Effects of anthropogenic activities on the molecular composition of urban organic aerosols: an ultrahigh resolution mass spectrometry study

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Abstract

The identification of the organic composition of atmospheric aerosols is necessary to develop effective air pollution mitigation strategies. However, the majority of the organic aerosol mass is poorly characterized and its detailed analysis is a major analytical challenge. In this study, we applied state-of-the-art direct infusion nano-electrospray (nanoESI) ultrahigh resolution mass spectrometry (UHR-MS) and liquid chromatography ESI Quadrupole Time-of-Flight (Q-TOF) MS for the analysis of the organic fraction of fine particulate matter ($PM_{2.5}$) from an urban location in Cork, Ireland. Comprehensive mass spectral data evaluation approaches (e.g., Kendrick Mass Defect and Van Krevelen) were used to identify compound classes and mass distributions of the detected species. Up to 850 elemental formulae were identified in negative mode nanoESI-UHR-MS. Nitrogen and/or sulfur containing organic species contributed up to 40% of the total identified formulae and exhibited strong diurnal variations suggesting the importance of night-time NO_3 chemistry at the site. The presence of a large number of oxidised aromatic and nitroaromatic compounds in the samples indicated a strong anthropogenic influence, i.e., from traffic emissions and burning of domestic solid fuel (DSF) material. Most of the identified biogenic secondary organic aerosol (SOA) compounds were later-generation nitrogen- and sulfur -containing products, indicating that SOA composition is strongly affected by anthropogenic oxidants such as NO_x and SO_2. Unsaturated and saturated C_{12}-C_{20} fatty acids were found to be most abundant homologs with composition reflecting primary marine origin. The results of this work demonstrate that the studied site is a very complex environment affected by a variety of anthropogenic activities and natural sources.

Introduction

Particulate matter (PM), also referred as atmospheric aerosols, is linked to air quality and climate. A significant fraction of PM is associated with organic carbon (OC) which can contribute up to 90% of the total aerosol mass in certain locations (Kanakidou et al., 2005). Organic aerosols can either be emitted directly (primary organic aerosol, POA) or formed through gas-to-particle conversion processes or oxidation of volatile organic compounds (VOCs) within the atmosphere (secondary organic aerosol, SOA). Various sources contribute to formation of PM and include anthropogenic sources such as use of diesel and petrol, burning of fossil fuel and biomass. Biogenic sources include VOCs emitted by vegetation. Urban environments provide very unique systems where both anthropogenic and biogenic emissions coexist resulting in the formation of extremely complex OA. For example, anthropogenic oxides of nitrogen (NO_x) are shown to react with a range of BVOCs causing high regional ozone concentrations (Chameides et al., 1988) as well as being responsible for formation of organonitrates, ON (e.g., Roberts, 1990; Day et al., 2010) and nitrooxy-organosulphates, NOS (Surratt et al., 2008) that are important SOA components.

The identification of organic composition of aerosols remains a major analytical challenge which results in a poor understanding of aerosol sources. But only a comprehensive knowledge of aerosol sources allows developing effective air pollution mitigation strategies. Considering that OA composed of thousands of organic compounds, which cover a wide range of polarities, volatilities and masses (Goldstein and Galbally, 2007), it is difficult to find a single analytical technique for their detailed chemical analysis at the molecular level. Conventional analytical methods based on gas chromatography (GC) and liquid chromatography (LC) mass spectrometry are very effective in the identification of specific marker compounds for certain aerosol sources such as biomass burning, vehicular and cooking contributions. However, these methods are not capable of resolving the highly complex mixtures with a wide variety of physico-chemical properties leading to a very large fraction of OC being unidentified. In a previous study at Cork harbour, Ireland, conducted during summer 2008 the detected marker compounds that are characteristic for domestic solid fuel burning, fungal spores and oxidation of isoprene and α- and β-pinene could only explain 20% of the OC (Kourtchev et al., 2011). Moreover, commonly used mass spectrometers, which are often used as detectors following chromatographic separation, do not have sufficient mass-resolving power to distinguish and differentiate all compounds present in the complex mixture of organic aerosol. Ultrahigh resolution mass spectrometry (UHRMS) methods have shown a great potential in solving this longstanding problem. UHRMS (i.e.,

Fourier transform ion cyclotron resonance MS and Orbitrap MS) have a mass resolution power that is at least one order of magnitude higher (~100 000) than conventional MS and thus, when coupled with soft ionisation techniques, can provide a detailed molecular composition of organic aerosol (Nizkorodov et al., 2011). Nano-electrospray (nanoESI) ionisation is a promising soft ionisation technique for the analysis of OA due to its high sensitivity toward a variety of analytes and low sample volume requirements (less than 5 μL are required for nanoESI analysis compared to at least 100 μL required by conventional ESI sources). In a direct infusion analysis of complex organic mixtures with conventional ESI sources the competition for ion formation, i.e., matrix effects, is one of the primary problems. The significantly lower flow rates employed by nanoESI decrease the droplet size and increase the charge concentration on the droplet resulting in less competition for ion formation and lower ion suppression (Love et al., 2011).

The objective of the current study is to apply nanoESI UHRMS to determine the molecular composition of urban $PM_{2.5}$ (particles with ≤2.5μm). Aerosol samples were collected at the industrial site in Cork Ireland during summer with the aim to obtain aerosol particles of mixed biogenic and anthropogenic origin. Considering that direct infusion analysis is a qualitative technique, aerosol samples were additionally analysed by LC - ESI Quadrupole Time-of-Flight (Q-TOF) MS for the NOS and organosulphates (OS) that reflect emissions from mixed sources. The results clearly demonstrate that the overall composition of OA is dominated by anthropogenic sources such as traffic and biomass burning and that the biogenic OA is significantly affected by anthropogenic oxidants (e.g., NO_x and SO_2).

Methodology

Ambient samples

Aerosol samples were collected at the Industrial Estate and Docks, Cork, Ireland (51°54′5 N, 8°24′38 W). A detailed description of the site is given elsewhere (Healy et al., 2010; Kourtchev et al., 2011). Briefly, the site is located approximately 3 km east of Cork city centre with a population of about 120,000. The site is located near a shipping berth, a main road and residential areas. The vegetation that surrounds the site manly consists of shrubs and native deciduous trees.

$PM_{2.5}$ aerosol samples were collected on quartz fiber filters (Pallflex Tissuquartz 2500QAT-UP, 150 mm diameter, preheated for 24 h at 650°C) using a High Volume (Digitel DHA-80, Switzerland) sampler with a flow rate of 500 L min^{-1}. In total 14 samples were collected during 3-19 September 2011. Considering relatively wet and cloudy weather prevailing

during the sampling period only five separate day and night samples were collected during 3-6 September, 2011. The remaining samples were collected at 24 hour (6 - 11 September, 2011) and 48 hour resolution (11 - 19 September, 2011) to enable sufficient collection of aerosol mass required for LC/MS analysis. The corresponding sampling collection time and dates are shown in Table S1.

Aerosol sample analysis

All ambient filters were analysed for organic carbon (OC) and elemental carbon (EC) using a thermal-optical transmission (TOT) technique (Birch and Cary, 1996).

For the UHRMS analysis, aerosol samples were extracted as described elsewhere (Kourtchev et al., 2013a). For each sample, a part of the quartz fibre filter (6–30 cm^2), depending on OC or total aerosol loading, was extracted three times with 5 mL of methanol (Optima® grade, Fisher Scientific) under ultrasonic agitation for 30 min in ice cold water. The three extracts were combined, filtered through a 0.2 μm ISO-Disc^{TM} PTFE filter (Supelco, Bellefonte, PA, USA) and reduced by volume to approximately 200 µL under a gentle stream of nitrogen. The final extracts were analysed using an ultrahigh resolution LTQ Orbitrap Velos mass spectrometer (Thermo Fisher, Bremen, Germany) equipped with a TriVersa Nanomate robotic nanoflow chip-based ESI source (Advion Biosciences, Ithaca NY, USA). The Orbitrap MS instrument calibration, settings and mass spectral data interpretation are described in the Supporting Information (SI). Double bond equivalent (DBE) for each individual formula was calculated using Xcalibur 2.1 (Thermo Fisher Scientific, USA) software. All molar ratios, DBE factors and chemical formulae presented in this paper refer to neutral molecules.

For LC/MS analysis, a part (20 cm^2) of the filter was spiked with internal recovery standard (0.6 µg camphorsulfonic acid). Aerosol samples were extracted in acetonitrile (grade) in a cooled ultrasonic bath for 20 minutes. Extracts were evaporated to dryness and reconstituted in 200 µL of 0.1 % acetic acid and 3 % acetonitrile in water. Sample extracts were analysed using a Dionex Ultimate 3000 HPLC system coupled through an ESI inlet to a Q-TOF mass spectrometer (microTOFq) (Bruker Daltonics GmbH, Bremen, Germany). The ESI-QTOF operating conditions are detailed in the SI.

Meteorological data

The meteorological data was obtained from the Cork Airport monitoring station. During the sampling period the wind was predominantly from west-southwesterly direction (Fig 1). The

period was accompanied by light/gentle (wind speed >2 m s^{-2}) and strong wind (>6 m s^{-2}) (Fig 1c) with the exception of two episodes corresponding to samples from 3 September and 13-15 September, which were characterised by very calm wind conditions (≤ 2 m s^{-2}) (Fig 1a and b).

The average air temperature and relative humidity were 12.5±2.0 ^{0}C and 90.2±9.5%, respectively. The whole sampling period, with exception of 3 September and 13-15 September 2011, was accompanied by at least light precipitation.

Results and discussion

High resolution nanoESI mass spectra of a day- and night- sample collected on 3 September and 4 September respectively are shown in Fig. 2. Throughout the sampling period very high variability between the molecular compositions was observed; however, despite this, all mass spectra appear to be mainly composed of compounds with molecular weight (MW) below 400Da. Although ions above 400 Da were observed in all samples up to the measured 650 Da range, their maximum contribution to the total number of formulae was less than 7%. The majorities of the ions with masses above 300 Da were nitrogen and/or sulfur containing species or oxidised aromatic compounds as described below. Depending on the sample, 271-849 elemental formulae were identified and included four subgroups: CHO, CHOS, CHON and CHONS. CHO was the most abundant subgroup in all samples (average 59.4±3.9% of the total formulae), followed by CHON (21.8±3.6%), CHOS (13.5±3.6%), and CHONS (5.2±2.4%). The highest number of molecular formulae (up to about 850) was observed during 3 September, when the wind speed fell below 2 m s^{-1} (Fig. 1a). Higher wind speeds were generally associated with greater dilution of aerosol as a larger volume of air passes over local emission sources.

Although only 5 out of 14 samples were collected during separate day and night periods, we could clearly observe an increase in the ratio of molecular formulae containing CHON and CHONS to the total number of peaks in night time samples (average 16% and 8%, respectively) compared to the day time samples. This difference is also apparent in the mass spectra shown in Figure 2. Generally, ON are formed in polluted air during the day through reaction with NO and at night through NO_3 radical-initiated reactions with alkenes (Day et al., 2010). The increased ratio of ON molecules during the night might indicate the importance of NO_3 chemistry at the sampling site or more pronounced partitioning into the particle phase. Similar diurnal trend for nitrogen containing compounds was observed for the aerosol samples collected at Bakersfield, USA (O'Brien et al., 2013). It should be noted,

however, that a significantly higher fraction of nitrogen containing compounds (up to 53%, by number) was observed in the latter study. The differences could be related to specific emissions of gas phase ammonia at the Bakersfield site, which is a region known for substantial agricultural livestock emissions. In this respect, O'Brien et al. (2013) suggested that about 50% of their nitrogen containing organic compounds could have been formed through reactions of gaseous ammonia with SOA components. The increased fraction of OS during the night in the Cork samples could be explained by enhanced gas-to-particle partitioning at the cooler night-time temperatures. It has been suggested that some of the volatile species (e.g., pinanediol nitrates) need cooler temperatures to partition to the particle phase where they are subsequently sulphated (e.g., Surratt et al., 2008).

The average elemental ratios for molecules containing CHO compared to the total number of formulas showed rather low variation throughout the sampling period with 0.39±0.04 and 1.28±0.09 (mean value ± standard deviation) for O/C and H/C, respectively. These values are comparable to average O/C obtained using UHRMS from mixed urban-rural aerosol from Bakersfield, USA: 0.33 and 0.37 during a day and night, respectively (O'Brien et al., 2013). However, higher values were reported for urban aerosol from Cambridge, UK: 0.55-0.6 (Rincón et al., 2012) and boreal forest aerosol from Hyytiälä, Finland: 0.52 (Kourtchev et al., 2013a). Generally, higher O/C values are given for SOA generated in laboratory experiments from BVOCs, e.g., α-pinene, 0.42-0.55 (Putman et al., 2012), limonene, 0.5-0.6 (Kundu et al., 2012), photo-oxidation of isoprene under low-NO_x conditions, 0.54 (Nguyen et al., 2011) and BVOC mixture containing α-, β-pinene, Δ_3-carene and isoprene, 0.58 (Kourtchev et al., 2013b).

Oxidised aromatics

The Van Krevelen (VK) diagram, which shows H/C and O/C ratios for each formula in a sample, can be used to describe the overall composition or evolution of organic mixtures (Van Krevelen, 1993; Nizkorodov et al., 2011). Figure 3a shows a VK diagram for a representative sample collected on 4 September 2011. It can be clearly seen from Figure 3a that the majority of the CHO molecules in these samples have O/C<0.5 and a large range of H/C (0.5-2.0). While molecules with high H/C ratios (≥1.5) and low O/C ratios (≤0.5) (area A in Fig. 4) are generally associated with aliphatic compounds, molecules with H/C ratios (≤1.0) and O/C ratios (≤0.5) (area B in Fig. 3) typically belong to oxidised aromatic hydrocarbons (Mazzoleni et al., 2012). In addition to oxidised aromatic hydrocarbons, the

low O/C and H/C cluster (area B) include a number N and S containing molecules. Such prevalence in the aerosol samples from Cork suggests very strong anthropogenic influence at the sampling site. In contrast, only a few ions were present in the aromatic region in aerosol from the pristine boreal forest site Hyytiälä, Finland (Fig. 3b) (Kourtchev et al., 2013a). Moreover, all of the compounds in area B in the Hyytiälä sample correspond to CHON molecules. Although the sampling site at Cork is located only 400m from the shipping berth, it is highly unlikely that the shipping emissions are responsible for the presence of a large number of oxidised aromatic hydrocarbons. A previous study conducted at this site during summer 2008 using an Aerosol Time-of-Flight (ATOF) MS indicated that shipping type aerosol particles were observed in short, sharp events and contributed only 1.5% to ambient $PM_{2.5}$ mass (Healy et al., 2010). On the other hand, the same study suggested that vehicular traffic is the largest source of ambient $PM_{2.5}$ mass in Cork Harbour during summer time. The presence of a very large number of species with high double bond equivalents (DBE) (≥6) (Fig. 4), which shows the degree of unsaturation of a molecule, supports the inferences derived from the Van Krevelen diagram (Fig. 3). It is worth mentioning that the compounds associated with high DBE were not observed in the pristine boreal aerosol at Hyytiälä associated with the clean Atlantic air masses (Fig 4, black circles) (Kourtchev et al., 2013a). Molecular formulae with elemental ratios reflective of SOA (Wozniak et al., 2008) (area C, Figure 3a and b) were present in most of the samples. Their contribution to the total number of formulae was found to be the highest during the days with the lowest wind speed (below 2 m s^{-1}, 3 September and 13-15 September) and can possibly be explained by a lower dilution of the aerosol.

Tracers for marine sources

The molecular composition of the aerosol samples was examined using Kendrick Mass (KM) analysis, which is used for the identification of homologous series of compounds differing only by the number of a specific base unit (e.g., a CH_2, CHO, groups). Kendrick mass of the CH_2 unit is calculated by re-normalising the exact IUPAC mass (14.01565) of CH_2 to 14.00000. The Kendrick Mass Defect (KMD) is calculated from the difference between the nominal mass of the molecule and the exact KM (Hughley et al., 2001). Depending on the sampling day, 95 to 97% of all peaks belong to CH_2 'homologous' series with >2 members. Figure 5 shows a KMD plot for the sample from 3 September 2011 (that has the highest influence from local emissions as indicated by the low wind speed) where KMD is expressed as a function of nominal KM. In this graph, all compounds with the same

base formula but different number of CH_2 groups have the same KMD value and thus appear on a horizontal line. Therefore, the identification of molecular composition of one compound in the homologous series allows elucidation of the remaining peaks in the series (Nizkorodov et al., 2011). Considering the chemical complexity of the aerosol samples, the identification of all series would be very impractical and speculative; therefore, in this study we concentrated on the series that exhibited temporal variations or contained ions with very high relative intensities (R.A >50%). Although due to competitive ionisation in the ESI direct infusion analysis of the aerosol samples with a complex matrix the ion intensities do not directly reflect the concentration of the molecules in the sample, it has been suggested that semi-qualitative information on the relative concentrations between samples can still be obtained (O'Brien et al., 2013). The distinguishably largest homologous series present in the samples begins with a KM of 101.9541 corresponding to $C_5H_{10}O_2$, and is possibly associated with a short chain unsaturated acid. This series included lauric acid (as identified by MS^2 analysis), which exhibited very high ion intensity (up to 60% R.A.) during most of the sampling period. Fatty acids, including lauric acid, can have multiple sources, which include marine biota (e.g., Tervahattu et al., 2002), plant waxes (e.g., Simoneit et al., 1988), and combustion of biomass material (e.g., Oros and Simoneit, 2001). The carbon number prevalence (even or odd) of the fatty acids is often used for aerosol source identification. During the sampling period, fatty acids exhibited strong even carbon number prevalence, which indicates the importance of marine sources but also included molecules with an odd carbon chain indicating their mixed origin. The site is located next to the river Lee, Lough Mahon and only 15 km from the Celtic Sea, where phytoplankton and algae are very abundant. Phytoplankton and algae are known to be an important source of fatty acids (e.g., Jeffries, 1970). The annual phytoplankton bloom in the Celtic Sea typically occurs from April to October (ICES, 2008), which coincides with the aerosol sampling period. Fatty acids can be emitted directly to the air or the dissolved material can be transferred to the air via bubble bursting processes in sea spray. In this respect, a fair amount of sea salt in ambient particles at the Cork harbour have been reported previously (Healy et al., 2010).

Biomass burning markers

N and/or S containing molecules had shorter homologous series compared to those associated with CHO species (Fig. 5). Similar observations were reported for urban aerosol from Cambridge, UK (Rincón et al., 2012) and boreal forest aerosol Hyytiälä, Finland (Kourtchev et al., 2013a). Rincón et al. (2012) suggested that atmospheric oxidation reactions

resulting in the incorporation of sulfur and nitrogen functional groups do not conserve homologous series but rather lead to a wide range of possible reaction products. The longest N containing series had 10 homologues beginning with $C_6H_5NO_3$. Based on the MS^2 analysis this molecule was tentatively identified as nitrophenol. Although nitrophenols can originate from various sources including decomposition of herbicides and insecticides and burning of coal and wood (Shafer and Schonherr, 1985) in urban environments primary motor vehicle emissions are believed to be their major source (e.g., Tremp et al., 1993). Nitrophenols (2-nitrophenol and 4-nitrophenol) have been previously observed in aerosol from urban locations e.g., Rome, Italy (Cecinato et al., 2005), Mainz, Germany (Zhang et al., 2010) and were mainly attributed to traffic emissions.

Another nitrogen containing series that is worth reporting included molecules with the following molecular formulae: $C_6H_5NO_4$, $C_7H_7NO_4$, $C_8H_9NO_4$, $C_9H_{11}NO_4$ and $C_{10}H_{13}NO_4$. These species were tentatively identified as nitroaromatic compounds (NACs), e.g., nitrocatechols, nitrophenols, nitroguaiacols and nitrosalicylic acids. NACs have been recently detected in aerosol samples from urban location, e.g., Ljubljana, Slovenia (Kitanovski et al., 2012) and rural environments e.g., Saxony, Germany (Iinuma et al., 2010), K-Puszta, Hungary (Claeys et al., 2012) and Hyytiälä, Finland (Kourtchev et al., 2013a) and were mainly attributed to biomass burning sources. The R.A. of these species showed a very high correlation between each other in all Cork samples (Fig. 6) supporting their common origin. Although NACs were observed throughout the whole sampling period, the highest intensities of these molecules (up to R.A. 50%) were observed during 3 September and 13-15 September, which coincided with the highest OC concentration, the lowest temperature and the lowest wind speed. This trend was also apparent in the Principal Component Analysis (PCA, for method details see SI), where NACs are found to be closely correlated to each other, moderately correlated to OC and EC and anticorrelated with temperature and wind speed (Fig. 7). A previous study of $PM_{2.5}$ aerosol in Cork harbor reported that biomass burning in particular, combustion of domestic solid fuel (DSF), i.e., peat, coal, wood and smokeless coal, is a substantial source of OC and $PM_{2.5}$ even during summer (Kourtchev et al., 2011; Healy et al., 2010).

The study by Kourtchev et al., (2011) used anhydrosugars, i.e., levoglucosan, mannosan, galactosan and 1,6-anhydro-*β*-*D*-glucofuranose as marker compounds to estimate the contribution of DSF burning. These anhydrosugars, structural isomers with a molecular formula $C_6H_{10}O_5$, were also observed in all examined samples at *m/z* 161.0456. Although, an ion at *m/z* 161.0456 exhibited the highest intensity (R.A. 20-25%) during 3 September

(sample TQ1) and 13-15 September (TQ12), it is only moderately correlated with the NACs as indicated in the bidimentional plane defined by the first two principal components of the PCA (Fig. 7). Competitive ionisation or ion suppression due to the presence of other matrix compounds could be a reason for these observations. Despite this, the fairly high abundance of the ion corresponding to the anhydrosugars with molecular formula $C_6H_{10}O_5$ suggests that DSF burning is a major source of aerosol in Cork harbor. Similarly to the NACs, the anhydrosugars ($C_6H_{10}O_5$) were moderately correlated to OC and EC and anticorrelated with temperature and wind speed (Fig. 7). In addition, the PCA clearly supports the unique composition of the two samples from 3 and 13-15 September as they form a cluster separate from all other samples.

Anthropogenic aging of biogenic SOA

Another very intensive ion (R.A. up to 85%) at *m/z* 294.0654 observed in almost all samples corresponded to a species with molecular formula $C_{10}H_{17}NSO_7$. This molecule has been previously identified as *α-/β*-pinene related NOS MW295 (Surratt et al., 2009; Gómez-González et al., 2011) and was observed in various sampling locations including a Belgian forest site at Brasschaat that is severely impacted by urban pollution (Gómez-González et al., 2011), rural background sites at Birkenes (Norway), Lille Valby (Denmark) and Vavihill (Sweden) (Yttri et al., 2011) and Hyytiälä (Finland) (Yttri et al., 2011; Kourtchev et al, 2013a). The OS and NOS are generally formed through heterogenous reactions of BVOCs involving acidic sulfur aerosol (Surratt et al., 2008), which is primarily derived from anthropogenic sources and therefore reflect anthropogenic influences at the sampling site. In general, N and S containing compounds have very high ionisation efficiencies, and thus the high abundance of the corresponding ions in the samples could be explained not only by relatively high concentration of the compound but also by their favorable ionisation. LC/MS analyses confirmed that the NOS MW295 was one of the major species in the Cork harbor samples. Depending on the sampling day the concentration of NOS MW295 as determined by LC/MS varied between 0.06 and 2.08 ng m^{-3} with its maximum concentration peaking at night-time. These values are comparable to concentration ranges (0.6-3.6 ng m^{-3}) for $PM_{2.5}$ aerosol from a Belgian forest site (Gómez-González et al., 2011). The later study also observed night-time concentration increase of the NOS MW295 and linked it to enhanced gas-to-particle partitioning at the cooler night-time temperatures or formation through night-time chemistry with NO_x. 3-methyl-1,2,3-butanetricarboxylic (3-MBTCA), another *α*- and *β*-pinene oxidation product (Szmigieslki et al., 2007), was detected in all studied samples in the

concentration range 0.03-0.28 ng m^{-3}. 3-MBTCA has been previously identified as an OH-initiated oxidation product of pinonic acid and was proposed as a suitable tracer for the chemical aging of biogenic secondary organic aerosol (SOA) by OH radicals (Müller et al., 2012).

Considering that increased concentration of α- and β-pinene derived NOS MW 295 was observed during the time when the wind speed was the lowest ($\leq$2 m s^{-1}) we can suggest that the BVOC precursor responsible for the formation of this compound was rapidly oxidised by the anthropohgenic oxidants (e.g., NOx). This is also confirmed by a presence of 3-MBTCA and absence of the first generation α - and β-pinene oxidation products (e.g., pinic acid and pinonic acid) in the samples. However, the lower air dilution during the days with the lowest wind speed could also be responsible for these observations.

Another important BVOC derived NOS MW297 with the molecular formula $C_9H_{15}NO_8S$ was detected in the Cork samples by both direct infusion UHRMS and LC/MS analyses. This molecule was previously identified as a limonene oxidation product (Surratt et al., 2008) and was detected in various rural background sites (Yttri et al., 2011). The observed concentrations of limonene derived NOS (0.2 ng m^{-3}) in Cork site was lower than those reported previously for rural background sites (0.5-1.5 ng m^{-3}) (Yttri et al., 2011). The difference can be explained by the type of vegetation and the density of the limonene emitting species in Cork.

Among the identified OS, the presence of $C_5H_{12}SO_7$ in the Cork samples is worth reporting as it is considered to be a tracer for isoprene, which is an important BVOC emitted by terrestrial vegetation. This tracer compound was previously identified as C_5 organosulphate MW 216 and was suggested to be derived from isoprene epoxydiol isomers (Surratt et al., 2010).

A complete list of OS and NOS detected by direct infusion nanoESI UHRMS in one sample associated with local emissions is shown in the Table S2. Although the alternatively applied LC/MS method was able to detect (above detection limit) only two OS and two NOS compared to (22-119 formulae) and (9-89 formulae), respectively identified by the direct infusion nanoESI UHRMS, it provides invaluable quantitative information on the contribution of specific OS and NOS in the aerosol mass.

Conclusions

In this study we applied direct infusion nanoESI UHR-MS and LC/ESI-(Q-TOF) MS for the analysis of the organic fraction of 14 summer $PM_{2.5}$ samples from an urban location in Cork, Ireland. Up to 850 elemental formulae were identified with direct infusion analysis. The most

predominant groups of identified compounds included molecules with CHO, CHON and CHOS. The occurrence and abundance of ions corresponding to nitrogen containing species (likely ON) exhibited very strong night-time prevalence suggesting importance of NO_3 chemistry at the site.

Van Krevelen and DBE distributions along with relatively low elemental O/C and H/C ratios indicated the presence of a large number of oxidised (poly-)aromatic compounds in the samples, suggesting that the site is strongly influenced by traffic emissions. The distinguishable homologous series in the KMD diagram contained saturated and unsaturated fatty acid characteristic for primary marine emissions. The longest nitrogen containing series included NACs, e.g., nitrocatechols, nitrophenols, nitroguaiacols and nitrosalicylic acids derived from burning of DSF material. Most of the biogenic secondary organic aerosol (SOA) compounds were found to later-generation SOA components such as NOS and OS. The absence of major 'fresh' biogenic SOA components, such as pinic and *cis*-pinonic acid, which are precursors for some of the identified OS and NOS, suggests a strong influence of anthropogenic pollutants such as NO_x and SO_2 at the site, which might have quickly further oxidised these first-generation SOA components. This conclusion is supported by the presence of 3-MBTCA, a tracer for the aged biogenic secondary SOA, which was present in all samples.

The results of this work demonstrate that the studied site is a very complex environment dominated by a variety of industrial and domestic activities. Primary and secondary natural sources of organic aerosol mass were also identified and it was suggested that anthropogenic gaseous oxidants efficiently and significantly affect the composition of biogenic SOA at this location resulting in a large number of nitrogen- and sulfur-containing organic compounds.

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Figures and captions:

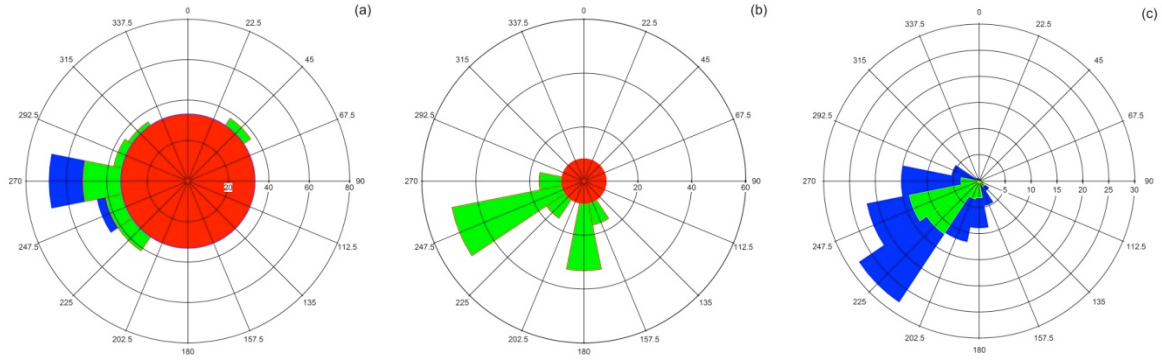


Figure 1. Wind roses for (a) 3 September, 2011; (b) 13-15 September, 2011 and (c) the rest of the sampling period for 4-13 September and 15-19 September, 2011. The colour represent the wind speed: blue > 6 m s^{-2} (strong wind); green >2 m s^{-2} (light/gentle wind) and red < 2 m s^{-2} (calm wind conditions).

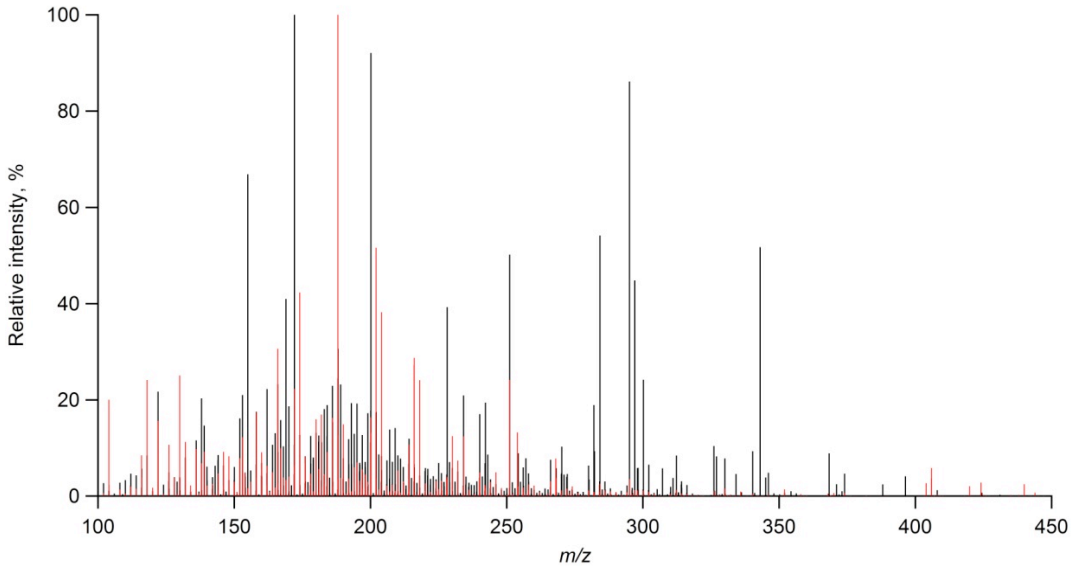
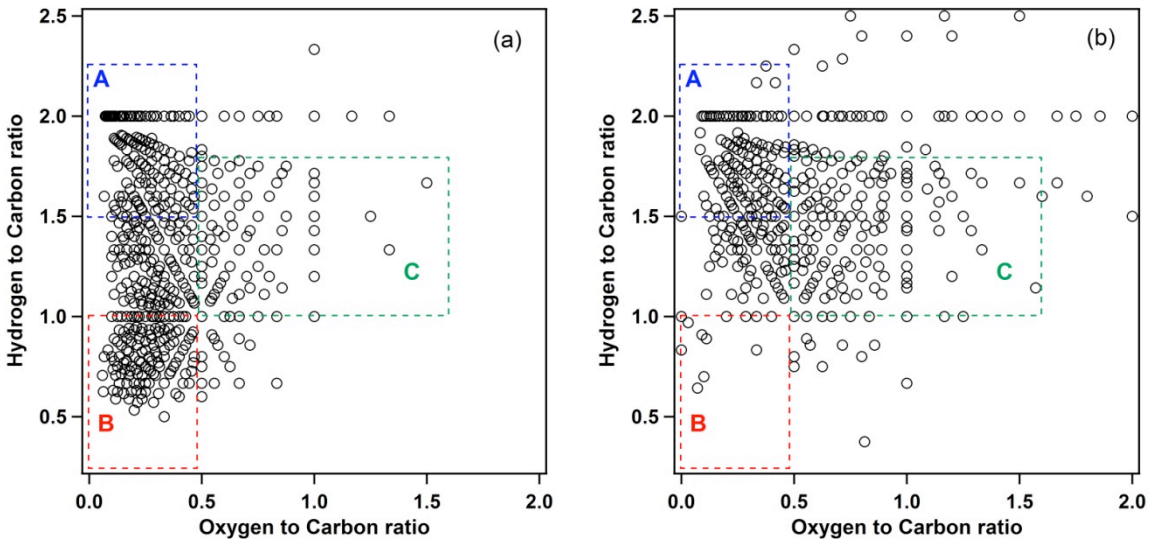


Figure 2. Direct infusion negative-nanoESI UHRMS blank corrected mass spectra obtained for the representative day (in red) and night (in black) organic aerosol samples from Cork, Ireland.



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552 Figure 3. Van Krevelen (VK) diagrams for all detected ions in the aerosol samples from (a)
553 an urban environment at Cork, Ireland, and (b) a remote boreal forest, Hyytiälä, Finland;
554 Areas 'A', 'B' and 'C' indicate differences in the number of ions tentatively attributed to
555 aliphatic, aromatic and secondary organic aerosol (SOA) species, respectively. All ions in
556 the area 'B' of the boreal forest sample correspond to CHON molecules. The corresponding
557 VK for the Hyytiälä's sample in Kourtchev et al. (2013a) only showed CHO and CHOS
558 molecules.

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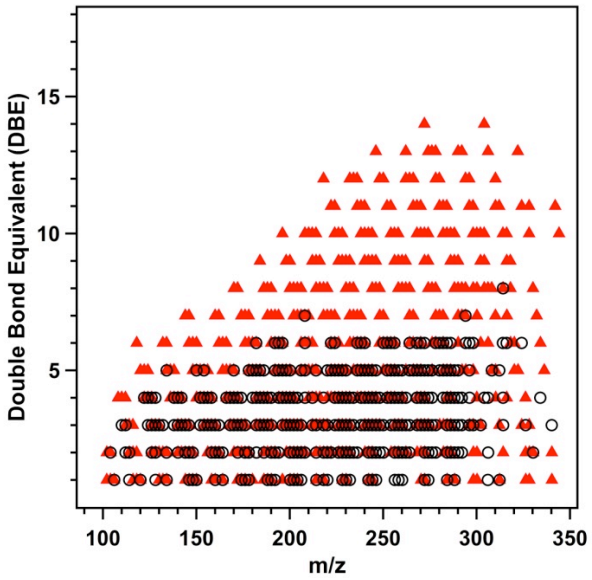
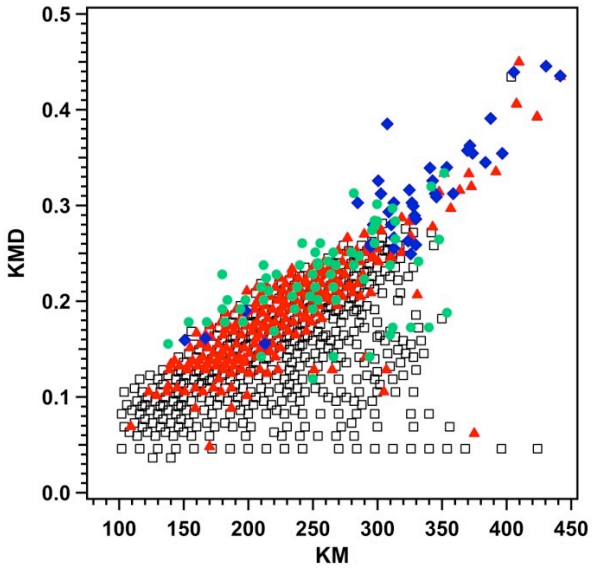


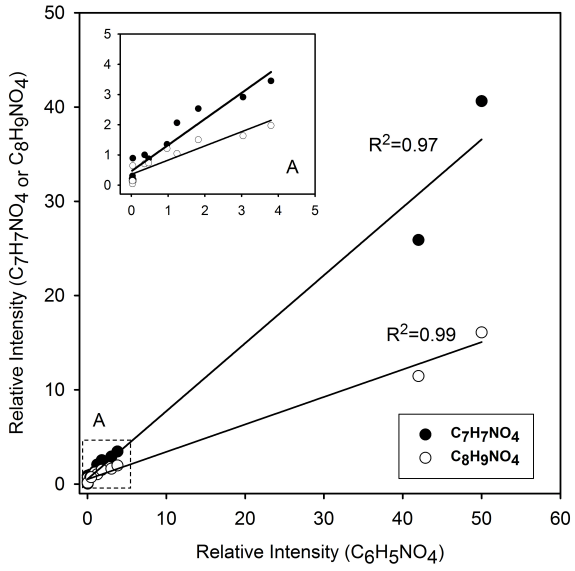
560

561 Figure 4. Double bond equivalents (DBE) vs. mass to charge ratio (*m/z*) for CHO molecules
562 in the samples associated with local emissions from an urban site in Cork, Ireland collected
563 on 3 September, 2011 (red triangles) and a boreal forest site at Hyytiälä, Finland, collected on
564 17 August 2011 (black circles).



565

566 Figure 5. CH_2-Kendrick mass defect (KMD) vs. nominal Kendrick mass (KM) for CHO
567 (black squares), CHON (red triangles), CHOS (green circles) and CHONS (blue diamonds)
568 species in the aerosol sample from Cork, Ireland, associated with local emissions (from 3
569 September, 2011).



570

571 Figure 6. Correlation of relative intensities (RA) for nitroaromatic compounds (NACs) during
572 the sampling period (3-17 September 2011) in Cork samples. The insert 'A' shows the strong
573 correlation of these species even at low RA.

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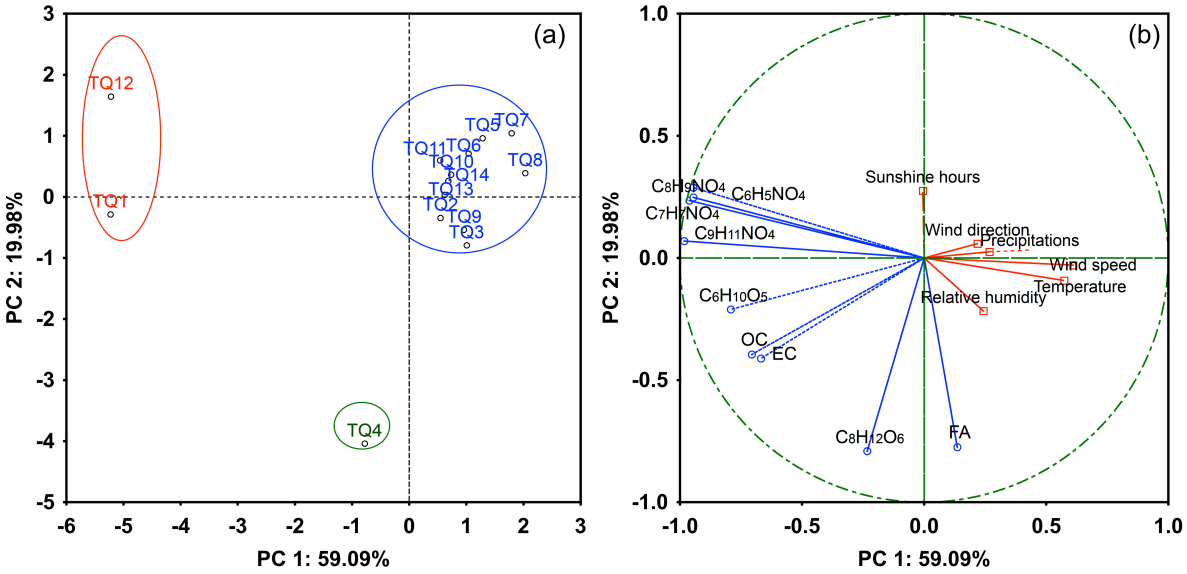

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577 Figure 7. Scores (a) and loadings (b) of the first two principal components obtained from the
578 principal components analysis and explaining the 79.07% of variance of the dataset. Red,
579 blue and green ellipses show three distinct clusters in the scores plot (a). Vectors in blue and
580 in red represent the active and supplementary variables in the loadings plot (b). Abbreviation
581 FA corresponds to the ratio of even to odd carbon number of the detected fatty acids.

582

583