Characterization of CHOS compounds in rainwater from continental and coastal storms by ultrahigh resolution mass spectrometry

Ralph N. Mead a,*, J. David Felix a, G. Brooks Avery a, Robert J. Kieber a, Joan D. Willey a, David C. Podgorski b

a Department of Chemistry and Biochemistry, University of North Carolina Wilmington, Wilmington, NC 28403-5932, USA
b Future Fuels Institute, National High Magnetic Field Laboratory, Florida State University, 1800 East Paul Dirac Dr., Tallahassee, FL 32310-4005, USA

HIGHLIGHTS

- Differences in CHOS compounds in precipitation from two different air mass back-trajectories.
- Presence of organo-sulfate and reduced organo-sulfur species in precipitation.
- Highly condensed reduced organo-sulfur compounds only in continental precipitation.

ARTICLE INFO

Article history:
Received 10 September 2014
Received in revised form
21 January 2015
Accepted 23 January 2015
Available online 24 January 2015

Keywords:
Rainwater
CHOS
FT-ICRMS
Ultrahigh resolution mass spectrometry

ABSTRACT

Rainwater from four continental and three coastal storms was collected and analyzed by (-) ESI Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). This study presents a comprehensive comparison of the CHOS molecular formulas of rainwater dissolved organic matter from these two different storm trajectories. There were 899 and 695 total molecular formula assignments in the continental and coastal storms respectively. Of these, 33% and 15% were unique to continental and coastal storms. Kendrick mass analysis of methylene units highlighted oligomers present in both storm types illustrating their ubiquitous occurrence in atmospheric waters. There was also evidence of organo-sulfate containing molecular formulas as well as highly condensed aromatic structures containing one sulfur and one oxygen. These condensed aromatic sulfur containing structures likely originate from fossil fuel sources and were only detected in continental derived rainwater.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Elucidating the composition of rainwater dissolved organic matter (DOM) has remained at the forefront of atmospheric research principally because of its central role in a host of fundamentally important atmospheric processes (Mullahay et al., 2011; Willey et al., 2012). Rainwater DOM is a complex heterogeneous mixture of organic compounds, the composition of which remains to a large extent unknown (Altieri et al., 2012; Mitra et al., 2013). This is particularly true when describing organic entities that contain one or more sulfur atoms (Zhao et al., 2013). Organo-sulfur containing compounds play a pivotal role in the formation of secondary organic aerosols (SOA) (Karambelas et al., 2014; Surratt et al., 2007) leading to high molecular weight oligomers. These compounds are of particular interest in the chemistry of the troposphere because they can enhance hydroscopicity of droplets acting as cloud condensation nuclei (Hung et al., 2014).

Unraveling the composition of organic sulfur species in atmospheric waters is hindered primarily by the difficulty in describing molecular formulas of a suite of analytes present in very low abundances in a complex matrix. Recent analyses of atmospheric waters by Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) demonstrated that individual molecular formulas of organic moieties can be assigned with great accuracy. Altieri et al. (2009) used FT-ICR MS to investigate the provenance and elemental composition of rainwater organic sulfur species in rain from an anthropogenically impacted location in New Jersey, USA. The authors suggested that the organo-sulfates likely
contributed to the large percentage of uncharacterized water-soluble organic carbon species in atmospheric organic matter and that several organo-sulfates could be used as tracers for SOA formed under highly acidic conditions. Sulfur containing molecular formulas were also found in cloud water dissolved organic matter were CHOS compounds with reduced forms of S were observed in addition to organo sulfates (Zhao et al., 2013).

Altieri et al. (2009) and Zhao et al. (2013) were important studies because they demonstrated the utility of FT-ICR MS in describing organo-sulfur species in atmospheric waters. One of the most important uncertainties regarding organo-sulfur speciation is how the molecular distribution of the various species is influenced by storm origin as determined by air mass back trajectory. The significance of storm origin on organic matter composition was underscored in a recent study by Mead et al. (2013) utilizing FT-ICR MS to analyze H2CO compounds in rainwater collected from both continental and coastal derived storms. Approximately 25% of the roughly 2000 assigned CHO molecular formulas were unique to each storm classification indicating the importance of air mass back trajectory on the composition of rainwater DOM. Analysis of the unique molecular formula assignments highlighted distinct groupings of various bio- and geo-molecular classes with coastal storms containing unique formulas representative of carbohydrate-like compounds while continental storms had lipid-like formulas. Mead et al. (2013) also found that continental storms contained condensed aromatic structures derived from fossil fuel combustion sources similar to black carbon which were not present in coastal rain events. The present study represents the first detailed analysis of organo-sulfur containing compounds in rainwater by FT-ICR MS collected on an event basis from a series of continental and coastal storms at one geographical location. The data generated therefore provide the most comprehensive examination to date of the chemical formulas of the organo-sulfur containing components of rainwater DOM from various air-mass back trajectories.

2. Methods

2.1. Sample collection

Precipitation event samples were collected on the University of North Carolina Wilmington campus (34°13.9’N, 77°52.7’W) located approximately 8.5 km from the Atlantic Ocean. Automatic Sensing Wet/Dry Precipitation Collectors (four Aerochem-Metrics (ACM) Model 301) were used to collect samples. The precipitation collectors housed 4 L glass beaker placed within a HDPE plastic bucket. All glassware used for rain collection, filtration apparatus and storage containers were baked at 450 °C in a muffle furnace for a minimum of 4 h to remove organics prior to use. Real time precipitation maps were used to define the end of precipitation events. Once collected, the rainwater was filtered (0.2 µm pore size, poly-sulfone) and stored at 4 °C prior to analysis. Meteorological data including rain amounts, rain duration, time of day, surface temperature and airmass back trajectory were also recorded.

Storm events were classified using air-mass back-trajectories generated by the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) developed at the National Oceanic Atmospheric Administration Air Resources Laboratory using the web based version (Draxler and Hess, 1998). Storms were visually classified as continental when the air mass was predominately over land and as coastal if there were significant marine influences (Avery et al., 2006a, 2006b; Kieber et al., 2006a, 2005; Southwell et al., 2010; Willey et al., 2009, 2000).

2.2. Sample handling and mass spectrometry

All sample preparation, mass spectrometric acquisition and data processing was the same as described in an earlier study (Mead et al., 2013). Filtered rainwater was lyophilized and reconstituted in methanol prior to FT-ICR MS analysis. Lyophilization was chosen as the pre-concentration technique because C18 SPE recovers on average only 36% of DOM total integrated fluorescence (Miller et al., 2009) suggesting most of the chromophoric material is hydrophilic and not effectively bound to the C18 non-polar stationary phase. A second study comparing solution state 1H NMR C18 extractable rainwater DOM to freeze dried rainwater DOM also reported considerable differences between the two preparation techniques. The freeze-dried sample had a richer, more abundant 1H NMR spectra compared to the analogous C18 SPE fractionated rain sample (Seaton et al., 2013).

FT-ICR MS spectra were acquired with a passively shielded 9.4 T superconducting magnet (Oxford Instruments, Abingdon, Oxfordshire OX13 5QX United Kingdom) located at the National High Magnetic Field Laboratory in Tallahassee, Florida (Kaiser et al., 2011). Spectra were acquired over a m/z range of 155–1200 Da. Time-domain transient signals were collected and processed by a modified 1D ICR data acquisition system (Blakney et al., 2011). Sample was directly infused at a flow rate of 0.3 µL min⁻¹ and negative ions were produced at atmospheric pressure by an external electrospray source with needle voltage at ≈ 2300 V (Gonsier et al., 2011). Ions were accumulated in the first radio frequency (rf)-only octopole for approximately 0.5 s before transfer through a quadrupole into a second rf-only octopole where they were collisionally cooled with helium gas, then transferred through a rf-only quadrupole to a seven segment open cylindrical cell with capacitively coupled excitation electrodes similar to the configuration of Tolmachev et al. (2008). Chirp excitation (~700-90 kHz at a sweep rate of 50 Hz µs⁻¹ and 360 Vp-p amplitude) accelerated the ions to a detectable cyclotron radius (Tolmachev et al., 2008). Approximately 100–200 time-domain acquisitions were co-added, Hanning-apodized, and zero-filled once prior to fast Fourier transform and magnitude calculation. Frequency was converted to m/z by the quadrupolar electric trapping potential approximation (Ledford et al., 1984; Shi et al., 2000). Spectra were internally calibrated from extended homologous alkylation series (compounds that differ in elemental composition by integer multiples of CH2) of high relative abundance. Mass accuracy for all assignments was equal to or less than 500 ppb. Given the reproducibility of (−) ESI FT-ICR MS between replicates, single measurements were done (KidoSoule et al., 2010; Mesfioui et al., 2012).

Molecular formulas were assigned from measured m/z values with the Predator Analysis algorithm developed at the National High Magnetic Field Laboratory. Elemental constraints for the assignment of DOM molecular formulas were C2n-100, H4,2n-200, O0-20 and S0-1 and are based upon the literature (Kujawinski and Behn, 2006). Every signal in the mass spectra for which a unique molecular formula could be assigned was sorted by elemental composition (C, H, O, and S). The double bond equivalents parameter (DBE = number of rings plus double bonds to carbon) measures hydrogen deficiency and is calculated from the elemental composition, CnH2nX2OySz (DBE = C – h/2 + n/2 + 1) as determined by FT-ICR mass spectrometry (Kramer et al., 2004; Stenson et al., 2003). Each molecular formula was assigned an aromaticity index (AI) based on the system proposed by Koch and Dittmar (Koch and Dittmar, 2006). Formulas are conservatively classified as non-aromatic (AI < 0.5), aromatic (AI > 0.5) and condensed aromatic (AI > 0.67). Individual storm event data from the same storm classification was pooled and considered as one. This was done to mitigate any mass spectral peak differences observed between
samples due to variations in concentration, ionization efficiencies and salt content between samples. The data presented and discussed in this study are unique to each storm type. In other words, if an assigned molecular formula occurred in both storm types it was not considered in this study.

3. Results and discussion

3.1. Rainwater bulk properties

A total of seven rain samples collected from both continental (4) and coastal (3) rain events were analyzed. A description of the chemical characteristics of each rain event and corresponding back trajectories can be found elsewhere (Mead et al., 2013). There was a higher percentage of unique molecular formula assignments in continental derived storms compared to coastal storms with almost double the molecular formula assignments of CHOS compounds (Table 1). The average unique molar ratios of O:C and H:C of all CHOS assignments for continental derived storms were 0.4 ± 0.4 and 1.2 ± 0.4 respectively. Similarly the coastal derived storm average O:C and H:C unique molar ratios were 0.5 ± 0.2 and 1.5 ± 0.4 respectively. The average unique molecular weight of continental and coastal storms were 345 ± 89 and 427 ± 67 respectively. Although continental derived storms have almost double the unique CHOS compounds as coastal rain, it appears there are only subtle differences between the rainwater CHOS containing formulas that are unique to each storm type. As a comparison to this study, terrestrial derived rainwater from southeastern United States was analyzed by FT-ICR MS and the distribution of CHOS molecular formulas was 14% of the total number of molecular formula assignments (Mitra et al., 2013). The O:C and H:C of the CHOS compounds from the same study were 0.34 and 1.5, respectively. Although the elemental ratios of formulas detected in this study and the work by Mitra et al. (2013) are similar, it is impossible to state that identical compounds are shared in the two sample sets. However, the similarity does suggest that the DOM isolated from rainwater at these different locations is similar in molecular composition.

3.2. van Krevelen analysis

The van Krevelen plot is a means to graphically represent the elemental ratios from assigned molecular formulas. Distinct patterns emerge based upon when the O:C is plotted vs. the H:C. van Krevelen plots have been used to characterize distinct classes of organic matter found in atmospheric waters such as lipid-like material and condensed aromatic hydrocarbons (Altieri et al., 2012; Mitra et al., 2013; Wozniak et al., 2008). Clear differences have been observed in the composition of dissolved organic matter based upon the van Krevelen plots of CHO containing compounds in continental and coastal storms from a previous study (Mead et al., 2013).

The van Krevelen plot of CHOS containing compounds had clear differences between coastal and continental derived storms (Fig. 1). A conservative description of the source of the compound can be inferred based upon the location of the formula assignment in the van Krevelen plot (Kim et al., 2003). There are a series of coastal derived formulas with high H:C between 1.5 and 2 and low O:C between 0.2 and 0.3 that can be considered lipid-like based upon the elemental ratios of lipids. A clear delineation of formulas can be

<table>
<thead>
<tr>
<th>Storm type</th>
<th>Total assignments</th>
<th>Unique assignments</th>
<th>% Unique</th>
<th>Average (±SD) unique O:C</th>
<th>Average (±SD) unique H:C</th>
<th>Average (±SD) unique MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continental</td>
<td>899</td>
<td>294</td>
<td>33</td>
<td>0.4 ± 0.4</td>
<td>1.2 ± 0.4</td>
<td>345 ± 89</td>
</tr>
<tr>
<td>Coastal</td>
<td>695</td>
<td>107</td>
<td>15</td>
<td>0.5 ± 0.2</td>
<td>1.5 ± 0.4</td>
<td>427 ± 67</td>
</tr>
</tbody>
</table>
derived from continental storms as indicated by the near vertical line with H:C approximately 0.4–1.5 and O:C approximately 0.1. Molecular formulas with low H:C are typical of condensed aromatic hydrocarbons that originate from many sources. One possible source of these condensed aromatics may be from biomass burning in continental storms that would not be generated in coastal or marine dominated events.

### 3.3. CH₂O and S distribution

The double bond equivalent (DBE) distribution of all unique formulas for both storm types was plotted vs. number of carbons (Fig. 2). DBE is a means to investigate the hydrogen deficiency of molecular formulas compared to the corresponding saturated n-alkane with the same number of carbons. For example, hexane (C₆H₁₄) has a DBE = 0 while 1-hexene (C₆H₁₂) has a DBE = 1 representing the replacement of 2 hydrogens with a double bond. In addition to accounting for double bonds to carbon, DBE also accounts for saturated rings and carbonyl functionalities. The DBE of the molecular formulas assigned to continental storms ranged from 0 to 20 while the DBE for coastal storms ranged from 0 to 9 (Fig. 2). The difference in DBE distribution indicates that continental storms contain compounds that are significantly more unsaturated/condensed relative to coastal storms. Continental storms also have a broader carbon number distribution with a range of C₅–C₃₅ relative to the carbon number distribution of coastal storms C₈–C₂₈. Of the total formulas unique to continental storms, 26% have DBE > 10 while all formulas unique to coastal storms have DBE < 10. The contrast in DBE between coastal and continental derived events indicates that approximately a quarter of the unique molecular formulas in continental storms are highly condensed/unsaturated.

The heteroatom class distributions of oxygen in unique sulfur-containing formulas for both storm types are presented in Fig. 3a and b. Fifty six percent of continental and 97% of coastal derived storms respectively have O:S > 4 while 37% of continental derived storms have O:S < 4 and none of the coastal derived storms have O:S < 4. The distribution of oxygen and carbon in sulfur-containing formulas are illustrated in Fig. 4 keeping in mind the number of sulfur atoms is one thus the data illustrates the distribution of sulfur containing compounds between storm types. Continental storms have the broadest distribution of oxygen and carbon-containing compounds while the distribution of the same atoms in coastal derived storms is relatively truncated. This further highlights the differences in source and/or processing of rainwater dissolved organic matter in the two storm types.

One possible form of S is an organo-sulfate (R-O-SO₃H) functional group, which has been observed before in atmospheric water samples (Altieri et al., 2009; Schmitt-Kopplin et al., 2010). Organosulfates...
sulfate compounds can form through a variety of mechanisms but are typically produced via secondary reaction products (Hatch et al., 2011; Nguyen et al., 2012). Acid-catalyzed epoxide ring-opening reactions have been shown to yield organosulfates from a number of biogenic VOCs, including isoprene (Lin et al., 2012; Surratt et al., 2010), 2-methyl-3-buten2-ol (Zhang et al., 2012, 2014) or monoterpenes (Linuma et al., 2009, 2007; Surratt et al., 2008). A number of other organosulfates have been observed (including nitrated derivatives) from biogenic VOC oxidation products (Surratt et al., 2008) and anthropogenic sources (Staudt et al., 2014), but the formation mechanisms remain unclear. Recent studies have also suggested the role of sulfate radical anions in solution (Nozière et al., 2010).

The elemental ratio of O:S can be used as a proxy for the occurrence of organo-sulfate functional groups given the constraints of one S atom used in the assigned formulas. Therefore, if organo-sulfate functionalities are present then O:S ratio will be equal to four. Both storm types contain formulas with O:S = 4 but there were also numerous assignments with O:S > 4 in the lower left portion of the van Krevelen plot with relatively low H:C and O:C are of particular interest. The region of the van Krevelen plot where these compounds are typically not reported and/or observed in atmospheric waters. Potential sources of reduced S containing compounds are fossil fuel combustion products (Nishioka, 1988; Panda et al., 2007; Sinninghe Damsté et al., 1999).

### 3.4. Highly condensed organo-sulfur formulas

The series of molecular formulas in the lower left portion of the van Krevelen plot with relatively low H:C and O:C are of particular interest. The region of the van Krevelen plot where these compounds are located indicate that they are condensed cyclic structures. The aromaticity index (AI) proposed by Koch and Dittmar is one method to assign a value to rank formulas and their associated compounds based on aromaticity (Koch and Dittmar, 2006). If a formula has AI ≥ 0.67, the corresponding compound(s) are considered to be condensed aromatics, if the AI > 0.5 then the compound is considered aromatic, and if the AI is <0.5 then the compound is considered to be relatively saturated. All molecular formula assignments in this study with an AI ≥ 0.67 contain one oxygen and one sulfur (Table 2). Possible structures for several of these compounds are presented in Fig. 5 in mind there are many isomers and these are just one possibility. There are a series of formula assignments in Table 2 that differ by 2 hydrogen atoms suggesting successive hydrogenation (e.g. \( \text{C}_{16}\text{H}_{32}\text{OS} \) and \( \text{C}_{18}\text{H}_{34}\text{OS} \)). One possible structural series displayed in Fig. 5a and b differ by just 2 hydrogens from hydrogenation of a double bond within the ring system. Organic sulfur functional groups have been detected before in polycyclic aromatic hydrocarbons from a variety of human activities such as combustion of diesel and coal (Tolosa et al., 1996).

### 4. Implications and conclusions

This study represents the first comprehensive examination of CHOS containing molecular formulas from different air mass back trajectories. Continental rain contained a number of organo-sulfate CHOS compounds based upon the observed O:S ratio. Of particular interest was the occurrence of highly condensed aromatic structures containing only one S and one O in continental derived rainwater. To the best of our knowledge, this is the first study to definitively demonstrate the occurrence of these compounds. These molecules may arise from anthropogenic or natural sources but their highly condensed nature suggests that they are derived from combustion processes (Mead et al., 2013).

The formation of CHOS containing compounds can occur via reaction with an organic compound dissolved in atmospheric waters from natural and anthropogenic sources and an atmospheric oxidant forming low volatile highly water soluble products (Hatch et al., 2011; Shapiro et al., 2009). However, what is not understood presently is the role of changing rainwater DOM chemistry on this process. For example, increasing peroxide concentrations in rainwater (Mullaugh et al., 2011) may oxidize CHOS compounds thereby increasing their water solubility and decreasing their atmospheric lifetime. This may be especially important for condensed CHOS structures with conjugated pi systems that are
potentially chromophoric. Removing these compounds from atmospheric waters faster may have an impact on solar actinic flux and photochemical processes. Ethanol derived from biofuels may impact the formation and/or decay of CHOS compounds in rainwater by influencing the oxidizing capacity of atmospheric waters (Kieber et al., 2014; Millet et al., 2012).

Acknowledgments

The authors thank the National Science Foundation for financial support under grant AGS-1003078. Work performed at the National High Magnetic Field Laboratory was supported by NSF Division of Materials Research through DMR-11-57490, BP/The Gulf of Mexico Research Initiative to the Deep-C Consortium, the Future Fuels Institute, and the State of Florida.

References


