

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

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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.

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.

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).

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

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.

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.

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.

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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.

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.

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

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.

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.

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

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,

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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.

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.

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.

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.

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

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

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.

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

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

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

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

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

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)."

Pg 31421 Line 9: "trajectories"

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

Pg 31426 Line 10: "shortening"

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

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