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**Atmospheric
Chemistry
and Physics
Discussions**

# Interactive comment on "Insights into dissolved organic matter complexity in rainwater from continental and coastal storms by ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry" by R. N. Mead et al.

**Anonymous Referee #1**
Received and published: 30 January 2013

The authors analyse the rainwater samples for organic composition using FTICR-MS. The rainwater samples are classified by airmass backtrajectories and differences in composition are observed. The presence of black carbon is also identified by observation of aromatic structures, and oxygenated fragments are associated to these structures. The manuscript is fairly well presented and the work is relevant for the atmospheric science community. The manuscript is recommended for publication in Atmospheric Chemistry and Physics after the following comments have been addressed.


General comments:
Is the author's suggestion that composition in O:C and H:C space indicates presence of cellulose-like material, or the aged/processed products coincidentally fall in this regime? This would be a question of whether the high O:C ratio is determined by source or atmospheric processing. Russell et al. (2010) reported (through spectroscopy measurements) that marine aerosol appears to be naturally high in O:C ratio due to hydroxide groups in polysaccharides, so this may be a relevant point to discuss.

Response: The areas defined within the van Krevelen plot are modeled after Kim et al., 2003 and are based upon the characteristic H:C and O:C ratios of common biomolecules such as cellulose. The classifications are meant to be a conservative assessment of the organic matter present. If a molecular formula has elemental ratios that place it within the cellulose predefined area it is not conclusive the unknown is cellulose. All that can be said is the ratio of H:C and O:C is cellulose-like. The molecular formulas that fall within the cellulose region are dominated by highly oxygenated species but without further structure elucidation techniques it is hard to differentiate what the major source is.

The manuscript has been edited to include this point from lines 211-218.

Regarding the discussion beginning on p. 31421, line 1: Does this study support

or provide evidence against the view that as aerosols read the end of their lifetime, their chemical composition converges on a narrow range of chemical composition (e.g., Jimenez et al., 2009)? While O:C still indicates aerosol lifetime/ opportunity for aqueous-phase processing, it appears that even at the point at which these aerosols are removed from the atmosphere by wet deposition, the measurement techniques used here suggest that source characteristics are retained when viewed by a soft ionization method. Recent work (e.g., Aumont et al., 2012) suggests that gas-phase processing may be insufficient to produce highly oxidised species.

Response: This is a very interesting point however there are limited data so further discussion would be speculation at this point.

While the authors state that compositions reported in this study are not directly comparable with Altieri et al. (2008, 2009) because of differences in origin/trajectory, could broad comparisons be raised to determine whether products of aqueous-phase reactions might produce similar O:C ratios and repeating monomeric groups?

Response: The Altieri et al 2009 data is difficult to compare to this study for several reasons. The rainwater analyzed had a higher DOC concentration (>200 μM) than this study, sample data was pooled from different trajectories and the mass range scanned by the mass spectrometer was different (50-500 Da) than this study (155-1200 Da).

In section 3.3 and 3.4 of this manuscript there is a discussion regarding the occurrence of oligomers in precipitation and potential sources as identified by Altier et al., 2008 (and others).

Specific comments:
p. 31425, line 1: can an approximate/average lifetime be proposed from rainfall frequency in the region?

Response: We are unsure as to the reviewer's comments. The sentence this is referring to is for the broad classification of dissolved organic matter. No quantification was done in the data presented. However, the paper by Willey et al 2000 ( Global Biogeochemical Cycles, 14, 139-148) provides an annual flux of dissolved organic carbon from rainwater to the study site in Wilmington, NC.

p. 31425, line 12: Could fragmentation or incomplete ioniastion in the mass spec lead to the underestimation of functionality (i.e., observation of monofunctionality) of the aromatic structure identified as BC?

Response: Negative mode electrospray ionization (- ESI) is considered a soft ionization technique giving M-1 ions. Stenson et al., 2003 (Analytical Chemistry, 75, 1275-1284) has shown how ESI-FT-ICR produces singly charged molecular species with no fragmentation in dissolved organic matter isolated from the Suwannee River. ESI is susceptible to ion suppression therefore samples from the same back trajectory were

pooled and compared to the other trajectory to eliminate ionization variability.

p. 31425, line 26 (also p. 31426, line 9): The reason for the wet deposition and removal is probably not so much by (partial) functionalisation—one would not expect BC to be so soluble from the proposed structures—but the mixing with other water soluble components (e.g., Petters et al., 2006; R. Zhang et al., 2008).

Response: We appreciate the reviewers suggestion and have added to the text association with DOM as a way to increase apparent solubility of the functionalized BC.
The text has been edited from 302-310.

p. 31425, line 26: isn't the observation of marine aerosol by the authors' procedure predicated on the occurrence of wet deposition? So lack of observation does not necessarily indicate absence of transport.

Response: Based upon the collection of rain at our station and related back to origin through back trajectory, there appears to be little to no marine influence. If there are marine aerosols transporting inland they appear not to be deposited through precipitation events.

p. 31426, line 13: Recent studies by Cappa et al. (2012) and Sedlacek et al. (2012) might suggest that prior estimates of the impact of BC on climate change is not as significant as reported earlier (e.g., Jacobson, 2001).

Response: The latest information from Cappa and Sedlacek have been incorporated in the text. The sentence now reads "This has significant ramifications towards climate change because atmospheric BC is a suspected chromophore that reemits adsorbed sunlight at longer wavelengths thereby warming the lower atmosphere."

Fig. 1. Why are the two boxes for coal, and as the other reviewer notes, no mention of amino sugars in the Figure elsewhere.

Response: The amino sugars have been removed from the figure. The areas within the van Krevlen pot were assigned according to Kim et al., 2003. The areas highlighted are typical given the elemental composition of coal.