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Discussions

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

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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 (FTICR-MS).
5 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 FTICR-MS. Approximately 25 % of the roughly 2000 assigned CHO molecular formulas are unique to each storm classification indicating the importance of air mass back trajectory on the composition of rainwater dissolved organic matter (DOM). Anal-
10 ysis 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 with 13 unique methylene oligomers in continental storms suggesting oligomer forma-
15 tion is ubiquitous in rainwater albeit different for each storm classification. Oligomers of small acids and $C_3H_4O_2$ were detected in both storm types indicating their processing may be similar in both back trajectories. Black carbon (BC) was detected in continental storms with phenol moieties that are not as oxidized as aquatic DOM black carbon. The discovery of BC in continental rainwater has significant ramifications towards climate
20 change, because atmospheric BC is such a potent chromophore that reemits absorbed sunlight at longer wavelengths thereby warming the lower atmosphere.

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 com-
25 bined (Willey et al., 2000a). Rain is a significant source of DOM to surface seawater ($90 \times 10^{12} \, \mathrm{g\,C\,yr^{-1}}$), 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., 2000b). DOM plays a central role in many important rainwater reactions including free radical generation and trace metal complexation. Recent studies also demonstrate that a significant fraction of DOM is chromophoric suggesting this ma-
5 terial 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 con-
10 strained. 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 (^{13}C and ^{14}C) to estimate the relative contribution of natural and anthropogenic inputs to rainwa-
15 ter 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
20 altering the composition of rain DOM (e.g., 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 ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) (Nizkorodov et al., 2011; Altieri et al., 2009, 2012). FTICR-MS offers ultra-high resolving power to assign
25 molecular formulas at environmentally relevant concentrations in complex aquatic matrices such as natural waters (Stenson et al., 2003b). 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

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present study represents the first detailed analysis of C, H, O containing compounds in rain water by FTICR-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 event rain samples which housed a 4 l glass beaker placed within a HDPE plastic bucket. Samples were collected on an event basis, less than 12 h after precipitation stopped. 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 was baked at 450 °C in a muffle furnace for a minimum of 4 h to remove organics prior to use. Meteorological data including rain amounts, rain duration, time of day, surface temperature and storm origin were also recorded. Real time precipitation maps were used to define the end of specific rain events, which initiated the sampling process.

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 that the rainwater water freezes within minutes. Once frozen the round bottom flask containing the sample was placed on a Labconco 4.5 Freezone lyophilizer

until dry usually within 4–5 h and dissolved in HPLC grade methanol prior to FTICR-MS analysis. Lyophilization was chosen as pre-concentration technique to recover as much of the rainwater DOM as possible. It has been found that C_{18} SPE (solid phase extraction) 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 C_{18} non-polar stationary phase. A second study compared solution state ^{1}H NMR of C_{18} 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 ^{1}H NMR spectrum compared to the analogous C_{18} SPE fractionated rain sample (Seaton et al., 2012).

FTICR-MS data were acquired with a passively shielded 9.4 Tesla superconducting magnet (Oxford Instruments, Abingdon, Oxfordshire OX13 5QX UK) located at the National High Magnetic Field Laboratory in Tallahassee, Florida (Kaiser et al., 2011). Data were acquired over a scan range of m/z 155–1200. 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

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internally calibrated from extended homologous alkylation series (compounds that differ in elemental composition by integer multiples of CH_2) of high relative abundance. Mass accuracy for all assignments was equal to or less than 500 ppb. Given the reproducibility of (-) ESI FTICR-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 NHMFL. Elemental constraints for the assignment of DOM molecular formulas were 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 FTICR-mass spectrometry (Kramer et al., 2004; Stenson et al., 2003a). Each molecular formula was assigned an aromaticity index (AI) based on the system proposed by Koch and Dittmar (2006). Here, 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 were 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 (HYSPLIT) model 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(MRF) model to produce the forecast wind fields. Beginning at the end of each recorded rain event at the UNCW rain site, a 72 h hind-cast was generated starting at the 500 m level. This was chosen to repre-
5 sent 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 coastal storms a mixture of continental and marine influences (Avery et al., 2006a,b; Kieber et al., 2006b). Storms classified according to this scheme have been shown to reveal clear
10 differences between coastal and continental rain events in both inorganic and organic constituents (Avery et al., 2006a,b; Kieber et al., 2005, 2006a; Southwell et al., 2010; Willey et al., 2009).

3 Results and discussion

3.1 Bulk parameters

15 A total of seven rain samples collected from both continental and coastal storms types (S1) were analyzed in this study. Back trajectories of each storm can be found in Supplement section (S2). The volume of each event ranged from 1.52–18.8 mm while DOM concentrations ranged from 49–312 µM which are typical of previously reported values for this site suggesting these events were representative (Willey et al., 2000a).
20 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
25 1.2 and 1.4 respectively while the O : C ratio for both storm types were 0.4. The average molecular weight of the unique formulas was 422 and 432 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 assignment in the continental storm was $C_8H_{16}O_8$ with elemental ratios of H : C 2 and O : C 1. In comparison, an assigned molecular formula from a coastal storm was $C_9H_{18}O_9$ 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 FTICR-MS. This approach has been used extensively in the organic geochemical studies of fossil fuels (Majid 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). Diagenetic processes can be identified within the van Krevelen plot as well as methylation/demethylation, oxidation/reduction and decarboxylation reactions. 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 on 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. 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 were only from continental trajectory (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) (Hughey 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).

$$\text{KM} = \text{IUPAC mass measured} \left[\frac{14.0000}{14.01565} \right] \tag{1}$$

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

$$\text{KMD} = [\text{NM} - \text{KM}] \tag{2}$$

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).

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

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
5 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., 2003b). 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
10 storms had 10 and 11 families respectively. Several series highlighted in Fig. 2 lie within predetermined areas on the van Krevelen plot including cellulose ($C_{20}H_{30}O_{14}$), char ($C_{16}H_8O_7$) and lipid ($C_{13}H_{26}O_2$) like materials. Of particular interest is the lipid-like component with assigned molecular formula $C_{12}H_{24}O_2(CH_2)_{1-14}$ that was only detected in continental storms. All individual homologues in this family have a KMD of
15 0.04605 and a DBE of 1. One possible starting structure based upon this information is tridecanoic acid ($C_{13}H_{26}O_2$) with 1 DBE rendering the remainder of the homologue series tetradecanoic through heptacosanoic acid. 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).

20 ## 3.4 Oligomers

Recently it has been shown that esterification of small molecular weight acids (e.g., oxalic) and β-hydroxy-acids produces 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
25 leading to the constant addition of $C_3H_4O_2$. Some oligomers identified in this study

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have been observed before in laboratory studies involving photo-oxidation of methyl-glyoxal and glycolaldehyde (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 concentration 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 ($C_2H_2O_3$) and six additions of $C_3H_4O_2$ to yield a final molecular formula assignment of $C_{20}H_{26}O_{15}$. 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 suggest the DOM is relatively more oxidized than continental rainwater DOM.

3.5 Black carbon

Black carbon (BC) derived from combustion sources is an important component of the global carbon cycle that has been detected in a variety of environmental settings including aerosols and ocean sediments (Goldberg, 1985; Chylek et al., 1999). Annual atmospheric aerosol emissions of BC from biomass burning and fossil fuels are estimated at $3281\,\mathrm{Gg\,yr^{-1}}$ and $2710\,\mathrm{Gg\,yr^{-1}}$, respectively (Bond et al., 2004). Atmospheric BC is recognized as a potent chromophore, absorbing shortwave radiation and re-emitting this energy at longer wavelengths thereby warming the lower atmosphere (Chylek et al., 1996). The radiocarbon age of BC isolated from the water-soluble component of aerosols is estimated to be 2050 yr bp where 20 % of the BC originated from fossil fuel sources (Wozniak et al., 2008).

While BC has 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 in continental storms (Fig. 1). The molecular formulas all had aromaticity index (AI) 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 BC component is DBE/C ratio where a ratio greater than 0.7 indicates condensed aromatic structures (Hockaday et al., 2006). Approximately 40 % of the assigned formulas in this study were higher than the 0.7 threshold suggesting the presence of BC in continental rainwater (Table 3).

The BC assigned formulas in this study are all mono-oxygenated which is in stark contrast to BC 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 BC in rainwater are proposed in Fig. 3 for several formula assignments that were generated taking the unique assigned formulas and current knowledge regarding black carbon composition (Hockaday et al., 2006). 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.

Unprocessed BC is emitted as particulate organic matter with very limited water solubility. The BC identified in this study is partially oxidized by atmospheric processes enhancing its water solubility. Oxidation of soot has been proposed in earlier studies yielding a series of water-soluble compounds (Decesari et al., 2002). The significance of this study is highlighted by the proposed molecular structures (Fig. 3) of BC 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
5 dissolved organic matter by FTICR-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
10 storms in various bio- and geo-molecule classes such as lipids, amino sugars, proteins and cellulose. This study highlights the variation in DOM composition between different air-mass back trajectories and greatly expands upon earlier rainwater FTICR-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
15 2 is that it does not closely resemble marine DOM with regards to molecular weight range and complexity by other FTICR-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;
20 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
25 directly adjacent to the coast. The results of the current study suggest marine sources of HULIS are not transported far inland since the marine DOM was not observed in

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marine origin rain collected at our coastal location approximately 10 km from the At-lantic Ocean.

Natural and anthropogenic impacts on the chemistry of atmospheric waters have been well documented, but this is the first study to characterize black carbon in rain-water at the molecular level. This has significant ramifications towards climate change, because atmospheric BC is such a potent chromophore that reemits adsorbed sun-light at longer wavelengths thereby warming the lower atmosphere. Understanding the molecular level composition of black carbon is also important in determining its trans-formation in the lower atmosphere, because as BC is oxidized it becomes more hy-drophilic thus significantly shorting its lifetime via washout (McMeeking et al., 2011). The processing of BC may accelerate in the future as potent oxidants such as hy-drogen 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 black carbon change.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/31413/2012/ acpd-12-31413-2012-supplement.pdf.

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Table 1. Total assigned CHO 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 CHO Formulas	Unique Formulas	% Unique Formula	Unique Mean ± (SD) H : C	Unique Mean ± (SD) O : C	Unique Mean MW
Continental	1989	465	23.4	1.2 ± (0.4)	0.4 ± (0.2)	422 ± (117)
Coastal	2001	486	24.3	1.4 ± (0.4)	0.4 ± (0.3)	434 ± (83)

Table 2. Parent acid and $C_3H_4O_2$ oligomer series detected in all continental and coastal storms. Each addition of $C_3H_4O_2$ to the parent acid is denoted by corresponding number (n) and results in a loss of water.

Parent Acid	Number (n) of $C_3H_4O_2$ 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

Table 3. Proposed neutral molecular formulas of the black carbon (BC) compounds.

						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 (2006).
[d] Double bond equivalents normalized to number of carbon.

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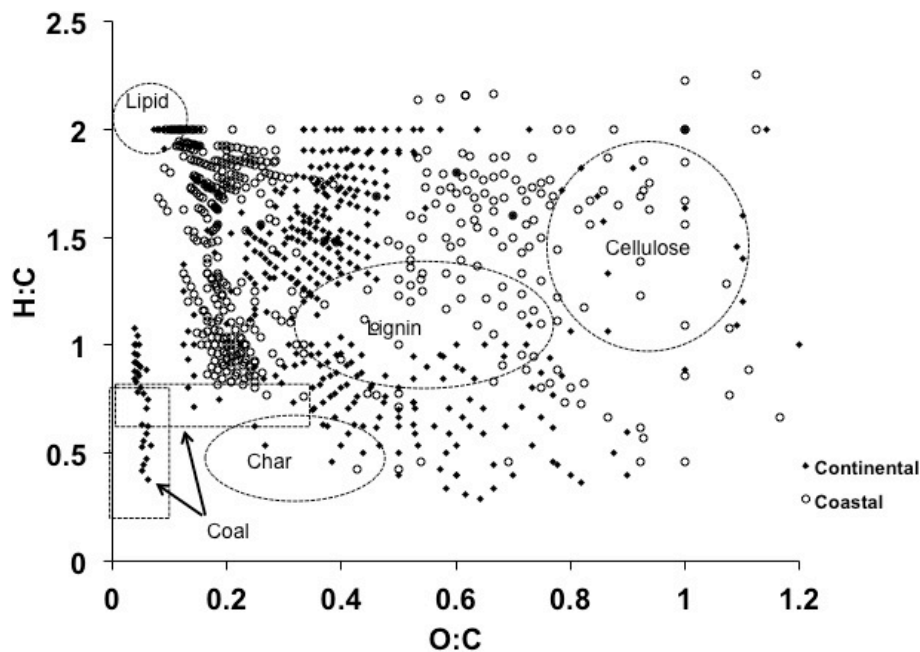Printer-friendly Version

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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). AS represents amino sugars.
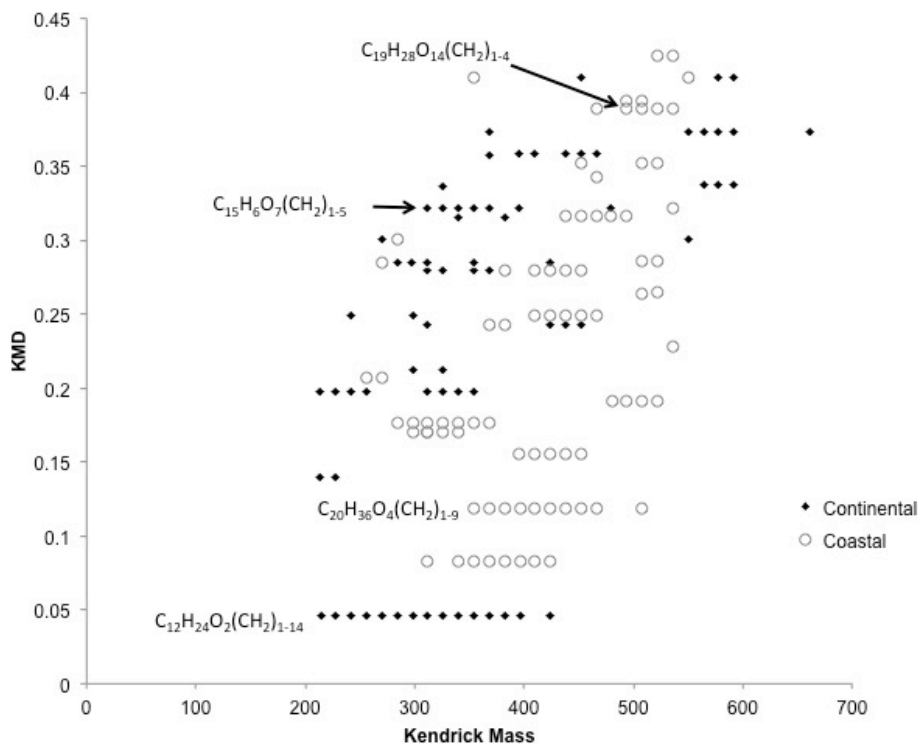
Fig. 2. Kendrick mass plot of neutral unique molecular formulas normalized to CH_2 for continental and coastal storms. Horizontal lines with the same Kendrick mass defect represent molecular formula families that increase by one methylene unit.

$C_{17}H_{12}O$

$C_{17}H_{14}O$

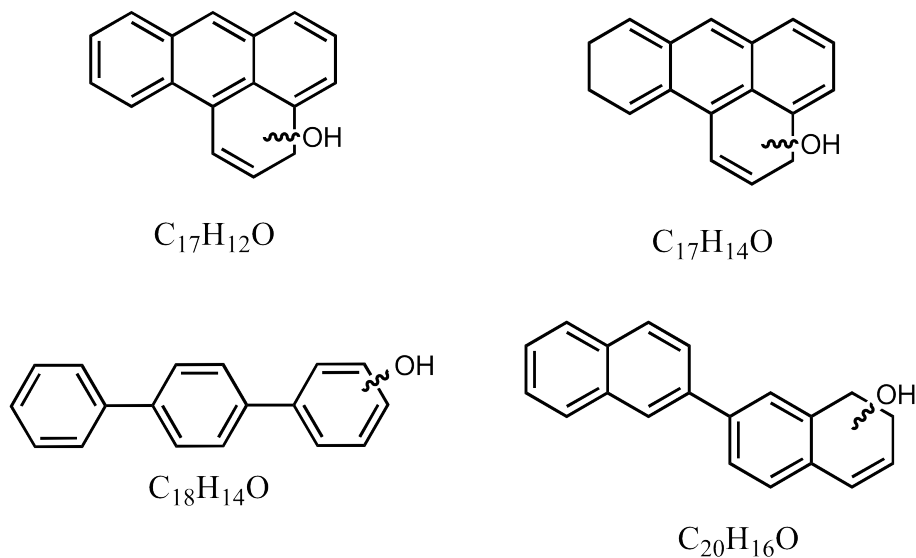$C_{18}H_{14}O$

$C_{20}H_{16}O$

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

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