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DOI:

[10.1016/j.atmosenv.2017.10.007](https://doi.org/10.1016/j.atmosenv.2017.10.007)

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Document Version

Peer reviewed version

Citation for published version (Harvard):

Dall'Osto, M, Healy, RM, Wenger, JC, O'Dowd, C, Ovadnevaite, J, Ceburnis, D, Harrison, R & Beddows, D 2017, 'Distinct high molecular weight organic compound (HMW-OC) types in aerosol particles collected at a coastal urban site', *Atmospheric Environment*, vol. 171, pp. 118-125. <https://doi.org/10.1016/j.atmosenv.2017.10.007>

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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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#Now at Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment and Climate Change, Toronto, Canada

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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.

1 **ABSTRACT**

2

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

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2 **1. INTRODUCTION**

3

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

16

17 Oligomeric species have been identified as an important component of SOA in
18 laboratory studies (Jang and Kamens, 2001, Jang et al., 2002, Kalberer et al., 2004).
19 Oligomer formation in the particle phase has been attributed to a variety of chemical
20 reaction pathways (Hallquist et al., 2009) including heterogeneous acid-catalysed
21 reactions (Jang and Kamens, 2001, Jang et al., 2001; 2002), and aqueous chemistry
22 within clouds (Lim et al., 2010). Although it has been found that the aqueous phase
23 reactions of organic vapours can lead to higher molecular weight products than
24 equivalent reactions in the gas phase, the role of the liquid phase of aerosols in SOA
25 formation is still largely unknown (Beardsley et al., 2013). It is also important to note
26 that oligomers in aerosols are not only formed via secondary mechanisms, but also
27 include direct primary emissions from terrestrial, marine and biomass burning primary
28 sources (Decesari et al., 2000, Reid et al., 2005). Detection and characterization of
29 oligomeric species in aerosols is important as they are expected to significantly affect
30 gas-particle partitioning, hygroscopic growth, particle reactivity, and health effects
31 (Kanakidou et al., 2005). However, oligomers are not often clearly observed in
32 ambient aerosols and there is uncertainty over the extent of their relevance under

1 atmospheric conditions (Kourtchev et al., 2016). Denkenberger et al (2007) and
2 Gross et al (2006) detected high molecular weight species thought to be oligomers in
3 field and chamber measurements respectively using an Aerosol Time-of-Flight Mass
4 Spectrometer (ATOFMS) but were not able to make detailed mechanistic inferences.

5 Sea salt (SS) is also a source of atmospheric aerosols, and can contribute up to 80%
6 of particle levels in the air in coastal areas (Seinfeld and Pandis, 2006; Gant et al.,
7 2015). Most SS aerosol particles are formed through interaction between the ocean
8 surface and wind, resulting in breaking waves and bursting bubbles (Lewis and
9 Schwartz, 2004). SS aerosols are the most abundant aerosols in the coastal
10 atmosphere and thus act as pre-existing particulate matter for SOA formation. Unlike
11 NaCl aerosols that have a clear phase transition, SS aerosols have a very low
12 efflorescence relative humidity and have been shown to hold water at low RH.
13 Therefore, SS aerosols act as a medium for aqueous phase reactions in marine
14 environments. During transport through the atmosphere, SS particles commonly
15 react with gases and other types of aerosol particles and in the process change
16 composition. The composition and shape affect hygroscopicity and light scattering,
17 both of which influence their climate impacts. For example, in anthropogenically
18 influenced atmospheres, many SS particles become internally mixed with sulfate and
19 nitrate (Gard et al., 1998; Adachi and Buseck, 2015). However, there is a large range
20 of reactivities within sea salt aerosol particles (Ault et al., 2013a,b; 2014). Recently,
21 Laskin et al. (2012a) reported substantial chemical reactivity of sea salt particles with
22 secondary organics that has been largely overlooked in atmospheric aerosol
23 chemistry. It was shown that that chloride components in sea salt particles may
24 effectively react with organic acids releasing HCl gas to the atmosphere, leaving
25 behind particles depleted in chloride and enriched in the corresponding organic salts.
26 Other studies have also shown that, under atmospheric conditions, the presence of
27 SS aerosols significantly increased the SOA yields of aromatic hydrocarbons,
28 compared to seedless conditions or the presence of pure NaCl seeds (Beardsley et
29 al., 2013).

30

31 Due to the potential climatic impacts of atmospheric organic species, there has been
32 growing interest in the effects of organics on the hygroscopicity and phase transition

1 of inorganic aerosol. Despite great efforts devoted to understanding the
2 hygroscopicity of mixed organic/inorganic aerosols, current knowledge of the
3 interaction between organics and inorganics in mixed droplets at the molecular level
4 is still very limited (Yu et al., 2011). Developing a better understanding of the factors
5 controlling heterogeneous chemical reactions on the surface of atmospheric aerosols
6 is challenging because the complex composition, structure and heterogeneous
7 distribution of species make predicting the degree of reactivity of each particle
8 difficult (Ault et al., 2013a,b; 2014). Bulk ensemble measurements provide valuable
9 information, but the implicit assumption of internal mixing can lead to discrepancies
10 between models and measurements because the average value may not accurately
11 represent the aerosol population when multiple populations are present (Healy et al,
12 2014). The rates of heterogeneous reactions of trace gases with aerosol particles are
13 complex functions of particle chemical composition, morphology, and phase state.
14 Currently, the majority of model parameterizations of heterogeneous reaction kinetics
15 focus on the population average of aerosol particle mass, assuming that individual
16 particles have the same chemical composition as the average state (Ryder et al.,
17 2014). There is, however, a lack of knowledge on the sources and formation
18 mechanisms of oligomeric species.

19

20 In recent years aerosol mass spectrometry has become available as a powerful tool
21 for the on-line chemical characterization of individual aerosol particles (Murphy,
22 2007) or small aerosol ensembles (Canagaratna et al., 2007). Measurement of
23 particle composition by on-line mass spectrometry has developed extensively over
24 the last two decades and is currently the fastest growing area of atmospheric aerosol
25 research (Laskin et al., 2012b). The importance of oligomeric species in ambient
26 organic aerosol has not received sufficient attention because evidence of such
27 compounds in the atmosphere is very scarce (Denkenberger et al., 2007; Wang et
28 al., 2010, Duan et al., 2016). In this work we have identified and characterized three
29 unique types of HMW-OCs particles in ambient aerosol at an urban coastal location
30 in Cork, Ireland. Two different particle mass spectrometers were deployed: an
31 Aerosol Time-of-Flight Mass Spectrometer (ATOFMS) (Gard et al., 1997) and an
32 Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS)

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

10

11 **2. MATERIAL AND METHODS**

12

13 **2.1 Location**

14

15 The campaign took place from 1st to 22nd February 2009 (all times in this study are in
16 local time - LT) at the Tivoli Industrial Estate and Docks, Cork, Ireland (51°54'5 N,
17 8°24'38 W). A detailed description of the site is given elsewhere (Healy et al., 2009,
18 Healy et al , 2010). Briefly, the site is located in the Port of Cork, approximately 3 km
19 east of Cork city centre. Residential areas surround the site on all sides except the
20 north and northeast.

21

22 **2.2 On-line Aerosol Techniques**

23

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

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

3

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

13

14 **2.3 Processing of Mass spectrometer data**

15

16 The data generated by the two mass spectrometers has been processed, analysed
17 and reported in detail in a previous publication (Dall'Osto et al. 2013). Briefly, Positive
18 Matrix Factorization (PMF) was applied to the HR-ToF-AMS organic matrix and a
19 five-factor solution was found, supported both mathematically and with external
20 correlations with parallel gaseous, aerosol off-line and ATOFMS measurements. The
21 AMS_PMF organic aerosol (OA) factors HOA (“hydrocarbon-like” OA), LV-OOA (“low
22 volatility oxygenated” OA), BBOA (“biomass burning” OA), PCOA (“peat and coal”
23 OA) and COA (“cooking” OA) comprised 20%, 19%, 23%, 21% and 18% of the total
24 non-refractory organic mass, respectively. The ATOFMS dataset was reduced to 10
25 single particle types which accounted for around 97% of the detected particles.
26 Based on composition, temporal profile and other factors, the clusters were attributed
27 to the following source categories; domestic solid fuel combustion (~61%), secondary
28 aerosols (~27%), traffic (~5%), sea salt (~3%) and shipping (~1%). A follow up study
29 (Dall'Osto et al., 2014) characterized the fine PM component using factor analysis
30 applied to the array of on-line and off-line aerosol measurements. Five aerosol
31 sources were apportioned, three of primary origin (Traffic, domestic solid fuel burning

1 or urban and regional origin, up to 61–70% of $PM_{2.5}$) and two mainly of secondary
2 origin (secondary organic aerosol of urban and regional origin, up to 30–39% of
3 $PM_{2.5}$). Overall, there are clear benefits from applying factor analysis to results
4 obtained from multiple on line aerosol techniques (ATOFMS and AMS), allowing for
5 better source apportionment (Dall’Osto et al., 2013; 2014). In the ATOFMS analysis
6 performed here, we focussed on the remaining 2.7% (36,538 in number) of detected
7 particles which were classified by ART-2a into three distinct classes. They can be
8 described as predominantly organic particle types presenting a systematic High
9 Molecular Weight (HMW) signal. Whilst these three particle types only represent
10 about 3% of the whole ATOFMS dataset, we argue that these single particle mass
11 spectra provide important new information on the sources and processes affecting
12 oligomer formation in an urban area affected by anthropogenic primary sources (i.e.
13 traffic, biomass burning), as well natural coastal sources (i.e. sea salt), during winter
14 time. In a separate analysis, the YAADA ATOFMS dataset was also queried to return
15 mass spectra meeting the following criteria: a signal in the m/z range -250 to m/z -
16 500 that is greater than 0.01 of the total relative peak area, as per previous studies
17 (Pratt et al., 2012, Denkenberger et al., 2007). The query returned approximately
18 33,000 particles, or about 3% of the total dataset, implying that the three oligomer
19 ATOFMS Art-2a particle classes do represent the majority of the oligomer signal
20 detected in single particle ATOFMS mass spectra.

21

22 **3. RESULTS AND DISCUSSION**

23

24 Measurement of both positive and negative ions within the dual polarity mass
25 spectrometer for each individual particle provides the ability to identify aerosol
26 sources and examine its mixing with secondary species (Pratt and Prather, 2010).
27 The three ATOFMS oligomer particle types were characterized by high mass
28 negative ions in the 200-400 mass/charge range with repetitive spacing of 12,14, and
29 16, characteristic of oligomeric species. By contrast, a corresponding oligomeric
30 pattern was not observed in the positive ion mass spectra. Furthermore, the positive
31 mass spectrum was not generated for most (>95%) of the particles comprising the
32 three categories herein presented. Processes occurring during particle ablation and

1 ionization can influence the mass spectra produced by the ATOFMS. These effects
2 remain poorly characterized for complex atmospheric particles, and they include
3 shot-to-shot variability due to laser inhomogeneities and matrix effects caused by
4 reactions within the laser plume (Neubauer et al., 1998; Gross et al., 2000; Reilly et
5 al., 2000, Hatch et al., 2014; Giorio et al., 2015). At the mass spectral level,
6 composition dependent matrix effects can also lead to differing instrumental
7 sensitivities for the same chemical species depending on the presence or relative
8 abundance of other constituent species within the same particle (Liu et al., 2000).
9 Alkylammonium sulfate particles have been shown to readily absorb water at low
10 relative humidities (<45 %) (Chan and Chan, 2013; Hu et al., 2014), and particle-
11 bound water has been shown to suppress negative ion formation in mass
12 spectrometers (Neubauer et al., 1997, 1998). In contrast, negative species with the
13 highest electron affinity are detected most easily and with higher ion peak areas
14 (Schoolcraft et al., 2001; Reinard and Johnston, 2008). The detection of the HMW-
15 OCs as negative ions suggests that the species are deprotonated oxidized organics;
16 the mass/charge difference pattern can be attributed to the loss of carbon atoms, -
17 CH₂ groups, and oxygen atoms (Denkenberger et al., 2007). Previous ATOFMS
18 particles producing only negative ion mass spectra with sulfate and sulfuric acid ion
19 markers were labeled as externally mixed sulfate particles (Pratt and Prather 2010;
20 Pratt et al., 2010), although further studies are needed to fully understand the
21 uncertainties associated with ATOFMS measurements (Healy et al., 2012)

22

23 **3.1 Characterization of the oligomer ATOFMS single particle mass spectra**

24

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

30

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 \rightarrow m/z -138) and nitroguaiacols (m/z -168 \rightarrow 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.

Fig. 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.

1 The observed pattern of the oligomeric species in the negative ion mass spectra is
2 similar to that obtained in previous experiments. Oligomeric species were detected
3 from m/z 200-450 with a mass difference pattern of 14 and 16 Da in water-soluble
4 organic matter extracted from filter sampling in Zurich (Baltensperger et al., 2005;
5 Samburova et al., 2005; Kalberer et al., 2004;2006). In chamber studies, Gross et al.
6 (2006) showed the real-time detection of HMW-OCs with a spacing of 14-16 Da from
7 m/z -200 to -750 via ATOFMS as photooxidation products of 1,3,5-trimethylbenzene
8 and α -pinene/1,3,5-trimethylbenzene. In that study, the shape of the off-line LDI-MS
9 pattern showed good agreement with the shape of the oligomeric mass spectral
10 patterns acquired with the ATOFMS.

11

12 The three HMW-OCs ATOFMS particle types were all distributed in the submicron
13 mode ($<1\mu\text{m}$). The smallest mode was observed for particle type OLI-BBOA (250-
14 300nm), followed by OLI-NIT (400nm). In contrast, particle type OLI-SS was found to
15 be distributed in the largest detected particles, at about 800-900 nm. Such
16 differences are likely due to the different aerosol sources associated to the three
17 particle types, where an attempted apportionment is described in the next sub
18 section.

19

20 **3.2 Temporal profiles and possible source apportionment of oligomer particles**

21

22 The temporal trends of the three oligomer particle types are shown in Figure 2. It
23 should be noticed that whilst OLI-NIT and OLI-BBOA present similar trends, ART-2a
24 cluster OLI-SS presents a different pattern. Furthermore, the OLI-SS particle type
25 occurs mainly during the period of 4th-9th February, when clean marine Polar air
26 masses were encountered (Dall'Osto et al., 2013). During this period, the ATOFMS
27 detected higher particle number concentrations of pure NaCl (Figure 2 middle panel),
28 low anthropogenic NO_x gaseous concentrations and higher than average ozone
29 concentrations for this location (Figure 2 top panel). The temporal trends of the three
30 oligomer particle types were correlated with the main ATOFMS and AMS aerosol
31 classes described in Dall'Osto et al. (2013). Cluster OLI-SS was found to be highly

1 correlated only with ATOFMS-NaCl ($r=0.81$), and not with other ATOFMS nor AMS
2 particle types ($r<\pm 0.2$). By contrast, cluster OLI-BBOA was highly correlated with
3 ATOFMS OC-EC-SUL (Domestic solid fuel combustion, $r=0.87$), and not with other
4 ATOFMS particle types ($r<\pm 0.2$). It is valuable to remember in this context that in
5 Northern Europe not only wood but also other solid fuels such as coal, peat and
6 smokeless fuels are also strong contributors (Allan et al., 2010; Healy et al., 2009;
7 Dall'Osto et al., 2013; 2014). For this reason, the ATOFMS particle type is herein
8 defined with the general name of ATOFMS OC-EC-SUL, representing domestic solid
9 fuel combustion. However, it is interesting to note that cluster OLI-BBOA correlated
10 more with AMS PMF BBOA (Biomass Burning OA, $r=0.74$) than AMS PMF PCOA
11 (Peat and coal, $r=0.45$), hence the name OLI-BBOA. The reason for this is not clear
12 and further work is needed to draw conclusions. Cluster OLI-NIT was found
13 correlated with ATOFMS OC-EC-NIT (Secondary nitrate aerosol internally mixed with
14 EC, $r=0.71$) and AMF Nitrate ($r=0.84$), and not with other particle types ($r<\pm 0.2$). In
15 ATOFMS studies, usually the negative spectrum is vital for identifying secondary
16 species such as sulfate and nitrate, while the positive spectrum is used for metals
17 such as Na, Al, Ca, K and Fe (Gross et al., 2000). As mentioned at the beginning
18 above, the three ATOFMS particle types were mainly characterized by negative
19 single particle mass spectra. By investigating the few (<5%) positive single particle
20 mass spectra belonging to each class, it was found that cluster OLI-NIT and OLI-
21 BBOA were rich in m/z 39 (K) whereas cluster OLI-SS was found rich in m/z 23 and
22 m/z 81 (Na and Na_2Cl), confirming the association with biomass burning and sea salt,
23 respectively. The reported associations suggest that the three HMW-OCs types are
24 associated with three different possible sources: evening winter time primary
25 biomass burning (OLI-BBOA), night time nitrate formation (OLI-NIT) and day time
26 reaction with sea salt (OLI-SS). Biomass burning (BB) is considered as one of the
27 greatest primary sources of organic aerosols in the atmosphere (Kitanovski et al.,
28 2012 a, b). Atmospheric nitro-aromatic compounds such as nitrocatechols present
29 relatively high concentrations in urban areas and have been related to biomass
30 burning. Kitanovski et al. (2012 a, b) found significant correlations between these
31 analytes and biomass burning, occurring mainly during winter time.

32

1 Some consideration of the diurnal profiles of the three particle types (Figure 3) can
2 also be made. OLI-BBOA clearly spiked during evening times at about 9pm in
3 association with primary domestic solid fuel combustion emissions. Cluster OLI-NIT
4 shows the strongest diurnal variation with a clear night time predominance. However,
5 a peak at about 9am may also be seen coinciding with traffic rush hours. By contrast,
6 cluster OLI-SS shows a unique diurnal trend spiking at 3-4pm, concomitant with the
7 highest ozone concentrations and strongest solar radiation values. We are unable to
8 check in the negative mass spectra (Figure 1) for specific ion markers that can be
9 attributed to photochemical reactions. However, several peaks were found enhanced
10 in the OLI-SS single particle mass spectra (e.g. m/z -109, -121, -135, -137, -152, -
11 163, -209, -223, -237, -254, -269, -284, Figure 1), some of which (m/z -121, -137)
12 were previously associated with secondary organic formation (Dall'Osto and
13 Harrison, 2012); suggesting different aerosol formation mechanisms relative to OLI-
14 BBOA and OLI-NIT. It is worth remembering that most ambient studies reported so
15 far have focused on summer conditions. For example, the pioneering study of
16 Denkenberger et al. (2007) found that the highest degree of oligomerization
17 depended on season (more HMW-OCs were detected in the summer), particle size
18 and acidity. Recent, Dual et al. (2016) reported abundant ion peaks in the m/z 200–
19 850 range detected in aerosols appearing during heavy haze days, whereas these
20 were negligible on a clear day, indicating the existence of HMW-OCs in the
21 wintertime haze. Our results suggest that at least three different oligomeric species in
22 a coastal region during winter time can be a complex mixture of different sources and
23 processes.

24

25 **3.3 Marine versus Stagnant periods**

26

27 As described in our previous study (Dall'Osto et al., 2013) two different
28 meteorological periods were experienced during the campaign: stagnant air mass
29 conditions (days 1–3 and 16–19 February, named “stagnant” period, Period S.) and
30 cold marine air mass (consecutive days: 4-9 February, named “marine” period,
31 Period M.). Period M. is characterized by colder Atlantic air masses (2.7 ± 2 °C) and
32 stronger winds ($4.9\pm 2\text{ms}^{-1}$) relative to Period S. (4.9 ± 3 °C and $3.7\pm 2\text{ms}^{-1}$). Briefly,

1 higher concentrations of anthropogenic aerosol constituents were observed for
2 Period S. as a consequence of low dispersion conditions. In contrast, more NaCl was
3 observed as expected during Period M. Indeed, 81% of the total OLI-SS classified
4 during the field study were observed in Period S. The HR-ToF-AMS dataset was
5 queried to support the existence of specific oligomer species during this period.
6 Unfortunately, signals attributable to oligomer species were not found. Although this
7 could confirm that these particles contribute little to particle mass concentrations, it is
8 also possible that the HMW-OCs did not survive the high temperatures used in the
9 vaporizer. However, we tested if m/z peaks attributable to C-Cl bonds - supportive of
10 sea salt internally mixed with organic matter - could be detected. Figure 4 shows for
11 the two different periods - as expected - higher signal due to AMS BBOA ($C_2H_4O_2$,
12 m/z 60.444, marker for levoglucosan, Alfarra et al., 2007) for the Period S (relative to
13 Period M.) and vice versa for AMS NaCl peaks (m/z 58, NaCl, Ovadnevaite et al.,
14 2012). It is interesting to note that the temporal trends of C-Cl peaks (C_2Cl) confirms
15 higher amounts of these species in period M, indeed suggesting the presence of
16 organic material in sea salt enriched air masses. Halogens could take part in the
17 aging process of organic aerosols, and gas-phase photochemical halogenation may
18 generate additional low-volatile compounds, which condense onto the existing
19 particles (Ofner et al., 2012).

20

21 **3.4 Atmospheric implications**

22

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

1

2 Our study shows that the detected HMW-OCs likely contain nitrogen-containing
3 organic compounds; which have drawn attention owing to their impact on aerosol
4 chemistry and physics. Specifically, they represent an important part of aerosol
5 brown carbon, which possess good abilities to absorb ultraviolet and visible sunlight,
6 thus influencing the radiative forcing of the Earth. As pointed out by Shapiro et al.
7 (2009) and Yu et al. (2011) all those products mentioned before do not contribute
8 substantially to SOA mass. However, due to the high absorption coefficients of some
9 nitrogen-containing reaction products, an important influence on the optical and
10 radiative properties of ambient aerosols cannot be excluded (Bones et al., 2010).
11 Among them, nitrocatechols and their homologues have recently been associated
12 with biomass burning. Our study shows that these organic nitrogen components may
13 be internally mixed with different types of HMW-OCs, potentially formed via a number
14 of different atmospheric primary and secondary processes (Wang et al., 2010).

15

16 As pointed out by Laskin et al. (2012b), the chemical reactivity of sea salt particles
17 with secondary organics has been largely overlooked in atmospheric aerosol
18 chemistry. Our results show that HMW-OCs may be formed on sea salt particles
19 during daylight in winter periods in Cork. Adachi and Buseck (2015) recently showed
20 that sea-salt particles were major components in the samples of an urban area and
21 that they changed their composition and shape within 3 h of travel from the ocean.
22 Nearly half of the aerosol particles in samples collected from the LA area originated
23 as sea salt, and most had reacted at least in part to form sulfate, nitrate, or both,
24 resulting in Cl loss. Such atmospheric aging likely modifies the acidity, hygroscopic,
25 and optical properties of particles. Current climate and atmospheric chemistry models
26 assume that all sea salt particles react as if they are pure NaCl (Ault et al., 2013a, b;
27 2014) . However, a number of distinct particle types exist (including sea salt, organic
28 carbon, and biological particles) as well as mixtures of these and, within each
29 particle type, there is a range of single-particle chemical composition. Internally
30 mixed sea salt - organic carbon particles are twice as likely not to undergo extensive
31 reaction compared to those identified as sea salt (Ault et al., 2013a, b; 2014). Such
32 non-equidimensional shapes influence light scattering (Adachi and Buseck, 2015)

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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.

ACKNOWLEDGMENTS

This work was funded by the Ireland Higher Education Authority Programme for Research in Third Level Institutes (PRTL1) – Cycle 5, and the Irish Environmental Protection Agency. Additional founding by the Spanish Ministry of Economy through projects BIO-NUC (CGL2013-49020-R), and by the EU through the FP7-PEOPLE-2013-IOF programme (Project number 624680, MANU – Marine Aerosol NUcleations) and the Ramon y Cajal fellowship (RYC-2012-11922). The National Centre for Atmospheric Science NCAS Birmingham group is funded by the UK Natural Environment Research Council.

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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 (OLIomer- Biomass Burning Organic Aerosols), OLI-NI (OLIomer-NITrate) and OLI-SS (OLIomers 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 O₃ (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).

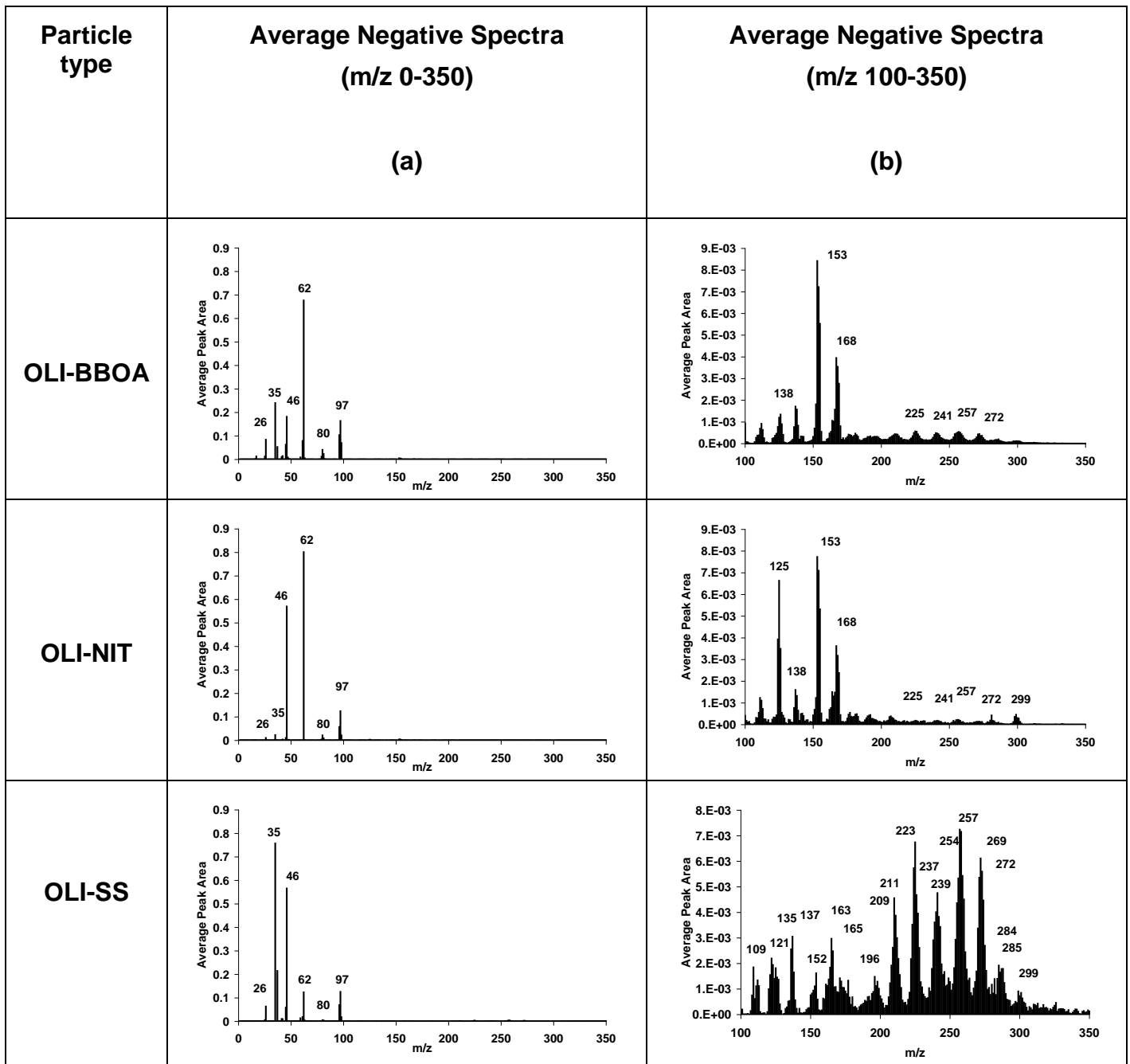
Figure 3. Diurnal profiles of the three oligomer ATOFMS particle types detected. At the bottom average temperature (T) and Relative Humidity (RH) are also shown. Data are presented as averages of the entire field study (03-22/02/2009).

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; Alfara et al., 2007, Sea Spray (SS, Ovadnevaite et al., 2012) and C-Cl bonds.

1 LIST OF FIGURES

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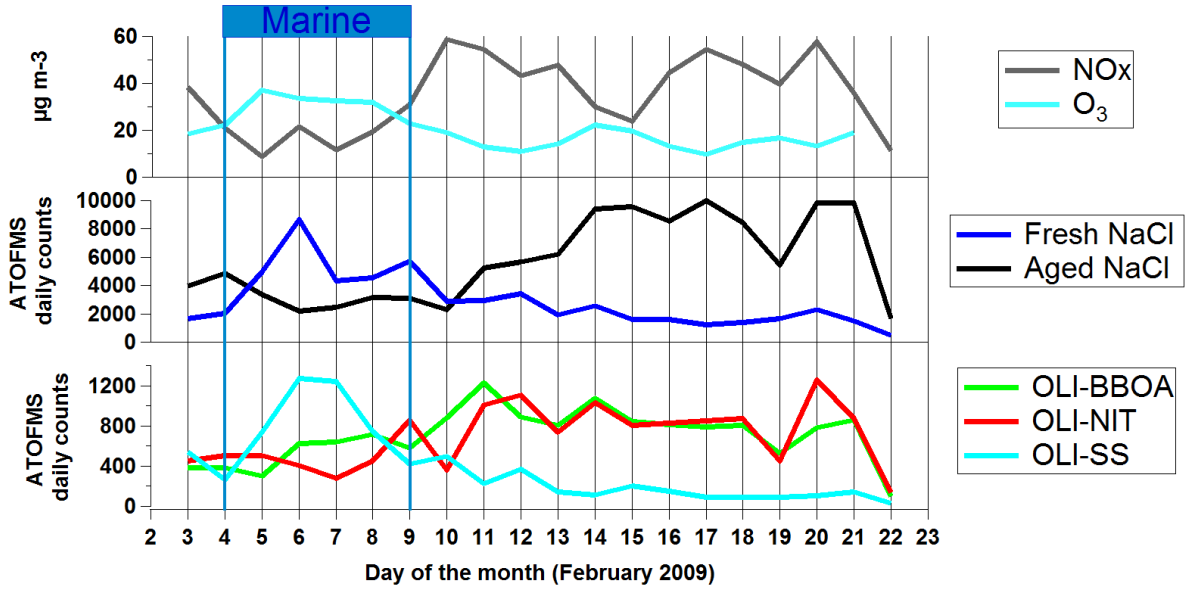
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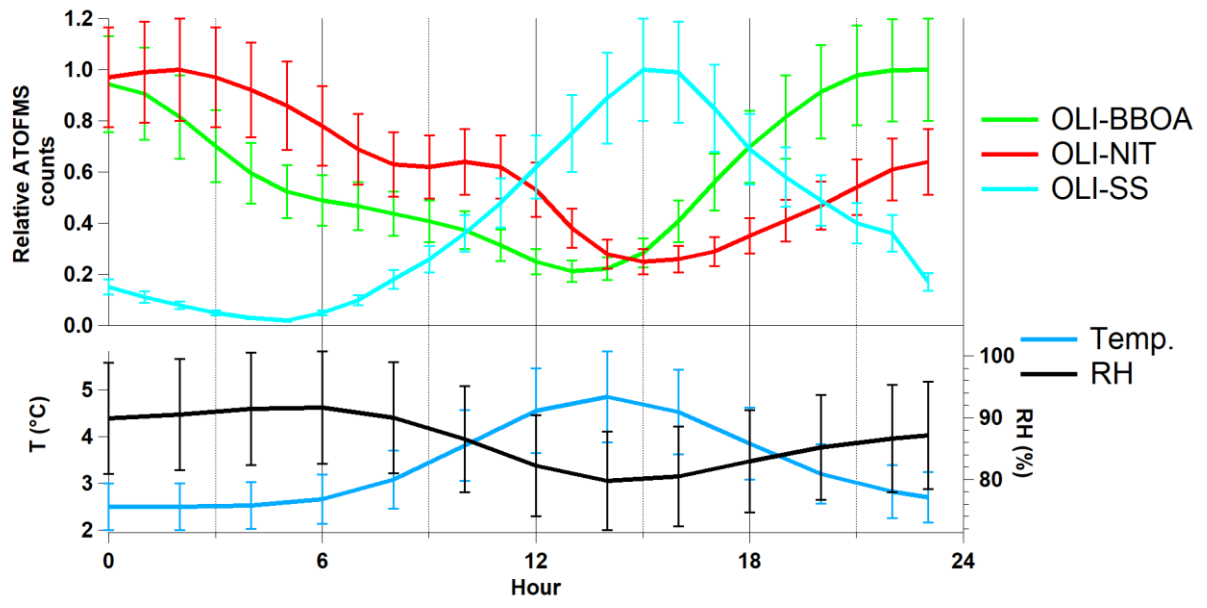
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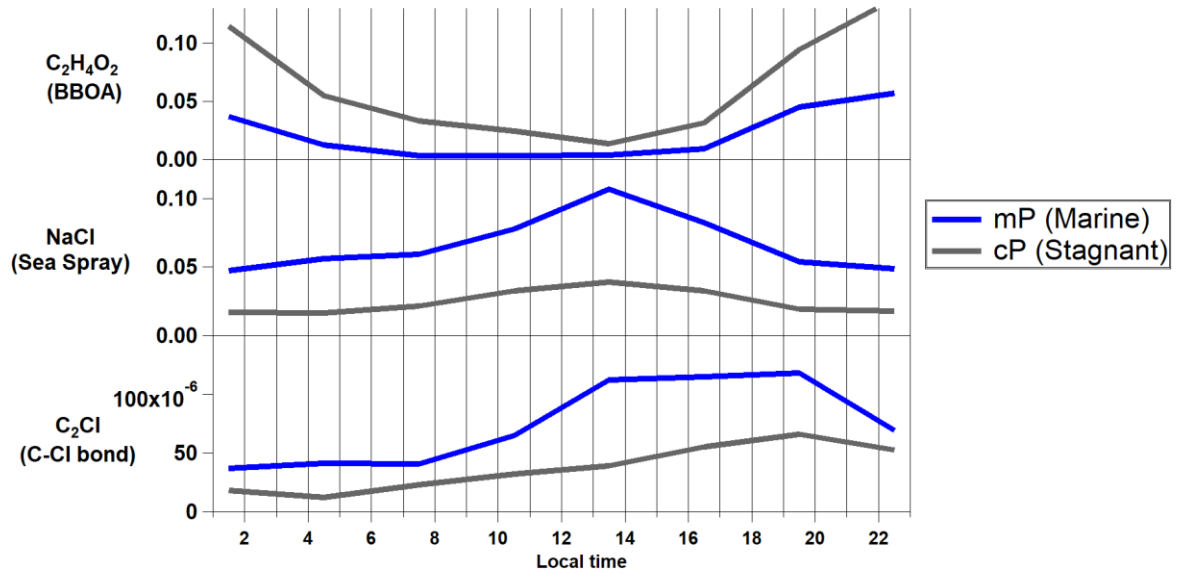
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