

# **Interactive comment on “Quality transformation of dissolved organic carbon during water transit through lakes: contrasting controls by photochemical and biological processes” by Martin Berggren et al.**

## **GENERAL COMMENTS**

In this work, the authors aim to determine the relevance of bio-and photo-degradation processes during the water transit time in individual lakes. The authors hypothesize that each process will prevail as a function of the color of the DOC compounds, so that biodegradation will target non-colored DOC while photo-degradation, colored DOC compounds. Using a complex data set at different temporal and spatial scales and including both field and experimental data, the authors found brown-water lakes to be dominated by biodegradation processes (not photo-degradation), which leads to their persistent brown-water color.

The authors present these results as contrasting with the current paradigm of loss of colored constituents of DOC along the inland waters continuum. However, they do not provide such a continuum (i.e. accumulated water residence time along the landscape), they do not evaluate the molecular composition of DOC and, the presented here are net changes (i.e. including production and degradation of DOC) but they are not discussed as so. I consider the partitioning between photo and bio-degradation processes a key question to complete our knowledge on the pathways of C processing in inland waters. But because of this relevance, I ponder indispensable that the authors clarify those concerns above and the ones specified below (such as properly assessing the role of hydrology, improving the characterization of DOC or providing the complete results -the last specially affecting Figure 2-) before this manuscript can be considered for publication. I hope these comments are helpful and constructive.

## **SPECIFIC COMMENTS**

### **Abstract**

P1 L17: “photo-chemistry qualitatively dominated”...what does qualitatively mean here? That the changes in DOC quality were dominated by photo-decay? That you assess that in a qualitative (i.e. non-quantitative) way? Clarify in the text.

Also, photo-chemistry dominated the DOC or the CDOM transformation in headwater lakes? How is the production of non-colored DOC evaluated? Clarify in the text.

P1 L19: Was there a systematic relationship between color loss and WTT in clear-water lakes? Add this information also.

### **Introduction**

P2 L17: Maybe biodegradation processes do not affect colored DOC preferentially, but that they do affect it at all has a stronger impact on the inland waters C budget than the consumption of in-situ produced DOC. Add information on the DOC sources and their relevance on the C budget here.

P2 L22: Available references on “efficient” photo processing, showing how polyphenolic, aromatic compounds are mostly affected by photo reactivity (assessed at a molecular level) in black and boreal waters, are missing (e.g. Stubbins et al. 2010 L&O, Kellerman et al. 2014 Nat. Comm. and references therein).

P2 L27: I agree with the authors that the assessment of the variability of WTT within systems is very relevant. However, without assessing how that variability is linked to changes in color of runoff DOC, it is hard to attribute the changes in the lake just to in-situ biogeochemical processing. Clarify that here and incorporate that perspective throughout the text -see comments below-.

## Methods

P3 L16: modify this sentence into “lakes are located in the boreal region, where nutrients” and provide a reference of that distribution.

P3 L30-32: Although, low effects of pH on the optical properties of DOM have been reported at the most frequent inland water’s pH range (i.e. 5.5-7.5), they can be important at lower pH values (< 4.5), such as the ones included in this study. Accordingly, add a paragraph in the discussion stating which lakes presented these low pH values (i.e. 3.4) and how could that affect your absorbance measurements (some useful literature: Pullin and Cabanis et al., 2003, *Geochim. Cosmochim. Acta.*; Patel-Sorrentino et al., 2002 *Wat. Res.*; , Spencer et al., 2007, *Wat. Res.*).

P4 L6: Consider reporting Catchment area/ Lake area ratio as a more relevant variable to discuss epilimnetic WTT than catchment area alone.

P5 L3: Why using only 3 wavelengths if the whole spectra were available? Given the aim of the study, much more robust conclusions could be reached if other widespread descriptors such as SUVA<sub>254</sub> and slope analysis were included, and I recommend their inclusion. Those descriptors are widespread, and in particular, spectral slope analysis, is recognized to provide further insight into DOM composition than absorption coefficients alone (see Helms et al. 2009 L&O, Loiselle et al. 2009 L&O). Package “cdom” in R could be a useful tool to perform that exploration.

P5: Calculations for outflow are not provided but they are presented in Figure 1. Add this information here.

P6 L17: Are all the other catchments spatially independent? Even if the inlet streams are considered negligible, what about the accumulated time in the catchment (*sensu* Müller et al. 2013 *Aq. Sci.*)?

P6 L27: The relative contribution of LMWC to total DOC (%) should be used instead of the total concentration of organic acids. A higher total sum of organic acids could be just due to a higher DOC concentration. Thus, to clarify if samples have a higher relative contribution of LMWC compounds or just higher DOC, the relative contribution of LMWC to total DOC (%) should be used, and ideally both (LMWC for each sample and in % and in mgC L<sup>-1</sup>) shown in the Supplementary Information.

Also, is the correlation between a<sub>254</sub>:a<sub>365</sub> and the organic acids positive or negative? Should be stated.

P7 L13: Bacteria might dominate the biomass, but still be predated by heterotrophic flagellates. How does the bacterial abundance looked during the experiments?

Moreover, 450 days is a very long period, which effects would have both the predation and the death of the bacterial community and subsequent mineralization of that biomass on the results? How fair is it to consider that these results reproduce the biodegradation process occurring in the field where lakes behave like chemostats not like batch incubations? Justify in the text, and discuss later the implications and assumptions that have to be done to compare both results in the discussion.

P7 L18: I agree that microbial processing can happen in the entire water column, but I believe the simultaneous action of UV and biodegradation cannot be discarded. On the one side and mainly, because photo-mineralization rates are faster than biodegradation rates. On the other side, because there are several situations where the entering water will be exposed to both ( i) water in the hypolimnion, would have been initially exposed to both UV and microbes when entering the lake, ii) under ice conditions, microbial activity would also be minimal due to low water temperature iii) during the ice-free period and at that latitude, daylight is almost for 24h). Thus, both processes are likely to occur also simultaneously or following the inverse sequence (photodeg --> biodeg). Justify that, considering the number of papers using the opposite approach.

The authors could also perform a much deeper exploration of the changes between layers with the temporal data available and in light of the results shown in Fig.2 on that direction.

P7 L25: Similarly for photo-decay than for bio-decay: even if a radiation equivalent to two years was applied, there was no water renewal considered. Discuss how well you expect this results to reproduce the process in the field.

P8L8: Where the assumptions fulfilled?

P8L11: Specify which variables are set as the fixed effects and as the random effects here.

## **Results**

P8 L24: Is “the most dynamic lake” also the smaller lake (volume)? The one with bigger catchment? I missed that in the discussion later and to discuss the controls on the trends on WTT and color in the epi- and hypolimnion.

P9 paragraph 3.4: There are no details provided on what is considered “change” in the incubations. Also, changes in DOC and ideally DOC decay rate should be shown in Fig. 3

P9 L30: Provide details (e.g. units) of this calculation. Also, only the ones in Fig. 2 were included, or all the sites? Clarify. Also, looking at these figures, how does the reader know which are the “clearest” and “darkest” lakes? different symbols should be used. Moreover, that categorization should be clearly defined and the cut-off between both justified previously and based on values previously reported in the literature. Also, in Table 1, it should be an additional categorical variable stating if a lake is “clear” or “brown”.

## Discussion

P10 L10: Which impact could it have that WTT does not span a whole hydrological year? Discuss here.

P10 L13: “the quantitative photo-bleaching in the Björntjärna catchment”, what do the authors mean? Was there a quantitative evaluation of that? What is the total DOC photo-bleached in the catchment? Also were those studies (Lindell et al. 2000; Vachon et al. 2016) using a similar approach?

P10 L17: If I am correct, now comes the only available definition of “brown” lakes. Also...what other variables define a brown or clear- water lake??

Could the authors relate these categories with e.g. morphological variables? (e.g. volume, catchment/lake area, peatland presence, etc). It feels somehow poor to discuss the change in color using a categorical variable built upon that same parameter. I recommend to provide a full multi-parametrical characterization of the two groups.

P10 L20: Müller et al. 2013 evaluated the influence of lateral water inputs. Could later inputs explain the patterns found here? Was there some assessment of lateral fluxes in the systems (e.g. groundwater inputs) so as to discard that from happening in some of the other brown-water lakes?? Discuss in the text.

P10 L30: How is it in Fig. S1b evaluated the contribution of runoff to total water and DOC? The authors do not explicitly evaluate this and they should do so. According to that figure, as runoff increased, WTT decreased. Therefore, we could expect the exported water/DOC during episodic flows to be flushed away from lakes also. As WTT turns longer after the flow, the DOC sources and thus composition, should also recover. To avoid that interpretation, the authors should explicitly evaluate the contribution of runoff to the budget, and discuss more in depth differences found in that sense between the different type of lakes (i.e. above and below one hydrological year, clear and brown) and their layers (epi vs. hypolimnion).

P11 L13: I consider the authors cannot conclude this, as there cannot be confident on the evaluation of the inputs performed, and that should be discussed at that point. Thus, “DOC accumulation can overcome degradation even in some small individual unproductive lakes” and it can be due to reduced degradation or to lateral terrestrial inputs. Add that discussion.

P11 L17: The authors should evaluate these processes always as a net result of production vs consumption. Thus, in brown-water lakes, the apparent decrease in LMWC is due to consumption above production. Opposite would hold true for clear-water lakes. Implications of acknowledging that are apparent and results need to be discussed under that light.

P12 L1: Thus, the total color loss might be the same in both type of lakes, but the relative loss in brown water much lower. So... if the brown water lakes correspond to the headwater and lower WTT lakes, terrestrial inputs being more important and frequent (lower WTT), could that color loss in brown lakes (even if just representing a small fraction of the total color) be indeed more important at the landscape level?

Discuss, and as previously stated, provide a better characterization (including morphology and relation with the catchment, especially with terrestrial inputs) of the two lake types (clear vs brown).

P12 L20: What does it mean that it eventually “takes over”? Which mechanism could then explain it? Are there no other environmental or morphological factors that can explain that? Which could be the temporal threshold and could that be related with the hydrology? Include these questions in the discussion.

P11 L23: I believe it is very bold to interpret the incubation results that way. They give us an idea of the changes caused by one mechanism, but they do not exclude other mechanisms to happen. All the potential processes that could produce these changes in in-situ lake CDOM should be discussed.

### **Summary and conclusions**

The first sentence sounds contradictory. If only headwater lakes are being evaluated, then, it cannot be assessed a general freshwaters pattern.

I believe the fact that headwater streams present “a sustained level of pigmentation regardless of WTT variations” is extremely interesting, and the relationship of that with hydrology and input sources deserves a much deeper exploration, and I encourage the authors to move towards that direction. Otherwise, the affirmation that “the results may not conform to the general reported pattern of selective removal of colored constituents” without providing an evaluation of the DOC sources variability, does not hold firmly.

### **Tables and figures**

**Table 1:** Provide volume or depth information. Provide the categorical variable: clear or brown.

**Figure 1:** use different symbol for inlet or black color, it cannot be distinguished. Also, add definition of the outlet calculation in methods. Without that information... Shouldn't "out" WTT be longer than "epi" WTT? Answer and clarify in the text.

**Figure 2:** I recommend fully re-working this figure and splitting it in two if needed. Above all, all data should be provided, for all lakes and layers, significant or not, so that the relationships not shown here could be evaluated by the reader. Moreover:

- The reader should be able to identify the lakes, to assess if the trends in the two layers are opposed or similar in each system.
- Also, it is impossible to assess the adequacy of the fittings without the points even if p-value is reported, and that is very important information.
- It is not clear which are the clear and which the brown water lakes, include that information in the legend.
- There seems to be two groups also as a function of WTT, how does that influence the results? e.g. in Fig 2d, where epilimnion and hypolimnion present completely opposite trends for the two age groups.
- Consider providing a summary table with the results of all the regressions, so the reader realizes how many fittings and which were not significant also.

**Figure 4.** It is not clear how that % is calculated (see previous comment). Also, are these changes significantly different from zero? Add that information as well as a zero-line. Clarify also in the caption that the slopes correspond to the ones in Fig. 2d. The reader should be able to identify to which line in Fig. 2d corresponds each dot in Fig. 4, modify accordingly.

**Figure 5:** The presence and contents of this figure should be re-evaluated once the suggested changes have been taken into account. Also, as it reads now, it is a bit like the chicken or the egg dilemma: are brown regime lakes brown because they have high water color? Or do they have color because of their brown regime? In other words, what is the progress on defining color regime only based on color?

#### **TECHNICAL COMMENTS**

P1 L13: "DOC quality and color"...if color and quality are considered separately, which variables are being used to describe quality besides absorbance? Isn't color quality of DOC? I suggest modifying into "changes in DOC color", as it most accurately describes the approach used here.

P1 L17: "Photo-chemistry" includes all the chemical effects of light, so that is not incorrect, but, as a "dominant process in DOC transformation in the epilimnia", do the authors specifically mean "photo-decay" or "photo-degradation"?

P1 L20: Would "moreover" be more appropriate than "instead"?

P2 L2: Consider changing "and to cause" into "and cause"

P3 L1: Consider changing "selected" into "selective"

P3 L28: absorbance or absorption coefficient?

P6 L27: Fig. A2 should be Fig. S2?

P7 L29: "was" should be "were"