

Responses to Associate Editor:

Dear Dr Koji Suzuki

Thank you for providing us an opportunity for subsequent revision of our manuscript. In this second iteration, we carefully edited the Abstract, text and figures following the criticism of the reviewers. We shortened and focused the Abstract, verified references, revised the Discussion, explained the relevance of CO₂ emissions to the DOC bio- and photo-degradation. We completely reorganized the Results presentation (first, biodegradation, then photodegradation with all measured parameters), as requested by 2nd reviewer.

The 2nd reviewer also suggested splitting the manuscript into two independent stories: a) spatial and temporal patterns in degradation, and b) the relationship between degradation and trace metals. He/she argues that this will improve the readability and shorten the length of the document. However, our intention, when submitting to Biogeosciences, was to avoid disintegrating results, given that the journal considers rather lengthy manuscripts. It is natural that the relationships between DOM bio- and photodegradation and trace elements are assessed across spatial and temporal scale.

We constructed our discussion around three main issues of this work: (1) comparison between bio- and photo-degradation of DOM, (2) possible impact of DOM degradation on CO₂ emissions, and (3) examining the link between DOM degradation and trace metal pattern. We made sure the consistence of presentation between results and discussion and revised some parts of Discussion for clarity.

We also revised the conclusions, via presenting broader implications of the study and the recommendations, as requested by the reviewer.

Our point by point response is provided below.

Responses to Reviewer # 1

The authors have made visible progress after the first round of revision. They have argued the links between OM degradation and TE, which has been questioned by both Rev #1 and #2. The hypothesis of these links and the novelty of this study become more focused in the revision.

We appreciate positive evaluation of our work by the reviewer.

Given that the linkage of OM degradation with TE is the significant novelty of this study, it is important for the authors to add TE's conclusion in the "Synopsis" part. This addition will further enhance the clarity and impact of the study.

We agree with this valuable proposition and modified the Synopsis as following:

"In boreal humic waters of a forest lake and a bog, the rate of dissolved organic matter photodegradation is four times higher than that of biodegradation. However, given the shallow (0.5 m) light-penetrating layer, the biodegradation provides the largest contribution to CO₂ emission from water surfaces. A few trace metals were partially removed (1-10 %) during photo- and biodegradation, via precipitation of Fe(III) hydroxides after destabilization of organo-ferric colloids and organic complexes"

I am confused by the authors' response that they have shortened the Abstract. However, I found that the "Abstract" in the main revision text did not change—or at least, it is different from the "Response."

The comment is well taken. According to the Editor, there is no limit on word number for the Abstract in this journal. Now we shortened the Abstract to only 330 words, revised some sentences for clarity and made sure it is consistent between recommendations provided by the Editorial office.

Please use the same DOI citation form in the "Reference" section.

We verified and added wherever necessary the DOI citations in the references and revised as requested.

Responses to Reviewer No 2

The authors present a revised version of the manuscript. They have addressed many of the previous comments, but the manuscript still needs improvement.

We carefully revised the manuscript following the comments of reviewer

1. Is the term "DOC or DOM" missing in the title? – **Added 'dissolved organic matter'**

2. Please summarize the abstract. Usually, it should not exceed 200 words (standard of many journals but please check with the handling editor).

We strongly revised the abstract, refocused and shortened it to 330 words. Please note that there is no formal word limit for the Abstract in Biogeosciences.

3. Lines 75-81. This manuscript does not address differences in degradation between POC and DOC; therefore, mentioning this in the introduction is completely irrelevant. The authors can simply explain in the methods section why samples were filtered.

We agree with this pertinent remark and removed relevant text from the Introduction. We specified 'DOM' bio- and photodegradation in the Methods (sections 2.2.1 and 2.2.2) as recommended by the reviewer.

4. Line 91. Consider changing "elevated" for "high". - **Revised as recommended.**

5. Line 94. Please improve clarity.

We removed this sentence from the introduction because it is not directly relevant to the present study.

6. The link between degradation and trace metals is still not clear in the manuscript. The topic is barely mentioned in the introduction and it appears after explaining the study design and the first hypothesis.

In response to this comment, we introduced the importance of studying coupled DOM – trace metal transformation in natural waters from the very beginning of the Introduction (L 75-77, 82-87 of the revised manuscript).

In my opinion, this remains the main issue of the manuscript, not because of the lack of novelty but rather the lack of a coherent story. The authors should either address a) spatial and temporal patterns in degradation, or b) the relationship between degradation and trace metals. This would also solve the issues of readability and length of the document.

We disagree with the suggestion of splitting the manuscript into two separate stories (articles). Our intention, when submitting to Biogeosciences, was to avoid fractionation of scientific results, given that this journal considers rather lengthy manuscripts. It is natural that the relationships between DOM bio- and photodegradation and trace elements are considered across spatial and temporal scale. It is not feasible to discuss the behavior of trace metals, which are tightly linked to DOM, without analyzing the degradability of DOM.

7. Line 280. The acronym "GET" is not used anywhere else in the manuscript, please delete.

Fixed

8. The discussion is not easy to follow. The authors organized the results based on the parameters measured (concentrations, bacterial number, trace metals, optical parameters, etc), which results in text repetition. This is clear in the discussion, where once again it is mentioned which and where the degradation rates were higher or lower. Instead, the results should be presented as biodegradation (all the results), and then photodegradation (all results).

We agree with this pertinent remark and completely re-organized results presentation, via presenting two major sections (Biodegradation and Photodegradation) with relevant subsections (DOC, DOC quality, trace elements). This also led to reorganization and renumbering of figures.

In the next section, the authors can discuss properly and compare between the two. Overall, the manuscript can be simplified, which would make the scientific message clearer and stronger.

We constructed our discussion around three main issues of this work: (1) comparison between bio- and photo-degradation of DOM, (2) possible impact of DOM degradation on CO₂ emissions from water surfaces, and (3) examining the link between DOM degradation and trace metal pattern. We made sure the consistency of presentation between results and discussion and revised some parts of Discussion for clarity. We would like to simplify the manuscript, but the study deals with multiple issues (two totally different processes) which act on both 'classic' organic matter and 'less common' trace metal' objects. These processes are considered across different spatial (hydrological continuum, different horizons of the water column) and temporal (seasons) scale. Due to breadth and multi-disciplinarity of adopted approach, simplifying the results and their discussion as requested by the reviewer would mean simply removing part of our findings. For the moment, we would like to preserve the integrity of our experimental design and main findings.

9. Section 4.2. This is another example of the lack of a clear message in the manuscript. Are the CO₂ fluxes important in this paper? Because according to the aims and hypotheses, the focus of the paper are the degradation rates (lines 137-142) and partitioning of trace elements (lines 151-153). Yet, this section is as long as section 4.3, which is actually related to a hypothesis.

As stated in the first sentence of the Introduction, Organic Carbon (OC) processing via metabolic biological (heterotrophic bacteria uptake and respiration) and inorganic physico-chemical (photolysis) pathways is considered to be one of the major source of CO₂ supersaturation in surface waters and related C emissions (Lapierre et al., 2013; Tranvik et al., 2009). This was most important motivation of this study – to relate, for the first time for several diverse aquatic systems across seasons, experimentally measured rates of DOM degradation to in-situ measured CO₂

emissions. For this reason, we would like to preserve the section 4.2. of the Discussion. Following reviewer's remark, we added an explicatory sentence to the beginning of this section (L 562-567).

10. Lines 663-674. The conclusions are not just another summary of the results. What are the broader implications of the study and the recommendations?

A broad implication of obtained results is that, although DOM photodegradation rates were sizably higher compared to those of biodegradation, the rather thin photic layer in humic waters does not allow for significant contribution of photolysis in overall CO₂ emission from lake and bog surfaces. Our recommendations for further work are the following (L 669-676 of the revised manuscript): Further work is needed on biodegradation of photolytically altered DOM given that photo-oxidation is known to transform molecular structures into more bioavailable forms. The high seasonal dynamics and spatial variability in both photo- and biodegradability of DOM and related trace elements of humic surface waters in the boreal zone encountered in this study suggest the need for studying these processes during "shoulder seasons" (early spring and late autumn), the periods of maximal photo- and biodegradation, respectively. These efforts should be focused on the most dynamic components such as small streams and subsurface waters, which demonstrated the highest rates of both photo- and biodegradation.

11. Figure 5.D. The upper error bar of the piezometer at time 1 is outside the scale.
We revised this figure for clarity

12. Figure 6.D. The lower error bar of the piezometer at time 2 is outside the scale.
This was a misprint in s.d. evaluation; fixed.