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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

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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.

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 ionisation method. Recent work (e.g., Aumont et al., 2012) suggests that gas-phase processing may be insufficient to produce highly oxidised species. 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?

Specific comments:

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

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?

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).

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.

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).

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

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 31413, 2012.