Atmospheric Environment 171 (2017) 118–125

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Distinct high molecular weight organic compound (HMW-OC) types in aerosol particles collected at a coastal urban site

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ARTICLE INFO

Keywords:
Oligomers
High molecular weight organic compounds
ATOFMS
Sea salt
Mixing state

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., 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

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http://dx.doi.org/10.1016/j.atmosenv.2017.10.007
Received 13 April 2017; Received in revised form 25 September 2017; Accepted 4 October 2017

partitioning, hygroscopic growth, particle reactivity, and health effects. However, oligomers are not often clearly observed in ambient aerosols and there is uncertainty over the extent of their relevance under atmospheric conditions. 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; Gantt 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 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, 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 600° 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