



Insights into dissolved organic matter complexity in rainwater from continental and coastal storms by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry

R. N. Mead¹, K. M. Mullaugh¹, G. Brooks Avery¹, R. J. Kieber¹, J. D. Willey¹, and D. C. Podgorski²

¹Department of Chemistry and Biochemistry University of North Carolina, Wilmington, NC 28403-5932, USA

²National High Magnetic Field Laboratory 1800 East Paul Dirac Dr., Tallahassee, FL 32310-4005, USA

Correspondence to: R. N. Mead (meadr@uncw.edu)

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Abstract. A series of seven rainwater samples were collected in Wilmington, North Carolina USA originating from both continental and coastal storms and analyzed by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). This data set is unique in that it represents a detailed comparison of the molecular level composition of DOM in rainwater collected from distinctly different air mass back trajectories by FT-ICR MS. Approximately 25 % of the roughly 2000 assigned CHO molecular formulas are unique to a single storm classification indicating the importance of air mass back trajectory on the composition of rainwater dissolved organic matter (DOM). Analysis of the unique molecular formula assignments highlighted distinct groupings of various bio- and geo-molecule classes with coastal storms containing unique formulas representative of lignin and cellulose-like formulas while continental storms had lipid-like formulas. A series of 18 distinct methylene oligomers were identified in coastal storms and 13 unique methylene oligomers in continental storms, suggesting oligomer formation is ubiquitous in rainwater albeit different for each storm classification. Oligomers of small acids and C₃H₄O₂ were detected in both storm types indicating their processing may be similar in both back trajectories. Condensed aromatic hydrocarbons were detected in continental storms with phenol moieties that are not as oxidized as similar compounds detected in aquatic DOM.

1 Introduction

Dissolved organic matter (DOM) is a major component of both marine and continental rain present in concentrations greater than nitric and sulfuric acids combined (Willey et al., 2000). Rain is a significant source of DOM to surface seawater (90×10^{12} g C yr⁻¹), equivalent to the magnitude of river input of DOM to the open ocean and half the magnitude of carbon buried in marine sediments per year on a global scale (Willey et al., 2000). DOM plays a central role in many important rainwater reactions including free radical generation and trace metal complexation (Witt et al., 2007; Faust and Zepp, 1993). Recent studies also demonstrate that a significant fraction of DOM is chromophoric, suggesting this material plays a pivotal role in the wavelength dependent spectral attenuation of solar radiation by atmospheric waters (Kieber et al., 2012; Muller et al., 2008; Santos et al., 2012).

Despite the global significance of DOM to climate change and the chemistry of the troposphere, its composition, source and patterns of variation remain poorly constrained. Attempts to characterize rainwater DOM have utilized a combination of spectroscopic and molecular level measurements such as nuclear magnetic resonance (NMR) and excitation emission fluorescence spectroscopy (EEMs) (Santos et al., 2012; Miller et al., 2009). Recent studies have also employed the isotopes of carbon (¹³C and ¹⁴C) to estimate the relative contribution of natural and anthropogenic inputs to rainwater organic matter (Avery et al., 2006b; Raymond, 2005).

Characterizing organic matter in rainwater is a challenge primarily because of the complexity and number of compounds present in the mixture. Usually chromatographic

or other preparative techniques (e.g., ultrafiltration or solid phase extraction) are performed prior to analysis to reduce the background or lessen matrix effects potentially altering the composition of rain DOM (Santos et al., 2012; Decesari et al., 2005). Recently there have been significant advances made in the characterization of rainwater DOM and aerosol water-soluble organic carbon using ultra high resolution Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) (Nizkorodov et al., 2011; Altieri et al., 2009, 2012). FT-ICR MS offers ultra-high resolving power to assign molecular formulas at environmentally relevant concentrations in complex aquatic matrices such as natural water (Stenson et al., 2003). A previous study using this powerful technique to characterize rainwater dissolved organic matter provided important compositional information of various combinations of C, H, O, N, S and P based upon season and back trajectory but did not look at C, H, O alone (Altieri et al., 2012). The present study represents the first detailed analysis of C, H, O containing compounds in rain water by FT-ICR MS collected on an event basis from a series of continental and coastal storms. The data generated provide the most comprehensive examination to date of the chemical formulas present in rainwater DOM of various air mass back trajectories.

2 Methods

2.1 Sample collection

Rainwater 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.

Four Aerochem Metrics (ACM) Model 301 Automatic Sensing Wet/Dry Precipitation Collectors were used to collect rain samples which housed a 4 L glass beaker placed within a HDPE plastic bucket. Rainwater samples were collected on an event basis and brought back to the laboratory less than 12 h after precipitation stopped. Real-time precipitation maps were used to define the end of specific rain events. Rainwater was filtered (0.2 µm pore size, polysulfone) and stored at 4 °C prior to analysis. 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 hours to remove organics prior to use. Meteorological data including rain amounts, rain duration, time of day, surface temperature and storm origin were also recorded.

2.2 Sample handling and mass spectrometry

All solvents used were purchased from Burdick and Jackson. Filtered rainwater was transferred to a 250 mL round bottom flask and flash frozen by placing the flask into a vessel containing a slurry of dry ice and acetone. The temperature of this mixture (−78 °C) is such the rainwater water freezes within minutes. Once frozen, the round bottom flask

containing the sample was placed on a Labconco 4.5 freeze-zone lyophilizer until dry – usually within 4–5 h – and dissolved in HPLC grade methanol prior to FT-ICR MS analysis. Lyophilization was chosen as the pre-concentration technique to recover as much of the rainwater DOM as possible. It has been found C₁₈ SPE only recovers on average 36 % of DOM total integrated fluorescence in rain samples (Miller et al., 2009). Based upon this most of the chromophoric material present in rainwater is hydrophilic and not effectively bound to the C₁₈ non-polar stationary phase. A second study compared solution state ¹H NMR of C₁₈ extractable rainwater DOM to freeze dried rainwater DOM and there was considerable difference 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). Dissolved organic carbon was analyzed with a high temperature catalytic oxidation using a Shimadzu TOC 5050 (Avery et al., 2004).

FT-ICR MS spectra were acquired with a passively shielded 9.4 Tesla 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 scan range of 155–1200 Da. Time-domain transient signals were collected and processed by a modular ICR data acquisition system (Blakney et al., 2011). Sample was sprayed 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 V_{p-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 (Mesfioui et al., 2012; Kido Soule et al., 2010).

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

Table 1. Total assigned C,H,O formulas, unique formulas to each storm type and % unique of total assigned CHO formulas for the rain events analyzed during this study.

Storm type	Total assigned C,H,O formulas	Unique formulas	% Unique formula	Unique mean \pm (SD)	Unique mean \pm (SD)	Unique Mean MW
				H : C	O : C	(g mol ⁻¹)
Continental	1989	465	23.4	1.2 \pm (0.4)	0.4 \pm (0.2)	422 \pm (117)
Coastal	2001	486	24.3	1.4 \pm (0.4)	0.4 \pm (0.3)	434 \pm (83)

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, N and S). For this manuscript only C, H and O will be discussed while the other elements will be presented in another, future manuscript. The double bond equivalents parameter (DBE = number of rings plus double bonds to carbon) measures hydrogen deficiency and is calculated from the elemental composition, C_cH_hN_nO_oS_s (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). Here, formulas are conservatively classified as non-aromatic (AI < 0.5), aromatic (AI > 0.5) and condensed aromatic (AI \geq 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.

2.3 Storm classification

Storm events were classified using air-mass back trajectories generated by the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPPLIT) developed at the National Oceanic Atmospheric Administration Air Resources Laboratory using the web based version (Draxler and Hess, 1998). The trajectories were calculated using pre-processed gridded horizontal and vertical wind fields generated at 6 h intervals from the National Center for Environmental Prediction's Global Data Assimilation System (GDAS) using the medium range forecast model (MRF) to produce the forecast wind fields. Beginning at the end of each recorded rain event at the UNCW rain site, a 72 h hindcast was generated starting at the 500 m level. This was chosen to represent the air mass near the well-mixed boundary layer likely to contribute more heavily to in-cloud processes and wet deposition (Walker et al., 2000). Storms were visually classified as continental where the air mass was strictly over land and as coastal if there was any marine influence (Avery et al., 2006a, b; Kieber et al., 2006b). Storms classified according to this scheme have been shown to reveal clear differences between coastal and continental rain events in both inorganic, isotopic and organic constituents. (Avery et al., 2006a, b; Kieber et

al., 2005, 2006a; Southwell et al., 2010; Willey et al., 2000, 2009).

3 Results and discussion

3.1 Bulk parameters

A total of seven rain samples collected from both continental (4) and coastal (3) storm types (S1) were analyzed in this study. Back trajectories of each storm can be found in the Supplement Sect. S2. The amount of each event ranged from 1.52–18.8 mm while dissolved organic carbon concentrations ranged from 49–312 μ M which are typical of previously reported values for this site suggesting these events were representative (Willey et al., 2000). Each combined storm type had approximately 2000 identifiable CHO formulas of which nearly 25 % were unique, in other words not common, to the storm types (Table 1). This is similar to other studies where the distribution of unique CHO formulas was 13 % to 36 % of the total assigned from rain events originating from continental sources (Altieri et al., 2009). The average H : C elemental ratios for continental and coastal rain were 1.2 \pm 0.4 and 1.4 \pm 0.4, respectively while the O : C ratio for continental storm types was 0.4 \pm 0.2 and coastal 0.4 \pm 0.3. The average molecular weight of the unique formulas was 422 \pm 177 (g mol⁻¹) and 432 \pm 83 (g mol⁻¹) for continental and coastal storm types respectively. These elemental ratios are not statistically different from one another but instead there are molecular formulas with different numbers and combinations of CHO that have similar elemental ratios between storm types. For example, one molecular formula assignments in the continental storm was C₈H₁₆O₈ and elemental ratios of H : C 2 and O : C 1. In comparison, an assigned molecular formula from a coastal storm was C₉H₁₈O₉ with elemental ratios of H : C 2; and O : C 1. This is just one example of similar elemental ratios between storm types but different molecular formulas.

3.2 van Krevelen analysis

van Krevelen plots visually present the molar ratios of H : C (ordinate) and O : C (abscissa) of assigned formulas generated by FT-ICR MS. This approach has been used extensively in the organic geochemical studies of fossil fuels (Majid

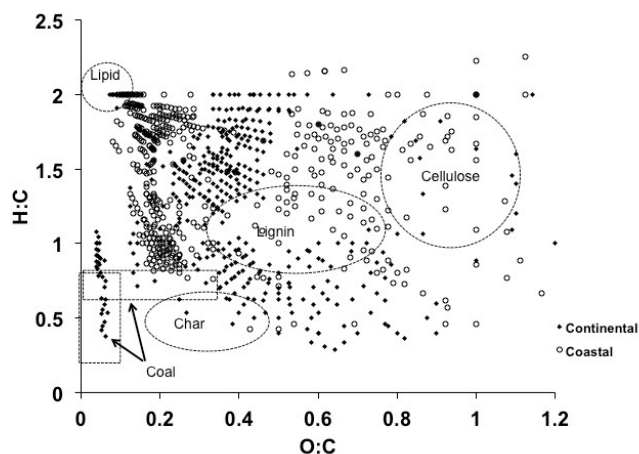


Fig. 1. van Krevelen plot of unique assigned formulas containing CHO in continental and coastal storms. The indicated areas are based upon earlier literature descriptions (Kim et al., 2003).

et al., 1991; Curiale and Gibling, 1994; Bostick and Daws, 1994). The van Krevelen analysis can be used to identify biological/geochemical classes of organic compounds in dissolved organic matter by distinct elemental ratios (Wu et al., 2004; Kim et al., 2003). Areas within the van Krevelen diagram can also be classified according to molar ratio ranges which allows for a conservative assessment of the type of organic matter present in the DOM (Podgorski et al., 2011).

The van Krevelen plots of the unique molecular formulas for continental and coastal storms are presented in Fig. 1. Coastal storms had major groupings of unique formulas representative of cellulose-like compounds while continental storms had lipid- and soot/black carbon-like formulas. Upon closer examination of Fig. 1 it is evident that there are assigned formulas from coastal storms that have a high O : C ratio (> 0.6) not found in continental rain. In fact, 26 % of the unique formulas in coastal storms had O : C ratio > 0.6 while continental derived storms had only 15 % of the unique formulas with O : C ratio > 0.6 . The highly oxidized state of coastal storm derived DOM may shed light into the environmental processing that occurred to form the material. It has been hypothesized that aerosol organic matter “ages” or becomes more oxidized as exposure to atmospheric processing increases (Jimenez et al., 2009). A similar process may be occurring for rainwater DOM where as the atmospheric residence time of rain DOM sources increases during transport over the oceans, the O : C ratio increases concurrently.

A second hypothesis that may explain the highly oxidized DOM in coastal rainwater might have to do with an increase in polysaccharides from bubble bursting processes at the ocean surface. This process has been shown to aerosolize carbohydrates into the atmosphere (Russell et al., 2010). However, the O : C ratio of monosaccharides such as pentose or hexose is 1 while disaccharides such as sucrose is 0.91. Few of the coastal O : C ratios in Fig. 1 approach one suggest-

ing carbohydrates from bubble bursting may make a minor contribution to the coastal precipitation and no contribution to terrestrial storms. Highly oxidized rainwater DOM (O : C ≈ 3.0) over a scan range of 50–500 m/z has also been observed from an urban industrialized location in New Jersey, USA; however, direct comparison should be made with caution because the rainwater data in this study was only from continental trajectories (Altieri et al., 2009).

3.3 Kendrick mass analysis

The van Krevelen plot of the unique formulas of continental and coastal storms revealed possible homologous sets or families of compounds that differ in mass by CH_2 units (Fig. 1). These homologous series can be explored further by determining the Kendrick mass (KM) (Hughes et al., 2001; Kendrick, 1963). This is determined by taking the measured IUPAC mass and normalizing to 14.0000 u instead of the IUPAC 14.01565 u as shown in Eq. (1).

$$\text{KM} = \text{IUPAC mass measured} \left(\frac{14.0000}{14.01565} \right) \quad (1)$$

The Kendrick mass defect (KMD) can then be calculated using Eq. (2), which determines the difference between the nominal mass and the Kendrick mass.

$$\text{KMD} = [\text{NM} - \text{KM}] \quad (2)$$

Plotting KMD vs. Kendrick mass provides a visual means of identifying homologous sets differing by CH_2 (Fig. 2). It is possible to have similar KMD values for different homologous series therefore presorting data using z^* (Eq. 3) ensures membership within a homologous series is due to differences in CH_2 unit (Hsu et al., 1992).

$$z^* = \left(\text{modulus} \left[\frac{\text{NM}}{14} \right] \right) - 14 \quad (3)$$

Taking the unique assigned formulas and plotting the KMD vs. Kendrick mass of $z^* = -10$ reveals several homologous sets in the continental and coastal storms. The z^* value of -10 was chosen for this study since this represents differences between formulas of exactly 14 caused by addition of a CH_2 unit (Stenson et al., 2003). Several homologous series are observed when plotting KMD vs. Kendrick mass for a z^* of -10 that differ by CH_2 units (Fig. 2). If a homologous set is considered to contain a minimum of three formulas, as represented by a point, then the continental and coastal storms had 10 and 11 families, respectively. Several series highlighted in Fig. 2 lie within predetermined areas on the van Krevelen plot including cellulose ($\text{C}_{20}\text{H}_{30}\text{O}_{14}$), char ($\text{C}_{16}\text{H}_8\text{O}_7$), protein ($\text{C}_{20}\text{H}_{38}\text{O}_4$) and lipid ($\text{C}_{13}\text{H}_{26}\text{O}_2$) like materials. Of particular interest is the lipid like component with assigned molecular formula $\text{C}_{12}\text{H}_{24}\text{O}_2$ (CH_2) $_{1-14}$ that was only detected in continental storms. All individual homologues in this family have a KMD of 0.04605 and a

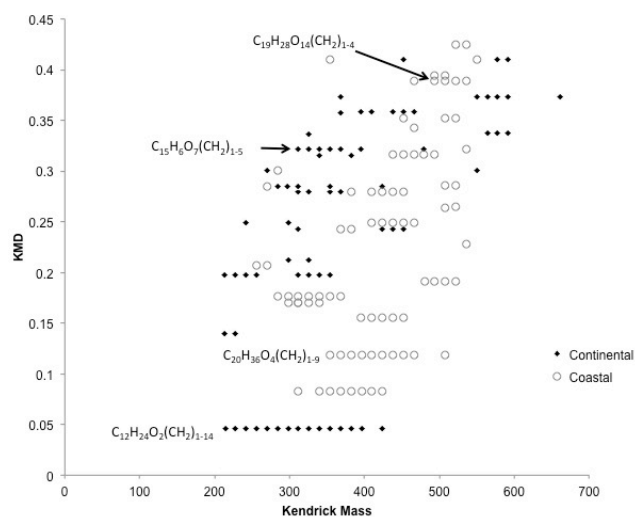


Fig. 2. Kendrick mass plot of neutral unique molecular formulas normalized to CH_2 for continental and coastal storms presorted at $z^* = -10$. Horizontal lines with the same Kendrick mass defect represent molecular formula families that increase by one methylene unit.

DBE of 1. One possible starting structure based upon this information is tridecanoic acid ($\text{C}_{13}\text{H}_{26}\text{O}_2$) with 1 DBE rendering the remainder of the homologue series tetradecanoic through heptacosanoic acid. Long chain fatty acids have been observed in aerosols originating from plant waxes (Elias et al., 1999; Bi et al., 2008) but this is the first time long chain fatty acids have been determined in rainwater although linear acids with fewer than 5 carbons have been observed previously (Avery et al., 2006a).

3.4 Oligomers

Recently it has been shown that esterification of small molecular weight acids (e.g., oxalic) and β -hydroxy-acids can produce oligomers detected in rain and fog waters (Altieri et al., 2009; Mazzoleni et al., 2010). The oligomer series begins by either radical or acid catalyzed esterification of an organic acid with a hydroxyacid with loss of water leading to the constant addition of $\text{C}_3\text{H}_4\text{O}_2$. Some oligomers identified in this study have been observed before in laboratory studies involving photo-oxidation of methylglyoxal and glycoaldehyde (Altieri et al., 2008; Perri et al., 2009). There were several oligomer series in this study that belong to families of mono and dicarboxylic acids found in the common formula assignments for both continental and coastal waters (Table 2). The presence of these oligomers in both continental and coastal rainwater samples suggests their widespread occurrence in atmospheric waters. Many of the same acids have been measured in precipitation collected at the same station as in this study (Avery et al., 2006a). The acids were detected year round but varied by season and trajectory. For example, formic acid has the highest annual volume weighted concen-

Table 2. Parent acid and $\text{C}_3\text{H}_4\text{O}_2$ oligomer series detected in all continental and coastal storms. Each addition of $\text{C}_3\text{H}_4\text{O}_2$ to the parent acid is denoted by corresponding number (n) and results in a loss of water.

Parent acid	Number (n) of $\text{C}_3\text{H}_4\text{O}_2$ additions
Acetic	2,3,4,5,6
Formic	3,4,5,6
Glyoxylic	3,4,5
Glycolic	3,4,5
Lactic	2,3,4,5
Maleic	2,3,4,5
Malonic	2,3,4
Oxalic	2,3,4
Pyruvic	2,3,4,5
Succinic	2,3,4

tration in precipitation and is the most abundant during the growing season in precipitation originating from coastal and continental storms. However, in the current study, there was one oligomer series found only in coastal storms with a parent formula of glyoxylic acid ($\text{C}_2\text{H}_2\text{O}_3$) and six additions of $\text{C}_3\text{H}_4\text{O}_2$ to yield a final molecular formula assignment of $\text{C}_{20}\text{H}_{26}\text{O}_{15}$. This oligomer has an H : C and O : C ratio of 1.3 and 0.75, respectively, putting it in the cellulose portion of the van Krevelen plot (Fig. 1). The location of this compound on the plot and the fact it was only detected in coastal storms suggests the DOM is relatively more oxidized than continental rainwater DOM.

3.5 Condensed aromatic hydrocarbons

Condensed aromatic hydrocarbons have been detected by FT-ICR MS in a variety of environmental settings including water-soluble organic carbon and aquatic dissolved organic matter (Sleighter and Hatcher, 2007; Wozniak et al., 2008). It has been hypothesized that one possible source of these condensed aromatic hydrocarbons is derived from combustion sources and initially classified it as black carbon based upon elemental ratios of molecular formulas generated by FT-ICR MS measurements (Hockaday et al., 2006a; Stubbins et al., 2010). However, there is debate regarding the exact nature of this material and the corresponding classification as black carbon and other forms of combustion derived products (Andreae and Gelencser, 2006). Therefore, the condensed hydrocarbons in this study will be considered a mixture of all possible sources of combustion-derived compounds since only FT-ICR MS data was collected.

While condensed hydrocarbons have been observed in many environmental matrices there are currently limited studies documenting its presence in rainwater (Chylek et al., 1999; Hadley and Kirchstetter, 2012). The van Krevelen diagram of unique assignments had molecular formulas with elemental ratios typical of char and coal like material

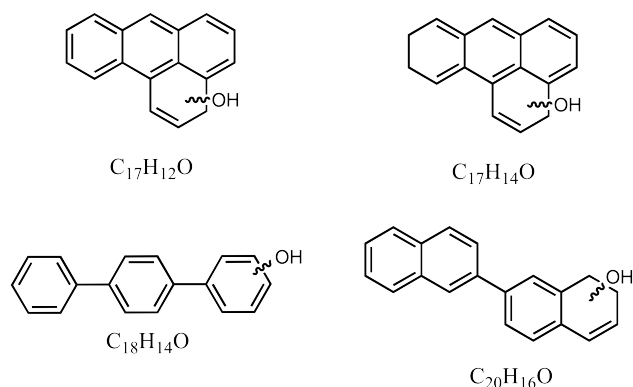


Fig. 3. Proposed condensed aromatic hydrocarbon structures based upon the assigned molecular formulas. The position of the hydroxyl group is uncertain as indicated by the wavy bond on the structure.

in continental storms (Fig. 1). The molecular formulas all had aromaticity index (A.I.) values greater than 0.5, which can be classified as aromatic or condensed aromatic structures (Table 3) (Koch and Dittmar, 2006). Another proxy to further validate condensed aromatic hydrocarbon component is DBE/C ratio where a ratio greater than 0.7 indicates condensed aromatic structures (Hockaday et al., 2006b). Approximately 40 % of the assigned formulas in this study were higher than the 0.7 threshold suggesting the presence of condensed aromatic hydrocarbons in continental rainwater (Table 3).

The condensed aromatic hydrocarbon assigned formulas in this study are all mono-oxygenated which is in stark contrast to condensed aromatic hydrocarbons identified in aquatic DOM and soils which are much more highly oxygenated with carboxylic functional groups (Kramer et al., 2004; Kim et al., 2004). A phenol moiety is hypothesized as the functional group as opposed to an ether because the phenolic proton is slightly acidic making these compounds ionizable by (–) mode ESI. Potential structures of condensed hydrocarbons in rainwater are proposed in Fig. 3 for several formula assignments which were generated taking the unique assigned formulas and current knowledge regarding black carbon composition (Hockaday et al., 2006b). The proposed structures were based upon the type and number of atoms present and further constrained by the double bond equivalents. All proposed structures had aromatic moieties with one hydroxyl group whose position on the structure, given the possibility of isomers, is uncertain.

The detection of condensed aromatic hydrocarbons identified in this study may be due to the partially oxidized nature of it through photochemical processes which in turn will increase its water solubility. Oxidation of soot has been proposed in earlier studies yielding a series of water-soluble compounds (Decesari et al., 2002). It has been also suggested the partitioning of condensed aromatic hydrocarbons with other oxidized carbonaceous particles alters the

hydrophobic-hydrophilic balance thus increasing the apparent water solubility (Petters et al., 2006). Whichever mechanism is occurring, the significance of this study is highlighted by the proposed molecular structures (Fig. 3) of condensed aromatic hydrocarbons and sheds insight into the oxidation state of this material as it is scavenged by rain in the atmosphere.

4 Implications

Data presented in the current study represent the first detailed analysis of rain water dissolved organic matter by FT-ICR MS collected on an event basis from a series of continental and coastal storms. This study highlights the complexity of rainwater DOM where approximately 2000 CHO formulas were found in each trajectory class with the type and distribution of organics dependent on storm origin. Analysis of the unique assignments suggested distinct groupings of organic matter in continental and coastal storms in various bio- and geo-molecule classes such as lipids, condensed hydrocarbons, aromatics and cellulose. This study highlights the variation in DOM composition between different air-mass back trajectories and greatly expands upon earlier rainwater FT-ICR MS data where samples were pooled or were collected from a single storm type.

One interesting characteristic of rainwater DOM suggested by the data in Figs. 1 and 2 is that it does not closely resemble marine DOM with regards to molecular weight range and complexity by other FT-ICR MS studies (Sleighter and Hatcher, 2008). This dissimilarity sheds light on the uncertainty regarding the origin of humic like substances (HULIS) in atmospheric waters. Earlier proposed sources of HULIS include biomass burning, secondary organic aerosols and marine sources (Mayol-Bracero et al., 2002; Hung et al., 2005; Cavalli et al., 2004). The marine sources of HULIS have been hypothesized to originate from bubble bursting processes where marine water DOM is ejected into the atmosphere as a fine aerosol which contributes 27 % HULIS to the water soluble organic carbon fraction of a fine mode marine aerosol (Cavalli et al., 2004). It should be noted that this earlier study was conducted on aerosols collected directly adjacent to the coast. The results of the current study suggest marine sources of HULIS are not transported far inland since it was not observed in coastal origin rain collected at our location approximately 10 km from the Atlantic Ocean.

Natural and anthropogenic impacts on the chemistry of atmospheric waters have been well documented but this is the first study to characterize condensed aromatic hydrocarbons in rainwater at the molecular level. This has significant ramifications towards climate change because black carbon may be associated with condensed aromatic hydrocarbons that are a suspected chromophore that reemits adsorbed sunlight at longer wavelengths thereby warming the lower atmosphere (Cappa et al., 2012; Sedlacek et al., 2012). Understanding

Table 3. Proposed neutral molecular formulas of the condensed aromatic hydrocarbons.

						MW ^a	DBE ^b	A.I. ^c	DBE/C ^d	H : C	O : C
C	15	H	8	O	1	204	12	0.80	0.80	0.47	0.07
C	16	H	6	O	1	214	14	0.87	0.88	0.31	0.06
C	16	H	10	O	1	218	12	0.87	0.75	0.56	0.06
C	16	H	12	O	1	220	11	0.87	0.69	0.69	0.06
C	17	H	8	O	1	228	14	0.93	0.82	0.41	0.06
C	17	H	12	O	1	232	12	0.93	0.71	0.65	0.06
C	17	H	14	O	1	234	11	0.93	0.65	0.76	0.06
C	18	H	8	O	1	240	15	1.00	0.83	0.39	0.06
C	18	H	10	O	1	242	14	1.00	0.78	0.50	0.06
C	18	H	14	O	1	246	12	1.00	0.67	0.72	0.06
C	19	H	8	O	1	252	16	1.07	0.84	0.37	0.05
C	19	H	10	O	1	254	15	1.07	0.79	0.47	0.05
C	19	H	12	O	1	256	14	1.07	0.74	0.58	0.05
C	20	H	16	O	1	272	13	1.13	0.65	0.75	0.05
C	20	H	18	O	1	274	12	1.13	0.60	0.85	0.05
C	21	H	18	O	1	286	13	1.20	0.62	0.81	0.05
C	22	H	20	O	1	300	13	1.27	0.59	0.86	0.05
C	22	H	22	O	1	302	12	1.27	0.55	0.95	0.05
C	23	H	20	O	1	312	14	1.33	0.61	0.83	0.04
C	23	H	22	O	1	314	13	1.33	0.57	0.91	0.04
C	23	H	24	O	1	316	12	1.33	0.52	1.00	0.04
C	24	H	20	O	1	324	15	1.40	0.63	0.79	0.04
C	24	H	22	O	1	326	14	1.40	0.58	0.88	0.04
C	24	H	24	O	1	328	13	1.40	0.54	0.96	0.04
C	25	H	22	O	1	338	15	1.47	0.60	0.84	0.04
C	26	H	22	O	1	350	16	1.53	0.62	0.81	0.04
C	26	H	24	O	1	352	15	1.53	0.58	0.88	0.04
C	26	H	26	O	1	354	14	1.53	0.54	0.96	0.04

^a Molecular weight calculated using the average atomic weight of the atoms in the assigned molecular formulas.

^b Double bond equivalents is a measure of the number of rings and double bonds calculated using the equation in the text.

^c Aromaticity index is calculated as described by Koch and Dittmar (Koch and Dittmar, 2006).

^d Double bond equivalents normalized to number of carbon.

the molecular level composition of condensed aromatic hydrocarbons is also important in determining its transformation in the lower atmosphere because as condensed aromatic hydrocarbons are oxidized it becomes more hydrophilic thus significantly shortening its lifetime via washout (McMeeking et al., 2011). The processing of condensed aromatic hydrocarbons may accelerate in the future as potent oxidants such as hydrogen peroxide increase in concentration due to the continued desulfurization of the atmosphere (Mullaugh et al., 2011). This in turn has significant implications towards climate prediction models, especially as natural and anthropogenic emissions of condensed hydrocarbons change.

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