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Interactive comment on “Molecular characterization of dissolved organic matter from subtropical wetlands: a comparative study through the analysis of optical properties, NMR and FTICR/MS” by N. Hertkorn et al.

Anonymous Referee #2

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In general, the paper is hard to follow with so much information describing some data and on the hand lacking a clear conclusion and explanation of the observations and linking it to the geochemical and the environmental conditions in each ecosystem. I think the authors lost an opportunity to compare and link between the NMR and the ICR results. Each section appeared to be separate from the section before it or after it. The paper needs to be re-organized and focused on the main conclusions. I personally don't think the optical priorities data are needed, as well as the comparison between the terrestrial DOM and the marine DOM samples. It might be worth mentioning how

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different these samples are from each other (which is not surprising), however I would only spend few sentences on that and not 2-3 paragraphs. This paper needs major changes. The data sets on the other hand are extensive and would be a great addition to the DOM society and a substantial contribution to scientific progress.

Abstract: “I don’t think this sentence add anything to the abstract and a result I suggest deleting it. “Analogies were such that an established excitation emission matrix fluorescence parallel 15 factor analysis (EEM-PARAFAC) model for the Everglades was perfectly applicable to the other two wetlands”) The abstract contains a lot of information. I suggest rewriting it to summarize the main points of the study only. Introduction: The authors of the paper fail to include references of main groups that are known for using FT ICR MS, NMR in their organic matter characterization, rather, it appears that the authors are mainly referencing their papers. Experimental: What time of the year did the sampling take place in the everglades? It was confusing to me which FCE samples were collected in 2011 and which was collected over the years. “Sampling was performed during 2011 for the Florida coastal Everglades (FCE; for SPE-DOM) and during the summer 2010 for the Pantanal (PAN) and the Okavango Delta (OKA) as part of on-going research programs. For EEM-PARAFAC comparisons, multiple samples collected monthly over several years (Chen et al., 2013) for the FCE, 38 samples collected along a trans-Okavango gradient (Cawley et al., 2012), and 22 samples collected in different sub-environments of the Pantanal wetland (rivers, lagoons, marshes; unpublished) were used to assess differences and similarities.” How representative are these 6 samples to their ecosystems? The number of samples chosen for this study is too low for such a detailed comparison. Are these the samples that were collected for the ICR? Or these are the summary of the 38 samples? I am still confused on which samples are included in this study. “For the Florida Coastal Everglades (FCE), samples were collected from the freshwater marsh, peat-soil dominated Shark River Slough (FCE-L) and the marl-soil dominated Taylor Slough (FCE-S), from the Okavango Delta 13717 BGD 12, 13711–13765, 2015 Molecular characterization of dissolved organic matter from subtropical wetlands N. Hertkorn et al. Title Page

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Abstract Introduction Conclusions References Tables Figures J I J I Back Close Full Screen / Esc Printer-friendly Version Interactive Discussion Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper | (OKA) seasonal floodplain (OKA-L) and occasional floodplain (OKA-S) along the Boro River (Cawley et al., 2012), and the Paraguay River (PAN-L) and a wetland channel in Pantanal National Park (PAN-S; Chacra de Solange) for the Pantanal (PAN).”

“How long were the extracts stored in the freezer? From my experience, even if the samples are stored in MeOH, you will see changes in OM composition with time. “the isolated SPE-DOM extracts (referred from here on as DOM for the NMR and FT-ICRMS data) were stored in pre-combusted glass vials and kept in a freezer until analyzed.”

“How was the concentration of the extracts in an organic solvent measured? “Diluted SPEDOM ($5 \mu\text{g mL}^{-1}$ 15 in methanol) were injected into the electrospray source using a microliter pump at a flow rate of $120 \mu\text{L h}^{-1}$ with a nebulizer gas pressure of 138 kPa and a drying gas pressure of 103 kPa”.

“What was the number of unassigned peaks? “Final formulae were generated and categorized into groups containing CHO, CHNO, CHOS or 13720 BGD 12, 13711–13765, 2015 Molecular characterization of dissolved organic matter from subtropical wetlands N. Hertkorn et al. Title Page Abstract Introduction Conclusions References Tables Figures J I J I Back Close Full Screen / Esc Printer-friendly Version Interactive Discussion Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper | CHNOS molecular compositions which were used to reconstruct the group-selective mass spectra (Schmitt-Kopplin et al., 2010).”

Results section: “I don’t think the optical properties added anything to this study. I think the problem is with the low number of samples used for comparison. Considering that the authors spend more time and space explaining the NMR and the ICR data, I would suggest removing the optical properties data to the supporting information.”

“Why was the NMR done on the SPE samples? Why not the original samples? Freeze drying the samples then dissolving them in D₂O would be less biased than using SPE.”

“The IHSS extraction protocol utilizes strong acids and bases which could (or is) altering the composition of organic matter. I personally don’t recommend this protocol.”

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Can you elaborate on what you mean by “identical source materials”. A sample description would be useful here. The whole section “Extraction selectivity of dissolved organic matter” appears out of place. Maybe move to supporting information and summarize main conclusion in the manuscript? Maybe the methods section? The NMR section is very detailed. It is very easy to get lost. Why not focus on the main results and conclusions only. What do you attribute the reason of the high number of unassigned formulas? (table 3) DID you compare the samples using Kendrick plots that utilize all the observed masses? A PCA or NMDS or both the NMR and the ICR data could be useful.

Biogeochemical significance: The biological significant paragraph fails to explain the main factors behind the differences or lack of differences observed between the samples. A summary of the main conclusions is lacking. Each section in this manuscript appears to be separate from the other and rarely linked to one another. A paragraph that links all the observations from different techniques is lacking.

Interactive comment on Biogeosciences Discuss., 12, 13711, 2015.

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