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Biogeosciences Discussions

Interactive comment on "Chemodiversity of Dissolved Organic Matter in the Amazon Basin" *by* Michael Gonsior et al.

Anonymous Referee #2

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Anonymous Referee 2 Comments for Biogeosciences Discussions manuscript "Chemodiversity of dissolved organic matter in the Amazon Basin" MS number: bg-2016-72

Overall: The manuscript by Gonsior and coauthors compares the DOM quality using traditional optical methods (EEM, PARAFAC) with more specialized FT-ICR-MS and statistical methods in three different water types in the Amazon Basin. They present some interesting data and it is exciting that they saw definite relationships between the optical and molecular methods and the unique chemical signals between the three rivers. I think this paper would be improved by some rearrangement and additional content and clarification, especially regarding which samples are in the confluence of the Amazon River and how that relates to removal of DOM through adsorption and/or coagulation, currently the data presented does not clearly support DOM removal.

Specific Comments: For the most part, the sampling locations are divided into Rio Negro, Rio Madeira and Rio Tapajos. However, there are a couple of other location that are also presented e.g., Rio Jamari (abstract and tables), Solimoes River (discussion); additional information needs to be presented to give context to these locations or include the data under the three main location.

Are all of the samples from the Tapajos River in the confluence? It is not clear what stations are part of the confluence and which samples are just part of the river stem or flooded lakes. This needs to be clarified throughout the manuscript, but especially in the results and the discussion since a main point of your paper is the removal of DOM upon the mixing of rivers. In the current version of the manuscript the data is not presented to clearly demonstrate that DOM is being removed.

Pg 1, Line 21: Are all the samples from the Tapajos in the confluence? reword if this is not the case.

Pg 2, Line 19: Is it the removal of CDOM and suspended sediments that cause the waters to be clearer or the lack of CDOM and low suspended particle load due to clear waters draining weathered areas? Please clarify, add context, and/or estimates for each if available.

Pg 2, Lines 29-34: How do clear waters fit into this? Add information if available or add a statement to the effect that no information is available for clear waters.

Pg 2, Lines 29-34: Tie this paragraph into how it would relate to your study; link to changes in chemical compounds

Pg 3, Line 16: How many surface water samples were collected in the main stem of the river? Include range as you do for the lake samples. Specify how many and which samples were collected in the confluence vs the main stem.

Pg 3, Line 23: Add temperature and duration that filters were combusted.

Pg 4, Line 1: Samples were kept cool when? During extraction, until frozen? Please

clarify.

Pg 5, Line 1: What was the pH of the original river waters? If not pH 4-5, why was this pH chosen instead of a more neutral pH? Did you observe a pH dependence for your EEMs if samples were run at pH 4-5 vs pH 7-8?

Pg 7, Lines 3-7: The Solimoes River has not been mentioned before and no data are presented that show a decrease in DOM from the Rio Negro; the values for the flooded lakes and main river stem are almost identical for DOC. If the Solimoes River is just used as a comparison from another study, data needs to be presented that shows DOM removal occurred in the Rio Negro (DOC values and/or FT-ICR-MS figures from above and below the confluence).

Pg 7, Lines 9-19: This paragraph would benefit from some reorganization and clarification to allow this paragraph to flow better and increase understanding. Move the sentence "Very low abundance. . ." (lines 11-12) after the discussion about Rio Madeira and/or provide more context for the sentence, especially related to the boreal lakes and link to the next paragraph "The Tapajos areas contained. . ." (lines 17-19). Simplify the sentence "The unique and diverse. . ." (lines 13-15), are these the same or different unique compounds from the first sentence or the other unique compounds with unknown origin? Provide context as to how growing soy beans could cause unique compounds.

Pg 7, Line 23: How does Fmax3 relate to the Rio Negro? Fmax3 looks like it would also be a dominant component in Rio Negro in the example EEM in Fig. S2 and you state that Fmax 3 and 4 typically were correlated.

Pg 7-8, Lines 32-1: Unclear how the coagulation of analogous molecular ions fit into this paragraph. Suggest removing sentence.

Pg 8, Line 13-14: This sentence is vague and needs clarification. I agree that light attenuation would be different for the various sampling locations due to the differences

in the water characteristics, but how is this related to the unique compounds.

Pg 8, Lines 14-16: Additional discussion needs to be made to support this statement. No data is presented that suggests removal or transport of FDOM on particles or that you observed a loss of FDOM in the study area. If additional data are given to support the adsorption/coagulation, this statement could be expanded upon to tie into the bigger picture of biogeochemical cycling.

Pg 8, Lines 17-19: Please present evidence that the differences in the DOC concentration are a result of adsorption or coagulation besides just a difference in FT-ICR-MS. These three rivers seem to have very different geology in their headwaters that could also be responsible for the differences in DOC concentrations. This is especially relevant to the Rio Tapajos waters that should have a very low particle load.

Pg 8, Line 22: Could you provide some data to support the removal of HMW compounds from this river? Possibly a comparison of EEMs or FT-ICR-MS from upstream (lower particle load) and downstream (higher particle load)

Pg 9, Line 22-25: Additional information or clarification is needed for this section as stated previously regarding removal. The plants in the region may not vary substantially throughout the region but there is likely additional factors for the differences in DOC concentrations than just adsorption to mineral particles or coagulation with metals, likely a result of the geology in the different regions. Also no data is shown to support DOM removal through mixing.

Pg 16: Table 2: Rio Jamari is only mentioned in this table and the abstract. Provide some context for this location, is it another white water river like Rio Madeira? Or was this what the river was called after confluence with the Amazon River?

Pg 16: Table 2: It is not clear which data set is after the confluence with the Amazon River. Please provide clarification as Rio Tapajos has the same labeling (flooded lakes and main stem river) as the other rivers.

Pg 21, Fig. 5: To increase the understanding for readers unfamiliar with heat maps, include color bar legend and labels for the various axes.

Fig. S1: Are these stations for the flooded lake sites only or all sampling locations? Add text to caption for clarity. Can you provide additional information and make the map marker a different color for stations that were within the confluence with the Amazon River.

Technical Comments: Introduction:

Pg 2, Line 9-10: Switch “clear waters” and “white waters” since that is the order you talk about them.

Pg 2, Line 9: I suggest rewording the beginning of this paragraph to “Amazon tributaries vary in their coloration and opacity due to their origin and reactivity and have traditionally been classified as “black waters”, “white waters” and “clear waters”. These three water types play a continuing role. . .”

Pg 2, Line 11: Suggest using a different word than “processing” and simplifying “such as through”

Pg 2, Line 12: Change “has” to “have”

Pg 2, Line 23: Reword. Possibly to “High CDOM in black waters and suspended sediment concentrations in white waters limit light. . .”

Pg 3, Line 2-3: Reword. “It is unclear how previous work. . .or microbial processes, reflect the authentic. . .”

Pg 3, Line 10: Change “By applying” to “Using”

Pg 3, Line 10: Correct “overall”

Pg 3, Line 11: Simplify sentence by removing “moreover”

Pg 3, Line 13: Change “issues” to “relationships”

Materials and Methods: Pg 3, Line 16: Remove “by”

Pg 3, Line 17: Check number of lakes sampled, in Fig. S1, n=10,n=10, n=9 for Madeira, Negro, and Tapajos Rivers respectively. Should it be “9-10 lakes”? Or correct Figure S1.

Pg 3, Line 20: Move “either”; “were filtered and solid phase extracted either immediately after collection. . .or within three hours”

Pg 3, Lines 25-26: Reword sentence to “Formic acid was used instead of HCl to prevent possible chloride ion adduct formation. . .”

Pg 3, Line 28: Reword line 28 to include “pH 2, formic acid” from line 30, since this is the first occurrence of “acidified Milli-Q water”; if defined in line 28, do not need to include in line 30.

Pg 4, Line 4-5: Is this the range for all samples and location? Reword: “DOC concentrations for all samples ranged from 3-10 mg L-1, so only 1 L of sample water was filtered through the SPE cartridges to prevent overloading the 1 g cartridges.”

Pg 4, Line 8-9: Move manufacture’s name: “. . .performed by an automated FOSS® colorimetric flow injection analysis (FIA) system, according to the quality control guidelines recommended by the manufacturer”

Ultrahigh Resolution Mass Spectrometry Pg 4: I would recommend rearranging this paragraph so you introduce what you did before providing explanation.

Pg 4, Line 15-16: Did your instrument achieve a mass accuracy of less than 0.2 ppm? If so please clarify. State what your instrument did rather than saying what is typically achieved.

Pg 4, Line 25-26: Possibly move this sentence “All SPE samples. . .” to the beginning of the paragraph so the reader knows what you did prior to additional explanation.

Excitation Emission Matrix Fluorescence and Parallel Factor Analysis: Pg 4, Line 29-

30: Rearrange sentence: “CDOM was recovered almost quantitatively (>90

Pg 4, Line 30: Add volume to sentence “XX hundred uL. . .” or add a transition, “SPE-DOM samples were prepared by drying 100 uL of methanolic SPE-DOM. . .”

Pg 5, Line 12-13: This sentence could be simplified to “The maximum intensities of the components (Fmax) for each sample was exported and used for all subsequent statistical analyses.”

Pg 5, Line 25: Which “two normalized data sets” are you referring to?

Results and Discussion: Pg 6, Line 2-6: Break into two sentences, “. . .and Rio Madeira. Conversely, at high m/z, e.g. NM 601. . .”

Pg 6, Line 10: Add “however” “However, the intensity-weighted. . .” Since the decreasing trend was not the same for elemental ratios as for the DBE.

Pg 6, Line 11: Replace ‘that’ with ‘the’ or ‘the same’, “did not follow the same decreasing trend. . .”

Pg 6, Line 14-16: Be more specific with how the different formulae were different in the various water types, e.g. instead of ‘noticeably lower’ maybe use ‘approximately 50

Pg 6, Line 22: Clarify that these 6118 molecular formulae are for all the samples from all the waters combined and link to the top 6 panels of Fig. 2 “All Amazon DOM signatures”

Pg 6, Combine paragraph (lines 18-24) and next paragraph (25-27) or tie them together better.

Pg 6, Line 25: Remove “only”

Pg 6, Line 25-26: Tie this sentence to the lower 6 panels of Fig 2, possibly by using “ubiquitous” instead of “common”.

Pg 7, Line 3: The phrase “disk-shaped” is odd, is there a better word choice.

Pg 7, Line 19: Add ‘found’, “signatures found in all”

Pg 7, Line 24: Provide reference for conjugated π-systems.

Pg 7, Line 29: add “to” “remarkably close to the results”

Pg 8, Line 7: Change ‘However’ to ‘For example’ or reword. This sentence seems like it is in support of the previous discussion that the optical properties could be related to specific molecular characteristics.

Pg 8, Lines 21-22: Simplify sentence: “The DOC data were in agreement with the FT-ICR-MS and EEM-PARAFAC results. . .”

Pg 8-9, Line 32-2: Simplify and reword. Possibly “One unique CHO cluster consisted of hydrogen-deficient (low H/C), but highly oxygenated (high O/C) molecular ions and had a strong positive correlation with all Rio Negro samples (Fig. S6). Similarly, the Fmax components 3 and 4 were highly correlated to a cluster of high molecular weight molecular ions likely aromatic in origin (Fig. 5 and S6).” Tie this back to lignin.

Pg 9, Lines 6-9: Simplify the sentence “Components Fmax 3 and 4. . .” (lines 6-9) to “However, components Fmax 3 and 4 did not show any correlation with molecular ions in the CHNO pool, nor in the CHOS pool, supporting the supposition that these PARAFAC components were only derived from CHO molecules.” May fit better immediately after the rest of the discussion about Fmax 3 and 4, end of line 2.

Pg 9, Line 11: Remove comma and ‘was’.

Pg 9, Line 16: Reword: “Overall, Fmax 1, 2, and always correlated together as did Fmax 3 and 4.”

Pg 9, Line 21: Change ‘appearance’ to ‘compounds’.

Pg 9, Line 27: Reference Table 2 and highlight the similarities between the river and flooded lake.

Pg 9, Line 30-33: Split into two sentences.

Pg 9, Line 34: Be specific about which methods. ". . .without FT-ICR-MS and statistical analyses"

Tables: Pg 16: Table 2: Give number of samples collected for each location.

Figures: Pg 17: Should be Figure 1

Supplemental Figures: Rearrange supplemental figures so that they are numbered as they are listed in the text.

Fig. S1: Rearrange the station order since you always talk about them in the order Rio Negro, Madeira, and Tapajos.

Fig. S1: Since this is a supplementary figure, possible to make maps larger?

Fig. S6: To increase the understanding for readers unfamiliar with heat maps, include color bar legend and labels for the various axes.

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