14 April 2015

Dear Editors of *Biogeosciences*:

We greatly appreciate the detailed reviews of our manuscript. We have responded to all questions raised by the reviewers. We believe the manuscript has been improved substantially and re-submit it to *Biogeosciences*.

Best regards,

Neung-Hwan Oh

We would like to thank the reviewers for the thorough review which improved the original manuscript greatly. We revised the manuscript carefully following the reviewers' suggestions. Below, find reviewers' comments in normal font and our replies in blue.

Anonymous Referee #1

General Comments

This paper describes a study that compares laboratory and field measurements of UV/Vis and FDOM sensor measurements across gradients of temperature and turbidity. These sensors are often used as proxies for DOC concentrations in natural waters and this is the first study that I am aware of to directly compare the performance of these sensors. The authors suggest that the UV/Vis sensors are more sensitive to changes in turbidity than the FDOM sensors, while the FDOM data are suggested to be more sensitive to changes in temperature. I think that this is a worthwhile effort, but have a few concerns regarding the approach described in this paper.

My main concern is related to the fact that the authors simply show that temperature and turbidity differentially affect UV/Vis and FDOM sensor readings, but do not take the important step of showing how/if the sensor data can be corrected to provide reasonable proxies for DOC concentration. Specifically, uncorrected UV/Vis data are compared with temperature corrected (but not turbidity corrected) FDOM data. While it is important to show the varying influence of temperature and turbidity on the different types of sensor data (which the authors do well), it is also important to quantify how these varying influences can be accounted for to provide the most accurate estimates of DOC concentration from sensor data. Downing et al (2012) provide an excellent example of how corrections for FDOM sensor data can be derived and applied to estimate DOC concentrations. The manuscript would be strengthened by taking a similar approach for the FDOM and UV/Vis sensor data reported here.

This is a good point. We provided equations for temperature and turbidity correction (Eqs. 1 to 6) and applied the equation for the in-situ monitoring of the sensor signals (Fig. 4) following the example of Downing et al. (2012).

UV/Vis and FDOM sensor readings are made across a small range of turbidity and DOC concentrations. The authors suggest that this is because these small ranges are consistent with those observed in the study watershed. While this may be true, and informs future studies at this specific site, limiting the investigation to such small ranges does not allow for the results presented here to be applied in streams/rivers with broader ranges of environmental conditions.

We conducted new experiments over increased ranges of temperature and turbidity following the reviewer's suggestion (Figs. 2 & 3). We also strengthened discussion on the limitation of this study and what needs to be done for broad applications of the sensors (section 3.2).

Specific Comments

1. UV/Vis and FDOM sensor data can be used as proxies for DOC concentrations. The authors refer to the sensor data as proxies at certain locations in the text, but not consistently (e.g. see the third paragraph of section 2.1). I recommend that the sensor data are consistently referred to as proxies throughout the manuscript.

Done.
p.6, line21: e.g. "In order to examine the feasibility of using the UV/VIS and FDOM sensors as a proxy to estimate [DOC], …"

2. It is stated that the UV/Vis sensor obtains data across a range of wavelengths (220-720 nm) and that "global calibration" is used to estimate organic carbon concentrations. It would be helpful to be more specific, and state what wavelengths are used, and how they are used to estimate concentrations.

Good point. We also asked the company how the 'global calibration work' to estimate the DOC concentrations, but they refused to provide detailed information because it is the company's core know how. We copy and pasted their response here ("*Please understand that any detailed information regarding used wavelengths cannot be published because this is s::can core know how*").

3. It would be helpful to state the precision associated with the laboratory measurements of DOC concentrations.

Done.
p.7, line10: "Accuracy of the Shimadzu analyzer was verified by analyzing quality check (QC) solution (ERA, Colorado, USA) at a concentration similar to the sample [DOC]. The measurement error for a QC (4.8 mg L^{-1}) was 3% on average and < 0.1 mg L^{-1} for the other QC (0.5 mg L^{-1})."

4. Three IHSS reference materials and artificial stream water were used in the laboratory experiments. The artificial stream water was created by mixing leaves and soil from the study stream with DI water and then extracting the DOC from this mixture. This approach eliminates any contributions from other sources of DOM that would be found in natural waters (e.g. algal-derived DOM). Given that different sources of DOM have different absorbance and fluorescence characteristics (as stated at the end of the second to last paragraph of section 3.1.1, the second to last paragraph of section 3.1.2, and the third paragraph of section 3.2) it is difficult to use information gained from the laboratory results to improve our ability to interpret sensor measurements obtained in natural water samples. Therefore, it would be more informative to use actual stream water instead of artificial stream water for the laboratory experiments.

Good point. We conducted new laboratory experiments using storm water collected from the study site following the reviewer's suggestion and new, expanded results are provided in the revised manuscript.
p.7, line18: "In order to simulate field conditions, about 20 L of stream water was used for temperature and turbidity correction. The stream water had been collected from a forest watershed as detailed in the next section (2.3) at peak discharge using precombusted 2 L glass

bottles when the typhoon, "NAKRI" hit South Korea on August 2nd in 2014, and was kept frozen before the experiment."

5. Figure 1: There are no data between [DOC] _ 5 and 11 mg/L for the comparison of UV/Vis and FDOM readings of SRNOM as a function of DOC concentration. This data gap should be filled or the _11 mg/L sample should be removed from the analysis.

Done. The data point of high DOC concentration is removed from the analysis following the reviewer's suggestion (Fig. 1).

6. Are the slopes shown in figure 2a significantly different from zero?

Figure 2a is replaced with figures from new experiments and p-values are reported. Yes, the slopes were significantly different from zero. However, the slope was so low that its effect on temperature correction is negligible.
p.12, line 13: "The UV/VIS sensor outputs showed little variability with temperature change (slope: 0.009 to -0.004, R^2: 0.22 to 0.54, $p < 0.01$) in SRNOM, SRHA, and SRFA solutions (Fig. 2a) as well as in the forest stream water (Fig. 2d; slope: 0.001 to 0.002 RU $^oC^{-1}$, R^2: 0.03 to 0.04, $p < 0.01$). The slopes of the UV/VIS sensor outputs against temperature were less than 0.01 RU $^oC^{-1}$, indicating that the effect of temperature on UV/VIS sensor was negligible. Even if temperature of the forest stream water increased by 20^{o}C, the sensor outputs would increase only by ~0.03 RU, which is less than 1% of sensor readings of the forest stream (Fig. 2d)."

7. "BW" is referenced in figure 2, and I assume it is the artificial stream water, but it is not defined in the text. I recommend that this be defined in the methods section.

Done.
p.10, line3: "… a forested watershed, "Bukmoongol watershed" (BW; 35.0319 ^{o}N, 127.6050 ^{o}E) in Mt. Baekwoon located in Gwangyang city, South Korea."

8. Section 3.1.3: It is stated that the FDOM20 slightly decreased as a function of turbidity when [DOC] = 5.2 mg/L. It appears that there was a relatively large decrease in FDOM 20 (_20% decrease across a small range of turbidity (0-25 NTU)). Is the slope of this line significantly different from zero?

Figure 3 is replaced with new figures from new experiments and p-values are reported.

9. For the in situ data, I recommend either applying existing temperature and turbidity corrections to the sensor data (e.g. the corrections provided by Downing et al., 2012 for FDOM) or using the results shown in figures 2 and 3 (preferably over a broader range of turbidity and DOC concentrations) to generate corrected UV/Vis and FDOM sensor data specific to the study site. Comparing these corrected values against laboratory derived [DOC] data would provide useful insight into the performance/utility of the sensors as proxies for [DOC], which is the stated objective of the study. Such comparisons could be presented instead of the comparisons currently presented in Figure 5.

The sensors were tested over a broader range of temperature and turbidity and new figures were provided (Figs. 2 to 5). We also strengthened discussion on the limitation of this study and what needs to be done for broad applications of the sensors (section 3.2).

Technical Corrections:
1. There are many grammatical mistakes throughout the manuscript. The clarity of presentation would be improved by consultation with an experienced technical editor.

Grammatical errors will be edited in the final submission stage of the manuscript.

Interactive comment by J. Hur

In this work, the authors examined the possible environmental factors resulting in the changes in the signals produced from in-situ UV-Vis and fluorescence sensors. This kind of effort can make lots of contributions to more accurate estimate of DOC export from ecosystems, particularly from forested watersheds enriched with organic carbon. Overall, the manuscript is well-organized. It is nice to see the suggestions for proper use of the optical sensors in field for accurately monitoring DOC concentrations, which is based on sound experimental data. I have a few comments for the improvement of this manuscript.

(1) It seems insufficient to state the novelty of this work in comparison with the previous similar reports. Is that comparing/testing UV-VIS and fluorescence sensors at the same time? More explicit statement about the originality needs to be added in revision. Adding a new table can be an idea for a better comparison between this work and the prior studies with the detailed sensor types and the conditions provided.

We added a table on previous studies using the two types of the sensors following the suggestion (Table 1).
p.5, line5: "Although the UV/VIS and FDOM sensors have been used widely to estimate stream and river [DOC], to our knowledge, there is no study directly comparing the performance of the two types of sensors (Table 1)."

(2) Is there any possibility that the sensors manufactured by other companies could produce a little different trends and/or different degree of the sensitivity to temperature and turbidity. The related discussion is needed.

Good point. We added discussion on different models.
"Although we tested two specific models of UV/VIS and FDOM sensors, multiple models are available and we did not address variability of many sensors or variability within a model line. Sensor-specific as well as site-specific calibration would be necessary to use the sensors as a proxy of [DOC] considering that each sensor reacts differently to a range of temperature and turbidity. For example, four types of FDOM sensors showed different attenuation ratio to changes of turbidity although they all showed increasing trends of attenuation with increased turbidity (Downing et al., 2012). FDOM sensors with open path responded strongly to turbidity changes than that with close path (Downing et al., 2012)."

(3) As the authors indicated, the sensitivity of the sensors is likely to be dependent on the dominant components of DOM in water samples, especially for fluorescence sensor. In this regard, this study may be somewhat limited to generalize their findings into other fields (even into other forested watersheds). Please note that the in situ data of this study are produced from a single forested watershed over a limited time period. It would be nice to add the possible limitations or convincing statements over the further applications.

Good point. We added discussion on the limitation of this study and what factors should be considered for future application of the sensors.

p.16, line14: "The three storm events were not strong in terms of precipitation intensity and did not capture large variation of temperature and turbidity in the field and this is a limitation of this study. However, this can be also interpreted that the sensors can be employed to provide reliable, high resolution data for base flow conditions. Although it is demonstrated that the sensors can be compensated for temperature and turbidity to be used as a proxy of [DOC], there are several other factors that should be considered for successful application of the sensors in the field…"

Anonymous Referee #2

The manuscript by Yoo et al. is a concise method paper. It deals with different sensor systems for the detection of DOC and provides a comparison of the methods. Given that, the paper is rather technical and methodological and does not focus on processes or mechanisms. There are other papers available in the literature that did comparable things (eg Downing et al 2012) but the novelty in this MS is that they compared fluorescence sensors with absorbance sensors.

Fig 1 and the respective text in the results: Please provide a statistical test + outcome for your statement that the linear regressions are significantly different.

Figures are replaced with new figures from newly conducted experiments and p-values are reported (Figs. 1 & 2).

Temperature correction of fluorescence: There is a solid theoretical foundation for a temperature dependence of fluorescence and therefore a correction makes sense. It seems that the authors just used a linear correction (please provide more through information about the exact formula and parameters of the correction). I wondered whether the theory would also predict a linear relationship.

We revised the manuscript providing the exact formula and parameters of the correction (Eqs. 1 to 6).
p.13, line4: "We observed strong negative correlations of the FDOM sensor with temperature in the reference materials as well as in the the whole range of DOC concentrations from 1.1 to 10.5 mg L^{-1} of the forest stream (slope: -0.17 to -2.07 (ppb QSE) $^{o}C^{-1}$, R^2: 0.97 to 0.99, $p<0.001$), decreasing by ~1.4% in ppb QSE per 1^{o}C increase (Fig. 2b, 2e). This result is consistent with the former studies showing that FDOM signals decreased by an average of 0.8-1.5% per 1^{o}C increase over the range from ~1 to 25^{o}C (Downing et al., 2012; Watras et al., 2011).
A study on fluorescence of wetland-dominated lakes demonstrated that slope of the fluorescence against temperature increased as concentration decreased (Watras et al., 2011) and the same pattern was observed in this study (Fig. 2e). Temperature coefficent, ρ ($^{o}C^{-1}$) was estimated to be -0.017 ± 0.004 (mean ± SD) for the solutions of lab DOC from 1.1 to 10.5 mg L^{-1} at 20^{o}C."

The application of the sensors is not very convincing as the system did not react massively to the heavy hydrological disturbances. It would be more impressive to use a system where DOC increases over orders of magnitude and also turbidity reacts more strongly. I would assume that the applied linear corrections work fine over these narrow variation bands in DOC/turbidity. The larger the range of DOC/turbidity/temperature would be the higher is the chance of systematic deviations due to non-linearities. So, a more rigorous test in a more dynamic system would be more convincing.

Good point. We conducted new laboratory experiments over broader range of turbidity and limitation of this study is included in the discussion. Please check the sections, "3.1.3" and "3.2" as well as "4. Conclusions and Implications".