

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

### **Anonymous Referee #1**

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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,

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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.

Specific comments: Abstract, lines 22-24: “...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. Abstract, lines 25-26: This conclusion also not supported by the results - very speculative.

Page 2, line 5: Spencer et al. 2013 should be Spencer et al. 2012. Page 2, line 8: Weishaar et al. 2003 (missing reference) Page 5, line 7: “naphierian” should be Napierian Page 5, line 20: (Parker, 1968) missing reference Page 5, line 30: (Wunsch et al. 2015; Parker and Rees 1960) missing references Page 7, line 6: (Watras et al. 2011) missing reference 2.7 Hydrological and metrological data should be “Hydrological and meteorological data” Page 8, line 13: “The relative peak intensities of ubiquitous formulas were correlated with various parameters...” These results are not shown in the manuscript Page 9, line 12: “With 1000 m<sup>3</sup> s<sup>-1</sup> at SATURN-08, the seasonal discharge maximum was comparatively low (Fig. 3a).” The discharge is more like 10,000 m<sup>3</sup> s<sup>-1</sup>. This statement needs to be corrected. Page 9, lines 31-32: “The highest relative variability was observed in the DOM aromaticity indicator SUVA<sub>254</sub>, 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 autochthonous DOM. It would help if the authors better explain the need for using these indices and the observed variability. 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. Page 12, line 15: Correspondingly, during

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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. Pages 15-16, lines 33, 1: ...The high abundance of such molecular formulas during the spring freshet could therefore explain shifts in SUVA<sub>254</sub>, BIX, and HIX.” These shifts are not evident in any of the figures -too speculative. 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.

Figures: Fig. 2(b): It is not clear why a decreasing FDOM trend is observed at SATURN-05 between ~5/12 to ~8/13. 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. 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?

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