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Molecular characteristics of the water soluble organic matter in size-fractionated aerosols collected over the North Atlantic Ocean

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ABSTRACT

Size-fractionated aerosol impactor samples ($n = 3$) representing North American, North African, and marine air mass influences were collected over the North Atlantic Ocean as part of the 2011 US GEOTRACES cruise (GEOTRACES GA03), and a molecular-level chemical characterization of the water soluble organic matter (WSOM) was obtained using electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry. Remarkable differences were found between the molecular characteristics of WSOM from the fine (<0.49 μm) and coarse size fractions demonstrating the importance of collecting size-fractionated aerosols in order to obtain a full molecular characterization of aerosol WSOM. The greatest molecular complexity, as defined by the number of formulas in each fraction, was found in the <0.49 μm fraction of North American and North African-influenced aerosols, and in the >7.2 μm fraction of marine-influenced aerosols. Principal component analysis (PCA) showed the <0.49 μm fraction of the North American-influenced WSOM to be differentiated from all other size fractions by the prevalence of highly oxidized compounds, an indicator of atmospheric aging. The coarse fractions of the North American-influenced sample showed evidence of important contributions from low O/C (<0.2) and condensed aromatic compounds indicative of primary combustion-influenced organic matter (OM). The fine fractions of the marine and North African-influenced samples showed characteristics of a primary marine biological source including peptide-like, phospholipid-like, and carbohydrate-like molecular formulas. The coarse fractions of the marine sample and the 0.49–3.0 μm fraction of the North African-influenced sample were defined by molecular formulas at intermediate O/C (0.2 to 0.6) and high H/C (>1.5) ratios including many heteroatom (N, S, P) containing formulas. Condensed aromatic compounds, which originate from anthropogenic sources and can affect the global climate by absorbing solar radiation, as well as compounds that can be attributed to secondary organic aerosols (SOA), were found in all 17 WSOM fractions analyzed. This indicates the ubiquitous nature of these types of compounds across aerosol size fractions and air mass influences, even in aerosols collected over the middle of the ocean. These results provide an indication of size-fractionated aerosol composition, and future molecular characterization work should be paired with physical characteristics to inform size-fractionated and source-resolved models of aerosol OM impacts in the atmosphere.

1. Introduction

Organic matter (OM) contributes a significant proportion to aerosol mass, particularly to the fine fraction, of which it can comprise 20–90% (Kanakidou et al., 2005). Aerosol OM affects global climate directly by scattering and absorbing light interfering with the Earth's radiative balance and indirectly by acting as cloud condensation nuclei (Lohmann and Feichter, 2005; Yu et al., 2006). Further, OM from both natural and anthropogenic sources that enters the atmosphere has an effect on the Earth's biogeochemical cycles, because much of atmospheric OM is deposited to terrestrial and aquatic environments (Jacobson et al., 2000). To a large degree, the molecular composition of aerosol OM determines its environmental impact through effects on light scattering and absorption in the atmosphere (Andreae and Gelencsér, 2006), aerosol hygroscopicity and cloud condensation nuclei formation (Demou et al., 2003; Ellison et al., 1999), and biogeochemical impacts upon deposition (e.g., Paris and Desboeufs, 2013; Wozniak et al., 2013). The molecular composition of aerosol OM has been shown to vary with aerosol source (e.g., Decesari et al., 2007; Wozniak et al., 2014), atmospheric processing (e.g., Jimenez et al., 2009; Kroll et al., 2011), and particle size (e.g., Cavalli et al., 2004; Tagliavini et al., 2006), though the details of the various factors determining molecular composition, and by extension environmental impact, of aerosol OM are still uncertain.

Understanding the factors determining aerosol OM molecular composition in marine environments is a particular challenge due to the difficulty in collecting samples in remote environments, the multiple potential sources (e.g., marine, anthropogenic, continental dust,

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biomass burning) contributing to the OM mass, and atmospheric processing of OM during long range transport. Numerous studies on aerosols collected from various sources have shown the source dependence of aerosol composition (Carbone et al., 2010; Cavalli et al., 2004; Jayaratne et al., 2011; Radhi et al., 2010; Wozniak et al., 2012a, 2012b). Marine aerosol OM composition can vary depending on the relative abundance of anthropogenic and mineral dust continental aerosols, which have been photochemically aged to varying degrees during long range transport, relative to each other and to marine-derived aerosols (Andreae, 2007; Hawkins et al., 2010; Wozniak et al., 2014). Purely marine aerosols originate from bubble bursting at the ocean surface; they are dominated by inorganic sea salts, but also contain OM from biological and secondary sources (Bigg and Leck, 2008; O'Dowd and de Leeuw, 2007). Of the continentally-influenced aerosols that make their way into the marine atmosphere, the anthropogenically-influenced aerosols (collected from areas with significant combustion emissions) have higher proportions of OM as compared to mineral dust-influenced aerosols (Pósfai and Buseck, 2010; Putaud et al., 2004; Wozniak et al., 2013).

Recent studies have shown that aerosol OM characteristics vary with particle size. Generally speaking, marine aerosols are associated with coarse particle sizes due to the presence of inorganic salts (e.g., Cavalli et al., 2004), but O'Dowd et al. (2004) found that while sea salt was the dominant component of coarse marine aerosols, OM dominated the fine fraction during times of high biological activity. In continentally-influenced aerosols, anthropogenic aerosols have a larger concentration in the fine size fraction due to the presence of compounds associated with fossil fuel combustion, while the mass concentration of mineral dust aerosols lies in the coarse fraction (Flament et al., 2011; Ramanathan et al., 2001). Anthropogenic-influenced continental aerosols include coarse particles as well, such as those from road dust resuspension (Manoli et al., 2002) and from naturally occurring biogenic sources (Kavouras et al., 1999). Very fine, nucleation mode aerosols consist of secondary organic aerosols (SOA) formed in the atmosphere by gas-particle conversion processes such as nucleation, condensation and various chemical reactions, as well as small primary emitted particles from both natural and anthropogenic sources (Hallquist et al., 2009). Proton NMR studies have shown aerosols in the Amazon basin to have higher alkyl content in the fine fractions and higher alcohol content in the coarse fractions (Tagliavini et al., 2006). In studies of marine aerosols, proton NMR has shown stronger signals for hydrogens attached to carbons bound to heteroatoms in the fine fractions and stronger signals for hydrogens attached to carbons having alcohol and ether groups in the coarse fractions (Cavalli et al., 2004).

The challenge of obtaining a complete characterization of aerosol OM from several sources and varying reactivities is made even more difficult in marine aerosols which have significantly lower OM loadings compared to aerosols collected in terrestrial environments (e.g., O'Dowd et al., 2004; Hawkins et al., 2010; Wozniak et al., 2013) and thus stretches the limits of the available analytical techniques. Recently, electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FTICR-MS) has been used to successfully characterize a large fraction of complex water soluble organic matter (WSOM) in aerosols at the molecular level (e.g., Duarte and Duarte, 2011; Reemtsma et al., 2006; Schmitt-Kopplin et al., 2012; Wozniak et al., 2008, 2014), but to our knowledge, none have examined size-fractionated marine aerosol samples. Considering the fact that significant chemical differences, which show distinct impacts in the atmosphere, have been noted previously for size-fractionated aerosol OM, it is clear that the application of ESI FTICR-MS for aerosol OM characterization of size-fractionated aerosols will advance our understanding of aerosol OM environmental impacts.

In the present study, the molecular characteristics of WSOM isolated from size-fractionated aerosols collected over the North Atlantic Ocean as part of the 2011 US GEOTRACES cruise are investigated via ESI FTICR-MS. Principal component analysis (PCA) is performed to facilitate comparison of the molecular characteristics providing distinguishing molecular characteristics of the various size fractions and air mass influences that have bearing on aerosol environmental impacts.

2. Materials and methods

2.1. Sample collection, handling and storage

Cascade impactor aerosol samples were collected aboard the R/V Knorr along a trans-North Atlantic Ocean transect on November 8–9, December 1–2, and December 6–7, 2011 as part of the 2011 US GEOTRACES program cruise (www.geotraces.org) (Table 1, Fig. 1). A five stage Sierra-style slotted cascade impactor (Series 230 High Volume Cascade Impactor, Tisch Environmental) was deployed in a high volume aerosol sampler (model TSP 5170, Tisch Environmental) set to process approximately 1.2 m^3 air min^{-1}. The particle size range cutoffs for the five impactor stages and backing filter, based on 50% collection efficiency for spherical particles (Dp50), were estimated as follows: 1) >7.2 μm, 2) 3.0–7.2 μm, 3) 1.5–3.0 μm, 4) 0.95–1.5 μm, 5) 0.49–0.95 μm, and backing filter < 0.49 μm. Measuring the actual particle size distribution on each stage requires separate measurements and instrumentation which are beyond our capabilities and the scope of this work. The particle size cutoffs described by the manufacturer for the five impactor stages and backing filter are based on 50% collection efficiency for spherical particles (Dp50), meaning that the low end of the size ranges (e.g., 7.2 μm for stage 1, 3.0 μm for stage 2, etc.) represents the diameter at which 50% of particles with that diameter are collected. Thus, particle dispersion occurs, and a given impactor stage collects particles outside of the assigned particle diameter ranges, but we can be confident that the majority of the coarsest particles are captured on the first stage and progressively smaller particles are captured on the subsequent stages. The cutoffs and particle diameter ranges are based on experimental values obtained from calibration with mono-disperse aerosols as described in Willeke (1975). Data from Arimoto et al. (1997), suggest that variations in these cutoff diameters are due mostly to variations in the sampling flow rate, and these variations were less than 10% (1 SD) for flow rates that varied by a factor of more than 50%. Flow rates in this study were maintained at near constant rates of ~1.2 m^3 min^{-1}, and we can be confident that the cutoffs were consistent among the samples. Impactor samplers have also been suggested to suffer from particle bounce, wherein particles bounce off the impactor surface and are re-entrained into the sampler flow and sampled on the subsequent smaller cutoff stages, leading to erroneous size distributions (Walsh et al., 1978). However, Arimoto et al. (1997) argued that particle bounce is minimized by the use of Whatman cellulose filters and by humid marine conditions such as those observed in this study. Walsh et al. (1978) also suggest that these types of impactor samplers may suffer wall losses, but Morton et al. (2013), using the same samplers, found very good agreement between trace element loadings collected using bulk and impactor samplers concurrently, suggesting that particle wall losses were not a problem.

A total of 17 size-fractionated aerosol filters were collected: all six size fractions for the North American and marine-influenced samples, and five size fractions for the North African-influenced sample (stage 1 was not collected for this sample, thus stage 2 includes particle sizes >7.2 μm in addition to those from 3.0 to 7.2 μm). Acid-washed slotted Whatman 41 cellulose ester filters with dimensions of 14 cm × 14 cm and an acid-washed 20 cm × 25 cm Whatman 41 backing filter were utilized for collection. The cascade impactor sampler was deployed 14 m above sea level on the ship's flying bridge. Aerosol sampling was controlled with respect to wind sector and wind speed using an anemometer interfaced with a Campbell Scientific CR800 datalogger in order to avoid contamination from the ship's stack exhaust. Only when the wind was ±60° from the bow and >0.5 m/s was the sampler allowed to run. The sampler was automatically shut off when the wind did not meet the direction and speed requirements and would only restart