

## ***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.***

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We would like to thank the anonymous reviewer #2 for her / his constructive comments that helped to improve the manuscript. The response below contains the reviewers comments (marked with “RC2: ”) 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.

RC2: There was a significant difference between FDOM data between SATURN-08 (S8) and SATURN-05 (S5), and the relationship between FDOM and DOC only applies

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to S8. Although the authors gave some explanations in the paper, it may worth digging out more details, as the FDOM-DOC relationship is a major finding of the paper. The authors suggest that the difference of FDOM between the two stations might not be due to data quality, but rather local sources of changes down stream of S8. As they mentioned, there are historical data of DOC vs. FDOM in the lower Columbia River. I suggest they dig out those data and overlay their data to see if there is any consistency or inconsistency in all data and the relationship. If they believe there are something ‘unusual’ down stream of S8, can they try to use their available data to investigate the nature and effects of such sources? I think spending more effort into this may gain more insights into the FDOM and DOC relationship, making the conclusion stronger.

Response: A comparison of the FDOM / DOC relationship between SATURN-05 and SATURN-08 is not possible, since no historic FDOM measurements are readily available from USGS to our knowledge. However, CDOM absorbance at 254 nm and DOC at SATURN-05 were sampled by USGS from 1999 onwards. As a result of the reviewers comment, we investigated the USGS dataset to further investigate and provide more detail. In total, 185 samples spanning the years 1999 to 2016 are available to date (as of 08/23/2016). The overall relationship between DOC and CDOM absorbance at 254 nm was significant, but weak ( $R^2 = 0.42$ ,  $p < 0.001$ ). We were also able to reproduce the results listed in Spencer et al. (2012) for the years 2009-2010. However, we also found a significant span in the % explained variance between different time periods: The stepwise correlation analysis of two consecutive years (e.g. 1999-2000) showed  $R^2$ -values ranging from -0.18 (2007 2008) to 0.93 (2009 2010) (see table 5 in revised manuscript). 2005-2006 and 2009-2010 were the only periods for which the quality of the DOC/CDOM correlation was sufficient to compare to our study. From this more detailed investigation of the USGS data, we conclude that, in order to utilize in situ sensors for DOC predictions, it is important to continuously monitor the correlation between DOC and CDOM / FDOM. However, we would like to refrain from further speculating as to why the DOC-CDOM relationship appears spatially and temporally unstable, since we do not have sufficient information to do so. The same holds true

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for the differences in FDOM readings between SATURN-08 and SATURN-05. As mentioned in our response to reviewer 1, the sensors at SATURN-05 have since been recalibrated. As a consequence of this comment, we have revised the discussion in section 4.2 and 4.3, pages 13 and 14. We recognize the reviewers call for overlaying our own data with that of USGS. However, a meaningful, direct comparison between data obtained in this study and data collected by USGS is not feasible, due to the small overlap of samples ( $n = 4$ ).

RC2: In a few places in the introduction and abstract, the text seems to suggest river discharge is one of biogeochemical factors (e.g., p3 at the beginning), which is not. It is hydrology. Need to be consistent throughout the paper.

Response: We deleted “biogeochemical” on page 1, L. 23 and added “and hydrological” on page 3, L.1

RC2: p2, L2, the reference is still from 1981; I believe there should be newer update.

Response: We have replaced the citation with a more recent publication and adjusted the estimated flux accordingly.

RC2: Eq 1. Please specify what is the purpose of calculating napierian absorbance.

Response: The use of napierian absorbance is based on its common usage within the marine CDOM community and is thus intended to present data in a comparable unit.

RC2: p6, L21, what is LOBO?

Response: Land/Ocean Biogeochemical Observatory. We have added an explanation to the manuscript.

RC2: 6. Section 2.6, no performance metrics of the in-situ sensors were given. What are their precision/accuracy, data quality etc.? Need to be careful what the quality these sensors can deliver. They may not always give the data quality as suggested by the manufactures. Should more systematically describe how these sensors were used

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and calibrated, and how the data were quality controlled, and in what accuracy and precision these data can be trusted.

We have modified section 2.6 to provide better detail on the sensor maintenance and data processing and included performance metrics provided by the manufacturer in the supplementary material of this comment and the revised manuscript. We agree with the statement that performance as specified by the manufacturer might not be identical to field measurements. However, that is mainly caused by conditions that cannot be recreated in a laboratory environment. In our opinion, regular cleaning and inspection, as well as frequent recalibration by the manufacturer are appropriate to handle this challenge.

RC2: p6, L30, ‘No corrections were made to the in-situ nitrate and phosphate measurements’. Why not, since there are discreet samples for nutrients measured?

Response: In situ Nitrate correlated with an  $R^2$  of 0.99, thus no correction was necessary. For Phosphate, corrections were not feasible due to the fact that in situ concentrations were mostly below the limit of detection. Explanations were added to the manuscript to clarify the reviewers concern.

RC2: p9, L18, 65%. It is more like 60% to me.

Response: Thanks for pointing this out, the text was corrected to 61 %.

9. p10, L8, ‘parametric correlation analysis’. What is this analysis exactly? Linear analysis?

Response: The manuscript text was modified to clearly state that a parametric, linear correlation analysis was performed.

RC2: p10, L8-13. The description here is confusing. Fig. 5 did not show Flu vs. FDOM relationship. What the two relationships here mean or imply then?

Response: We added a figure to the supplement of this response (Supplement Fig. 1)

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to show the relationship between in situ and laboratory fluorescence. The reference in the parenthesis was modified accordingly. Moreover, a mistake in the reported R2 was corrected (R2 was 0.93 instead of 0.95). Please also note that we will provide Fig. 1 to the supplement of the revised manuscript.

RC2: Between Section 4 and Section 4.1, the text here does not seem follow a logic way for presentation. May want to organize it into one or few sub-sections.

Response: We have added two subsections that help to emphasize the structure of this part of the discussion.

RC2: p12, L15, says rainfall caused decline in phytoplankton abundance. Any data or figure to show?

Response: This was also pointed out by reviewer 1. We have expanded this conclusion by citing supporting data (significant inverse correlation between chl a and discharge in the respective two week window).

RC2: p12, L26, why there is increased terrestrial nitrate runoff in winter?

Response: Increased terrestrial runoff is likely a consequence of increased winter rainfall in the study area. This explanation was added to the manuscript.

RC2: p12, L33, 'high' rainfall during May 2013. But it says low rainfall before this?

Response: "High amount" was substituted with "frequent" to improve the explanation. The overall amount of rain in the season was low, but the frequent occurrence of rain in May likely led to an increased discharge.

RC2: p14, L8, -7.57 vs. -4.7. I think the measurement error margin was about 10 umol/L, correct? So the difference is within the error margin, is it not? If yes, the conclusion here is not valid. How much of difference is in slopes here? Can that slope difference tell us some information?

Response: The error of DOC measurements should be treated independently of the

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intercept uncertainty. The only available metric to judge the significance of the difference between the two intercepts is their respective standard error (SE). Since DOC and CDOM did not correlate well in Spencer et al. (2012), the SE is rather high (3.3) compared to our study (0.7). After reviewing this information, we decided to alter this part of the discussion. The modified version also discusses the slope values. Thank you for raising this point.

RC2: Figs 2 and 4. There are no captions for sub plots (a), (b),...

Response: More detailed explanation on panels was added to both figure captions.

RC2: Figure 10. Is there an explanation why USGS data are different than the modeled DOC?

Response: We do not have definitive explanations for the differences visible in Fig. 10. However, the most likely explanation for the differences is that differences originate from lateral input of organic matter between SATURN-08 and SATURN-05. In our opinion, further explanations are too speculative.

Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/bg-2016-263/bg-2016-263-AC2-supplement.pdf>

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