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Interactive comment on "Seasonal variability of dissolved organic matter in the Columbia River: In situ sensors elucidate biogeochemical and molecular analyses" *by* Urban Johannes Wünsch et al.

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We thank the anonymous reviewer for her / his constructive comments. The response below contains the reviewers comments (marked with "RC1: ") followed by our response (marked with "Response: "). Please note: As a consequence of this review, we will provide a revised version of the manuscript at a later time.

RC1: General Comments: In this manuscript the authors examined data such as FDOM,chlorophyll fluorescence, temperature, nitrate, and turbidity measured with in situ sensor platforms deployed at two locations in the lower Columbia River, USA

combined with discrete measurements of DOC concentrations, CDOM absorption and fluorescence in addition to molecular signatures using FT-ICR-MS during March – August 2013 (spring – summer). DOC fluxes for the sampling period were calculated based on the relationship between FDOM and DOC. Relationships between DOC and CDOM/FDOM optical indices (HIX, BIX, SUVA) were also investigated. Furthermore, molecular characteristics were examined for the spring events (phytoplankton bloom, rain event, freshet) and for the summer sampling period. While the overall measurement approach was good, the results and the interpretations of the results were weak and sometimes speculative. Many papers that were cited were missing from the reference list.

Response: The missing references were caused by an unfortunate bug in the citation management software. The list will be updated in the revised version of the manuscript.

RC1: Specific comments: Abstract, lines22-24: "....FDOM parameters correlated with major seasonal biogeochemical shifts in the river associated with phytoplankton blooms and river discharge and thus revealed predictable seasonal patterns in DOM quality." The results do not support this conclusion.

Response: Deleted "predictable" in the cited sentence. In our opinion, the remaining conclusion is supported by the results.

RC1: Abstract, lines 25-26: This conclusion also not supported by the results - very speculative.

Response: It is not clear which part of this conclusion is speculative. Lines 25-26 report results that are directly reflected in the FT-ICR-MS dataset. The conclusion "correlated significantly" was drawn by means of transparently described methods and datasets.

RC1: Page 2, line 5: Spencer et al. 2013 should be Spencer et al. 2012.

Response: The claim "flux from individual rivers can vary by several orders of magnitude, depending on watershed characteristics" is supported by table 1 in Spencer

2012, where annual discharge, watershed % wetland, as well as annual DOC yields are provided.

RC1: Page 2, line 8: Weishaar et al. 2003 (missing reference)

Response: See response to general comments. Reference will be provided in the revised manuscript.

RC1: Page 5, line 7: “naphierian” should be Napierian

Response: The spelling is corrected in the revised version of the manuscript

RC1: Page 5, line 20: (Parker, 1968) missing reference

Response: See response to general comments. Reference will be provided in the revised manuscript.

RC1: Page 5, line 30: (Wunsch et al. 2015; Parker and Rees 1960) missing references

Response: See response to general comments. Reference will be provided in the revised manuscript.

RC1: Page 7, line 6: (Watras et al. 2011) missing reference 2.7 Hydrological and metrological data should be “Hydrological and meteorological data”

Response: Reference added to the bibliography and spelling corrected.

RC1: Page 8, line 13: “The relative peak intensities of ubiquitous formulas were correlated with various parameters....” These results are not shown in the manuscript

Response: These results are shown in Fig. 9, mentioned in results section 3.3 (page 11), and discussed in the discussion section 4.2 (page 15).

RC1: Page 9, line 12: “With 1000 m3 s-1 at SATURN-08, the seasonal discharge maximum was comparatively low (Fig. 3a).” The discharge is more like 10,000 m3 s-1. This statement needs to be corrected.

Response: The statement is corrected in the revised version of the manuscript.

RC1: Page 9, lines 31-32: “The highest relative variability was observed in the DOM aromaticity indicator SUVA254, while the FI had the lowest variability..” The implications of using these optical indicators remains unclear. This is briefly addressed in the discussion section (Page 15) with the conclusion that DOM was clearly terrestrially dominated (which is expected) and low in authochthonous DOM. It would help if the authors better explain the need for using these indices and the observed variability.

Response: More detailed explanations for the interpretation of the optical indices were added to the methods section 2.4. We added another sentence explaining the need for optical indices in our study at the beginning of section 4.2 (page 15).

RC1: Page 11, line 6: “To elucidate this cluster analysis, we investigated the average seasonal changes of ubiquitous molecular formula abundances for all sampling times (Fig. 8, right panel).” It appears that the changes investigated were linked to events (spring bloom, spring freshet, spring rain event) rather than a seasonal study.

Response: The wording was changed to “changes between events”, we recognize the concern of the reviewer.

RC1: Page 12, line 15: Correspondingly, during early spring 2013, rainfall during the peak of the bloom contributed to increasing river discharge, causing a steep decline in phytoplankton abundance” This is not evident from Fig. 2.

Response: The statement refers to Fig. 2(a) and (c), in particular the highlighted part(grey): Declining chlorophyll a abundance and increasing river discharge. This inverse relationship is hard to identify since the graph provides an overview of the entire season. Our statement is supported by the inverse correlation of chlorophyll a and river discharge during this time (April 1st – April 13th, R2 = 0.76). Moreover, as stated in this paragraph, earlier studies by Sullivan et al. showed similar findings. To support our conclusion, this correlation will be mentioned in the revised manuscript.

RC1: Pages 15-16, lines 33, 1: ...The high abundance of such molecular formulas during the spring freshet could therefore explain shifts in SUVA254, BIX, and HIX." These shifts are not evident in any of the figures -too speculative.

Response: As explained in the cited paragraph, we state that CDOM-correlated formulas had low H/C ratios and above average double bond equivalents. These two FT-ICR-MS metrics, as well as the evident correlation (all together summarized in Fig. 9) increase the likelihood that this particular part of the FT-ICR-MS dataset explains CDOM and FDOM variability (as the presence of an aromatic ring is a prerequisite for fluorescence of organic matter). In this context, we also referred to previously published work by Kellerman et al. which established similar relationships with a bigger dataset in Swedish lakes.

RC1: Page 16, lines 13-14: "Shifts in the fluorescence index indicated increased levels of fresh microbial DOM, demonstrating the link between primary and secondary production." These shifts are not evident in the figures or tables and the link between primary and secondary production too speculative.

Response: With chlorophyll a, the only available parameter to estimate biological activity concerned primary production. However, the fluorescence index (Parlanti et al.) has previously been established as an indicator for freshly produced microbial DOM (derived from the degradation of algae). As such, the shifts are not evident from figures or tables, but our conclusion can be drawn from the context of the results. To emphasize the speculative nature of our conclusion, "demonstrating the link" was substituted by "indicating a possible link".

RC1: Figures: Fig. 2(b): It is not clear why a decreasing FDOM trend is observed at SATURN-05 between _5/12 to _8/13.

Response: These data were discussed in section 4, page 13, lines 26-31. We concluded that the differences in readings between the two stations were caused by disturbances. The reviewer is correct in stating that it is not clear why the decrease between

May and August 2013 was observed. At this point, we have no possible explanation other than technical problems with the sensor. Since the sensor was recalibrated in the meantime, it is not possible to further investigate the issue.

RC1: Fig. 5: If data points for May and June associated with the spring freshet are excluded it does not appear that DOC and FDOM are well correlated. Also, in Spencer et al. 2012, Columbia River exhibited weak relationship between CDOM absorption and DOC likely due to significant impoundment of waters within its watershed. This factor is rather complex but should be considered in this study.

Response: The reviewer is correct in stating that the relationship between DOC and FDOM would not be strong if data from May 2013 were excluded. However, DOC values were highest during that period and to obtain a robust model of in situ data, these elevated readings are vital for several technical reasons concerning the accuracy of the in situ readings: (1) In situ readings are always affected by disturbances from particles that might vary between months, (2) readings are always affected by seasonal changes in temperature, and (3) unknown factors such as sunlight, diurnal variations in the power supply (solar power). While we corrected for (2) as mentioned in the manuscript, other factors ((1) and (3)) are difficult to investigate and therefore not quantifiable. It is therefore highly likely that these readings (along with the 5 % precision of the DOC measurement) caused the relatively weak relationship between DOC and FDOM when the overall variation was small. We added a paragraph in the discussion (revised manuscript): "However, if data from May 2013 were excluded, the relationship between DOC and FDOM would not be significant. This is likely caused by factors contributing to the measurement uncertainty, such as variations in water turbidity, imperfect temperature correction and slight variation in FDOM quality at the wavelength pair used by the sensor."

RC1: Fig.7: Not clear what is being presented here. These are at two different stations (SATURN-08 and SATURN-05) but at least visually two plots look the same. Were the data from the two stations combined?

Response: The plot highlights unique molecular formulas at station SATURN-08 (b) and SATURN-05 (b) against the background of all molecular formulas (grey, both stations combined). The similarity the reviewer refers to might arise from the grey background, or (as stated throughout the manuscript) the fact that SPE-DOM from both stations was relatively similar. The figure legend was adopted for clarification.

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