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Title	Source apportionment of PM2.5 in Cork Harbour, Ireland using a combination of single particle mass spectrometry and quantitative semi-continuous measurements
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Publication date	2010-10-11
Original Citation	Healy, R. M., Hellebust, S., Kourtchev, I., Allanic, A., O'Connor, I. P., Bell, J. M., Healy, D. A., Sodeau, J. R., and Wenger, J. C. (2010) 'Source apportionment of PM2.5 in Cork Harbour, Ireland using a combination of single particle mass spectrometry and quantitative semi-continuous measurements', Atmospheric Chemistry and Physics, 10, pp. 9593-9613. doi:10.5194/acp-10-9593-2010, 2010
Type of publication	Article (peer-reviewed)
Link to publisher's version	10.5194/acp-10-9593-2010, 2010
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Atmos. Chem. Phys., 10, 9593–9613, 2010
www.atmos-chem-phys.net/10/9593/2010/
doi:10.5194/acp-10-9593-2010
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Atmospheric Chemistry and Physics

Source apportionment of $PM_{2.5}$ in Cork Harbour, Ireland using a combination of single particle mass spectrometry and quantitative semi-continuous measurements

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Received: 9 December 2009 – Published in Atmos. Chem. Phys. Discuss.: 18 January 2010
Revised: 24 August 2010 – Accepted: 4 October 2010 – Published: 11 October 2010

Abstract. 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 particle number, elemental carbon (EC), organic carbon (OC), sulfate and particulate matter smaller than 2.5 µm in diameter ($PM_{2.5}$). The temporality of the ambient ATOFMS particle classes was subsequently used in conjunction with the semi-continuous measurements to apportion $PM_{2.5}$ mass using positive matrix factorisation. 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, various combustion, domestic solid fuel combustion and shipping traffic with estimated contributions to the measured $PM_{2.5}$ mass of 23%, 14%, 13%, 11%, 5% and 1.5% respectively. Shipping traffic was found to contribute 18% of the measured particle number (20–600 nm mobility diameter), and thus may have important implications for human health considering the size and composition of ship exhaust particles. The positive matrix factorisation procedure enabled a more refined interpretation of the single particle results by providing source contributions to $PM_{2.5}$ mass, while the single particle data enabled the identification of additional factors not possible with typical semi-continuous measurements, including local shipping traffic.



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1 Introduction

Ambient particulate matter (PM) is known to adversely affect human health, and long-term exposure to ultrafine (less than 100 nm diameter) ambient particles is expected to lead to irreversible changes in lung structure and function (Maier et al., 2008). PM also affects climate, both directly by scattering and absorbing solar radiation, and indirectly by acting as cloud condensation nuclei (IPCC, 2001). Identification of the various sources of anthropogenic PM in urban environments has received considerable attention with traffic, biomass burning and industrial processes typically contributing significantly to mass concentrations of $PM_{2.5}$ (Castanho and Artaxo, 2001; Kim and Hopke, 2008; Godoy et al., 2009; Karanasiou et al., 2009; Mugica et al., 2009; Heo et al., 2009). However, refined apportionment of $PM_{2.5}$ is often hindered by the low temporal resolution of off-line analysis and a lack of knowledge of the mixing state of the particles collected.

Single particle mass spectrometry allows the simultaneous detection of internally mixed primary and secondary components of ambient PM including elemental and organic carbon, trace metals and ionic species with high temporal resolution (Sullivan and Prather, 2005). The internal mixing state of individual particles arising from specific anthropogenic and natural processes is often unique, and thus useful for identifying sources when combined with meteorological data (Reinard et al., 2007). 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

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(Reinard et al., 2007; Snyder et al., 2009; Liu et al., 2003; Bein et al., 2007; Pekney et al., 2006a; Bein et al., 2006). More spatiotemporally diffuse sources, such as light and heavy duty vehicular traffic and biomass burning, have also been identified using unique ATOFMS mass spectral signatures (Spencer et al., 2006; Silva et al., 1999; Moffet et al., 2008). More recently, 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, 2010).

The positive matrix factorisation (PMF) (Hopke, 2003) approach to source apportionment has recently been employed in the interpretation of data from aerosol mass spectrometers (Lanz et al., 2007; Dreyfus et al., 2009; Ulbrich et al., 2009; Allan et al., 2010) and has also been applied to a combination of data from an aerosol mass spectrometer and an aerosol time-of-flight mass spectrometer (Eatough et al., 2008). The latter study involved combining ATOFMS and time of flight aerosol mass spectrometry (ToF-AMS) data with continuous on-line and off-line quantitative measurements of $PM_{2.5}$, sulfate, nitrate, black carbon and several gas phase species in Riverside, California. PMF was performed with and without the mass spectral data, and the number of factors obtained rose from six to sixteen once the data was included. The additional factors introduced contributions from various local and regional sources including shipping activity, thus demonstrating the value of on-line measurements of particle composition. A detailed campaign performed in Pittsburgh, Pennsylvania, focused on the identification of sources of PM 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, 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 in order to apportion $PM_{2.5}$, but without including single particle data. 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 total $PM_{2.5}$ mass. PMF of temporal trends of various single particle classes generated using laser ablation mass spectrometry (LAMS) has been performed previously to identify sources of PM 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. 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 quantitative EC/OC data. Vehicular traffic was found to account for approximately two thirds of the organic carbon measured over an 18 day period.

The aim of this study was to identify and apportion local and regional sources of $PM_{2.5}$ in Cork Harbour using a combination of ATOFMS data and quantitative semi-continuous measurements of particle number, $PM_{2.5}$ mass, EC/OC and sulfate. ATOFMS mass spectral signatures for peat, coal and wood combustion particles were also obtained separately in order to apportion these sources more accurately in the ambient dataset. A PMF approach similar to that of Eatough et al. (2008) was employed for quantitative source apportionment based on the ATOFMS data collected.

2 Methodology

2.1 Sampling site and equipment

The sampling site is located at Tivoli Docks in the Port of Cork (51°54′5 N, 8°24′38 W), approximately 3 km east of Cork City centre (Fig. 1). Shipping berths are located 400–600 m to the southwest and west-southwest. The prevailing winds are southwesterly, and therefore the site is ideally positioned for the detection of ship plumes. The main road carrying traffic east out of the city and towards Dublin lies to the north of the site. Residential areas surround the site on all sides except the north and northeast. A suite of semi-continuous instrumentation was located at the site for the duration of the campaign; particulate SO_4^{2-} was monitored using a Thermo Electron model 5020 SPA instrument and EC/OC mass concentrations were measured using a thermal-optical carbon analyser (Sunset Laboratory Inc., 3rd generation field model) fitted with a cyclone to remove particles larger than 2.5 µm in diameter. A scanning mobility particle sizer (SMPS, TSI model 3081) measured the size distribution of particle number in the range 20–600 nm (mobility diameter) every 3 min. A TEOM (tapered element oscillating microbalance, Thermo Electron model 1400a) was located on-site for the measurement of $PM_{2.5}$ mass concentrations (averaged every 30 min). The ATOFMS (TSI model 3800) was fitted with an aerodynamic lens (TSI model AFL100) for the measurement of particles in the size range 100–3000 nm. The instrument is described in detail elsewhere (Dall'Osto et al., 2004). In short, particles are sampled through an orifice and accelerated through the aerodynamic lens to the sizing region of the instrument. Here, the aerodynamic diameter of particles is calculated based on their time of flight between two continuous wave lasers (Nd:YAG, 532 nm). Particles are



Fig. 1. Left panel: map of sampling site and surrounding area. Cork city lies 3 km to the west. The site (X) is positioned to the northeast of the nearby shipping berths (B) in the Port of Cork (yellow), surrounded by residential areas (blue), a shipping lane (green) and a main road (red). Right panel: Windrose for 7–28 August 2008.

then transmitted to the mass spectrometry region of the instrument and ionised using a Nd:YAG laser (266 nm). The resulting positive and negative ions are finally analysed using two collinear time-of-flight mass spectrometers. Wind speed, wind direction, temperature, humidity and rainfall were monitored using a Casella NOMAD weather station. All instruments sampled air through stainless steel tubing from a height of 4 m above ground level. Every instrument was located on site for three weeks from 7–28 August 2008, except for the SMPS which was on site from 14–28 August 2008.

2.2 Combustion experiment

Mass spectral signatures were obtained for coal, "smokeless" coal, peat and wood by burning each in turn for approximately 1 h in an outdoor stove and measuring the fresh combustion particles by ATOFMS. Each fuel was purchased locally in order to be representative of typical domestic output in the area. Specifically, commercially available compacted peat briquettes, bituminous coal, smokeless coal and ash wood were used. Peat is commonly used in Ireland for domestic space heating. Ash wood was used since it is widely available for sale in retail outlets in Cork City. 16 118 single particle mass spectra were generated during the experiment and clustered using the K-means algorithm ($K = 10$) as described in Sect. 2.4 (MacQueen, 1967). Coal, peat and wood burning particles were effectively clustered into separate classes although coal and smokeless coal did not exhibit sufficiently different mass spectra to be separated. These spectra were subsequently used to confirm the identification of classes in the ambient dataset.

2.3 ATOFMS data analysis

During the three week campaign 558 740 ATOFMS single particle mass spectra were generated and subsequently imported into ENCHILADA (Environmental Chemistry through Intelligent Data Analysis), a freeware single particle data analysis software package (Gross et al., 2010) and clustered using the K-means algorithm (MacQueen, 1967), ($K = 50$). ENCHILADA has been previously used to classify ATOFMS mass spectra generated from ambient particles at sites in Switzerland and East St. Louis, Illinois (Herich et al., 2008; Snyder et al., 2009). Inhomogeneous clusters were clustered again using K-means when necessary in order to refine particle classification. Those clusters with similar mass spectra and temporality were recombined to generate the following 14 particle classes; Coal, Peat, Wood, Sea salt, Shipping, Ca-traffic, EC-traffic, EC-phos, EC-MSA, EC-domestic, EC-background, EC-oil, ECOC, and Oligomer. These classes account for 94% of the particle mass spectra generated. The EC-phos and EC-MSA classes were generated from a single bimodal cluster that could not be separated further using K-means analysis. The two modes, which exhibited completely different temporalities, were thus separated by size. Particles of aerodynamic diameter less than 300 nm were classified as EC-phos and particles of aerodynamic diameter between 300 and 1000 nm were classified as EC-MSA. Hourly summed particle counts of each final particle class were subsequently used for positive matrix factorisation. Particle subclasses containing increased or additional signals for secondary species such as ammonium and nitrate were combined with their freshly emitted analogues during this analysis since they originate from the same source. In the absence of coincident aerodynamic particle sizer (APS) data, and knowledge of density and shape factor for the various classes, scaling procedures were not employed here (Qin et al., 2006). However, unscaled ATOFMS counts per hour were deemed suitable for PMF, as the size distributions of the various particle classes were not observed to shift significantly during the measurement period, which would alter their position along the transmission efficiency curve of the aerodynamic lens.

2.4 Positive Matrix Factorisation (PMF)

The identification of factors using PMF can be improved by the inclusion of single particle classes that have been unequivocally assigned to a source through their unique mass spectra (Eatough et al., 2008). As with the study of Eatough et al. (2008), the factorisation procedure has been applied to the previously clustered single particle mass spectra obtained by ATOFMS in this work. The clustering procedure provides hourly counts of identified particle classes that are treated as independent variables alongside hourly averages of measured EC, OC, SO_4 and $PM_{2.5}$ mass concentrations. Total SMPS counts in the size range 20–600 nm (mobility diameter) were integrated for each hour of the campaign and also included as a variable. By combining this information it is possible to apportion PM mass and particle number in a quantitative manner. Specific markers such as the ATOFMS classes used here are particularly useful for apportioning sources that are characterised by brief and/or irregular events or long-range emissions that bear no correlation to local events. The PMF model was developed using the USEPA PMF 3.0 software package available at www.epa.gov/scram001/receptorindex.htm. The uncertainty matrix associated with the data was calculated based on the instrumental level of detection and uncertainty (error fraction) as given by the manufacturer's documentation. The uncertainty used to describe the ATOFMS data was ±15% as in Eatough et al. (2008). For concentrations less than or equal to the method detection limit (MDL) provided, the uncertainty was calculated using the relationship (Polissar et al., 1998):

$$\text{Uncertainty} = \frac{5}{6} \cdot \text{MDL} \quad (1)$$

If the concentration was greater than the MDL provided, an alternative relationship was employed as follows:

$$\text{Uncertainty} = \sqrt{(\text{error fraction} \cdot \text{uncertainty})^2 + (\text{MDL})^2} \quad (2)$$

Experimentation with the number of factors was performed until the most reasonable results were obtained. Six-, seven- and eight-factor solutions were explored, with the six factor solution providing the most satisfactory result, as no useful information was gained by increasing the number of factors further. Estimation of the contribution of each factor to the total $PM_{2.5}$ mass was subsequently performed by scaling the PMF factor contributions against measured $PM_{2.5}$ mass by regression (Maykut et al., 2003; Shi et al., 2009).

3 Results and discussion

3.1 Semi-continuous measurements and meteorology

The mean ambient mass concentrations of organic carbon (OC), elemental carbon (EC), sulfate and $PM_{2.5}$ measured at the site for the duration of the campaign were 1.13, 0.61, 0.49 and 9.67 µg m^{-3}, respectively. Unfortunately, no mass concentrations were available for nitrate, chloride, ammonium or crustal material, which are expected to all contribute to $PM_{2.5}$ mass. However, ATOFMS data for single particles containing these species has been included for PMF instead. Concentration-time profiles for the semi-continuous measurements are given in Fig. 2. These values are broadly in line with those observed at a different site in Cork City from July–August 2001 (Yin et al., 2005). Seasonal variation of these variables has been discussed in detail in a previous article (Hellebust et al., 2010). Wind direction was predominantly southwesterly for the first and third weeks of the campaign and predominantly northwesterly from 14–23 August 2008. The average wind speed, air temperature and relative humidity were 4.7 m s^{-1}, 16 °C and 80% respectively. Rainfall was observed between 9–12 August 2008, 15–18 August 2008 and on 23 August 2008. Air mass back trajectories were calculated using the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) dispersion model (Draxler and Rolph, 2003). The first seventeen days of the campaign were characterised by clean North Atlantic and subarctic air masses, while air masses originating in North America influenced the site from 24–28 August 2008.

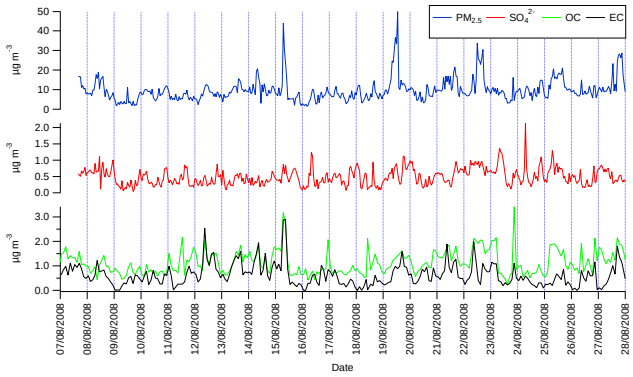


Fig. 2. Concentration-time profiles for $PM^{*}_{2.5}$, SO^{2-*}_{4}, organic carbon** and elemental carbon** for 7–28 August 2008. * Hourly averaged mass concentration. ** Bihourly averaged mass concentration.

3.2 ATOFMS particle classes

3.2.1 Peat

Coal, peat and wood combustion particles accounted for 41%, 10% and 9% of the total particles successfully ionised and detected by the ATOFMS, and were observed almost exclusively in the submicron size range. Although particle counts have not been scaled for size-related transmission efficiency through the aerodynamic lens or composition-dependent ionisation efficiency, the results indicate that even during the summer months, domestic solid fuel combustion is a source of $PM_{2.5}$ in Cork Harbour. Ambient domestic

Table 1. Ions observed in mass spectra for each ATOFMS particle class, represented by shaded areas.

	Coal-fresh	Coal-amm	Coal-amm-nit	Peat-fresh	Peat-nit	Wood-fresh	Wood-nit	Sea salt	Shipping	Ca-traffic	EC-traffic	EC-phos	EC-domestic	EC-background	EC-oil	EC-MSA	ECOC	Oligomer
$[C_n]^+/[C_nH_n]^+$	■	■	■	■	■	■	■		■	■	■	■	■	■	■	■	■	
$[C_n]^-$	■	■	■	■	■	■	■		■		■	■	■	■	■	■		
$[CN]^-/[CNO]^-$	■	■	■						■	■	■	■	■	■	■	■		■
$[C_2H_3O]^+$	■	■	■	■	■												■	
$[HCOO]^-$						■	■											
$[CH_3COO]^-$						■	■											■
$[COOHCOO]^-$						■	■									■		
$[Na]^+$	■	■	■	■	■	■	■	■	■		■		■	■	■		■	
$[Na_2O]^+/[Na_2OH]^+$								■										
$[Na_2Cl]^+/[NaCl_2]^-$								■										
$[Mg]^+$								■										
$[K]^+$	■	■	■	■	■	■	■						■	■	■		■	
$[K_2Cl]^+$						■	■				■							
$[Ca]^+$								■		■					■			
$[CaO]^+/[CaOH]^+$										■					■			
$[Ca_2O]^+$										■								
$[V]^+/[VO]^+$									■									
$[Ni]^+$									■									
$[Fe]^+$									■									
$[SO_2]^-$									■									
$[SO_3]^-/[HSO_3]^-$	■	■	■					■	■	■								■
$[SO_4]^-/[HSO_4]^-$	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■	■
$[CH_3SO_3]^-$																■		
$[NO_2]^-/[NO_3]^-$	■	■	■	■	■	■	■	■		■		■				■		■
$[Cl]^-$				■	■	■	■	■										■
$[NH_3]^+/[NH_4]^+$		■	■														■	
$[PO_2]^-$										■					■			
$[PO_3]^-$										■		■			■			
$[PO_4]^-$										■								

combustion particles were identified based on their similarity to particles generated from each fuel during the combustion experiment. Figures 3–5 compare average dual ion mass spectra for the freshly emitted ambient "Peat", "Coal" and "Wood" classes with those generated during the experiment. The prominent ions detected for the various classes are also included in Table 1. Peat particles are characterised by signals for sodium and potassium which dominate the positive ion mass spectra, along with carbon ions and hydrocarbon fragment ions (Fig. 3). Negative ion mass spectra for Peat particles contain many of the same ions observed for Coal but at very different relative intensities, with Peat particle spectra exhibiting additional signals for chloride and much lower signals for sulfate. This is the first reported identification of single particles formed through the combustion of peat, widely used as a domestic fuel not only in Ireland but also in parts of Northern Europe (Orru et al., 2009). The average dependence of Peat, Coal and Wood particles on time of day is shown in Fig. 6. The average diurnal profile for each particle class is very similar, increasing sharply from 18:00 to 21:00, and decreasing rapidly after 22:00, with a minimum during daytime hours. The periods of increasing and decreasing particle number can be explained by the local population lighting fires and allowing them to extinguish respectively. While very strongly dependent upon time of day, none of the domestic combustion classes exhibited an obvious dependence on wind direction due to the abundance of residential areas surrounding the site (Fig. 1). The clustering

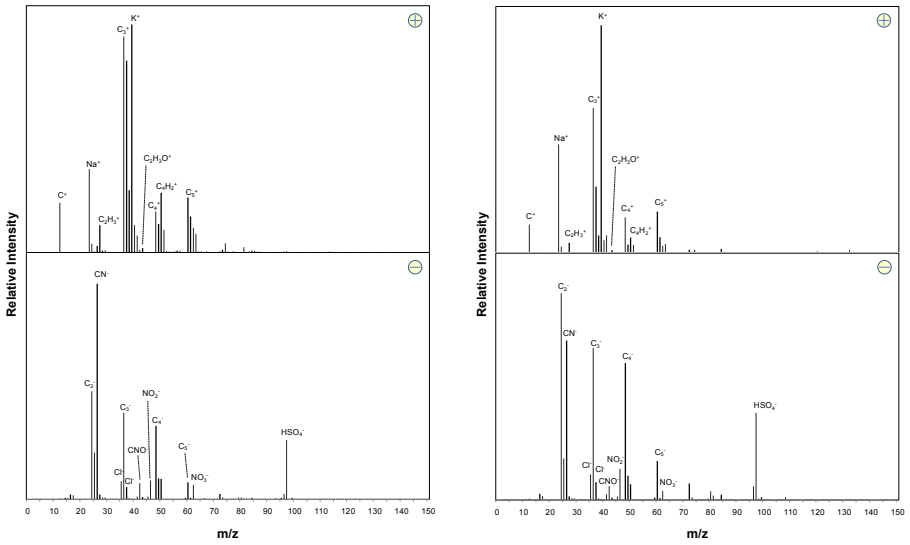


Fig. 3. Average dual ion mass spectra of ambient particles classified as "Peat" (left) and particles sampled during the peat combustion experiment (right).

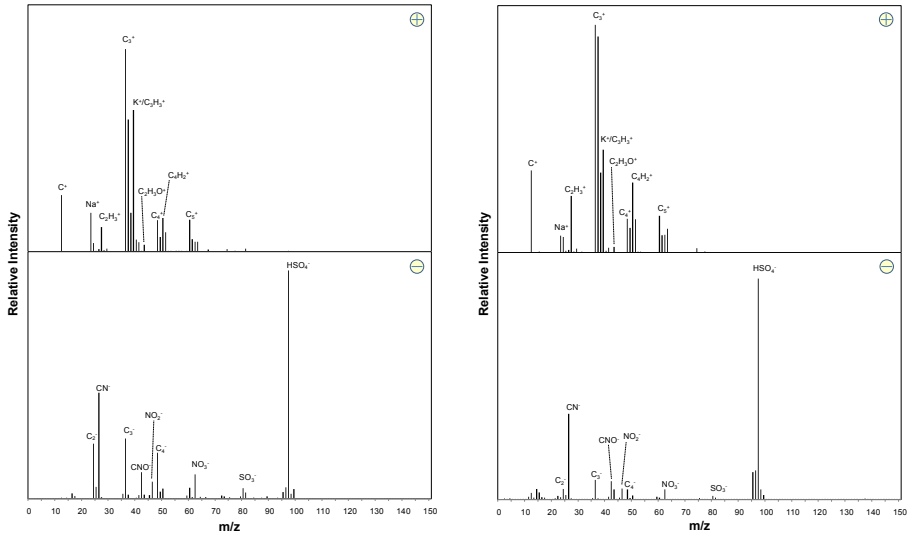


Fig. 4. Average dual ion mass spectra of ambient particles classified as "Coal" (left) and particles sampled during the coal combustion experiment (right).

procedure enabled the separation of freshly emitted and aged domestic combustion particles into subclasses based on their secondary composition, as described below. However, these subclasses were recombined for PMF as they originate from the same source.

3.2.2 Coal

Coal positive ion mass spectra are characterised by typical hydrocarbon fragment ions and a relatively low signal for sodium and potassium. Negative ion mass spectra contain peaks corresponding to elemental carbon, carbon-nitrogen adducts, nitrate, and sulfate. Although none of these ions are individually unique to the combustion of coal, there is a very strong similarity in the relative ion intensities of coal combustion particles detected during the combustion experiment and ambient coal combustion particles as shown in Fig. 4.

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. (2003), particles from coal-fired power generation facilities in Atlanta, GA were much larger in diameter

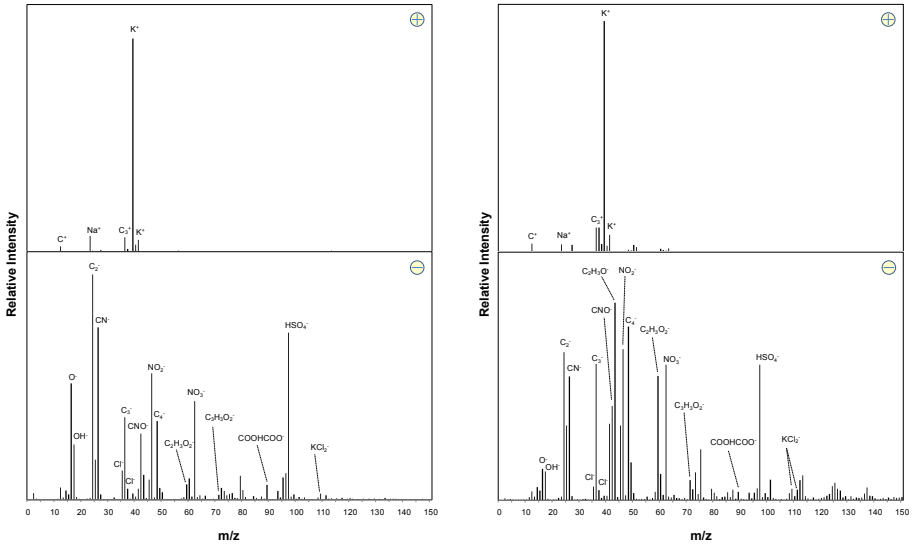


Fig. 5. Average dual ion mass spectra of ambient particles classified as "Wood" (left) and particles sampled during the wood combustion experiment (right).

exhibiting signals for lithium and iron that were not observed in our case, along with a comparatively low signal for sulfate. These inorganic particles arise from efficient conversion of carbonaceous material to CO_2 at high temperatures while the smaller domestic coal combustion particles observed in Cork contain carbonaceous material due to inefficient lower temperature combustion. 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 was observed in the coal combustion particles detected in this work (Fig. 4), 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 signals for carbon but not 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. 4).

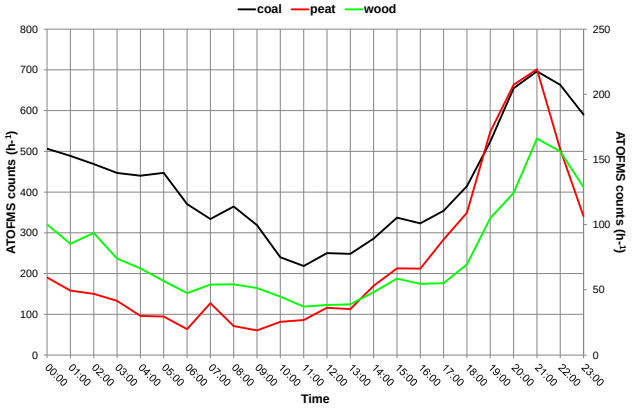


Fig. 6. Average diurnal trend for Coal, Peat and Wood ATOFMS particle counts for 7–28 August 2008.

3.2.3 Wood

Wood positive ion mass spectra are dominated by potassium atomic ions while signals for hydrocarbon fragments are almost completely suppressed. Signals are observed for chloride, carbon-nitrogen adducts, nitrate, sulfate, and often for potassium chloride (*m/z* 113, 115, $[K_2Cl]^+$) (Fig. 5). Similar ATOFMS mass spectra are commonly observed for particles arising from the combustion of biomass (Gard et al., 1997; Silva et al., 1999; Guazzotti et al., 2003; Moffet et al., 2008; Friedman et al., 2009). Compared to ambient "Wood" particles, those generated during the combustion experiment contain much higher signals at *m/z* −43 and −59, probably corresponding to the oxidised organic carbon fragment ions $[C_2H_3O]^-$ and $[CH_3COO]^-$ respectively (Silva et al., 1999;

Silva and Prather, 2000; Guazzotti et al., 2003). It is possible that semi-volatile oxidised organics in the combustion experiment particles may undergo evaporation in transit, or that a combination of different species of wood are burned in the local area resulting in these differences in negative ion mass spectra.

3.2.4 Peat, coal and wood subclasses

After the clustering procedure was performed for the ambient dataset, two aged coal particle subclasses were observed; one exhibiting an additional signal for ammonium termed "Coal-amm", and another containing a signal for ammonium and an increased signal for nitrate termed "Coal-amm-nit". Similarly, aged peat, "Peat-nit", and wood, "Wood-nit", particle subclasses were also observed which exhibited higher signals for nitrate but no additional signal for ammonium (Table 1). Cork City is surrounded by agricultural land and gas phase ammonia is expected to be ubiquitous. The absence of ammonium molecular ions in aged Peat and Wood mass spectra could be due to the presence of increased levels of potassium and sodium causing a suppression of ammonium signals coupled with the relatively low sensitivity of ATOFMS for ammonium (Spencer et al., 2006; Gross et al., 2000). However it is also possible that coal combustion particles, which contain much more sulfate than those produced by peat or wood combustion (Figs. 3–5), undergo heterogeneous reaction with gas phase ammonia more readily. This is supported by the fact that there is little or no delay between the appearance of fresh domestic coal particles and the Coal-amm subclass, indicating rapid uptake of ammonia.

The nitrated subclasses exhibit a dependence on later evening and early morning hours, indicating that they are aged and require more time to accumulate nitrate. The highest numbers of nitrated coal, peat and wood combustion particles were observed during four distinct events beginning on the evenings of the 11, 13, 14 and 22 August 2008. Each event coincided with a drop in wind speed to levels below $1\,m\,s^{-1}$ as shown in Fig. 7. It is important to note that meteorology such as this; low wind speed with possible nocturnal inversion, may result in a concentration enhancement of gas phase pollutants and particle number.

The low wind speed event of the evening of 22 August 2008 and early morning of 23 August 2008 is examined in detail in Fig. 8. The vast majority of particles present between 20:00 and 06:00 are known to arise from domestic peat, coal and wood combustion from the corresponding ATOFMS mass spectra. Between 06:00 and 07:00 traffic particles with smaller diameters dominate, before the wind speed increases again, dramatically reducing particle number. A ship plume from the nearby berths can also be observed between 08:00 and 09:00. This overnight period is also characterised by high relative humidity (87–99%) and a temperature drop of approximately 4 °C. Domestic fires are expected to be mostly extinguished by 00:00, however particle number does not decrease after this source is expected to be "switched off". In fact, a clear increase in SMPS particle number concentrations is observed between 23:00 and 03:00 (Fig. 8). Although no obvious growth in particle diameter is observed, the average signal for nitrate ($[NO_3]^-$, *m/z* −62) per particle detected by ATOFMS is observed to steadily increase at night, reaching a plateau at around 03:00 (Fig. 8). The average signal is used here because this is corrected for particle number, which is also increasing most likely due to meteorology. A simultaneous decrease is observed for the average potassium chloride signal ($[K_2Cl]^+$, *m/z* 113), indicating that for Wood particles, heterogeneous displacement of chloride with nitrate is at least partially responsible for nitrate accumulation. Single particle analysis of biomass burning particles of increasing age sampled in southern Africa has clearly demonstrated the replacement of chloride with nitrate and sulfate, probably through reaction with nitric acid and sulfuric acid respectively (Li et al., 2003).

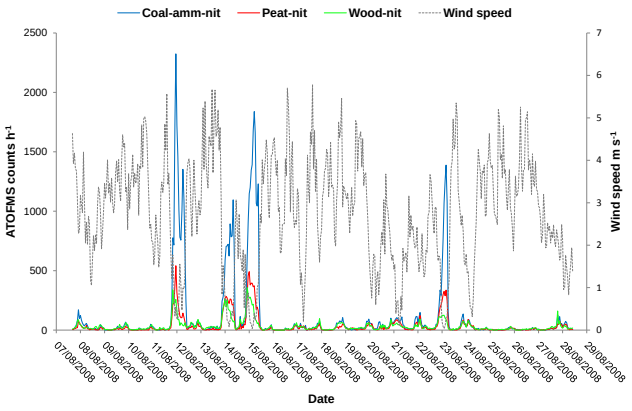


Fig. 7. Hourly integrated ATOFMS particle counts for the Coal-amm-nit, Peat-nit and Wood-nit subclasses and hourly averaged wind speed values for 7–28 August 2008.

The average signal for nitrate observed over the four low wind speed events for the three domestic combustion classes is given in Fig. 9. All three classes exhibit simultaneous elevated signals at night, reaching a maximum between 01:00 and 06:00. Wood particles accumulate the most nitrate on average, followed closely by coal particles. Unexpectedly, peat particles accumulate approximately half this amount. Periods of low wind speed allow locally emitted combustion particles to undergo prolonged mixing with gas phase NO_2. Under these conditions NO_2 can be oxidised to yield nitric acid on particle surfaces. In the presence of particle phase water, N_2O_5 and NO_3 can also be hydrolysed to form nitric acid, possibly an important pathway considering the high relative humidity observed at the site during these events (Mogili et al., 2006; Wang et al., 2009). Gas phase nitric acid or pre-existing ammonium nitrate can also be directly taken up by particles, with partitioning to the particle phase enhanced at lower temperatures (Sullivan et al., 2007). These processes

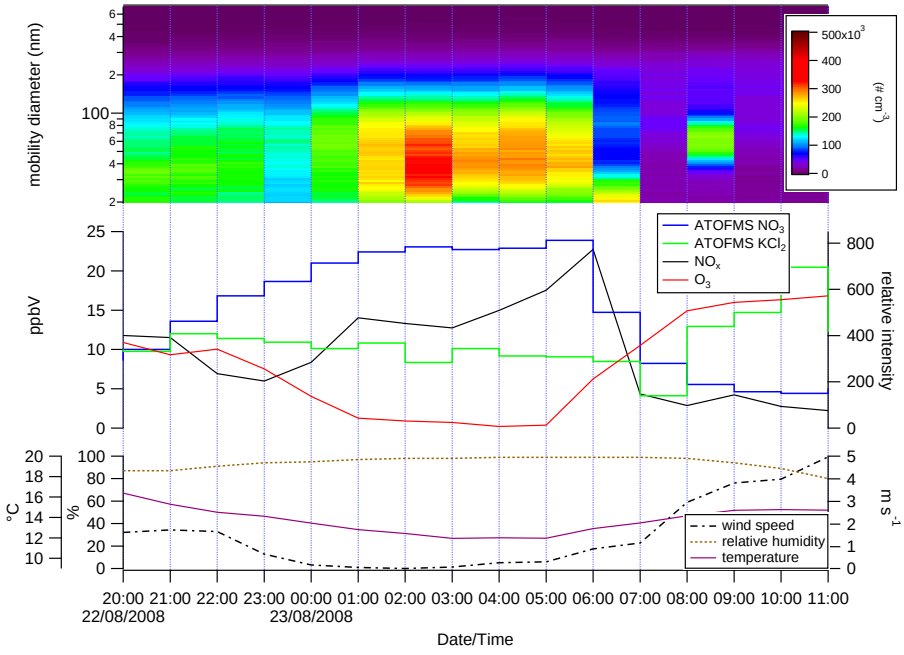


Fig. 8. Top panel: hourly integrated size resolved SMPS particle counts. Middle panel: hourly averaged ATOFMS signal for $[NO_3]^-$ and $[KCl_2]^+$, hourly averaged mixing ratios for NO_x and O_3. Bottom panel: hourly averaged wind speed, relative humidity and temperature.

most likely explain the accumulation of nitrate by domestic combustion particles, with additional input from heterogeneous chloride displacement in the case of Wood. While interesting in itself, this night-time processing is not expected to be a significant source of particulate nitrate in Cork, at least during the summer months, as the SMPS data does not reveal any obvious growth in mobility diameter. Hourly integrated ATOFMS size distributions for the Peat, Coal and Wood classes scaled to the SMPS data using an assumed density of 1.7 g cm^{-3} and shape factor of 1 (Reinard et al., 2007), also did not demonstrate obvious growth during this period. However, during the winter months, lower temperatures combined with elevated concentrations of domestic combustion particle numbers and NO_x may have a more pronounced effect on particle size.

3.2.5 Sea salt

Sea salt particles did not exhibit a strong dependence on time of day, although a slight dependence on westerly and southwesterly wind direction was observed, and exhibited a monomodal size distribution peaking at approximately 700 nm. These particles were characterised by the presence of sodium, chloride, magnesium and calcium atomic ions as per previous studies (Fig. 10) (Gard et al., 1998; Dall'Osto et al., 2004).

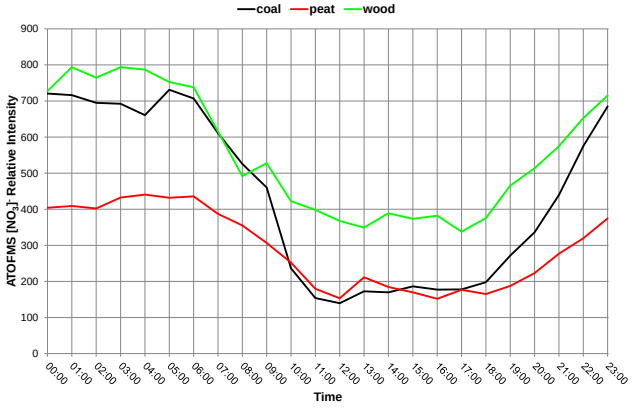


Fig. 9. Hourly averaged signal for nitrate for the Coal, Peat and Wood ATOFMS classes for the 4 low wind speed events (11–12 August 2008, 13–15 August 2008 and 22–23 August 2008).

3.2.6 Shipping

Shipping particles exhibited a very strong dependence on west-southwesterly wind direction but little or no dependence on time of day (Healy et al., 2009). 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 in every case through comparison with the Port of Cork shipping logs (Healy et al., 2009). The mass

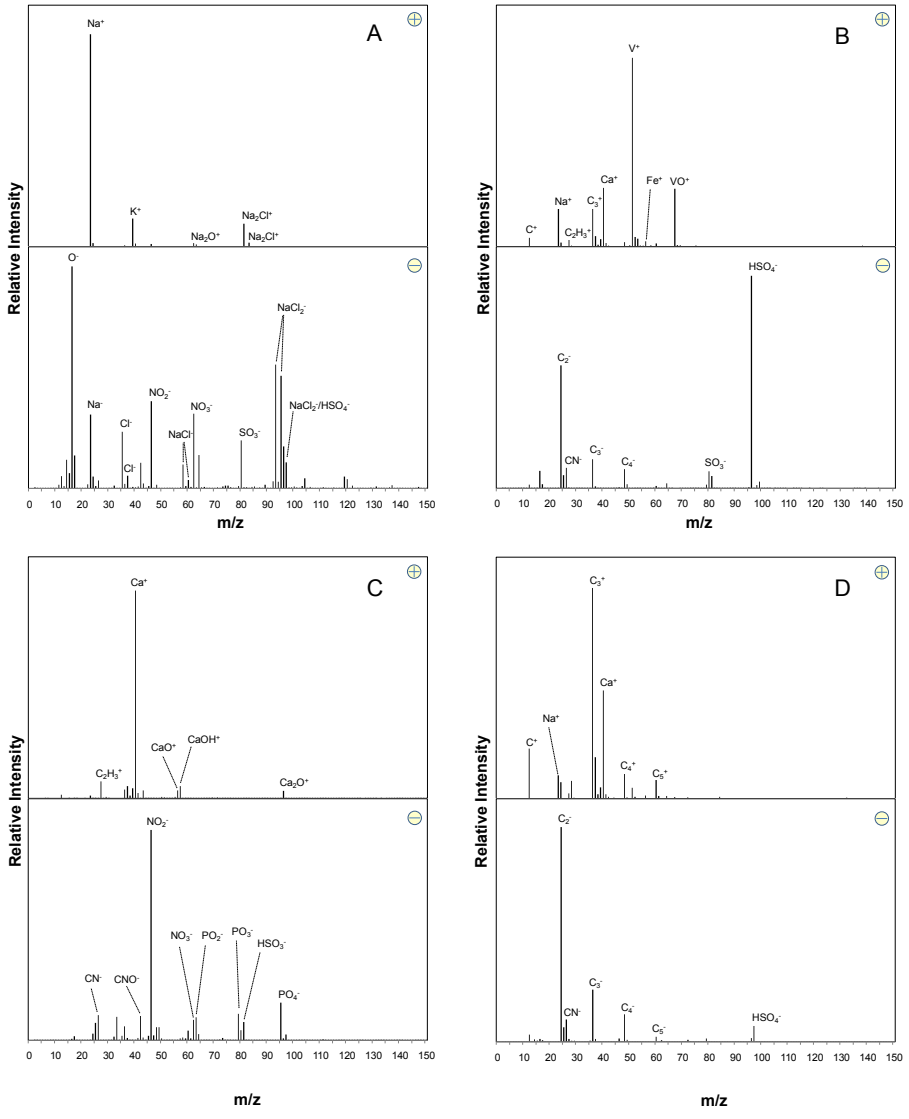


Fig. 10. Average dual ion mass spectra of ATOFMS particle classes; **(A)** Sea salt, **(B)** Shipping, **(C)** Ca-traffic, **(D)** EC-traffic.

spectra are characterised by the presence of organic and elemental carbon, sodium, calcium, iron, and nickel, along with a strong signal for sulfate (Fig. 10). 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 was thus attributed to the combustion of distillate fuel (Ault et al., 2009, 2010). Residual fuel oil combustion markers were observed in particle mass spectra for every ship plume measured in this work.

3.2.7 Elemental carbon and traffic classes

Three particle classes were observed that exhibited an obvious dependence on daytime vehicular traffic hours as shown in Fig. 11; Ca-traffic, EC-traffic and EC-phos. These classes peak on average between 08:00 and 17:00 and decrease dramatically between 00:00 and 06:00, as expected for vehicular activity. An additional increase is observed between 20:00 and 22:00 for EC-traffic although this may be partly due to incorrect classification of some domestic solid fuel combustion particles (EC-domestic), which exhibit almost identical negative ion mass spectra (Figs. 10 and 12). All three classes are commonly observed in roadside and dynamometer ATOFMS studies (Spencer et al., 2006; Suess and Prather, 2002; Shields et al., 2007; Sodeman et al., 2005; Toner et al., 2006; Toner et al., 2008).

The EC-domestic class is characterised by positive ion mass spectra containing high signals for sodium and potassium (Fig. 12). As shown in Fig. 11, this class exhibits a similar diurnal variation to those observed for the Peat, Coal and

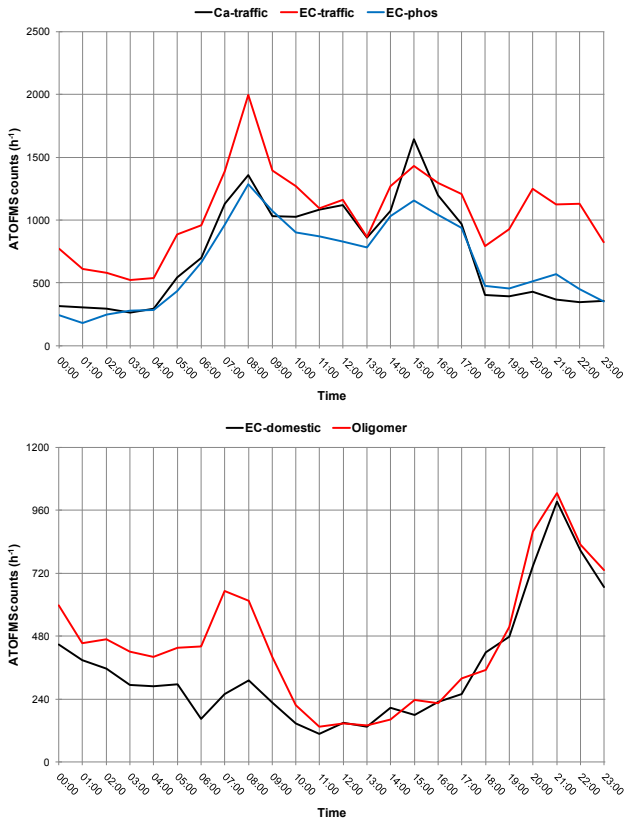


Fig. 11. Average diurnal trend for (top) Ca-traffic, EC-traffic and EC-phos and (bottom) EC-domestic and Oligomer particle counts for 7–28 August 2008. EC-phos and EC-domestic particle numbers have been multiplied by a factor of 3 and 1.5 respectively for comparative purposes.

Wood classes. This temporality, coupled with the presence of sodium and potassium atomic ions that are also observed for Peat and Coal (Figs. 3 and 4), indicate that domestic combustion is the most likely source of these particles. A nitrated subclass is not observed for this particle class, however, and is most likely explained by the poor hygroscopic growth factor of elemental carbon particles (Weingartner et al., 1997).

EC-background particles exhibit a bimodal size distribution in the range 100–1000 nm, peaking at 250 and 500 nm, and are characterised by higher order elemental carbon ions than any of the other classes. These particles do not exhibit any dependence on wind direction or time of day, suggesting multiple sources. There was no obvious difference in relative ion intensity for the mass spectra of the two modes. Similar single particle mass spectra have been collected using the LAMPAS-2 instrument in Germany (Vogt et al., 2003) and using ATOFMS in Athens, Greece (Dall'Osto and Harrison, 2006) and attributed to diesel exhaust and fossil fuel combustion, respectively.

EC-oil particles exhibit diameters in the range 150–1000 nm, peaking at approximately 250 nm and do not exhibit a strong dependence on wind direction or time of day. These particles exhibit positive ion mass spectra with signals for carbon, sodium, potassium and calcium (Fig. 13). Negative ion mass spectra are dominated by a large signal for phosphate. Similar particles have been observed in heavy duty vehicle exhaust using ATOFMS but without a signal for potassium, indicating that this class may contain some incorrectly classified domestic combustion particles and thus have more than one source (Toner et al., 2006).

3.2.8 EC-MSA

EC-MSA particles are approximately 300–1000 nm in diameter, peaking at 550 nm and have very similar positive ion mass spectra to EC-phos particles but do not contain any signal for $[PO_3]^-$ (Fig. 12). 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 an artificially higher relative intensity at *m/z* −95 than expected from the isotopic distribution of $NaCl_2^-$ (Fig. 10). 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. (2010), 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 relative to the negative elemental carbon ions and an additional signal corresponding to oxalate (*m/z* −89, $[COOHCOO]^-$). 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 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. 14.

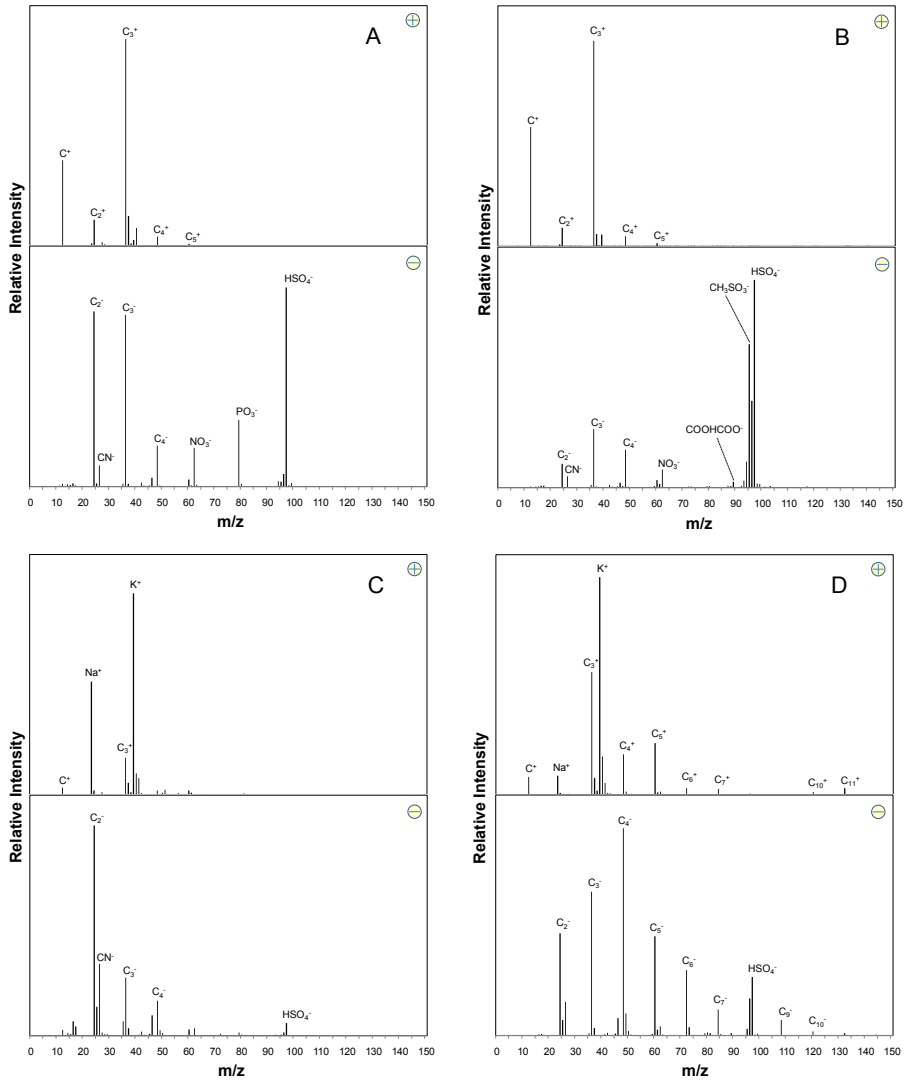


Fig. 12. Average dual ion mass spectra of ATOFMS particle classes; **(A)** EC-phos, **(B)** EC-MSA, **(C)** EC-domestic **(D)** EC-background.

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. 15, 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. 15, left and middle panels). Back-trajectories for air masses arriving at 100 and 200 m above ground level were also calculated yielding similar results. It may be possible that these particles are emitted by ships in the Atlantic Ocean, however no tracers for residual fuel oil were observed, indicating that if ships emit these particles they must arise from the combustion of distillate fuel (Ault et al., 2010). While it seems unlikely that many 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 O_3, CO, NO_y and VOCs originating in North America has been previously reported (Jennings et al., 1996; Forster et al., 2001; Stohl et al., 2003; Singh et al., 2006).

3.2.9 ECOC and oligomer

The ECOC class is characterised by hydrocarbon fragment ions, sulfate and although less obvious in Fig. 13 due to their relatively low signals, peaks are also consistently observed for ammonium and oxidised organic carbon (*m/z* 43, $[C_2H_3O]^+$). This class was previously tentatively identified by Healy et al. (2009) as transported ship exhaust particles

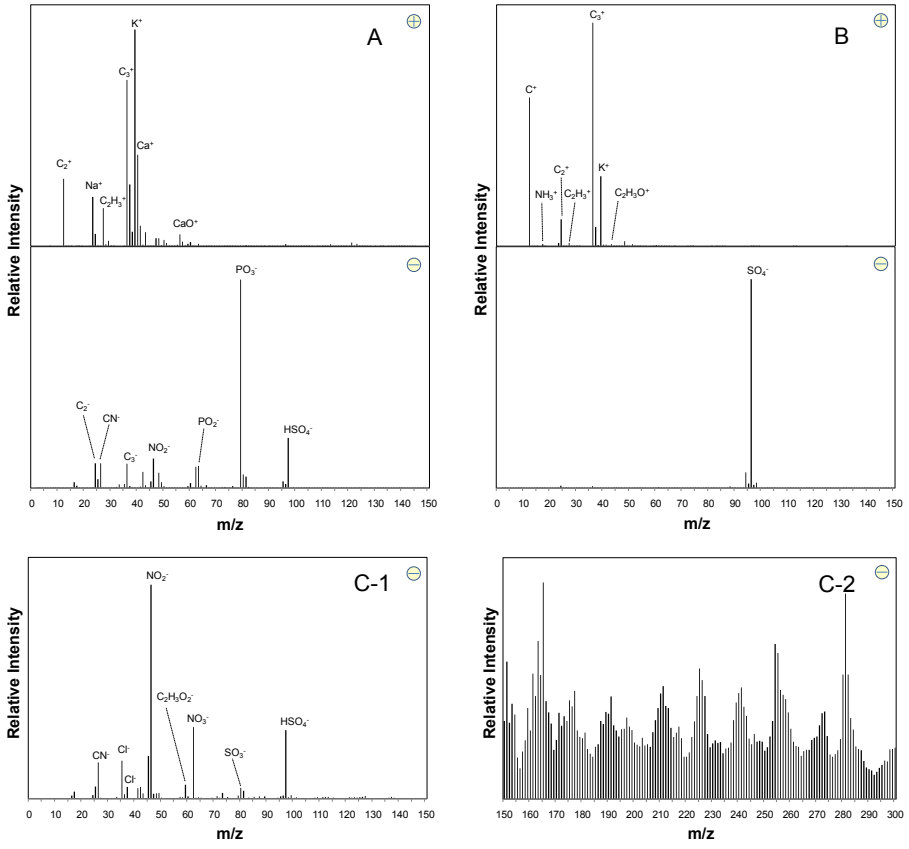


Fig. 13. Average dual ion mass spectra of ATOFMS particle classes; **(A)** EC-oil, **(B)** ECOC, and average negative ion mass spectra for (C-1) Oligomer (*m/z* 0–150) and (C-2) Oligomer (*m/z* 150–300).

due to their similarity to particles detected in San Diego using ATOFMS (Ault et al., 2009). However, the absence of any useful marker ions coupled with a lack of dependence on time of day or wind direction suggests multiple sources may emit these particles locally. PMF helps to resolve the sources of this class, as outlined below. 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).

The Oligomer class exhibits a very similar diurnal variation to the Coal, Peat and Wood combustion classes (Fig. 11). Analogous to the aged domestic combustion classes, the highest particle numbers for this class are observed during low wind speed conditions. Oligomer particle mass spectra exhibit little or no signal for positive ions. When positive ion signals are present they correspond to carbon atomic ions, oxidised carbon fragment ions, sodium and potassium atomic ions, which are also associated with domestic combustion. Negative ions are consistently observed for oxidised organic carbon, carbon-nitrogen adducts, chloride, nitrate and sulfate (Fig. 13). Higher mass negative ion signals are also observed up to *m/z* −400, but at much lower relative intensities (Fig. 13). ATOFMS particle mass spectra containing similar high mass negative ion signals have been identified as oligomer-containing, both in simulation chamber experiments and in ambient datasets (Gross et al., 2006; Denkenberger et al., 2007). In the latter study, several different aged

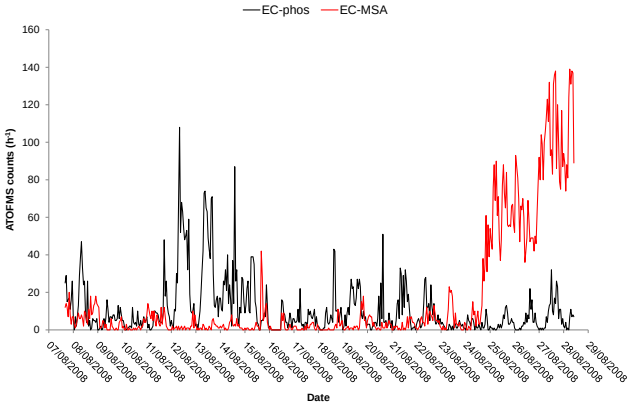


Fig. 14. Hourly integrated particle counts for EC-phos and EC-MSA particles for 7–28 August 2008.

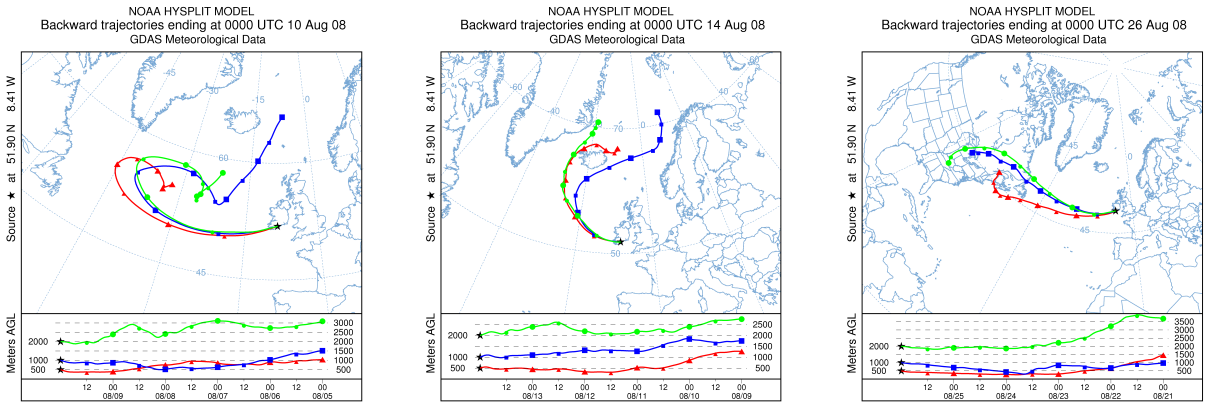


Fig. 15. 5 day back-trajectories for air masses arriving at Cork Harbour at 00:00 on 10 (left), 14 (middle) and 26 August 2008 (right).

particle types were found to contain oligomers, including vanadium-rich, amine-rich, organic carbon, and internally mixed organic/elemental carbon particles. Biomass burning particles did not contain any oligomeric species in that case. Ions that are typically used to identify significantly aged ambient particles by ATOFMS include m/z −125 and m/z −195, corresponding to $[H(NO_3)_2]^-$ and $[H_2SO_4HSO_4]^-$ respectively (Moffet et al., 2008; Denkenberger et al., 2007). These ions are absent for the Oligomer class identified in this work, suggesting that these particles may be relatively fresh compared to those observed by Denkenberger et al. (2007). 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. (2007), 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).

3.3 Source apportionment

PMF analysis was performed using the ATOFMS particle classes and quantitative EC/OC, sulfate, particle number and $PM_{2.5}$ data. Uncertainties were estimated as described above, but some data points were given higher uncertainty values based on assessment of their temporal trends in the context of all variables. The uncertainties for the following data points were increased significantly (to a value of 100); EC-oil on 21 August 2008 at 22:00 and 23:00 and EC-domestic on 21 August 2008 at 08:00. This is an increase of a factor of 50 compared to the average uncertainty for these two variables and 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). Six-, seven- and eight-factor solutions were explored. The six-factor solution appears to be the most appropriate to describe the data as no useful information is gained by further increasing the number of factors. The estimated contributions of each factor to the measured $PM_{2.5}$ mass and each variable are given in Table 2. Identification of further independent factors by PMF is dependent on having appropriate 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 is satisfactorily explained by the existing factors.

3.3.1 Traffic

The Traffic factor makes the largest contribution to ambient $PM_{2.5}$ mass (23%) and also 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. 10 and 12). 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

Table 2. Percentage variable contributions to the six factor PMF model and estimated percentage contribution of each factor to the measured ambient $PM_{2.5}$ mass. * Mobility diameter range 20–600 nm.

	Traffic	Marine	Long-range	Various combustion	Domestic combustion	Shipping
Quantitative measurements						
OC mass	20.65	19.93	18.05	16.16	20.90	4.31
EC mass	43.27	4.58	10.73	18.35	19.52	3.55
Sulfate mass	8.84	23.41	15.28	39.84	10.50	2.14
Particle number*	41.81	6.42	6.77	13.08	14.00	17.91
ATOFMS classes						
Coal	4.78	2.87	7.32	29.84	51.73	3.45
Peat	3.29	2.33	3.17	4.96	84.26	1.98
Wood	11.39	13.17	6.09	5.28	62.96	1.10
Sea salt	1.32	86.14	9.70	1.72	0.15	0.97
Shipping	0	0	0	0	0	100
Ca-traffic	82.76	4.42	8.47	0	0	4.35
EC-traffic	58.84	0.91	2.74	6.07	25.46	5.97
EC-phos	81.85	0	6.10	2.64	9.21	0.20
EC-MSA	0.83	5.92	89.89	3.04	0.31	0
EC-domestic	0	0	1.97	0	90.56	7.47
EC-background	27.57	1.35	11.45	35.38	17.79	6.47
EC-oil	51.98	0.64	0	23.70	23.67	0
ECOC	0	0	30.57	69.06	0	0.37
Oligomer	0.17	14.71	0	8.01	76.19	0.91
$PM_{2.5}$	22.92	13.68	12.68	10.68	4.87	1.49

using the methodology described. However, the PMF analysis enables this limitation to be observed, highlighting the value of the combined use of single particle mass spectrometry and PMF. 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; Dreyfus et al., 2009).

3.3.2 Marine

The Marine factor makes the largest contribution 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 $PM_{2.5}$ 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. 10). 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 at the same site in Cork Harbour using both principal component analysis (PCA) and PMF on semi-continuous data but without ATOFMS particle speciation (Hellebust et al., 2010). That study utilised measurements of NO, NO_2, O_3, SO_2, EC/OC, SO_4^{2-} 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 to the measured $PM_{2.5}$ mass in this work is lower, as expected considering the season and introduction of three new factors (Table 2). This 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.

3.3.3 Long-range transport

The Long-range transport factor was not resolved in the previous Cork Harbour study, due to the absence of ATOFMS mass spectral data (Hellebust et al., 2010). A very high contribution to the EC-MSA class was observed for this factor

indicating that it represents PM that has undergone transport through a marine environment. Contributions of 18%, 11% and 15% to OC, EC and sulfate mass respectively were observed. Although this regional episode only persisted for 4 days out of the total measurement period of 21 days it is estimated to contribute 13% to the $PM_{2.5}$ mass measured over the entire campaign. However, a considerable fraction of this mass is expected to be due to sea salt. This factor also accounts for 10% and 31% of the contribution to the Sea salt and ECOC ATOFMS classes, respectively.

3.3.4 Various combustion

The Various combustion factor exhibits contributions of 16%, 18% and 40% to OC, EC and sulfate mass, respectively. This factor is estimated to contribute 11% to the measured $PM_{2.5}$ mass. A power generation facility lies to the southeast of the sampling site, directly across the harbour, which burns diesel oil during peak times. A factor for power generation has been associated with this facility in the previous study performed at the same site (Hellebust et al., 2010). In that case, the factor was characterised by contributions to sulfate and OC, but not EC, consistent with high temperature combustion of fossil fuels. However, the dataset used spanned an entire year, and wind was often observed from the southeast. In this work, very few instances of southeasterly wind were observed (Fig. 1). Thus, the power generation facility is expected to influence $PM_{2.5}$ mass to a much lesser extent during this field study. Interestingly, a very high contribution to the ECOC particle class is observed (69%). This ATOFMS class exhibits signatures for internally mixed organic carbon and sulfate, particle phase species that could arise from high temperature fossil fuel combustion (Fig. 13). However, EC mass and the ATOFMS classes EC-oil, Coal and EC-background which also have contributions from this factor cannot be explained by this source. Thus it appears that this factor is influenced by contributions from other combustion sources.

3.3.5 Domestic solid fuel combustion

This factor is characterised by contributions of 52%, 84% and 63% to the Coal, Peat and Wood ATOFMS classes respectively. The lower values for Coal and Wood suggests that other sources are producing particles with mass spectra similar to those generated by domestic coal and wood combustion. Peat spectra are sufficiently unique to be almost exclusively attributed to domestic combustion. High contributions to the EC-domestic and Oligomer particle classes are also observed (91% and 76% respectively). This provides further support to indicate that oligomers are present in relatively fresh domestic combustion particles. This factor contributes 21% and 20% to the organic and elemental carbon measured, and is estimated to contribute 5% to the measured $PM_{2.5}$ mass.

3.3.6 Shipping

The shipping factor identified in this work was not identified in the previous study in Cork Harbour, due to the absence of complementary ATOFMS data in that case (Hellebust et al., 2010). 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 oil 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 include 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. It is important to note 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, 2010). A recent study involving PMF of trace metal and EC/OC data estimates that the contribution of shipping to $PM_{2.5}$ mass concentrations in Melilla, Spain is 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 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; Marmer et al., 2009; Viana et al., 2009; Pey et al., 2010), highlighting the need for corresponding source apportionment of PM in locations impacted by this source. Thus, knowledge of the relative contribution of fresh 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).

4 Conclusions

The contribution of various local and regional sources to ambient levels of $PM_{2.5}$ in Cork Harbour have been estimated using positive matrix factorisation and the identified sources are estimated to account for 66% of the measured $PM_{2.5}$ mass. The combination of pre-clustered ATOFMS classes with PMF allows for the identification of more sources than previous real-time monitoring or traditional off-line chemical analysis studies in Cork Harbour. The uptake of nitrate by domestic combustion particles was enhanced at night during low wind speed events, with heterogeneous reaction of nitric acid with potassium chloride also playing a role in the case of wood-burning particles. One class of carbonaceous particles containing methanesulfonic acid, a tracer for marine biological activity, is attributed to long range transport over the Atlantic Ocean, possibly originating in North America, although this source is not expected to have a significant impact upon air quality in Ireland. While local vehicular traffic was the largest source of ambient $PM_{2.5}$ mass in Cork Harbour during the sampling period, shipping traffic contributed significantly to ambient particle number concentrations (18%). Considering that fresh ship exhaust particles reside predominantly in the ultrafine mode and contain polycyclic aromatic hydrocarbons and transition metals with known toxicological effects, this source may have implications for human health in the area (Lippmann et al., 2006; Peltier et al., 2008; Murphy et al., 2009; Healy et al., 2009; Sodeau et al., 2009).

Acknowledgements. The authors would like to acknowledge the Port of Cork for providing a suitable sampling site and Darius Ceburnis (National University of Ireland Galway) for useful discussions regarding intercontinental transport. This research has been funded by the Higher Education Authority, Ireland under PRTLI cycle IV, the Irish Environmental Protection Agency (STRIVE programme, 2006-EH-MS-49, 2007-PhD-EH6 and BIOCHEA) and Science Foundation Ireland (07/RFP/CHEF520). Finally, the authors would also like to thank the anonymous reviewers for their constructive input which helped to improve the quality of the final version of this manuscript.

Edited by: N. Riemer

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