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Interactive comment on "Depth-dependent molecular composition and photoreactivity of dissolved organic matter in a Boreal Lake under winter and summer conditions" *by* M. Gonsior et al.

Anonymous Referee #2

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Here the authors present original data describing the variability in the molecular composition and photoreactivity of dissolved organic matter (DOM) with depth (bottom and surface) and across two seasons (winter and summer) in a Swedish boreal lake. The authors observed higher DOM concentrations in deep waters across seasons, a pattern they attribute to both a release of DOM from lake sediments during winter and summer, and to the photodegradation of surface DOM during summer. Following photodegradation experiments, the authors observed that the photo-alteration of the optical properties and molecular composition of DOM is not as extensive in surface waters as

in the lake bottom during summer or in the entire water column during winter, which suggests that solar radiations may quickly degrade and alter the photoreactive moieties of DOM exposed to light after ice melt. Based on the later observation, the authors stressed the importance of considering seasonality when assessing the yearly importance of DOM photo-mineralization as past studies have often been carried at times when DOM have already been exposed to light i.e. during summer. I think this is an important message and a novel contribution to the field. After reading the manuscript (especially P8961-L21 and Fig. 8), however, I was under the impression that the authors implied that the seasonal patterns in DOM composition they observed can mainly be explained in lakes by photochemistry (and its positive effect on microbial DOC degradation), and the release of DOM from the sediments. I am not arguing the possible importance of these processes, but I am not convinced that the microbial DOM processing per se can be completely discarded in explaining the observed patterns, given the evidence provided and for the reasons I detailed below. In my opinion, it would have been more convincing to show that microbes induce changes (or not) in the optical and molecular properties of DOM that differ from the changes induced by light only.

Specific comments:

Abstract:

L8: If photobleaching is not the sole factor explaining the higher DOC concentrations above the sediments, it seems logical to state here what other factor(s) might be involved. I suggest moving the later sentence about the release of DOC from sediments here.

Intro:

P8951-L16-18: While that may be true for humic or highly coloured lakes, it has been shown that light may in fact inhibit microbial degradation in more productive or algal-dominated systems e.g. Tranvik & Bertilsson 2001. As a side note, since this study was conducted in a humic lake, I would be more specific in the conclusions that the patterns observed and the proposed mechanisms underpinning these patterns may be particularly relevant in the case of humic lakes, but that they may differ with lake type.

P8951-L16: This paragraph starting is quite long and carries two distinct ideas: DOM photodegradation and release from the sediments. I suggest splitting for clarity.

P8952-L1: I would avoid using the word "concentration" when referring to CDOM thorough the manuscript as we don't really know how much of the DOM pool is actually chromophoric.

P8952-L17: Please provide proper referencing supporting the importance of re-dissolution.

Methods:

P8954-L14: How were the controls used in regard to the light exposed samples in the data treatment?

P8954-L23: Were the samples diluted prior to fluorescence measurements to minimize the inner filter effect as in Zepp et al. 2004? If not, how was that taken into account here as this effect may be quite important in highly coloured waters, and differ between the before and after the light treatment?

Results:

P8958-L14: Did the authors observed similar patterns in CDOM or fluorescence intensity? Some information on this should be presented in Table 1.

P8957-L26: I am a bit confused here regarding the inputs and "sinks" of DOC. There was a decrease in DOC concentrations of $\sim$ 4 mg L-1 between April and June, both at the surface and at the bottom. Yet the authors stated in the previous paragraph that a dilution or depletion was unlikely. Then what is the likely cause? Also, the difference in DOC between the surface and the bottom is quite small between April and June $\sim$0.5

mg L-1 (25.0-22.7 = 2.3 mg L-1 for April and 21.5-18.7=2.8 mg L-1 in June; Table 1), especially in regards to the change in total DOC. Was this difference significant given the measurement errors, and can it be that there was in fact inputs of DOC in the epilimnion compensating for the loss of DOC by photomineralization?

P8958-L5: I am still not convinced that the authors provided strong evidence of the importance of DOM release from the sediments to explain the patterns they observed. I would have expected to see some release rate measurements, or some comparison between the optical or molecular properties of the DOM standing just above the sediments and from the sediments themselves. Did the authors perform such measurements? Also, did the authors observe a similar pattern (i.e. higher DOC concentration near the sediments) in March as well, or was it constrained in April only when the sediments were anoxic?

P8958-L14: Here the authors should provide sufficient details on the results presented in the different figures (figure 6 should not be presented in the text before Fig. 4 and 5). Also, I would have expected to hear a bit about which fluorescent peaks were preferentially photodegraded in the experiments, and some discussion in regards to previous study e.g. Helms et al. 2013 and others.

P8958-L19-21: An alternative explanation for this result could be that CDOM or fluorescent DOM might also have been significantly degraded by microbes prior to the photobleaching experiments as recently shown for lakes e.g. Guillemette & del Giorgio 2012; Koehler et al. 2012; Kothawala et al. 2012.

P8959-L7-8: The statement about the solubility of oxidized DOM should be supported by the literature.

P8959-L14: Is this result consistent with what other studies have previously found (e.g. Stubbins et al. 2010)?

P8959-L20: I don't remember seeing rates of microbial decarboxylation specifically measured in Bastviken et al. 2004. Is it oxic respiration that is meant here? Also, I don't really follow the calculation that follows. How was the rate of 1.7 mg L-1 calculated, and what are the temporal units here? Or is it representing the total amount of DOC consumed over 2 months? If I get it right, the authors are trying to apportion how much of the DOC loss between April and June was due to microbial vs. photodegradation in the lake surface, and they come up with a 40% of total DOC loss potentially induced by solar irradiation. How exactly was that calculated, and where the 22 mg L-1 comes from? When looking at Table 1, I calculated a similar difference in DOC concentrations at the surface or at the bottom of the lake between the two sampling dates ($\sim$ 4 mg L-1), which contradicts a bit the importance of photomineralization in the surface. Could it be that the microbial degradation was simply higher than assumed based on Bastviken et al. 2004, and could thus explain most of the differences observed between April and June at the surface and bottom?

P8960: The discussion in the two paragraphs about how light induced changes in the optical and chemical properties, and in the size distribution of the DOM molecules is interesting, but should be put into context with previous work e.g. Helms et al. 2008; Stubbins et al. 2010; Helms et al. 2013 and others.

Technical comments:

P8951-L26: Remove space after CDOM

P8955-L3: Remove space SPE- DOM

P8956-L16: Give the full acronym for IUPAC

Legend Fig. 5: greater than 10%

Legend Fig. 6: Please indicate what the circles are referring to.

Relevant literature:

Guillemette F. & del Giorgio P.A. (2012). Simultaneous consumption and production of

fluorescent dissolved organic matter by lake bacterioplankton. Environ. Microbiol., 14, 1432-1443.

Helms J.R., Aron S., Jason D.R., Minor E.C., Kieber D.J. & Mopper K. (2008). Absorption Spectral Slopes and Slope Ratios as Indicators of Molecular Weight, Source, and Photobleaching of Chromophoric Dissolved Organic Matter. Limnology and Oceanography, 53, 955-969.

Helms J.R., Stubbins A., Perdue E.M., Green N.W., Chen H. & Mopper K. (2013). Photochemical bleaching of oceanic dissolved organic matter and its effect on absorption spectral slope and fluorescence. Marine Chemistry, 155, 81-91.

Koehler B., von Wachenfeldt E., Kothawala D. & Tranvik L.J. (2012). Reactivity continuum of dissolved organic carbon decomposition in lake water. J. Geophys. Res., 117, G01024.

Kothawala D.N., von Wachenfeldt E., Koehler B. & Tranvik L.J. (2012). Selective loss and preservation of lake water dissolved organic matter fluorescence during long-term dark incubations. Science of The Total Environment, 433, 238-246.

Stubbins A., Spencer R.G., Chen H., Hatcher P.G., Mopper K., Hernes P.J., Mwamba V.L., Mangangu A.M. & Wabakanghanzi J.N. (2010). Illuminated darkness: Molecular signatures of Congo River dissolved organic matter and its photochemical alteration as revealed by ultrahigh precision mass spectrometry. Limnology and Oceanography, 55, 1467.

Tranvik L.J. & Bertilsson S. (2001). Contrasting effects of solar UV radiation on dissolved organic sources for bacterial growth. Ecology Letters, 4, 458-463.

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