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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 #3
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General Comments

This study presents measurements of rain water by FTICR-MS. Some very interesting findings are presented, but the paper is weak in its current form. The differences explored between continental and coastal storms is very superficial. A detailed explanation of how DOM concentrations were measured is needed. Some clarification is need on the method and interpretation of results. The authors need to think hard about what is special about this work and what real, concrete conclusions can be drawn from their measurements. The implications section should be overhauled to focus on the specific conclusions rather than glorifying the observation of chromophores in rain water. Upon revision, this paper may be acceptable for publication.

Response:

We are pleased the reviewer finds merit in the data and its contribution to the literature. The information contained within the manuscript is novel because it represents the first and, to date, the only detailed molecular level characterization of rainwater DOM from different storm trajectories by FTICR-MS. As described and justified in the text the concrete conclusions are listed below, all of which are fundamentally new insights into organic matter composition in rainwater:

- **Molecular level** differences of rainwater derived DOM between coastal and continental storms.
- Confirmation of oligomers in both coastal and continental rainwater.
- Minimal contribution of marine derived dissolved organic matter to coastal rainwater.
- The first molecular level characterization of black carbon in rainwater and corresponding oxidation state.

Understanding the atmospheric processing of chromophoric DOM at a molecular level is important because CDOM makes up a large fraction of rainwater DOM and as such 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). One of the more interesting findings of the present study is the first time molecular formula and structure elucidation of black carbon (BC) in rainwater. This is a significant finding as BC is a known chromophore that emits radiation at longer wavelengths at varying levels thus warming surrounding atmosphere. Given this, chromophoric DOM in rainwater is important and a major implication of this study.

The dissolved organic matter (DOM), as described in the methods section, was isolated from rainwater by lyophilization. No processing of the sample other than this was done to obtain DOM for FTICR-MS analysis thereby minimizing sampling artifacts. The data presented has been processed and presented using accepted FTICR-MS techniques and methodology.

Specific Comments
Abstract, lines 5-7: How many studies have done detailed molecular level characterization of DOM in rainwater by ANY method? Perhaps this work is more unique than the authors are giving themselves credit for.

Response: This is the first and only study to date comparing C,H,O data obtained by ultra high resolution FTICR-MS of whole rain from different trajectories. There have been a few selected studies looking at individual compounds primarily focused on organic acids and small molecular weight aldehydes in rain but nothing approaching the comprehensiveness of this study.

Abstract, lines 12-13: It's a bit contrary to expectations for coastal storms to have lignin/cellulose characteristics and continental storms to have lipids. It's worth a short explanation in the abstract, and longer explanation in the main body (see later comment).

Response: The van Krevelen plot is a data reduction tool and is generated by taking the H:C and O:C ratios of assigned molecular formulas from the FTICR-MS experiment. Areas within the van Krevelen plot can be classified according to these molar ratios and related to typical compounds that have these same elemental compositions. The typical compounds used to delineate areas within the van Krevelen plot for this study are based upon the work of Kim et al., 2003. This approach has been used successfully before to classify the type of organic matter present and is considered a conservative way to determine the provenance of DOM. This is indicated by "lignin and cellulose-like" and "lipid-like" in the abstract.

Abstract: lines 14-15: How do the authors know the oligomers are secondary? Plant waxes are methylene oligomers.

Response: Altieri et al., 2008 demonstrated oligomerization resulting from the secondary formation of small molecular weight acids and $C_3H_4O_2$ occurred in laboratory experiments.

End of abstract: The implications of BC in rainwater should be left to the discussion because these particular conclusions are very general, and are not specific to the findings here.

Response: Removed the last sentence as requested.

Pg 31415 Line 29: What advantage is there to looking at C, H, O alone? Why would they look only at that when they have more elements to look at? It's not clear that the present study improves upon that characterization by looking at fewer compounds, so please explain.

Response: This paper is focused on C,H,O only because the inclusion of additional heteroatoms would result in an enormous data set which would be much too large for a succinct and focused manuscript. If all C,H,N,O,S were presented, for example, there would be approximately 5,000 molecular formulas to discuss resulting in a paper that would not have the in depth analysis needed. By presenting C,H,O only a much more in-depth examination and interpretation of the data is possible. The separating of C,H,O from C,H,O,N,S has been done successfully before in other studies employing FTICR-MS data of rainwater and surface water DOM (Altieri et al., 2009;D'Andrilli et al., 2010;Jaffé et al., 2012;Lin et al., 2012).

Pg 31417 Line 5: Based upon one study the authors are concluding that most chromophoric material in ALL rainwater is hydrophobic? It's a bit of a grand statement. It's reasonable that omitting extraction would preserve chemical heterogeneity, but the statement should be reworded.

Response: One of the main conclusions of an earlier study conducted by our laboratory (Miller et al., 2009) definitively demonstrated the relative proportion and fluorescent properties of hydrophilic vs. hydrophobic components in rainwater at this location. In that manuscript we report that a large fraction of rainwater DOM was composed of **hydrophilic** fluorescent material as opposed to surface water CDOM which is almost exclusively comprised of hydrophobic material. This is stated in the original submission below:

"Lyophilization was chosen as pre-concentration technique to recover as much of the rainwater DOM as possible. It has been found C_{18} 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 C_{18} non-polar stationary phase."

Pg 31418 Line 12: The authors claim in the introduction that previous work on FTICR-MS was different from theirs in that they are focusing on the C,H,O fragments but here they state they plan to publish results of the other elements in a forthcoming manuscript. Is there a reason that N and S cannot be included here? Does this merit two separate publications given that the methods, storm classification, and may

categories will overlap? It seems to me that the interpretation of the two storm types could be great improved by including N and S containing compounds and that perhaps one complete paper will have a higher impact that two nearly identical papers.

Response: As described above, the inclusion of the additional heteroatoms would result in a manuscript too large to provide an in-depth analysis and discussion. The separation of C,H,O from C,H,O,N,S is a common and accepted method to discuss FTICR-MS data. Some examples from the current literature where DOM from rainwater and surface waters include the following: (Altieri et al., 2009;D'Andrilli et al., 2010;Jaffé et al., 2012;Lin et al., 2012).

Pg 3149 Bulk parameters: I don't follow how exactly the DOM concentration was extracted from the spectral data. At the very least, it should be elaborated. It is not all obvious how one takes mass spectra and determines DOM. Also, DOM can be defined operationally, giving a different meaning in different methods. It is essential to be clear. Unless I understand how the DOM values are calculated, I cannot evaluate the interpretation of the data.

Response: There was a typo in section 31419 line 17 and was changed from DOM to dissolved organic carbon. A description was added to the method section describing how the DOC was measured. The DOM was isolated as described in the methods section by lyophilizing rainwater and then reconstituting in methanol prior to analysis by FTICR-MS.

Pg 31419 Bulk parameters: Include standard deviations in these values.

Response: Standard deviations have been added to the average values as requested.

Pg 31421 Line 1: The high O/C ratio in coastal, cellulose rain could be due to the source (ocean microlayer, rich in sugars) rather than atmospheric processing.

Response: The lines from 211-218 have been edited based upon Russell et al., 2010 to address this possibility.

Pg 31422 Line 18: It sounds like the continental fatty acids are originating from plant waxes. The authors should address this issue directly with some references for plant waxes and their oxidation products. For example, many plant waxes contain long saturated alkanes with ester groups that could easily become carboxylic acids.

Response: References and a short discussion have been added to the text from lines 249-252 however a more detailed discussion regarding the oxidation pathway was not included because of the limited data regarding oxidation processes rendering a detailed analysis as too speculative.

Pg 31423 Black Carbon: The first paragraph sounds like it belongs in the introduction.

Response: This is an important sentence to remind the reader of the pervasiveness of this material and its importance to the global carbon cycle.

Pg 31424: The labeling of these compounds as black carbon is a bit misleading. Is the absorption spectrum of these compounds constant across all wavelengths? If not then the term BC is not correct. Also, BC is usually distinguished from OC. Clearly these compounds are organic. Still, they could be found on or with soot particles. However, they themselves might very well be brown carbon, not black. Therefore the entire section on black carbon should really be rethought in the context of this distinction.

Response: The interpretation of the black carbon (BC) data was based upon several earlier FTICR-MS studies where BC has been detected and discussed. The labeling of the assigned molecular formulas as BC was based upon the molar ratios of H:C and O:C as described in the literature by several others (Wozniak et al., 2008;Kim et al., 2004;Kim et al., 2003;Kramer et al., 2004;Hockaday et al., 2006). Unfortunately there is no way to determine the absorption spectrum of the BC from the FTICR-MS data as requested.

Pg. 31424 Line 24: "Unprocessed BC is emitted as particulate organic matter" this is not correct. BC is associated with soot, and further, implies the elemental or near elemental graphite like fraction of soot (not organic). This indicates a real lack of familiarity with the subject.

Response: The comment regarding unprocessed BC emitted as particulate organic matter is addressed in an earlier study of BC by (Decesari et al., 2002). As Decesari et al. point out “Soot, a form of the material commonly referred to as black carbon, originates from combustion processes and is a mixture of elemental carbon (EC) and organic compounds (OC).”

Implications: In general this section includes too many grand overstatements about the findings. Specifically, it’s not clear what this study’s finding imply about the impact of BC on climate. "This has significant ramifications towards climate change" How? The finding of chromophores in rainwater is not new. I don’t see how this study gives more information about chromophores than others. Lines 10 and beyond draw grand conclusions from this study that are not merited.

Response: We completely agree with the reviewer that the finding of chromophoric material in rainwater is not new. Our group was the first to present a detailed study describing the ubiquitous nature of this material in precipitation in a publication over seven years ago (Kieber et al 2006). All subsequent studies of CDOM in precipitation including ours have utilized bulk analytical techniques such as fluorescence and absorbance spectroscopy to describe the properties of this colored material in rain. What is fundamentally new and novel about the current study is that it presents for the first time a detailed **molecular level** interpretation and analysis of the moieties responsible for the absorption of sunlight by rainwater.

We are unclear which specific statement(s) in the implications discussion the reviewer feels are unwarranted because the majority of the assertions were based directly on the data collected. For example the text from 31425 lines 8-13 reads “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, BC, 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.” Each of the points in the implication section is clearly justified by data and/or references in the body of the discussion of the manuscript. Another example is 31426 lines 3-5 “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 rainwater at the molecular level” which is entirely accurate based upon the literature to date. If the reviewer can provide concrete suggestions as to how to improve or correct specific statements made in implication section we would be happy to consider them.

Technical Corrections
Abstract line 13: It is unclear whether 18 unique methylene oligomers were found in coastal storms and 13 in continental OR whether the 18 in coastal storms was a total number. The "with" phrasing in line 14 is the most confusing part.

Response: The “with” the reviewer is referring to was a mistake. It has been replaced with “and”.

Abstract, line 14: Insert a comma before "suggesting"

Resposne: Done as requested.

Pg 31415 Line 4: Insert a comma before "suggesting"

Resposne: Done as requested.

Pg 31416 Line 12: Instead of "samples were collected" use "samples were retrieved" because it’s a bit confusing to say they were collected AFTER it stopped raining.

Response: The section has been completely rewritten to read: “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.”

Pg 31416 Line 24: Insert a comma after "once frozen" and on the next page (same sentence) use the m-dash around "usually within 4-5 hours" to offset it from the main clause

Response: Done as requested.

Pg 31417 Line 2: insert "the" before "pre-concentration"

Response: Done as requested.

Pg 31417 Line 12: "spectra" were acquired, specifically, not "data" and again on Line 15.

Response: Done as requested.

Pg 31418 Line 7: I didn’t see this acronym (NHMFL) explained earlier in the paper.

Response: NHMFL has been changed to National High Magnetic Field Laboratory

Pg 31418 Line 27: insert a period after the reference.

Response: Done as requested.

Pg 31419 Line 7: This sentence is awkward and missing a verb. Consider "Storms were visually classified as continental where the air mass was strictly over land and as coastal if there was any marine influence (ref)."

Response: Done as requested.

Pg 31421 Line 9: "trajectories"

Response: Done as requested.

Pg 31422 Line 22: change "produces" to "can produce"

Response: Done as requested.

Pg 31426 Line 10: "shortening"

Response: Done as requested.

References:

Altieri, K. E., Turpin, B. J., and Seitzinger, S. P.: Composition of Dissolved Organic Nitrogen in Continental Precipitation Investigated by Ultra-High Resolution FT-ICR Mass Spectrometry, Environmental Science & Technology, 43, 6950-6955, 10.1021/es9007849, 2009.
D'Andrilli, J., Chanton, J. P., Glaser, P. H., and Cooper, W. T.: Characterization of dissolved organic matter in northern peatland soil porewaters by ultra high resolution mass spectrometry, Organic Geochemistry, 41, 791-799, http://dx.doi.org/10.1016/j.orggeochem.2010.05.009, 2010.
Decesari, S., Facchini, M. C., Matta, E., Mircea, M., Fuzzi, S., Chughtai, A. R., and Smith, D. M.: Water soluble organic compounds formed by oxidation of soot, Atmos. Environ., 36, 1827-1832, 10.1016/s1352-2310(02)00141-3, 2002.
Hockaday, W. C., Grannas, A. M., Kim, S., and Hatcher, P. G.: Direct molecular evidence for the degradation and mobility of black carbon in soils from ultrahigh-resolution mass spectral analysis of dissolved organic matter from a fire-impacted forest soil, Organic Geochemistry, 37, 501-510, Doi 10.1016/J.Orggeochem.2005.11.003, 2006.
Jaffé, R., Yamashita, Y., Maie, N., Cooper, W. T., Dittmar, T., Dodds, W. K., Jones, J. B., Myoshi, T., Ortiz-Zayas, J. R., Podgorski, D. C., and Watanabe, A.: Dissolved Organic Matter in Headwater Streams: Compositional Variability across Climatic Regions of North America, Geochimica et Cosmochimica Acta, 94, 95-108, http://dx.doi.org/10.1016/j.gca.2012.06.031, 2012.
Kieber, R. J., Adams, M. B., Willey, J. D., Whitehead, R. F., Avery Jr, G. B., Mullaugh, K. M., and Mead, R. N.: Short term temporal variability in the photochemically mediated alteration of chromophoric dissolved organic matter (CDOM) in rainwater, Atmos. Environ., 50, 112-119, 10.1016/j.atmosenv.2011.12.054, 2012.
Kim, S., Kramer, R. W., and Hatcher, P. G.: Graphical method for analysis of ultrahigh-resolution broadband mass spectra of natural organic matter, the van Krevelen diagram, Analytical Chemistry, 75, 5336-5344, 10.1021/ac034415p, 2003.
Kim, S. W., Kaplan, L. A., Benner, R., and Hatcher, P. G.: Hydrogen-deficient molecules in natural riverine water samples - evidence for the existence of black carbon in DOM, Marine Chemistry, 92, 225-234, 10.1016/j.marchem.2004.06.042, 2004.
Kramer, R. W., Kujawinski, E. B., and Hatcher, P. G.: Identification of black carbon derived structures in a volcanic ash soil humic acid by Fourier transform ion cyclotron resonance mass spectrometry, Environmental Science & Technology, 38, 3387-3395, Doi 10.1021/Es030124m, 2004.
Lin, P., Yu, J. Z., Engling, G., and Kalberer, M.: Organosulfates in Humic-like Substance Fraction Isolated from Aerosols at Seven Locations in East Asia: A Study by Ultra-High-Resolution Mass Spectrometry, Environmental Science & Technology, 46, 13118-13127, 10.1021/es303570v, 2012.
Miller, C., Gordon, K. G., Kieber, R. J., Willey, J. D., and Seaton, P. J.: Chemical characteristics of chromophoric dissolved organic matter in rainwater, Atmos. Environ., 43, 2497-2502, 10.1016/j.atmosenv.2009.01.056, 2009.
Muller, C. L., Baker, A., Hutchinson, R., Fairchild, I. J., and Kidd, C.: Analysis of rainwater dissolved organic carbon compounds using fluorescence

spectrophotometry, Atmos. Environ., 42, 8036-8045, 10.1016/j.atmosenv.2008.06.042, 2008.
Santos, P. S. M., Santos, E. B. H., and Duarte, A. C.: First spectroscopic study on the structural features of dissolved organic matter isolated from rainwater in different seasons, Sci. Total Environ., 426, 172-179, 10.1016/j.scitotenv.2012.03.023, 2012.
Wozniak, A. S., Bauer, J. E., Sleighter, R. L., Dickhut, R. M., and Hatcher, P. G.: Technical Note: Molecular characterization of aerosol-derived water soluble organic carbon using ultrahigh resolution electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry, Atmospheric Chemistry and Physics, 8, 5099-5111, 2008.