bein et al., 2007; Pekney et al., 2006b). In that case PMF analysis was performed using the ICP-MS trace metal data, quantitative measurements of nitrate, sulfate and EC/OC but without including the single particle data, in order to apportion PM_{2.5}. Factors were generated corresponding to traffic, crustal material, regional transport, secondary nitrate, cooking and wood burning, steel production, and a gallium-rich factor was associated with coal burning. Several coal-fired power stations surrounding the site were identified as point sources of PM_{2.5}, with gallium identified as a possible tracer for coal combustion, although this source was estimated to contribute only 3% to the PM_{2.5} mass measured. PMF of temporal trends of various single particle classes generated using laser ablation mass spectrometry (LAMS) has been performed previously to identify sources of particulate matter in Toronto, Canada (Owega et al., 2004). Factors were obtained corresponding to sources of locally emitted and Saharan dust, road salt, wood burning, organic nitrates and aluminium-fluoride particles. However, no corresponding PM_{2.5} mass concentration or semi-continuous quantitative data was included or apportioned in that case.”

Comment:

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.

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Response:

The latter two ship emission articles were already referenced in the Results and Discussion section of the original manuscript. Furthermore the authors did not wish to repeat the findings of the recently published ship exhaust article (Healy et al., 2009). The first reference (Ault et al., 2010) was not published at the time of submission. However, additional lines have now been added to the Introduction, Paragraph 2 as follows: “More recently, single ship exhaust particles arising from the combustion of residual fuel oil have also been successfully identified and characterised using ATOFMS. Freshly emitted and regionally transported particles associated with this source containing internally mixed vanadium, nickel, iron and sulfate have been detected in Cork Harbour and in the Port of Los Angeles (Healy et al., 2009; Ault et al., 2009; Ault et al., 2010).” Also, the Results and Discussion section entitled “Source Apportionment: Shipping” has been greatly expanded in length and detail to incorporate a more in-depth discussion and literature review of the impact of in-port ship emissions on health, and the importance of assessing the contribution of this source as accurately as possible: “The shipping factor identified in this work was not identified in a previous study involving PMF of real-time monitoring data in Cork Harbour, due to the absence of complementary ATOFMS data in that case (Hellebust et al., 2010b). A contribution of 100% is observed for the ATOFMS Shipping class for this factor. This is expected, as these unique residual fuel oil combustion particles are emitted exclusively from container and liquid bulk vessels arriving and departing from the nearby shipping berths, with no input from other sources (Healy et al., 2009). Factors for residual oil combustion were not observed in either the Pittsburgh or Toronto PMF studies where single particle instruments were employed (Pekney et al., 2006b; Owega et al., 2004). However a factor for residual fuel oil was observed in Riverside, California using PMF of ATOFMS, AMS and other semi-continuous data and attributed to possible shipping or refining in the Los Angeles Harbour (Eatough et al., 2008), although the contribution to PM_{2.5} mass in that case was estimated to be negligible compared to other local and regional sources. Residual fuel oil combustion factors are often observed in PMF studies that in-

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clude trace metal analysis and identified using Ni and V (Godoy et al., 2009; Castanho and Artaxo, 2001; Kim and Hopke, 2008). However, the relative contribution of oil combustion particles from refining, industry, domestic heating and shipping can be difficult to separate (Isakson et al., 2001; Kim and Hopke, 2008; Eatough et al., 2008; Viana et al., 2009). Although shipping traffic is estimated to contribute only 1.5% to the ambient PM_{2.5} mass measured in this work, it contributes 18% to the total number of particles detected by the SMPS. This value is second only to traffic with a contribution of 42%. Thus it appears that local shipping traffic can contribute significantly to local ambient particle number in the size range 20–600 nm (mobility diameter) in Cork Harbour. What is important to note here is that while vehicular emissions are highly regulated, emissions arising from the combustion of residual fuel oil by ocean-going vessels are not (Fridell et al., 2008). The effect of regionally transported shipping emissions on air quality and health in coastal areas has come to the fore recently, with an estimated 60 000 deaths per annum attributed to this source, a number expected to rise over the next decade with an increase in global shipping activity (Corbett et al., 2007). A recent modelling study estimated that ship emissions could soon become one of the major sources of air pollution in Southern California, with some regions subject to a threefold increase in contribution to ambient PM_{2.5} mass concentrations from this source between 2002 and 2020 (Vutukuru and Dabdub, 2008). However, in-port ship emissions also need to be considered, in particular for cities with substantial shipping activity (Symeonidis et al., 2004; Ault et al., 2009; Tzannatos, 2009; Viana et al., 2009; Pey et al., 2009; Pey et al., 2010). A recent study involving PMF of trace metal and EC/OC data estimates the contribution of shipping to PM_{2.5} mass concentrations in Melilla Spain at 14% using V/Ni ratios (Viana et al., 2009). PMF of similar data collected at five sites in Seattle, estimates a contribution to PM_{2.5} mass of 4–6% from residual oil combustion, with the Port of Seattle identified as the most likely source (Kim and Hopke, 2008). Although the relative contribution of shipping to ambient PM_{2.5} is lower in our case, freshly emitted ship exhaust particle numbers reside predominantly in the ultrafine mode (Fridell et al., 2008; Healy et al., 2009; Ault et al., 2010), and epidemiological research suggests that

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fine or ultrafine particle number concentrations may represent a more accurate metric than PM_{2.5} mass concentrations when estimating the health impacts of anthropogenic particulate sources (Ibald-Mulli et al., 2002; Kreyling et al., 2006; Hoek et al., 2010). Several recent articles have focused on estimating the regional and global impact of emissions from shipping (Eyring et al., 2007; Petzold et al., 2008; Jalkanen et al., 2009; Marmar et al., 2009; Viana et al., 2009; Pey et al., 2010), highlighting the need for corresponding source apportionment of particulate matter in locations impacted by this source. Thus, knowledge of the relative contribution of ship exhaust particles of unregulated composition to air quality in a port environment is of particular importance considering the growth of shipping activity worldwide and the expected resultant effect on human health (Winebrake et al., 2009; Dalsøren et al., 2010)."

Comment:

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.

Response:

Although single particles attributed to coal-fired power generation facilities have been detected by single particle mass spectrometry in previous studies (Liu et al., 2003; Pekney et al., 2006a; Bein et al., 2007), and attributed to possible domestic combustion in two studies (Guazzotti et al., 2003; Mira-Salama et al., 2008), the single particle mass spectra observed in this work are quite different. In the study of Liu et al., particles generated in local coal-fired power facilities in Atlanta, GA were similar to those observed here except for additional signals for lithium and iron, and a substantially lower signal for sulfate. In the comprehensive study of Bein et al. (2007), gallium-

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containing particles internally mixed with sodium, potassium, silicon, iron and lead detected in Pittsburgh, Pennsylvania were attributed to local coal-fired power generation facilities. Single particles detected by ATOFMS during the Indian Ocean Experiment (INDOEX) that contained lithium and potassium were attributed to possible domestic and small-scale industrial coal combustion (Guazzotti et al., 2003). However, no discernible signal for gallium or lithium is detected in the coal combustion particle mass spectra in this work, indicating that while these may represent appropriate tracers for coal-fired power generation in Pittsburgh and Atlanta respectively (Bein et al., 2007; Liu et al., 2003), they are not necessarily useful tracers for domestic combustion of coal of a different origin. The single particles attributed to domestic coal burning by Mira-Salama et al. (2008) in Poland are also very different to those sampled in our case as no signal was observed for sulfate in that study. Varying origin of coal, and possibly conditions of combustion, may result in very different single particle mass spectra, and thus the collection of “standard” single particle mass spectra generated from the combustion of locally sourced fuels in a domestic stove proved invaluable to the correct assignment of these particles in the ambient dataset in our case. The relative intensities of sodium, potassium, carbon/hydrocarbon and sulfate ions were particularly useful, and the similarity of the “standard” particles and ambient particles is very strong as shown in Figure 1. The recurrent daily temporal variability and high correlation with off-line measurements of organic tracers in this work provide further evidence to confirm the source. Thus, “standard” particles should be generated or measured where possible in single particle studies. Several additions including appropriate references have been made to section “ATOFMS particle classes: Coal, Peat and Wood”, paragraph 1 as follows: “Particles attributed to coal-fired power generation facilities have been detected by single particle mass spectrometry in previous studies (Liu et al., 2003; Pekney et al., 2006a; Bein et al., 2007), however the single particle mass spectra observed in this work are quite different. In the study of Liu et al., particles generated in local coal-fired power generation facilities in Atlanta, GA were similar to those observed in this manuscript except for additional signals for lithium and iron,

C1904

and a substantially lower signal for sulfate. In the comprehensive study of Bein et al. (2007), gallium-containing particles internally mixed with sodium, potassium, silicon, iron and lead detected in Pittsburgh, Pennsylvania were attributed to coal-fired power generation facilities. Particles measured by ATOFMS in an aerosol outflow from Asia that were assigned to coal burning exhibited different spectra to those observed in this work, sharing many of the same positive ions but with an additional signal for lithium (Guazzotti et al., 2003). However no discernible signal for lithium or gallium is detected in the coal combustion particles detected in this work (Fig. 1), indicating that while these metals may represent useful tracers for locally mined coal (Bein et al., 2007), they are not necessarily useful tracers for domestic combustion of coal of a different origin. Single particle mass spectra generated with a single particle analysis and sizing system (SPASS) containing a signal for carbon but not for sulfate, were attributed to a fresh domestic coal combustion source in a recent study performed in Krakow, Poland (Mira-Salama et al., 2008). In that case, however, no combustion spectra were generated to confirm the source. In this work, a strong signal for sulfate was consistently observed even in freshly emitted coal combustion particles, demonstrating the value of collecting “standard” mass spectra where possible (Fig. 1).” A reference to the article of (Gard et al., 1997) which also describes wood burning mass spectra has been added to the reference of Silva et al. in the section “ATOFMS particle classes: Coal, Peat and Wood”, paragraph 3, as follows: “Similar ATOFMS mass spectra have been observed for particles arising from the combustion of various plant species indigenous to California (Gard et al., 1997; Silva et al., 1999)”

Comment:

Figures 4 & 5: Due to the large temporal variability of the “coal-amm-nit” and “peatnit” 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?

Response:

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In this case the authors did not intend to suggest that the nitrated subclasses appear in significant numbers on each day of the campaign, but it is difficult to illustrate the strong dependence these species have on time of day when they do appear if using Fig. 5 alone. While these particles are observed at the highest levels during four separate low wind speed events (Fig. 5), when present they exhibit a strong dependence on time of day that the authors wished to illustrate. The temporal shift between nitrated and non-nitrated subclasses would not be clearly seen in Fig. 5 and this is the reason for the inclusion of Fig. 4. The particle classes that are presented in Fig. 4 and not presented in Fig. 5 are the non-nitrated subclasses; freshly emitted coal, peat and wood combustion particles. These species do follow a very reproducible daily pattern, as illustrated in Fig. 4, but were not included in Fig. 5 as the plot would be too complex, and the relationship between wind speed and particle counts would not be as easy to identify.

Comment:

Page 1048, lines 7-10: Why is adsorption, condensation, or hydrolysis expected to be 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).

Response:

This is an interesting point. It is difficult to determine what fraction of the nitrate uptake is through heterogeneous reaction of KCl and NaCl salts with nitric acid to release gas phase HCl (Gard et al., 1998; Li et al., 2003), and what fraction is formed through hydrolysis of N₂O₅ or NO₃ at particle surfaces (Mogili et al., 2006; Wang et al., 2009).

C1906

Although single particle analysis of biomass burning particles of increasing age sampled in southern Africa clearly demonstrates the replacement of chloride with nitrate and sulfate, probably through reaction with nitric and sulfuric acid respectively, the relative humidity was quite low in that case (20-40%) (Li et al., 2003). More recently, similar depletion of particle phase chlorine has been observed in biomass burning particles measured by AMS arising from biomass burning in the Yucatan region of Mexico (Yokelson et al., 2009). The nitrated wood-burning particle class observed in this work is defined by dramatically higher signals for nitrate when compared to the fresh wood-burning class, but very little difference is observed in the signal for sulfate, indicating that while heterogeneous reaction with nitric acid may play a part, reaction with sulfuric acid is of comparatively little importance. The signals for K₂Cl⁺ (m/z 113, 115) and Cl (m/z -35, -37) are also lower in the aged wood-nit particles, by a factor of approximately 2, but these species remain present and thus chloride does not appear to be completely displaced overnight, although this reaction may proceed further downwind of the sampling site as particles are dispersed when wind speed increases in the early morning following each episode (Fig. 5). It is possible that both mechanisms play a part in nitrate uptake in the case of this study. There is a dramatically higher alkali metal concentration in wood particles compared to coal particles, with peat particle alkali metal concentrations lying in between the two (Figs. 1-3). Thus heterogeneous reaction with nitric acid to displace chloride should be most relevant for wood burning particles. In fact, as noted by Reviewer 1, there is little or no delay in the appearance of the nitrated wood burning particle class compared to the fresh counterpart, a trend also observed for the fresh and nitrated sea salt classes, and although the authors originally attributed this to the comparatively high hygroscopicity of wood burning particles accelerating N₂O₅ and NO₃ hydrolysis, it is indeed likely that rapid heterogeneous reaction with nitric acid may also be responsible (Gard et al., 1998; Li et al., 2003). However, the obvious delay in uptake of nitrate in the case of coal and peat burning particles (Fig. 4) indicates that their relatively low hygroscopicity is inhibiting the uptake of water and subsequent hydrolysis of N₂O₅ or NO₃ at particle surfaces, a humidity-dependent pro-

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cess that has been previously observed for carbonaceous particles in Shanghai (Wang et al., 2009).

In order to address this issue, the following lines have been removed from the manuscript “While it may be possible that some sodium and potassium cations on coal, peat and wood combustion particle surfaces are available for heterogeneous reaction with gas phase nitric acid, simple uptake through adsorption, condensation or N₂O₅/NO₃ hydrolysis are expected to be the dominant processes.”

Additional discussion has been added to the manuscript in the “ATOFMS particle classes: Coal, Peat and Wood” section, paragraph 4 as follows: “Single particle analysis of biomass burning particles of increasing age sampled in southern Africa clearly demonstrates the replacement of chloride with nitrate and sulfate, probably through reaction with nitric and sulfuric acid respectively, although the relative humidity was relatively low in that case (20-40%) (Li et al., 2003). More recently, similar depletion of particle phase chlorine has been observed in biomass burning particles measured by AMS arising from biomass burning in the Yucatan region of Mexico (Yokelson et al., 2009).”

The following addition has been made to the “ATOFMS particle classes: Coal, Peat and Wood” section, paragraph 5: “However, heterogeneous chemistry may also play a role in this processing. There is little or no delay in the appearance of the nitrated wood burning particle class compared to the fresh counterpart, a trend also observed for the fresh and nitrated sea salt classes. The Wood-nit particle class is defined by dramatically higher signals for nitrate when compared to the Wood-fresh class, but very little difference is observed in the average signal for sulfate between the two classes, indicating that while heterogeneous reaction with nitric acid may play a part, reaction with sulfuric acid is of comparatively little importance. The average signals for K₂Cl⁺ (m/z 113, 115) and Cl (m/z -35, -37) are lower in the Wood-nit particle class compared to Wood-fresh, by a factor of approximately 2, but these species remain present and thus chloride does not appear to be completely displaced overnight, although this re-

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action may proceed further downwind of the sampling site as particles are dispersed when wind speed increases in the early morning following each episode (Fig. 5). It is possible that both heterogeneous reaction and N₂O₅/NO₃ hydrolysis play a part in nitrate uptake in the case of wood burning particles. There is a dramatically higher alkali metal concentration in wood particles compared to coal particles, with peat particle alkali metal concentrations lying in between the two (Figs. 1-3). Thus heterogeneous reaction with nitric acid should be most relevant for wood burning particles. However, the obvious delay in uptake of nitrate in the case of coal and peat burning particles (Fig. 4) indicates that their relatively low hygroscopicity is inhibiting the uptake of water and that the subsequent hydrolysis of N₂O₅ or NO₃ at particle surfaces is the dominant mechanism for nitrate uptake for these particle classes (Wang et al., 2009).”

Comment:

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

Response:

The authors' previous article (Healy et al., 2009) involves the description of this source signature in detail, including comparison with the findings of Ault et al. (2009). However the more recent article of Ault et al. (2010) was not published when the original manuscript was submitted. The “ATOFMS particle classes: Shipping” section has been rewritten and expanded to include the findings of Ault et al. (2010) as follows:

“Shipping particles exhibited a very strong dependence on west-south-westerly wind direction but little or no dependence on time of day and accounted for approximately 4% of the particles ionised. These particles contain tracers for residual fuel oil and were observed in short, sharp events that could be directly attributed to ships entering and departing from the nearby shipping berths. This was confirmed through comparison with the Port of Cork shipping logs as outlined in a previous article (Healy et al., 2009). The positive ion mass spectra are characterised by organic and elemental carbon (m/z

C1909

12, [C]⁺; 27, [C₂H₃]⁺; 36, [C₃]⁺; 37, [C₃H]⁺, sodium (m/z 23, [Na]⁺), calcium (m/z 40, [Ca]⁺), iron (m/z 56, [Fe]⁺), vanadium (m/z 51, [V]⁺; 67, [VO]⁺) and nickel (m/z 58, [Ni]⁺) ions. Negative ion mass spectra contain signals for elemental carbon (m/z -12, [C]⁻; -24, [C₂]⁻; -36, [C₃]⁻; -48, [C₄]⁻), carbon-nitrogen adducts (m/z -42, [CN]⁻) and sulfate (m/z -64, [SO₂]⁻; -80, [SO₃]⁻; 81, [HSO₃]⁻; -97, [HSO₄]⁻) ions (Fig. 6). These spectra are very similar to those recently measured using ATOFMS and attributed to ship exhaust in the Port of Los Angeles, however in that case a second class of ship exhaust soot particles was also identified that did not contain residual fuel oil tracers such as vanadium and nickel and attributed to the combustion of distillate fuel (Ault et al., 2009; Ault et al., 2010). Particles containing vanadium were found to be relatively sulfate-enriched, indicating that vanadium or other transition metal impurities found in residual fuel oil combustion particles may catalyse the oxidation of SO₂ (Ault et al., 2010). Residual fuel oil combustion particles were detected for every ship plume measured in this work (Healy et al., 2009).”

Comment:

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.

Response:

The discussion regarding particle classes known to arise from vehicular emission was purposefully kept to a minimal length as the authors believe that the findings do not break any new ground scientifically, are in agreement with the previous single particle studies referenced in the manuscript, and serve only to confirm the local vehicular traffic source. Nevertheless, additional detail regarding particle size distributions has now

C1910

been included in the “ATOFS particle classes” sections, and to improve the clarity of the revised manuscript these sections are now rearranged as follows (EC-MSA has been assigned its own section due to the inclusion of a more thorough discussion): Coal, Peat and Wood Sea salt Shipping Elemental carbon and traffic classes EC-MSA ECOC and Oligomer The articles of Toner et al. (2006, 2008) regarding single particles arising from vehicular exhaust are already discussed briefly in the manuscript. However additional references have now been included as follows:

Section “ATOFS particle classes: Elemental carbon and traffic classes”, paragraph 2: “Ca-traffic positive ion spectra are characterised by signals for calcium (m/z 40, [Ca]⁺) and calcium oxide/hydroxide adducts (m/z 56, [CaO]⁺; 57, [CaOH]⁺; 96, [Ca₂O]⁺), and negative ion mass spectra contain signals for nitrate (m/z -46, [NO₂]⁻; -62, [NO₃]⁻), phosphate (m/z -63, [PO₂]⁻; -79, [PO₃]⁻; -95, [PO₄]⁻) and sulfate (m/z -81, [HSO₃]⁻; -97, [HSO₄]⁻). Similar single particle mass spectra have also previously been detected by ATOFS in heavy duty diesel vehicle dynamometer studies (Suess and Prather, 2002; Shields et al., 2007), and particles containing internally mixed calcium, phosphate, and elemental carbon, along with a wide range of various other internally mixed particle classes, have been detected by ATOFS in a light duty vehicle dynamometer study (Sodeman et al., 2005).”

Section “ATOFS particle classes: Elemental carbon and traffic classes”, paragraph 3: Negative ion spectra contain signals for elemental carbon (m/z -12, [C]⁻; -24, [C₂]⁻;...-84, [C₇]⁻) and a relatively low response for sulfate (m/z -97, [HSO₄]⁻) (Fig. 6). Similar particles have been observed previously by ATOFS in freshly emitted vehicle exhaust both in laboratory dynamometer studies and at a roadside site (Toner et al., 2006; Toner et al., 2008; Shields et al., 2007). Section “ATOFS particle classes: Elemental carbon and traffic classes”, paragraph 6: “Similar single particle mass spectra were collected using the LAMPAS-2 instrument both at a rural site, and a site next to an Autobahn in Germany, and attributed to diesel exhaust (Vogt et al., 2003).”

Comment:

C1911

Page 1052, last paragraph: While it is noted in Figure 8 that m/z -95 may be attributed to methanesulfonate, this is not discussed thoroughly 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". Based on the temporal trend in Figure 9, it would seem as though there was a local background of these particles as well.

Response:

This is a very interesting point, and we would like to thank the reviewer for these comments. Although m/z -95 was attributed to either phosphate or methanesulfonate (MSA) in the original manuscript, it seems more likely that MSA is the correct assignment in light of a recently published article regarding the identification of a variety of single particle classes that contain this species in Riverside, California (Gaston et al., 2010). The EC-phos-fresh and EC-phos-aged classes in this work could not be separated by the K-means algorithm due to the strong similarity of their mass spectra and were thus originally observed as a single bimodal class. A cut-off of 300 nm (aerodynamic diameter) was chosen. Particles smaller than 300 nm were termed EC-phos-fresh (now shortened to EC-phos), while those larger than 300 nm were originally termed EC-phos-aged (now renamed EC-MSA in the manuscript). However, this is not a very refined separation, because in reality the 2 modes overlap and what appears to be the minor local background referred to by Reviewer 1 in Fig. 9 arises as a result of this. The mass spectra differ only in that EC-phos spectra have a peak at m/z -79 confirming phosphate, while EC-MSA spectra do not contain this peak, but instead exhibit a peak at m/z -95 corresponding to MSA, a peak at m/z -89 corresponding to oxalate and a more intense signal for sulfate. MSA is a well established tracer for marine phytoplankton activity (Andreae and Crutzen, 1997; Hallquist et al., 2009; Gaston et al., 2010), and the presence of this species supports the theory that the EC-MSA particle class has undergone transport over at least part of the Atlantic Ocean. In the study of Gaston et al. (2010), vanadium-containing particles were observed to be enriched with

C1912

MSA relative to the other MSA-containing single particle classes that originated from coastal California, indicating that vanadium might represent a catalyst for MSA production. Interestingly, none of the other particle classes observed in this work are internally mixed with MSA, except possibly the sea salt class which appears to have an artificially higher relative intensity at m/z -95 than expected from the isotopic distribution of NaCl_2 , although this is difficult to determine definitively. However, a wide range of inorganic and carbonaceous particle classes transported from the coast of California were found to be internally mixed with MSA by the time they were detected by ATOFMS in Riverside (Gaston et al., 2010). This again reinforces the theory that all other carbonaceous particle classes observed in this work arise from local sources, except EC-MSA. Further discussion and details of appropriate additions to the manuscript are outlined in the response to the next comment.

Comment:

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?

Response:

This point is related to the previous comment and reply. While the authors agree that the likelihood of particles originating in North America undergoing intercontinental transport (ICT) to Ireland while surviving deposition processes is low, it is still possible, but is expected to have a negligible impact upon air quality (D. Ceburnis, personal communication, 2010). While there are relatively few direct measurements of particles from North America arriving at sites in Europe (Holloway et al., 2003), ICT of North American black carbon and forest fire particles to Ireland and Western Europe respectively, and ICT of Saharan dust particles to North America have been previously reported (Jennings et al., 1996; Forster et al., 2001; Singh et al., 2006; Owega et al., 2004). Direct advection of ozone from North America to Ireland has also been reported, contributing up to 20 ppbv during ICT events (Li et al., 2002). This source assignment

C1913

has been made by the authors through a process of elimination. EC-MSA is the only carbonaceous particle class that does not exhibit the temporality of local sources. Instead the temporality is strongly associated with a sustained shift in air mass origin (Fig. 10). EC-MSA is the only carbonaceous particle class containing MSA, a tracer for marine phytoplankton emissions (Fig. 8) (Gaston et al., 2010). Therefore the remaining sources of these particles are expected to be either oceanic activity or anthropogenic sources in the Atlantic Ocean or further west. Biological marine activity was ruled out as a source due to the presence of elemental carbon ions typically associated with combustion processes in the negative ion mass spectra, however biological activity is expected to be the source of the internally mixed MSA (Fig. 8). Even though the calculated HYSPLIT back-trajectories included in the manuscript are expected to become less reliable when projected over 5 days, assignment of EC-MSA particles to anthropogenic sources in North America should not be ruled out (Jennings et al., 1996; Forster et al., 2001; Singh et al., 2006), although admittedly a specific source or source region cannot be comprehensively identified. A new section entitled "ATOFMS particle classes: EC-MSA" has been written to address this point and the previous point raised by the reviewer: The following lines have been removed from the manuscript: "However, a strong signal is observed instead at m/z -95, possibly due to $[\text{PO}_4]^-$, suggesting that EC-phos-aged particles may represent an oxidised or aged form of EC-phos-fresh particles. When compared to EC-phos-fresh mass spectra, a much higher signal is observed for sulfate (m/z -97, $[\text{HSO}_4]^-$) relative to the negative elemental carbon ions and an additional signal corresponding to oxalate (m/z -89, $[\text{COOHCOO}]^-$) is also present. Assuming that both EC-phos-fresh and EC-phos-aged particles are generated in the same way" "Another possible assignment for the fragment at m/z -95 ion is methanesulfonate $[\text{CH}_3\text{SO}_3]^-$ (Silva and Prather, 2000). Methylsulfonic acid aerosol can be formed through the oxidation of biogenic dimethylsulfide emitted from ocean surfaces (Andreae and Crutzen, 1997; Hallquist et al., 2009), and may have been accumulated by EC-phos-aged particles during transatlantic transport. This class may thus represent vehicle exhaust particles originally emitted in North America or Canada that have

C1914

undergone oxidation and accumulation processes in transit before arriving at the Cork Harbour site." The new "ATOFMS particle classes: EC-MSA" section now reads: "EC-MSA particles are approximately 300-1000 nm in diameter, peaking at 550 nm, account for approximately 1.5% of the particles ionised, and have very similar positive ion mass spectra to EC-phos particles but do not contain any signal for $[\text{PO}_3]^-$ in the negative ion mode (Fig. 8). However, a strong signal is observed instead at m/z -95, assigned to methanesulfonate (MSA) (Silva and Prather, 2000; Gaston et al., 2010). MSA is a well established tracer for marine phytoplankton activity (Andreae and Crutzen, 1997; Hallquist et al., 2009; Gaston et al., 2010), and indicates that the EC-MSA particle class has undergone transport over at least part of the Atlantic Ocean. Interestingly, none of the other particle classes observed in this work are internally mixed with MSA, except possibly the Sea salt class which appears to have a higher relative intensity at m/z -95 than expected from the isotopic distribution of NaCl_2^- (Fig. 6). Although a wide range of inorganic and carbonaceous particle classes transported from the coast of California were found to be internally mixed with MSA by the time they were detected by ATOFMS in Riverside (Gaston et al., 2010), EC-MSA is the only carbonaceous single particle class in this work that contains this species. In the case of Gaston et al., vanadium-containing particles were observed to be enriched with MSA relative to the other classes, indicating that vanadium might represent a catalyst for MSA production. However, vanadium-rich shipping particles observed in this work were not internally mixed with MSA, presumably because they are emitted so close to the sampling site (400-600 m) (Healy et al., 2009). EC-MSA spectra also exhibit an intense signal for sulfate (m/z -97, $[\text{HSO}_4]^-$) relative to the negative elemental carbon ions and an additional signal corresponding to oxalate (m/z -89, $[\text{COOHCOO}]^-$). This suggests that uptake of sulfate and oxalic acid may have occurred during transport, a process previously observed for transported mineral dust particles in Asia (Sullivan and Prather, 2007). Oxalic acid has also been detected in single particles arising from biomass and fossil fuel combustion processes in Mexico City and Shanghai, and may be directly emitted at source or formed through the oxidation of biogenic and anthropogenic volatile organic

C1915

compounds (VOCs) in the gas or aqueous phases (Moffet et al., 2008; Carlton et al., 2007; Hallquist et al., 2009; Yang et al., 2009). EC-MSA particles do not appear in any significant number until the last 4 days of the campaign (24-28 August 2008), during which elevated counts are consistently observed as shown in Fig. 9. These particles do not exhibit any dependence on time of day but are strongly dependent on west-southwesterly wind direction. 5 day air mass back-trajectories, calculated using the HYSPLIT dispersion model (Draxler and Rolph, 2003), demonstrate that air masses arriving at 500, 1000 and 2000 m above the site during this 4 day period originated in North America (Fig. 10, right panel), while for the rest of the campaign (7-23 August 2008) similar 5 day back-trajectories show that air masses consistently originated in the North Atlantic and Arctic Oceans (Fig. 10, left and middle panels). Back-trajectories for air masses arriving at 100 and 200 m above ground level were also calculated yielding similar results. While it seems unlikely that anthropogenic particles would survive deposition processes during intercontinental transport over the Atlantic Ocean, transport to Europe of black carbon and boreal forest fire particles and anthropogenic trace gases including O₃, CO, NO_y and VOCs originating in North America has been previously reported (Jennings et al., 1996; Forster et al., 2001; Singh et al., 2006; Stohl et al., 2003).”

Comment:

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

Response:

In PMF, each data point is weighted according to its associated uncertainty. For the variables in question, EC-oil and EC-domestic, the average uncertainty calculated as described on page 1043, excluding the data points mentioned on page 1056, was approximately 2 particles. By setting the uncertainty to 100 we ensure that these data points do not influence the solution because they are down-weighted significantly com-

C1916

pared to the other points. The PMF solution seeks to minimise an object function which is a function of the prediction error and the measurement uncertainty. Thus, the higher the uncertainty, the less influence the prediction error for the data point has upon the solution (see e.g. (Paatero, 1999)).

The following sentence has been included in section 2.5, paragraph 2: “The higher the uncertainty given for a specific data point, the less influence it has on the solution (Paatero, 1999).”

The following sentence has been added to the section “Source Apportionment”, paragraph 1: “This is an increase of a factor of 50 compared to the average uncertainty for those two variables. This ensures that these particular data points do not exert any influence on the resulting factors resolved, as they will be significantly down-weighted compared to the remaining measurements (Paatero, 1999).”

Comment:

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.

Response:

The studies of Pekney et al. (2006) and Owega et al. (2004) both differ from the methodology described in this manuscript as outlined in the response to some of the earlier comments. The former study involved using single particle data to help confirm sources identified using PMF analysis of off-line ICP-MS results, but the single particle data was not included in the analysis. The latter study involved PMF analysis of single particle mass spectra only, without including or apportioning any other semi-continuous quantitative data. Direct comparisons to these studies, and other PMF analyses of urban PM_{2.5} composition, have been included in the manuscript as follows:

C1917

Additional detail has been added to the manuscript Introduction as follows: “A detailed campaign performed in Pittsburgh, Pennsylvania, focused on the identification of sources of particulate matter using a single particle mass spectrometer and off-line analysis of high-volume and micro-orifice uniform-deposit impactor (MOUDI) samples of PM using inductively coupled plasma-mass spectrometry (ICP-MS) (Pekney et al., 2006a; Bein et al., 2006; Bein et al., 2007; Pekney et al., 2006b). In that case PMF analysis was performed using the ICP-MS trace metal data, quantitative measurements of nitrate, sulfate and EC/OC but without including the single particle data, in order to apportion PM_{2.5}. Factors were generated corresponding to traffic, crustal material, regional transport, secondary nitrate, cooking and wood burning, steel production, and a gallium-rich factor was associated with coal burning. Several coal-fired power stations surrounding the site were identified as point sources of PM_{2.5}, with gallium identified as a possible tracer for coal combustion, although this source was estimated to contribute only 3% to the PM_{2.5} mass measured. PMF of temporal trends of various single particle classes generated using laser ablation mass spectrometry (LAMS) has been performed previously to identify sources of particulate matter in Toronto, Canada (Owega et al., 2004). Factors were obtained corresponding to sources of locally emitted and Saharan dust, road salt, wood burning, organic nitrates and aluminium-fluoride particles. However, no corresponding PM_{2.5} mass concentration or semi-continuous quantitative data was included or apportioned in that case.”

The Results and Discussion has been expanded as follows: The “Source Apportionment: Traffic” section now reads: “The Traffic factor contributes the most to the ambient PM_{2.5} mass (23%) and contributes significantly to particle number (42%), EC mass (43%), and the Ca-traffic and EC-phos ATOFMS particle classes (83% and 82% respectively). The high contributions to the ATOFMS classes indicate that their classification as traffic exhaust particles is correct. The contribution to EC-traffic is lower at 59%, and the Domestic solid fuel combustion factor contributes 25% to the EC-traffic class. This can be explained by the similarity of EC-traffic and EC-domestic negative ion mass spectra (Figs. 6 and 8). During the clustering procedure, this similarity

C1918

leads to an incomplete separation of particles from two different sources and although the multiple other single particle classes arising from these sources can be isolated efficiently these two classes cannot be completely separated using the methodology described. However, the subsequent PMF analysis enables this limitation to be observed, highlighting the value of combining these two approaches. The high traffic contribution to PM_{2.5} in this work demonstrates the dominance of local sources and is comparatively higher than that observed in the Pittsburgh study (11%), although this can be explained by the dominance of regionally transported PM_{2.5} in that case (Pekney et al., 2006b). Traffic is typically a dominant factor in PMF studies of urban PM_{2.5} (Castanho and Artaxo, 2001; Godoy et al., 2009; Mugica et al., 2009).”

The “Source Apportionment: Power Generation” section now reads: “The Power generation factor represents a source which would not have been identified by ATOFMS particle classification without PMF analysis, and exhibits variable contributions of 16%, 18% and 40% to OC mass, EC mass and sulfate mass respectively. This factor is estimated to contribute 11% to the measured PM_{2.5} mass. This value is relatively high compared to the 3% contribution of coal-fired power generation to PM_{2.5} mass in Pittsburgh (Pekney et al., 2006b). A coal-fired power generation facility lies to the southeast of the sampling site, directly across the harbour and explains the relatively high contribution to the ATOFMS Coal class (30%) (Hellebust et al., 2010b). A high contribution to the ECOC particle class is also observed (69%), which indicates that this class is accounted for almost exclusively by the Long-range transport and Power generation factors. A contribution of 35% to the EC-background class is observed, although this class is distributed among several other factors suggesting input from every combustion source.”

The “Source Apportionment: Shipping” section has been greatly expanded to include a more detailed comparison with previous PMF studies as outlined above.

Comment:

C1919

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.

Response:

MSA-containing particles have been observed in previous single particle studies as referenced in the manuscript, and the possibility of undetected particles was suggested because there is a contribution to OC mass from the marine factor. However, MSA-containing particles are observed in this work, and it is possible that there is an MSA contribution in the sea salt spectra as mentioned above and illustrated in Fig. 6. Therefore the following lines have been removed from the manuscript: "There is no additional ATOFMS class that is covariant with sea salt, suggesting that the instrument is unable to detect these particles. This could be due to the absence of any chemical species that can absorb the wavelength of the UV laser (266 nm)."

Although this work and the previous article of Hellebust et al. (2010b) shared a common goal of source identification of PM_{2.5}, the findings reported here are far more detailed and highlight the advantages of combining single particle mass spectrometry with PMF. The previous article was focused on the applicability of using real-time measurements of trace gases, EC/OC, particulate sulfate and PM_{2.5} mass with PMF analysis to estimate the relative input of major local sources of PM_{2.5} (Hellebust et al., 2010b). This work is focused on the investigation of single particle composition in an in-port urban environment. New findings regarding sources of PM_{2.5} including shipping traffic and possible ICT have been made possible, as knowledge of single particle mixing state is a powerful tool when separating the input from various anthropogenic processes. The "Source Apportionment: Marine" section has been amended and the previous results of Hellebust et al. (2010b) are expanded upon as follows: "The Marine

C1920

factor contributes the most to the ATOFMS Sea salt class as expected (86%), and contributes 14% to the PM_{2.5} mass. Interestingly, this factor also has the second highest contribution to OC mass (20%), indicating that biological activity in the Atlantic Ocean is contributing to particulate matter in Cork Harbour. There is no additional ATOFMS class that is covariant with sea salt, however there may be a contribution from internally mixed MSA in the sea salt mass spectra at m/z -95 (Fig. 6). MSA has recently been detected internally mixed with several types of carbonaceous and inorganic single particle classes in California (Gaston et al., 2010). This factor was not observed in a previous study using both principal component analysis (PCA) and PMF on semi-continuous data from the same site, but without ATOFMS particle speciation (Hellebust et al., 2010b). That study involved using cost-effective measurements of NO, NO₂, O₃, SO₂, EC/OC, SO₄²⁻ and PM_{2.5}, in combination with temporal and wind averaging to estimate major sources of PM_{2.5} in Cork Harbour. The data was collected over a longer period (May-August 2008), and only three factors corresponding to traffic, domestic combustion and power generation were identified and estimated to contribute 19%, 14% and 31% to the measured PM_{2.5} mass respectively. The absence of single particle composition and mixing state data led to a far less refined source apportionment in that case. The contribution of domestic solid fuel combustion and power generation to the measured PM_{2.5} mass in this work are lower, as expected considering the introduction of three new factors (Table 3). The introduction of additional factors is analogous to the work of Eatough et al. (2008), who also observed additional factors when ATOFMS and AMS datasets were added to existing real-time monitoring data."

Comment:

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 conclu-

C1921

sion should be examined further and reconsidered.

Response:

While pure ammonium sulfate is typically the most important “missing” single particle type in ATOFMS field studies (Wenzel et al., 2003; Spencer et al., 2008), simulation chamber experiments involving α -pinene photooxidation have also resulted in the formation of particles that could not be successfully ionised using ATOFMS (Gross et al., 2006). However when a mixture of α -pinene and 1,3,5-trimethylbenzene was photooxidised in that study, the resulting SOA was successfully ionised by the desorption/ionisation laser, indicating that 1,3,5-trimethylbenzene photooxidation products were required for efficient absorption at 266 nm. While pure biogenic SOA is unlikely to be formed in the urban environment in this work, it could in theory represent a missing particle type, although the expected ubiquity of ammonia at the site suggests that pure ammonium sulfate represents a more likely missing particle class (Healy et al., 2009). However, pure ammonium sulfate should have been detected by the online particulate sulfate measurements. The fact that the variance in the measured sulfate is explained by the reported PMF factors suggests that pure ammonium sulfate may not constitute a significant independent source of PM in this dataset, although it may account for some of the error in the “prediction” of sulfate. Crustal dust should absorb at 266 nm. In this case the authors referred to the transmission efficiency of larger particles through the aerodynamic lens as an obstacle to the detection of these species at low number concentrations, although it seems unlikely that the lower end of the size distribution of windblown soil or dust particles would not overlap with the upper limit of the lens (3 μ m), especially when sea salt is detected successfully. This source was suggested as it has been identified at a nearby site using off-line analysis in a previous study (Hellebust et al., 2010a). However, the absence of an ATOFMS class for crustal material suggests that it does not represent a detectable or significant source of PM_{2.5} during this particular campaign.

In response to the reviewer’s comments the following lines have been removed from
C1922

the Conclusions section: “Approximately 33% of the measured PM_{2.5} mass remains unaccounted for and possible missing sources include crustal material and biogenic secondary organic aerosol. A factor for crustal material was identified in a previous study focused on the off-line analysis of the metal content of PM_{2.5} collected at a different site in Cork Harbour, and was estimated to contribute 11% to the measured PM_{2.5} mass (Hellebust et al., 2010a). It is possible that crustal and biogenic SOA particles were not detected by ATOFMS due to inefficient transmission through the aerodynamic lens or inefficient absorption of the UV laser.”

The following lines have been added to section “Source Apportionment”, paragraph 1: “Approximately 33% of the measured PM_{2.5} mass remains unaccounted for and can possibly be explained by particles that are not detected by the ATOFMS such as pure ammonium sulfate (Wenzel et al., 2003). Identification of further independent factors by PMF is dependent on having appropriate source markers for specific source groups with a variance that is not explained by the factors already identified. Therefore it is difficult to speculate as to which emission sources are not identified as long as the variance in the measured variables are satisfactorily explained by the existing factors.”

Reviewer 1: 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.

Response:

The proposed change has been made. These lines now read: “An aerosol time-of-flight mass spectrometer (ATOFMS) was deployed for the measurement of the size resolved chemical composition of single particles at a site in Cork Harbour, Ireland for three weeks in August 2008. The ATOFMS was co-located with a suite of semi-continuous instrumentation for the measurement of elemental carbon (EC), organic carbon (OC), sulfate, particle number and PM_{2.5} mass.”

C1923

Comment:

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).

Response:

These changes have now been made.

Comment:

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

Response:

“Shipping traffic” is now used in both instances to clarify this source.

Comment:

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

Response:

These changes have now been made. This line now reads: “Aerosol time-of-flight mass spectrometry (ATOFMS) and other single particle mass spectrometry techniques have been employed in several field studies to identify point sources of PM_{2.5} including steel manufacturing, smelting, refining and power generation facilities (Reinard et al., 2007; Snyder et al., 2009; Liu et al., 2003; Bein et al., 2007; Pekney et al., 2006a; Bein et al., 2006).”

Comment:

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

C1924

Response:

“Diffuse” in this case refers to the spatial distribution of the source; it is not a point source but is distributed around the site in almost every direction

Comment:

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

Response:

This part has been changed to read as follows: “More recently, sources of organic aerosol in Wilmington, Delaware, were apportioned using a photoionisation aerosol mass spectrometer (PIAMS) (Dreyfus et al., 2009). The mass spectral data was modelled using PMF and these results were combined with elemental and organic carbon (EC/OC) quantitative data.”

Comment:

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

Response:

This is not a typo. It is a valid spelling of the word.

Comment:

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

Response:

The following line has been added: “Air mass back trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPPLIT) dispersion model (Draxler and Rolph, 2003).”

Comment:

C1925

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

Response:

This line now reads: "In the ambient dataset, aged coal particle subclasses were also observed; one exhibiting an additional signal for ammonium (m/z 17, $[\text{NH}_3]^+$; 18, $[\text{NH}_4]^+$), "Coal-amm", and another containing a signal for ammonium and an increased signal for nitrate (m/z -46, $[\text{NO}_2]^-$; -62, $[\text{NO}_3]^-$), "Coal-amm-nit".

Comment:

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

Response:

An additional line has been added as follows: "Wood-nit particles appear with little or no delay from Wood-fresh particles, while there is an obvious temporal shift of 2 h and 4-5 h between fresh and nitrated peat and coal particles respectively."

Comment:

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.

Response:

This class has been renamed ECOC in the revised manuscript for clarity and to facilitate comparison with previous single particle studies.

Comment:

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

C1926

Response:

This line now reads: "A similar class was also observed in Athens during a previous ATOFMS study, but due to a lack of dependence upon time of day could not be attributed to specific sources in that case (Dall'Osto and Harrison, 2006)."

Comment:

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"?

Response:

In this case, during the clustering procedure, the similarity of the negative ion spectra of EC-traffic and EC-domestic particles leads to an incomplete separation of particles from two different sources. This is indeed due to two sources producing very similar chemical fingerprints, and although the multiple other single particle classes arising from these sources can be separated efficiently as described in the manuscript, these two classes cannot be completely separated using the methodology described. Thus "incorrect classification" is admittedly not the best term to use. These lines now read: "The contribution to EC-traffic is lower at 59%, and the Domestic solid fuel combustion factor contributes 25% to the EC-traffic class. This can be explained by the similarity of EC-traffic and EC-domestic negative ion mass spectra (Figs. 6 and 8). During the clustering procedure this similarity leads to an incomplete separation of particles from two different sources, and although the multiple other single particle classes arising from these sources can be isolated efficiently these two classes cannot be completely separated using the methodology described. However, the subsequent PMF analysis enables this limitation to be observed, highlighting the value of combining these two approaches."

Comment:

C1927

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

The following reference has now been added: "(Hellebust et al., 2010b)"

Reviewer 2 General Comments:

This manuscript describes a thorough and careful analysis of the sources contributing to PM_{2.5} in Cork Harbor, in Ireland. The authors use established methods, especially PMF, to work with data from a variety of instruments including single particle mass spectra (ATOFMS), quantitative EC, OC, sulfate, PM_{2.5} mass, and particle number. They carried out PMF using the temporal trends observed after clustering the single particle data, which is emerging as the most useful way to include single-particle data in PMF models. The authors include single-particle measurements of potential sources (smokeless coal, peat, and wood) to better characterize their contributions in the PMF model. The paper is within the scope of ACP and will be of interest to ACP readers, although this could be enhanced as described below. Overall, while this paper does not break new ground in methodology, it applies an established method to a new location in a new way. This detailed study of a shipping harbor should be of great interest to those trying to characterize the sources of pollution from such locations, and the authors should do much more to focus in on this aspect of their work and to put it into the context of other work that examines particles in such locations (e.g. Ault, et al., Environ. Sci. Technol., 2009, 43, 3500.).

Response:

In response to earlier comments from Reviewer 1, the Introduction and "Source Apportionment: Shipping" sections have been greatly expanded to incorporate discussion of the relevant single particle studies, PCA and PMF studies, and other PM_{2.5} trace metal analysis studies regarding particulate matter emissions from shipping in various port environments. The authors believe that the methodology described herein allows for an accurate apportionment of PM_{2.5} mass and particle number concentrations arising

C1928

from the combustion of residual fuel oil on ocean-going vessels, and various other sources, in an urban in-port environment.

Comment:

The authors have done a careful job of presenting the work they did, and the manuscript is generally well organized and well written (see detailed comments below). It is an appropriate length, and all of the figures are important. In the course of their analysis, the authors note trends in the detection of single-particle spectra that correspond with their wood, peat, and smokeless-coal particle types, with associated nitrate in the mass spectra. They note that the addition of nitrate occurs temporally in that order and propose that this might be a measure of the relative hygroscopicity of the particle types, with the more hygroscopic particles taking up nitrate more quickly. This seems to be borne out by the data that they reference, but it would be nice to test this hypothesis with laboratory measurements of the hygroscopicity.

Response:

Additional hygroscopicity tests would be ideal using the appropriate instrumentation, a hygroscopic tandem differential mobility analyser (HTDMA) for example, attached to a simulation chamber into which the combustion particles are introduced. This would allow the measurement of growth factors for the various fuel combustion particles in order to validate the hypothesis. Unfortunately HTDMA instrumentation is not available to us, although as outlined above, heterogeneous reaction with nitric acid may also represent a competing mechanism for nitrate uptake for combustion particles in Cork Harbour, in particular for potassium-rich wood-burning particles. Discussion of the competing processes is included in the response to previous comments and the manuscript has been amended to take this into account. Admittedly, without the appropriate instrumentation this remains a hypothesis.

Comment:

C1929

The authors also note that oligomers are detected in particles that they say correspond with relatively fresh domestic solid fuel combustion classes. They note that the particles appear to be formed rapidly as compared to reported rates of detection in smog chamber experiments. The authors should note that in those referenced experiments, the particles were nucleating in the absence of seed particles, and thus the observed formation rates for oligomers include the nucleation of particles as well. The spectrum shown in Figure 11c indicates that the oligomers are found in particles that contain other materials (sulfates, nitrates, etc.), and thus it could be likely that they form on pre-existing particles.

Response:

This is a good point. Typically in simulation chamber experiments performed in the absence of seed particles an induction period, often on the order of hours, is observed during which photooxidation products reach high enough concentrations to nucleate secondary organic aerosol (Dommen et al., 2006; Gross et al., 2006; Healy et al., 2008). In urban environments, however, pre-existing particles should provide surfaces for heterogeneous or particle phase accretion reactions leading to oligomer formation that could be catalysed by the presence of sulfuric or nitric acid (Jang et al., 2002; Barsanti and Pankow, 2004, 2005; Liggio et al., 2005). Internally mixed nitrate and sulfate were detected in oligomer-containing single particles by ATOFMS in Riverside, California (Denkenberger et al., 2007). Increased particle acidity was also found to accelerate oligomer formation in that case. The lack of positive ion mass spectra in this manuscript hinders the source identification of oligomer-containing particles, however when positive spectra are present, signals are observed for sodium and potassium. Thus oligomer-containing particles may arise from accelerated accretion/oligomerisation reactions on relatively acidic coal combustion particles for example. The fact that the highest concentrations are observed for this class during low wind speed events suggests that these reactions do require a period of mixing with gas phase reactants that can be taken up through oligomerisation reactions (Kalberer

C1930

et al., 2004; Denkenberger et al., 2007). The following lines have been removed from the "ATOFMS particle classes: ECOC and Oligomer" section: "This indicates that a significant fraction of these oligomer-containing particles are relatively fresh." The following lines have been added to the end of the "ATOFMS particle classes: ECOC and Oligomer" section: "The rate of formation of detectable oligomers in secondary organic aerosol simulation chamber studies is typically of the order of hours (Kalberer et al., 2004; Gross et al., 2006), although studies performed in the absence of seed aerosol are often characterised by long induction periods while oxidation products reach high enough concentrations to induce nucleation (Dommen et al., 2006; Gross et al., 2006; Healy et al., 2008). In the case of Denkenberger et al., increased particle acidity was observed to accelerate oligomer formation. Thus, in this work oligomer-containing particles may arise from accelerated accretion/oligomerisation reactions on relatively acidic particles such as the coal-fresh class (Jang et al., 2002; Barsanti and Pankow, 2004, 2005; Liggio et al., 2005). The fact that the highest concentrations are observed during low wind speed events suggests that these particles require a period of mixing with gas phase reactants that can be taken up through oligomerisation reactions (Kalberer et al., 2004; Denkenberger et al., 2007)."

Comment:

Overall, I would like the authors to focus their conclusions on the broader implications of their work, rather than on the methodology – how applicable is their work to other ports and how does it compare to the characterization of other ports that are in the literature, what are the prospects for using this method for characterizing larger areas or more complex areas, and how much does their conclusion rely upon having the authentic sources measured?

Response:

The authors believe that the methodology described in this manuscript is applicable to other port environments. The advantage of performing such a study in Cork Harbour

C1931

is that the relatively small size of the city (population <300 000), and the reliably clean marine air masses arriving at the site result in primary particles from local sources dominating air quality, as described in the manuscript. The lack of any other particle type containing the residual fuel oil tracers V and Ni, along with the use of appropriate shipping logs, allows for a comprehensive source apportionment for particles arising from shipping in this location. Standard particle mass spectra for the predominant domestic fuels used in the area also allows for accurate apportionment of that source. Future similar studies in larger port cities will be more complex. Although the contributions from traffic and crustal material to ambient PM are often satisfactorily apportioned using traditional continuous monitoring and source apportionment methodologies, relative contributions from local and regional shipping, domestic oil combustion, refining and industry are much more difficult to separate (Godoy et al., 2009; Ault et al., 2009; Viana et al., 2009). The conclusions drawn in this work absolutely rely on the measurement of the authentic sources, in particular those regarding domestic combustion and shipping particles. However, the authors believe that the dissemination of these standard spectra among the scientific community, along with previously reported signature single particle mass spectra from various sources worldwide, enables future researchers to confidently confirm these sources in ambient datasets. In a similar way, previous dynamometer and roadside single particle studies instructed the traffic source identification in this work (Sodeman et al., 2005; Spencer et al., 2006; Toner et al., 2006; Toner et al., 2008). Now that the particular sources identified in this work are satisfactorily characterised, employing this methodology in other port locations should enable their relative contribution to PM_{2.5} and particle number concentration to be estimated. A comparison of the findings of this work with other PMF studies in port cities, with and without single particle mass spectrometry, is now included in the much expanded Shipping subsection of section 3.2, outlined earlier in reply to the comments of Reviewer 1. That discussion also includes the broader implications of our findings.

Reviewer 2 Specific comments:

C1932

1. Overall, I would suggest that the authors consider replacing the exhaustive lists of ions observed in the single-particle mass spectra that are included in the text with tables. This will decompress the text somewhat, make the text more readable, and make it easier to compare the ions observed in the various classes of particles.

Response:

A new table (Table 2) has now been included in the revised manuscript, summarising the ions observed for each particle class. This table is also now referenced in the manuscript. However, the authors believe that the description of the ions in the body of the text is also essential, as the presence or absence of particular ions is discussed in each case and compared with previous literature. In some cases the ions present, or their relative intensities, differ slightly between classes, for example for coal, peat and EC-domestic particles, and thus an adequate description is necessary. Such description of single particle classes is quite common in the literature (Dall'Osto and Harrison, 2006; Tan et al., 2002; Moffet et al., 2008).

Comment:

2. p. 1041, line 13-14: The authors discuss the separation of EC-phos-fresh and ECphos-aged, but do not comment there about whether these classes are different in any way other than size. The table suggested in comment 1, above, would make it easier to see this, and I would recommend adding a comment in the text as well.

Response:

These particle classes (now renamed EC-phos and EC-MSA respectively) exhibit very similar positive ion mass spectra, but the negative ion mass spectra are different, as outlined in the response to Reviewer 1. EC-phos spectra are characterised by a peak at m/z -79 corresponding to phosphate, while EC-MSA spectra do not have this peak but instead are characterised by peaks at m/z -89 and -95 corresponding to oxalate and methanesulfonate respectively. EC-phos particles are assigned to local traffic emis-

C1933

sions, and exhibit a pronounced diurnal cycle, while EC-MSA particles are associated with a shift in air mass origin and do not exhibit a dependence on time of day. These particles are instead assigned to intercontinental transport of anthropogenic particles from North America. The sections describing these classes have been expanded as described earlier, and EC-MSA has now been assigned an additional subsection due to the more detailed discussion included in earlier replies. A new table has also been included as described in the previous reply.

Comment:

3. p. 1043, line 10: The authors state that the number of factors used in their PMF calculations was varied until the “most reasonable” results were obtained. This phrase should be defined.

Response:

Six, seven and eight factor solutions were explored and the results of the various solutions are included in section “Source Apportionment”, paragraph 1. However, for clarity an additional line has been added to section 2.5, final paragraph: “Six-, seven- and eight-factor solutions were explored, with the six factor solution providing the most satisfactory result.”

Comment:

4. p. 1044, line 11: As there is expected to be relatively constant transmission through an aerodynamic lens in the size range for which it is designed, the authors might want to explain why there is expected to be little effect for not scaling for size-related transmission efficiency into the ATOFMS.

Response:

As the ATOFMS does not enable direct quantitative measurements due to size-dependent transmission efficiencies associated with the aerodynamic lens, and variable ionisation efficiencies depending on the particle matrix involved, scaling proce-

C1934

dures can be useful when attempting to quantify the contribution of various particle phase species to PM_{2.5} mass (Wenzel et al., 2003; Dall’Osto et al., 2006). However, an aerodynamic particle sizer (APS) is typically required to measure size distributions larger than about 800 nm. In our work, the SMPS system provided size distributions up to 600 nm only (mobility diameter), thus scaling procedures are limited as many of the particle classes measured exhibit aerodynamic diameters larger than this. However, the temporality of the various particle classes is the important aspect here. Assuming the particle transmission efficiencies and ionisation efficiencies of the identified classes did not change during the campaign, the temporality of each class can be used for PMF. In our case PMF analysis replaces scaling procedures as the particle number concentrations, EC/OC, sulfate and in particular PM_{2.5} mass concentrations we seek to apportion are instead reconstructed using the model. However, “missing” particles such as pure ammonium sulfate that are not ionised by the ATOFMS cannot be accounted for in this way. This phenomenon is discussed in previous replies.

Comment:

5. p. 1045, line 18: The authors discuss the strong signal for sulfate observed in the freshly emitted combustion particles from their source tests, which they note is different from the measurements observed by other researchers. However, they do not discuss the potential effect of their source tests being done in an outdoor stove. Could the outdoor air influence their observed spectra?

Response:

In theory, the outdoor air could have an influence on the standard combustion spectra either through rapid uptake of ammonium, nitrate, sulfate or organics, although these processes would have to be extremely rapid as the ATOFMS was located less than 5 m from the stove, and the sampled particles were exposed to ambient air for only a few seconds before detection. Therefore the internally mixed species detected are expected to be primary. We believe that the higher signal observed for sulfate in coal

C1935

particles detected in this work are a result of higher sulfur content in the coal used compared to previous studies. The origin of the coal appears to be important as gallium and lithium detected in previous single particle studies have been suggested as tracers for coal combustion particles measured in the US and Asia (Bein et al., 2007; Liu et al., 2003; Guazzotti et al., 2003), although these metals were not detected in our case, or in a previous single particle measurement campaign in Poland (Mira-Salama et al., 2008).

Comment:

6. Throughout the paper, the authors should more closely relate their findings to those that have been published, especially related to their source profiles. Coal has been sampled before with single-particle mass spectrometers (and should be referenced), but is this smokeless-coal different in some way? Similar questions arise with wood, which has been sampled and reported in numerous papers. Peat, I believe, is new to this work.

Response:

The Introduction, "ATOFMS particle classes: Coal, Peat and Wood" section and "Source Apportionment: Domestic combustion" section have been expanded to include much additional discussion and comparison with previous single particle studies of coal and wood combustion. These additions are included in the responses to Reviewer 1. The standard coal used for our combustion experiment was commercially available bituminous coal, while the commercially available smokeless coal is expected to contain lower levels of bituminous coal mixed and bound with anthracite. Interestingly, the mass spectra for coal and smokeless coal are practically identical and cannot be separated using the K-means algorithm in the case of this work. Therefore the relative contribution of these fuels to ambient air quality in Cork Harbour could not, unfortunately, be estimated.

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