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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 #1

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Gonsior et al. present novel data detailing the variability in dissolved organic matter (DOM) molecular quality with depth and in two seasons in a boreal lake. The paper provides important new information about how the quality of DOM varies with depth, particularly in surface waters, between winter, ice covered lake conditions and ice free conditions in the summer. Gonsior et al. show that DOM in deep waters is influenced by sediment derived inputs. Whereas surface summer waters shows signs of significant photodegradation and that further photodegradation of summer surface samples does not alter the molecular properties of the DOM as much as when DOM from deep

samples or surface samples under ice are irradiated – indicating that summer surface DOM is less photoreactive as it has already been photodegraded. Gonsior et al. conclude their abstract by stating that when researchers study the photo reactivity of lake DOM, they should consider how seasonal patterns of solar irradiance reaching surface waters alters not just DOM chemistry, but also its photoreactivity. This is certainly an important and often overlooked component of photoreaction rate determination in seasonally variable aquatic systems.

Comments on the manuscript:

Pg8951, L26 – Authors state that "CDOM typically dominates the DOM pool I these lakes". Consider revising as CDOM levels are reported only in absorbance units and not as concentrations. The true concentration of the colored components of the DOM pool are unknown and their absorbance is also often increased by high levels of iron. A more precise statement might be that these systems have high carbon normalized absorbance or SUVA, or that they are simply CDOM rich.

8952, L1 – "CDOM concentrations" – rephrase to CDOM levels, absorbance, or something other than concentration.

L11 – When talking about the loss of photolabile DOM in photoreactions cite the literature on this, such as:

Zhang, Y., H. Xie, et al. (2006). "Factors affecting the efficiency of carbon monoxide photoproduction in the St. Lawrence estuarine system (Canada)." Environmental Science & Technology 40(24): 7771-7777.

Moran, M. A., W. M. Sheldon, et al. (2000). "Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter." Limnology and Oceanography 45(6): 1254-1264.

Stubbins, A., J. Niggemann, et al. (2012). "Photo-lability of deep ocean dissolved black carbon." Biogeosciences 9(5): 1661-1670.

L14-18: These points about anoxia, redox, re-dissolution etc. should also be referenced.

Methods or early in results – detail DOC recoveries and how the optical properties of the CDOM compare to either the initial water before acidification if measured and literature values for similar environments.

8958, L5 – Photochemical experiments do not seem the best way to test the hypothesis that "DOM is released from the sediments" – this would be done by determining fluxes from sediments or comparing sediment leachate DOM molecular signatures with those of overlying waters. The photochemical experiments test whether summer surface DOM is photodegraded. Restate or remove this.

8959, L20 – "Microbial decarboxylation" is a overly specific term that suggests a mechanism whereby carboxyl groups are cleaved from DOM by microbes. I believe the authors mean respiration, whereby dissolved inorganic carbon is formed through the oxidation of DOC.

L24. The 1.7 mg L-1 is described as a rate, but has no temporal unit. Why? Is it per day, per second, per year?

L26 – how is the rate of DOC loss between April and June calculated?

8960, L3: Authors need to describe at least in modest detail the photochemical changes to optical properties and how these compare to previous work, how they are generally interpreted, and why in this case they indicate "limited photoreactivity".

L13-14: A shift to LMW has been shown during photochem in many previous studies using ultrafiltration and size exclusion (e.g. Thomson et al., 2004; Lou and Xie, 2006; Helms et al., 2008) and for whole waters using FT-ICR MS (e.g. Stubbins et al 2010).

Helms, J. R., A. Stubbins, et al. (2008). "Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter." Limnology and Oceanography 53(3): 955.

Lou, T. and H. Xie (2006). "Photochemical alteration of the molecular weight of dissolved organic matter." Chemosphere 65(11): 2333-2342.

Already cited: Thomson, J., A. Parkinson, et al. (2004). "Depolymerization of chromophoric natural organic matter." Environmental Science & Technology 38(12): 3360-3369.

Stubbins, A., R. G. Spencer, et al. (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(4): 1467.

Last paragraph about photo-bleached compounds needs to cite and place the current findings in the context of Kujawinski et al. 2006; Gonsior et al 2009; Stubbins et al. 2010; and Rossel, Vahatalo, Dittmar et al. 2013, all of which report somewhat similar findings. The author should know all of these FTMS refs.

8961, L5-20. Again cite literature showing that aromatics are lost and also connect this FTMS data to the optical data in the paper which also indicates that aromatics were lost.

8962 – When discussing the photolability of surface summer versus other times of year and deep samples, the authors should again turn to the literature which indicates photoractivity decreases with irradiation time:

Zhang, Y., H. Xie, et al. (2006). "Factors affecting the efficiency of carbon monoxide photoproduction in the St. Lawrence estuarine system (Canada)." Environmental Science & Technology 40(24): 7771-7777.

Moran, M. A., W. M. Sheldon, et al. (2000). "Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter." Limnology and Oceanography 45(6): 1254-1264.

Stubbins, A., J. Niggemann, et al. (2012). "Photo-lability of deep ocean dissolved black carbon." Biogeosciences 9(5): 1661-1670.

AND suggestions that samples from deep, aphotic waters are also more photoreactive than surface waters in other environments e.g. the ocean:

Mopper, K., X. Zhou, et al. (1991). "Photochemical degradation of dissolved organic carbon and its impact on the oceanic carbon cycle." Nature 353(6339): 60-62.

Interactive comment on Biogeosciences Discuss., 10, 8949, 2013.