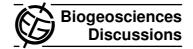
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Interactive Comment

Interactive comment on "High field NMR spectroscopy and FTICR mass spectrometry: powerful discovery tools for the molecular level characterization of marine dissolved organic matter from the South Atlantic Ocean" by N. Hertkorn et al.

Anonymous Referee #1

Received and published: 4 March 2012

General comments.

The paper presents novel, high quality and high value data. The employment of advanced NMR techniques and FTICR MS in concert is to be commended and offers novel insight beyond previous studies. However, the biogeochemical significance of the data and methods is not at the forefront of the paper. Instead the methods themselves take center stage. As written the manuscript may belong in a more analytical /

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chemical journal. Though the data certainly does provide a wealth of data of biogeochemical value this value is rather lost in the analytical detail. Therefore a rewrite is recommended in which the abstract is reduced and the conclusions elongated to draw together the strings of biogeochemical detail that are mentioned at various points in the paper. The authors should also consider restructuring the paper around biogeochemical themes as opposed to analytical ones. Perhaps addressing the nature of surface versus deep DOM, the nature of thermogenic DOM, CRAM, stoichiometry (C:N, H:C, O:C) etc bringing all lines of evidence to bare upon these subjects as opposed to the current layout which goes through the data as an analytical progression, pointing out when this data relates to the nature of DOM. It is recognized that the authors do bring together NMR data to address thermogenic DOM, but they do not incorporate FTMS in this discussion. This type of discussion, along with that in the section upon FTMS and NMR stoichiometry, provide examples of how the data might be reframed.

There is also limited reference to previous NMR studies of marine and other DOM when discussing the current data. This, along with some more reference to the observed general trends in oceanic DOM and the concepts derived from these observations, would strengthen the paper considerably (e.g. Hansell et al 2009 - Oceanography). Greater discussion of the similarities and differences between oceanic DOM and other OM, along with the placement of the analyzed samples in the oceanic DOM cycle, would offer more insight into why the DOM samples analyzed have the molecular character presented. This is key to emphasizing the biogeochemical significance of the work.

At present making detailed comments for the whole document does not appear instructive. Instead the key judgment criteria of the journal are listed with notes below to communicate the strong points and weaknesses simply and objectively. Following this there are section by section comments aimed at providing suggestions for restructuring beyond those noted above.

Though the current format requires refinement, the value of data is such that it should certainly be published and will represent a significant advance in the understanding of

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both the chemistry and biogeochemical cycling of oceanic DOM.

1. Does the paper address relevant scientific questions within the scope of BG?

Yes – although the analytical novelty is prominent rather than the biogeochemical significance

2. Does the paper present novel concepts, ideas, tools, or data?

Yes – the data included is particularly strong

3. Are substantial conclusions reached?

The conclusions section is weak given the novelty of the data. The vast majority of biogeochemical inferences scattered in the text are not reiterated in the conclusions. For this paper to be of value to a broader, biogeochemical audience an expended conclusions section is required. These expanded conclusions need to focus upon the biogeochemical significance of the work.

- 4. Are the scientific methods and assumptions valid and clearly outlined? The methods are valid and novel. The authors are commended for the level of analytical effort expended upon the samples.
- 5. Are the results sufficient to support the interpretations and conclusions?

Yes

6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)?

Yes – although the reference to an in house elemental formula assignment method with no discussion and no citation makes it impossible for other researchers to repeat the FTICR MS data work up (Section 2.3)

7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution?

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Yes. However, more previous NMR and other studies should be referred to when discussing the current data. There is limited discussion of the provenance of DOM in the various samples with respect to global ocean patterns in DOM biogeochemistry.

8. Does the title clearly reflect the contents of the paper?

Yes. Although a new title with reference to the biogeochemical insight provided would be beneficial.

9. Does the abstract provide a concise and complete summary?

The abstract is excessive in length and should be condensed. It would actually make a good model for a new conclusions section as it does present most of the biogeochemical insight gained.

10. Is the overall presentation well structured and clear?

The structure should be revised. The abstract is too long and the conclusions are incredibly light. Further details of potential restructuring are provided below in the section by section suggestions.

11. Is the language fluent and precise?

Yes

12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used?

Yes

13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated?

Yes – see section by section suggestions below.

14. Are the number and quality of references appropriate?

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Yes

15. Is the amount and quality of supplementary material appropriate?

Yes

Section by section comments

Abstract Conclusions

Too long. It should be reduced considerably and highlight the key biogeochemical findings. The current abstract may make a good starting place for and extended, biogeochem-centric conclusions section. The conclusions are currently too short and do not synthesize the impressive amount of data presented into a coherent expression of what has been learnt about the nature of DOM.

Methods

The methods section is good. Though perhaps some of the NMR details from the results and discussion should be move here.

Results

3.1

First sentence belongs in the methods. DOC, DON and C:N of natural water and PPL extract should be mentioned in the text rather than just noted in the table.

3.2

Bar the last paragraph, this whole section reads as introductory or methods material. The last paragraph should remain in the results and discussion. Some of the preceding text could be moved below the last paragraph to qualify the results.

3.3

Last line page 761 – "well visible" edit. Line 13 of page 762 – "very relevant" – relevant

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to what?

3.4

First paragraph appears to be a discussion of why a certain probe did not work, including review material. As the technique was not applicable and it appears data using this probe was not presented, then this piece can be struck or included as a few lines in the methods.

Within the first paragraph there is one orphaned mention of the nature of DOM: Page 765 – line 16 – "extensive intricacy". Intricacy of the DOM? Does this relate to latter discussions of molecular diversity? This is one of many instances where reworking the document around topics concerning the nature of DOM may provide a more coherent presentation of the information as it relates to DOM. It could be noted in a "molecular complexity" section that the 5mm probe did not work.

Paragraph 2 (page 765, 20-25) should be in the methods.

Page 767, line 8: "aliphatics appeared to have their signature changed" – How did it change? How does this relate to other information and the cycling of DOM? NMR based reverse mixing model: this is a methods section. It includes no results at all. The results appear later in reference to FTMS elemental ratios.

3.5 to 3.13

The rest of the sections are OK, yet the interesting findings about the chemistry of DOM from these exciting, cutting edge techniques is never truly brought together. The authors should endeavor to condense and distill the data into sections along the lines of the later 3.12.1 which does a good job of pulling the bulk organic matter, NMR and FTMS data together to offer insight into how and why DOM chemistry changes in the water bodies studied.

Interactive comment on Biogeosciences Discuss., 9, 745, 2012.

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