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Distinct High Molecular Weight Organic Compound (HMW-OC) types in aerosol particles collected at a coastal urban site

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KEYWORDS

Oligomers, High Molecular Weight Organic Compounds, ATOFMS, sea salt, mixing state.

HIGHLIGHTS

- Single particle mass spectra are collected at an urban coastal site.
- Three different types of HMW-OC are characterized.
- A unique HMW-OC type internally mixed with sea salt is found.

ABSTRACT

Organic oligomers were discovered in laboratory-generated atmospheric aerosol over a decade ago. However, evidence for the presence of oligomers in ambient aerosols is scarce and mechanisms for their formation have yet to be fully elucidated. In this work, three unique aerosol particle types internally mixed with High molecular weight organic compounds (HMW-OC) species - likely oligomers - were detected in ambient air using single particle Aerosol Time-Of-Flight Mass Spectrometry (ATOFMS) in Cork (Ireland) during winter 2009. These particle types can be described as follows: (1) HMW-OCs rich in organic nitrogen - possibly containing nitrocatechols and nitroguaiacols - originating from primary emissions of biomass burning particles during evening times; (2) HMW-OCs internally mixed with nitric acid, occurring in stagnant conditions during night time; and (3) HMW-OCs internally mixed with sea salt, likely formed via photochemical reactions during day time. The study exemplifies the power of methodologies capable of monitoring the simultaneous formation of organic and inorganic particle-phase reaction products. Primary emissions and atmospheric aging of different types of HMW-OC contributes to aerosol with a range of acidity, hygroscopic and optical properties, which can have different impacts on climate and health.

1. INTRODUCTION

Atmospheric aerosols impact global and regional climate, air quality and human health (Seinfeld and Pandis, 2006). Aerosols are typically complex mixtures of organic and inorganic species; the chemical composition being determined by the type of formation processes as well as chemical alteration within the troposphere through homogeneous, heterogeneous and multiphase reactions. Fine mode atmospheric aerosols contain a substantial fraction of organic matter which is largely secondary in nature (Zhang et al., 2007; Jimenez et al., 2009). These secondary organic aerosols (SOA) are formed from atmospheric oxidation of volatile organic compounds (VOCs) and consists of a mixture of oxygenated organic species whose composition is dependent on the degree of processing of the aerosol in the atmosphere. The precise mechanisms of formation and evolution of SOA are still highly uncertain (Hallquist et al., 2009).

Oligomeric species have been identified as an important component of SOA in laboratory studies (Jang and Kamens, 2001, Jang et al., 2002, Kalberer et al., 2004). Oligomer formation in the particle phase has been attributed to a variety of chemical reaction pathways (Hallquist et al., 2009) including heterogeneous acid-catalysed reactions (Jang and Kamens, 2001, Jang et al., 2001; 2002), and aqueous chemistry within clouds (Lim et al., 2010). Although it has been found that the aqueous phase reactions of organic vapours can lead to higher molecular weight products than equivalent reactions in the gas phase, the role of the liquid phase of aerosols in SOA formation is still largely unknown (Beardsley et al., 2013). It is also important to note that oligomers in aerosols are not only formed via secondary mechanisms, but also include direct primary emissions from terrestrial, marine and biomass burning primary sources (Decesari et al., 2000, Reid et al., 2005). Detection and characterization of oligomeric species in aerosols is important as they are expected to significantly affect gas-particle partitioning, hygroscopic growth, particle reactivity, and health effects (Kanakidou et al., 2005). However, oligomers are not often clearly observed in ambient aerosols and there is uncertainty over the extent of their relevance under atmospheric conditions (Kourtchev et al., 2016). Denkenberger et al (2007) and Gross et al (2006) detected high molecular weight species thought to be oligomers in field and chamber measurements respectively using an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) but were not able to make detailed mechanistic inferences.

Sea salt (SS) is also a source of atmospheric aerosols, and can contribute up to 80% of particle levels in the air in coastal areas (Seinfeld and Pandis, 2006; Gant et al., 2015). Most SS aerosol particles are formed through interaction between the ocean surface and wind, resulting in breaking waves and bursting bubbles (Lewis and Schwartz, 2004). SS aerosols are the most abundant aerosols in the coastal atmosphere and thus act as pre-existing particulate matter for SOA formation. Unlike NaCl aerosols that have a clear phase transition, SS aerosols have a very low efflorescence relative humidity and have been shown to hold water at low RH. Therefore, SS aerosols act as a medium for aqueous phase reactions in marine environments. During transport through the atmosphere, SS particles commonly react with gases and other types of aerosol particles and in the process change composition. The composition and shape affect hygroscopicity and light scattering, both of which influence their climate impacts. For example, in anthropogenically influenced atmospheres, many SS particles become internally mixed with sulfate and nitrate (Gard et al., 1998; Adachi and Buseck, 2015). However, there is a large range of reactivities within sea salt aerosol particles (Ault et al., 2013a,b; 2014). Recently, Laskin et al. (2012a) reported substantial chemical reactivity of sea salt particles with secondary organics that has been largely overlooked in atmospheric aerosol chemistry. It was shown that that chloride components in sea salt particles may effectively react with organic acids releasing HCl gas to the atmosphere, leaving behind particles depleted in chloride and enriched in the corresponding organic salts. Other studies have also shown that, under atmospheric conditions, the presence of SS aerosols significantly increased the SOA yields of aromatic hydrocarbons, compared to seedless conditions or the presence of pure NaCl seeds (Beardsley et al., 2013).

Due to the potential climatic impacts of atmospheric organic species, there has been growing interest in the effects of organics on the hygroscopicity and phase transition of inorganic aerosol. Despite great efforts devoted to understanding the hygroscopicity of mixed organic/inorganic aerosols, current knowledge of the interaction between organics and inorganics in mixed droplets at the molecular level is still very limited (Yu et al., 2011). Developing a better understanding of the factors controlling heterogeneous chemical reactions on the surface of atmospheric aerosols is challenging because the complex composition, structure and heterogeneous distribution of species make predicting the degree of reactivity of each particle difficult (Ault et al., 2013a,b; 2014). Bulk ensemble measurements provide valuable information, but the implicit assumption of internal mixing can lead to discrepancies between models and measurements because the average value may not accurately represent the aerosol population when multiple populations are present (Healy et al, 2014). The rates of heterogeneous reactions of trace gases with aerosol particles are complex functions of particle chemical composition, morphology, and phase state. Currently, the majority of model parameterizations of heterogeneous reaction kinetics focus on the population average of aerosol particle mass, assuming that individual particles have the same chemical composition as the average state (Ryder et al., 2014). There is, however, a lack of knowledge on the sources and formation mechanisms of oligomeric species.

In recent years aerosol mass spectrometry has become available as a powerful tool for the on-line chemical characterization of individual aerosol particles (Murphy, 2007) or small aerosol ensembles (Canagaratna et al., 2007). Measurement of particle composition by on-line mass spectrometry has developed extensively over the last two decades and is currently the fastest growing area of atmospheric aerosol research (Laskin et al., 2012b). The importance of oligomeric species in ambient organic aerosol has not received sufficient attention because evidence of such compounds in the atmosphere is very scarce (Denkenberger et al., 2007; Wang et al., 2010, Duan et al., 2016). In this work we have identified and characterized three unique types of HMW-OCs particles in ambient aerosol at an urban coastal location in Cork, Ireland. Two different particle mass spectrometers were deployed: an Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) (Gard et al., 1997) and an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS)

(DeCarlo et al., 2006). The ATOFMS in particular provides valuable information on both the composition and internal mixing state of single particles containing the HMW-OCs species, which in turn helps to determine their source and extent of chemical processing in the atmosphere. Small variations in the particle mixing state results in a characteristic mass spectra. As a result, a number of atmospheric processes and aerosol sources can be monitored in real time. In this paper we discuss not only information on the mass spectra, but also diurnal trends for particle counts over a four week period for the three different types of oligomer aerosols identified.

2. MATERIAL AND METHODS

2.1 Location

The campaign took place from 1st to 22nd February 2009 (all times in this study are in local time - LT) at the Tivoli 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., 2009, Healy et al , 2010). Briefly, the site is located in the Port of Cork, approximately 3 km east of Cork city centre. Residential areas surround the site on all sides except the north and northeast.

2.2 On-line Aerosol Techniques

The ATOFMS (Model 3800-100, TSI, Inc.) was used to measure bipolar mass spectra of individual aerosol particles (Gard et al., 1997; Su et al., 2004). The ATOFMS collected about 1,350,000 single particle positive and negative mass spectra. The TSI ATOFMS dataset was imported into YAADA (Yet Another ATOFMS Data Analyzer) and single particle mass spectra were clustered with Adaptive Resonance Theory neural network, ART-2a (Song et al., 1999). The parameters used for ART-2a were: learning rate 0.05, vigilance factor 0.85, and iterations 20.

Similar clusters obtained by ART-2a were manually merged (Dall’Osto and Harrison, 2006) so that the total number of clusters describing the whole dataset was reduced.

The HR-ToF-AMS focuses particles in the size range 50-600 nm (efficiency 100%) onto a hot surface (about 600º C) using an aerodynamic lens assembly (DeCarlo et al., 2006). Non-refractory particle components flash-evaporate on the hot surface; the evolving vapour is electron impact (70 eV) ionized and the ions are transported into an orthogonal extraction ToF-MS for high-resolution mass analysis. Mass concentrations and size distributions of the aerosol species measured with the HR-ToF-AMS were calculated using the methods outlined by DeCarlo et al. (2006). Standard ToF-AMS data analysis software packages (SQUIRREL v1.49 and PIKA v1.08) were used.

2.3 Processing of Mass spectrometer data

The data generated by the two mass spectrometers has been processed, analysed and reported in detail in a previous publication (Dall'Osto et al. 2013). Briefly, Positive Matrix Factorization (PMF) was applied to the HR-ToF-AMS organic matrix and a five-factor solution was found, supported both mathematically and with external correlations with parallel gaseous, aerosol off-line and ATOFMS measurements. The AMS_PMF organic aerosol (OA) factors HOA (“hydrocarbon-like” OA), LV-OOA (“low volatility oxygenated” OA), BBOA (“biomass burning” OA), PCOA (“peat and coal” OA) and COA (“cooking” OA) comprised 20%, 19%, 23%, 21% and 18% of the total non-refractory organic mass, respectively. The ATOFMS dataset was reduced to 10 single particle types which accounted for around 97% of the detected particles. Based on composition, temporal profile and other factors, the clusters were attributed to the following source categories; domestic solid fuel combustion (~61%), secondary aerosols (~27%), traffic (~5%), sea salt (~3%) and shipping (~1%). A follow up study (Dall’Osto et al., 2014) characterized the fine PM component using factor analysis applied to the array of on-line and off-line aerosol measurements. Five aerosol sources were apportioned, three of primary origin (Traffic, domestic solid fuel burning or urban and regional origin, up to 61–70% of $PM_{2.5}$) and two mainly of secondary origin (secondary organic aerosol of urban and regional origin, up to 30–39% of $PM_{2.5}$). Overall, there are clear benefits from applying factor analysis to results obtained from multiple on line aerosol techniques (ATOFMS and AMS), allowing for better source apportionment (Dall´Osto et al., 2013; 2014). In the ATOFMS analysis performed here, we focussed on the remaining 2.7% (36,538 in number) of detected particles which were classified by ART-2a into three distinct classes. They can be described as predominantly organic particle types presenting a systematic High Molecular Weight (HMW) signal. Whilst these three particle types only represent about 3% of the whole ATOFMS dataset, we argue that these single particle mass spectra provide important new information on the sources and processes affecting oligomer formation in an urban area affected by anthropogenic primary sources (i.e. traffic, biomass burning), as well natural coastal sources (i.e. sea salt), during winter time. In a separate analysis, the YAADA ATOFMS dataset was also queried to return mass spectra meeting the following criteria: a signal in the m/z range -250 to m/z -500 that is greater than 0.01 of the total relative peak area, as per previous studies (Pratt et al., 2012, Denkenberger et al., 2007). The query returned approximately 33,000 particles, or about 3% of the total dataset, implying that the three oligomer ATOFMS Art-2a particle classes do represent the majority of the oligomer signal detected in single particle ATOFMS mass spectra.

3. RESULTS AND DISCUSSION

Measurement of both positive and negative ions within the dual polarity mass spectrometer for each individual particle provides the ability to identify aerosol sources and examine its mixing with secondary species (Pratt and Prather, 2010). The three ATOFMS oligomer particle types were characterized by high mass negative ions in the 200-400 mass/charge range with repetitive spacing of 12,14, and 16, characteristic of oligomeric species. By contrast, a corresponding oligomeric pattern was not observed in the positive ion mass spectra. Furthermore, the positive mass spectrum was not generated for most (>95%) of the particles comprising the three categories herein presented. Processes occurring during particle ablation and ionization can influence the mass spectra produced by the ATOFMS. These effects remain poorly characterized for complex atmospheric particles, and they include shot-to-shot variability due to laser inhomogeneities and matrix effects caused by reactions within the laser plume (Neubauer et al., 1998; Gross et al., 2000; Reilly et al., 2000, Hatch et al., 2014; Giorio et al., 2015). At the mass spectral level, composition dependent matrix effects can also lead to differing instrumental sensitivities for the same chemical species depending on the presence or relative abundance of other constituent species within the same particle (Liu et al., 2000). Alkylaminium sulfate particles have been shown to readily absorb water at low relative humidities (<45 %) (Chan and Chan, 2013; Hu et al., 2014), and particle-bound water has been shown to suppress negative ion formation in mass spectrometers (Neubauer et al., 1997, 1998). In contrast, negative species with the highest electron affinity are detected most easily and with higher ion peak areas (Schoolcraft et al., 2001; Reinard and Johnston, 2008). The detection of the HMW-OCs as negative ions suggests that the species are deprotonated oxidized organics; the mass/charge difference pattern can be attributed to the loss of carbon atoms, -CH_2 groups, and oxygen atoms (Denkenberger et al., 2007). Previous ATOFMS particles producing only negative ion mass spectra with sulfate and sulfuric acid ion markers were labeled as externally mixed sulfate particles (Pratt and Prather 2010; Pratt et al., 2010), although further studies are needed to fully understand the uncertainties associated with ATOFMS measurements (Healy et al., 2012)

3.1 Characterization of the oligomer ATOFMS single particle mass spectra

The three ATOFMS oligomer particle mass spectra are shown in Figure 1 and are described below. Whilst in this section only particle mass spectra and aerosol size distributions are presented, in the following sections we describe diurnal profiles, temporal trends, source apportionment estimates, influence of meterology and atmospheric and biogeochemistry implications.

3.1.1 Particle type OLI-BBOA (Oligomer - Biomass Burning Organic Aerosol).

Fig. 1 (top) shows the negative mass spectrum; it is dominated by nitrate (m/z -46, m/z -62), chloride (m/z -35) and sulphate (m/z -80, m/z -97). The negative ion mass spectrum shows strong peaks at m/z - 26 $[CN]^-$ and m/z -42 $[CNO]^-$, indicating that the particles contain internally mixed organo-nitrogen species. Strong peaks at m/z -138, m/z -153, m/z -168 are unique and detected - for the first time to our knowledge - with the ATOFMS. These peaks could be attributed to transitions for methyl-nitrocatechols (m/z -168→m/z -138) and nitroguaiacols (m/z -168 → m/z -153).

A possible transition may be due to deprotonated methyl-nitrocatechols readily losing a NO radical [30 u (unified atomic mass units)], whereas deprotonated nitroguaiacols undergoing methyl radical loss (15 u) (Kitanovski et al., 2012a,b). Nitrocatechols and their homologues have recently been associated with biomass burning (Kitanovski et al., 2012a,b); further details are given in the following section. These substances are commonly associated with HULIS (humic-like substances), oligomeric material with strong polar, poly-acidic, and chromophoric properties (Decesari et al., 2000).

3.1.2 Particle type OLI-NIT (Oligomer - Nitrate).

Fig. 1 (middle) shows a negative mass spectrum mainly dominated by nitrate (m/z -46, m/z -62), with very minor presence of chloride (m/z -35), sulphate (m/z -80, m/z -97) and organic nitrogen (m/z -26, m/z -42). Strong peaks tentatively attributed to nitrocatechols (m/z - 138, m/z -153, m/z -168) can be seen. Interestingly, a strong peak at m/z −125 is due to $[H(NO_3)_2^-]$. In summary, this is an aerosol oligomer internally mixed with nitrate (m/z −46, −62 and −125).

3.1.3 Particle type OLI-SS (Oligomer - Sea Salt) aerosol.

Fic. 1(bottom) shows a negative mass spectrum mainly dominated by chloride (m/z -35), with little signal due to nitrate (m/z -46, m/z -62), sulphate (m/z -80, m/z -97) and organic nitrogen (m/z -26, m/z -42). Peaks possibly due to nitrocatechols (m/z - 138, m/z -153, m/z -168) are also weak in this particle type. Strong oligomer peaks can be seen for this particle type (Fig. 1bottom), relative to the previous two presented (Figure 1 top, 1 middle). The distinguishing aspect of this mass spectrum is a strong signal for chloride and oligomer species.

The observed pattern of the oligomeric species in the negative ion mass spectra is similar to that obtained in previous experiments. Oligomeric species were detected from m/z 200-450 with a mass difference pattern of 14 and 16 Da in water-soluble organic matter extracted from filter sampling in Zurich (Baltensperger et al., 2005; Samburova et al., 2005; Kalberer et al., 2004;2006). In chamber studies, Gross et al. (2006) showed the real-time detection of HMW-OCs with a spacing of 14-16 Da from m/z -200 to -750 via ATOFMS as photooxidation products of 1,3,5-trimethylbenzene and α-pinene/1,3,5-trimethylbenzene. In that study, the shape of the off-line LDI-MS pattern showed good agreement with the shape of the oligomeric mass spectral patterns acquired with the ATOFMS.

The three HMW-OCs ATOFMS particle types were all distributed in the submicron mode (<1µm). The smallest mode was observed for particle type OLI-BBOA (250-300nm), followed by OLI-NIT (400nm). In contrast, particle type OLI-SS was found to be distributed in the largest detected particles, at about 800-900 nm. Such differences are likely due to the different aerosol sources associated to the three particle types, where an attempted apportionment is described in the next sub section.

3.2 Temporal profiles and possible source apportionment of oligomer particles

The temporal trends of the three oligomer particle types are shown in Figure 2. It should be noticed that whilst OLI-NIT and OLI-BBOA present similar trends, ART-2a cluster OLI-SS presents a different pattern. Furthermore, the OLI-SS particle type occurs mainly during the period of 4th-9th February, when clean marine Polar air masses were encountered (Dall'Osto et al., 2013). During this period, the ATOFMS detected higher particle number concentrations of pure NaCl (Figure 2 middle panel), low anthropogenic NO_x gaseous concentrations and higher than average ozone concentrations for this location (Figure 2 top panel). The temporal trends of the three oligomer particle types were correlated with the main ATOFMS and AMS aerosol classes described in Dall´Osto et al. (2013). Cluster OLI-SS was found to be highly correlated only with ATOFMS-NaCl (r=0.81), and not with other ATOFMS nor AMS particle types (r<±0.2). By contrast, cluster OLI-BBOA was highly correlated with ATOFMS OC-EC-SUL (Domestic solid fuel combustion, r=0.87), and not with other ATOFMS particle types (r<±0.2). It is valuable to remember in this context that in Northern Europe not only wood but also other solid fuels such as coal, peat and smokeless fuels are also strong contributors (Allan et al., 2010; Healy et al., 2009; Dall´Osto et al., 2013; 2014). For this reason, the ATOFMS particle type is herein defined with the general name of ATOFMS OC-EC-SUL, representing domestic solid fuel combustion. However, it is interesting to note that cluster OLI-BBOA correlated more with AMS PMF BBOA (Biomass Burning OA, r=0.74) than AMS PMF PCOA (Peat and coal, r=0.45), hence the name OLI-BBOA. The reason for this is not clear and further work is needed to draw conclusions. Cluster OLI-NIT was found correlated with ATOFMS OC-EC-NIT (Secondary nitrate aerosol internally mixed with EC, r=0.71) and AMF Nitrate (r=0.84), and not with other particle types (r<±0.2). In ATOFMS studies, usually the negative spectrum is vital for identifying secondary species such as sulfate and nitrate, while the positive spectrum is used for metals such as Na, Al, Ca, K and Fe (Gross et al., 2000). As mentioned at the beginning above, the three ATOFMS particle types were mainly characterized by negative single particle mass spectra. By investigating the few (<5%) positive single particle mass spectra belonging to each class, it was found that cluster OLI-NIT and OLI-BBOA were rich in m/z 39 (K) whereas cluster OLI-SS was found rich in m/z 23 and m/z 81 (Na and Na_2Cl), confirming the association with biomass burning and sea salt, respectively. The reported associations suggest that the three HMW-OCs types are associated with three different possible sources: evening winter time primary biomass burning (OLI-BBOA), night time nitrate formation (OLI-NIT) and day time reaction with sea salt (OLI-SS). Biomass burning (BB) is considered as one of the greatest primary sources of organic aerosols in the atmosphere (Kitanovski et al., 2012 a, b). Atmospheric nitro-aromatic compounds such as nitrocatechols present relatively high concentrations in urban areas and have been related to biomass burning. Kitanovski et al. (2012 a, b) found significant correlations between these analytes and biomass burning, occurring mainly during winter time.

Some consideration of the diurnal profiles of the three particle types (Figure 3) can also be made. OLI-BBOA clearly spiked during evening times at about 9pm in association with primary domestic solid fuel combustion emissions. Cluster OLI-NIT shows the strongest diurnal variation with a clear night time predominance. However, a peak at about 9am may also be seen coinciding with traffic rush hours. By contrast, cluster OLI-SS shows a unique diurnal trend spiking at 3-4pm, concomitant with the highest ozone concentrations and strongest solar radiation values. We are unable to check in the negative mass spectra (Figure 1) for specific ion markers that can be attributed to photochemical reactions. However, several peaks were found enhanced in the OLI-SS single particle mass spectra (e.g. m/z -109, -121, -135, -137, -152, -163, -209, -223, -237, -254, -269, -284, Figure 1), some of which (m/z -121, -137) were previously associated with secondary organic formation (Dall´Osto and Harrison, 2012); suggesting different aerosol formation mechanisms relative to OLI-BBOA and OLI-NIT. It is worth remembering that most ambient studies reported so far have focused on summer conditions. For example, the pioneering study of Denkenberger et al. (2007) found that the highest degree of oligomerization depended on season (more HMW-OCs were detected in the summer), particle size and acidity. Recent, Dual et al. (2016) reported abundant ion peaks in the m/z 200–850 range detected in aerosols appearing during heavy haze days, whereas these were negligible on a clear day, indicating the existence of HMW-OCs in the wintertime haze. Our results suggest that at least three different oligomeric species in a coastal region during winter time can be a complex mixture of different sources and processes.

3.3 Marine versus Stagnant periods

As described in our previous study (Dall'Osto et al., 2013) two different meteorological periods were experienced during the campaign: stagnant air mass conditions (days 1–3 and 16–19 February, named “stagnant” period, Period S.) and cold marine air mass (consecutive days: 4-9 February, named “marine” period, Period M.). Period M. is characterized by colder Atlantic air masses (2.7±2 ºC) and stronger winds (4.9±2ms^{-1}) relative to Period S. (4.9±3 ºC and 3.7±2ms^{-1}). Briefly, higher concentrations of anthropogenic aerosol constituents were observed for Period S. as a consequence of low dispersion conditions. In contrast, more NaCl was observed as expected during Period M. Indeed, 81% of the total OLI-SS classified during the field study were observed in Period S. The HR-ToF-AMS dataset was queried to support the existence of specific oligomer species during this period. Unfortunately, signals attributable to oligomer species were not found. Although this could confirm that these particles contribute little to particle mass concentrations, it is also possible that the HMW-OCs did not survive the high temperatures used in the vaporizer. However, we tested if m/z peaks attributable to C-Cl bonds - supportive of sea salt internally mixed with organic matter - could be detected. Figure 4 shows for the two different periods - as expected - higher signal due to AMS BBOA ($C_2H_4O_2$, m/z 60.444, marker for levoglucosan, Alfarra et al., 2007) for the Period S (relative to Period M.) and vice versa for AMS NaCl peaks (m/z 58, NaCl, Ovadnevaite et al., 2012). It is interesting to note that the temporal trends of C-Cl peaks (C_2Cl) confirms higher amounts of these species in period M, indeed suggesting the presence of organic material in sea salt enriched air masses. Halogens could take part in the aging process of organic aerosols, and gas-phase photochemical halogenation may generate additional low-volatile compounds, which condense onto the existing particles (Ofner et al., 2012).

3.4 Atmospheric implications

Volatility and hygroscopicity are two key properties of organic aerosol components, and both are strongly related to chemical composition (Drozd et al., 2014). Because of the potential implications for partitioning/volatility, uptake coefficients, evaporation, and hygroscopicity, the irreversible transformation of volatile, soluble, and high-oxidation-state organic material into non-volatile material may be important in models of organic compound partitioning in the atmosphere. Cloud Condensation Nuclei (CCN) ability is directly related to the hygroscopicity of particles. Thus, for instance the CCN ability of the particle may be quite different when heterogeneous coverage formation and/or spatially heterogeneous reactions occur compared to when a particle is evenly coated and/or homogeneously reacted.

Our study shows that the detected HMW-OCs likely contain nitrogen-containing organic compounds; which have drawn attention owing to their impact on aerosol chemistry and physics. Specifically, they represent an important part of aerosol brown carbon, which possess good abilities to absorb ultraviolet and visible sunlight, thus influencing the radiative forcing of the Earth. As pointed out by Shapiro et al. (2009) and Yu et al. (2011) all those products mentioned before do not contribute substantially to SOA mass. However, due to the high absorption coefficients of some nitrogen-containing reaction products, an important influence on the optical and radiative properties of ambient aerosols cannot be excluded (Bones et al., 2010). Among them, nitrocatechols and their homologues have recently been associated with biomass burning. Our study shows that these organic nitrogen components may beinternally mixed with different types of HMW-OCs, potentially formed via a number of different atmospheric primary and secondary processes (Wang et al., 2010).

As pointed out by Laskin et al. (2012b), the chemical reactivity of sea salt particles with secondary organics has been largely overlooked in atmospheric aerosol chemistry. Our results show that HMW-OCs may be formed on sea salt particles during daylight in winter periods in Cork. Adachi and Buseck (2015) recently showed that sea-salt particles were major components in the samples of an urban area and that they changed their composition and shape within 3 h of travel from the ocean. Nearly half of the aerosol particles in samples collected from the LA area originated as sea salt, and most had reacted at least in part to form sulfate, nitrate, or both, resulting in Cl loss. Such atmospheric aging likely modifies the acidity, hygroscopic, and optical properties of particles. Current climate and atmospheric chemistry models assume that all sea salt particles react as if they are pure NaCl (Ault et al., 2013a, b; 2014) . However, a number of distinct particle types exist (including sea salt, organic carbon, and biological particles) as well as mixtures of these and, within each particle type, there is a range of single-particle chemical composition. Internally mixed sea salt - organic carbon particles are twice as likely not to undergo extensive reaction compared to those identified as sea salt (Ault et al., 2013a, b; 2014). Such non-equidimensional shapes influence light scattering (Adachi and Buseck, 2015)

Our findings may have implications also for marine biogeochemical cycles. Atmospheric deposition of reactive nitrogen (N) species from air pollutants is a significant source of exogenous nitrogen in marine ecosystems (Ito et al., 2014). The necessity of improving the process-based quantitative understanding of the chemical reactions of inorganic nitrogen species with organics in aerosol and cloud water is highlighted. Finally, it is worth remembering that as of 1995, 37% of the world's population lived within 100 km of a coast and that fraction has continued to increase. The different types of HMW-OCs presented here may also be of concern regarding their potential adverse health effects (Baltensperger et al., 2008). In summary, our single particle mass spectrometry measurements - taken in a European coastal location during winter time - has allowed us to shed some light on the mixing state of different types of HMW-OCs, including previously unreported modification of sea-salt particles in an urban atmosphere. Further studies are needed to examine multiphase atmospheric chemistry in coastal environments where marine air mixes with urban pollution.

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Figure Legend

Figure 1. ATOFMS ART-2a results for the three particle types (absolute values). Left part is the m/z 0-350 average single particle mass spectra, whereas in the right part the m/z 100-350 expanded is seen for OLI-BBOA (OLIgomer- Biomass Burning Organic Aerosols), OLI-NI (OLIgomer-NITrate) and OLI-SS (OLIgomers Sea Salt).

Figure 2. Temporal trends of oligomer ATOFMS species (bottom), ATOFMS particle types fresh and aged sea spray (middle) and gas measurements of NO_x and O_3 (top). In dash blue line (4-9/02/2009) is shown the clean marine Polar air mass period, as described in Dall´Osto et al. (2013, 2014).

Figure 3. Diurnal profiles of the three oligomer ATOFMS particle types detected. At the bottom average temperature (T) and Relative Humidity (RH) are also shown. Data are presented as averages of the entire field study (03-22/02/2009).

Figure 4. HR-ToF-AMS measurements for case studies mP (marine Polar, "Marine") and cP (continental Polar, "Stagnant") as described in Dall´Osto et al. (2013, 2014) for Biomass Burning markers (BBOA; Alfarra et al., 2007, Sea Spray (SS, Ovadnevaite et al., 2012) and C-Cl bonds.

LIST OF FIGURES

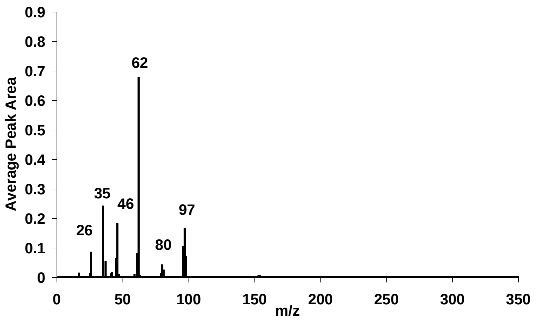
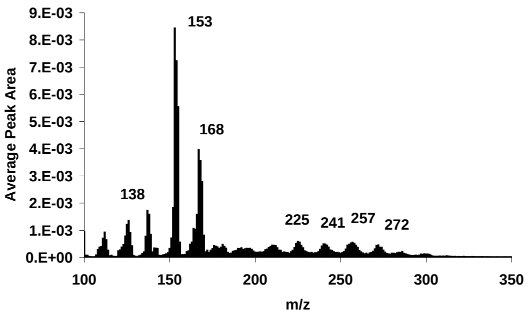
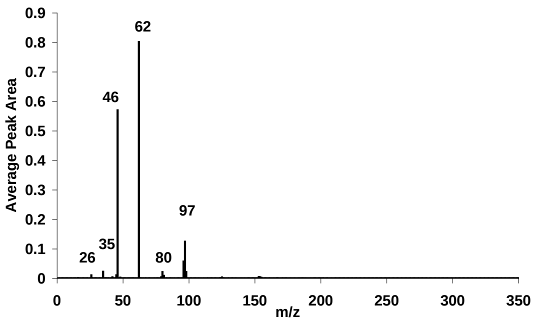
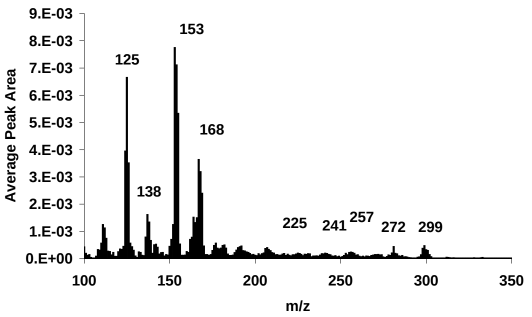
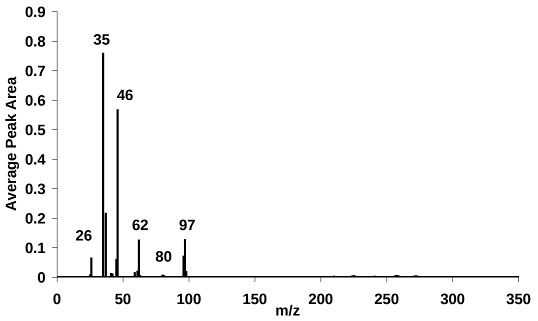
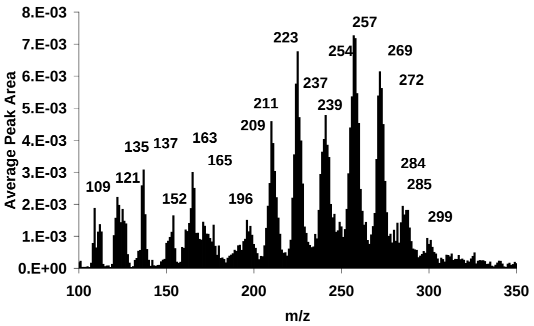
Particle type	Average Negative Spectra (m/z 0-350) (a)	Average Negative Spectra (m/z 100-350) (b)
OLI-BBOA		
OLI-NIT		
OLI-SS		

Figure 1. ATOFMS ART-2a results for the three particle types (absolute values). Left part is the m/z 0-350 average single particle mass spectra, whereas in the right part the m/z 100-350 expanded is seen for OLI-BBOA (OLIgomer- Biomass Burning Organic Aerosols), OLI-NI (OLIgomer-NITrate) and OLI-SS (OLIgomers Sea Salt).

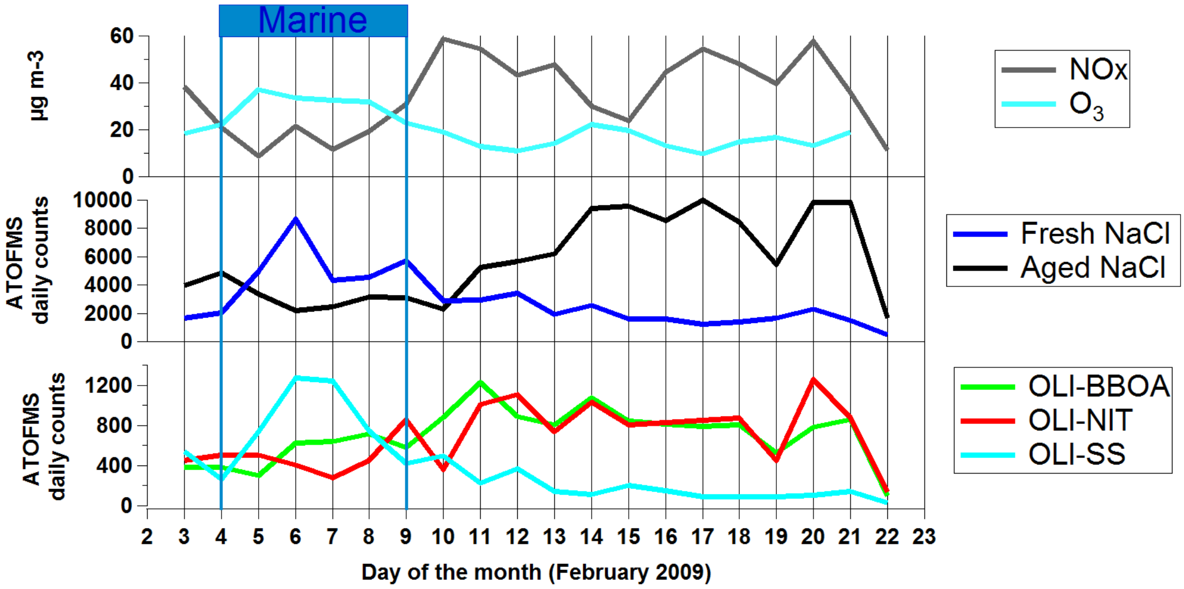


Figure 2. Temporal trends of oligomer ATOFMS species (bottom), ATOFMS particle types fresh and aged sea spray (middle) and gas measurements of NO_x and O_3 (top). In dash blue line (4-9/02/2009) is shown the clean marine Polar air mass period, as described in Dall´Osto et al. (2013, 2014).

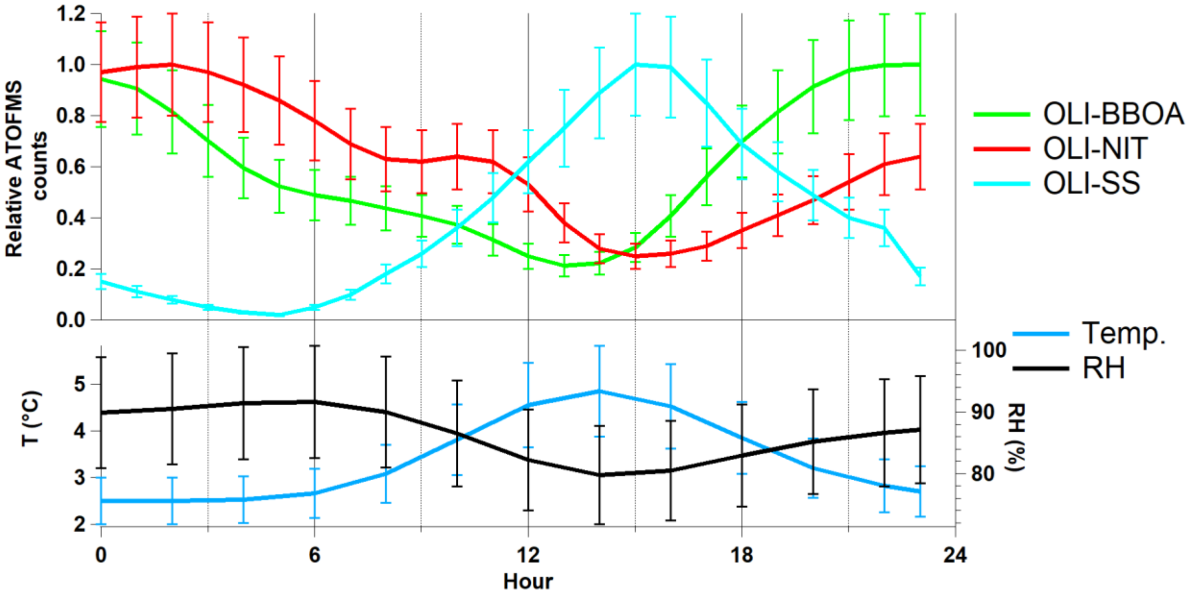


Figure 3. Diurnal profiles of the three oligomer ATOFMS particle types detected. At the bottom average temperature (T) and Relative Humidity (RH) are also shown. Data are presented as averages of the entire field study (03-22/02/2009).

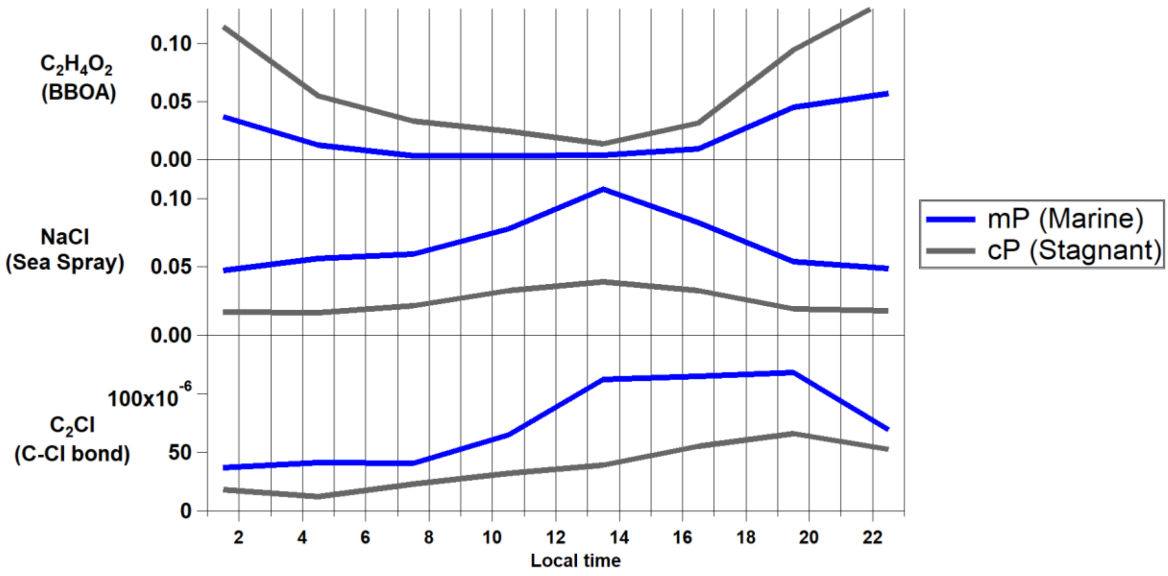


Figure 4. HR-ToF-AMS measurements for case studies mP (marine Polar, "Marine") and cP (continental Polar, "Stagnant") as described in Dall´Osto et al. (2013, 2014) for Biomass Burning markers (BBOA; Alfarra et al., 2007, Sea Spray (SS, Ovadnevaite et al., 2012) and C-Cl bonds.