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Interactive comment on "Partial coupling and differential regulation of biologically and photo-chemically labile dissolved organic carbon across boreal aquatic networks" *by* J.-F. Lapierre and P. A. del Giorgio

Anonymous Referee #1

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Review summary: The goal of this study is to understand patterns in lability of aquatic DOC to biological and photochemical degradation across boreal lakes, rivers and wetlands. This is important because we don't fully understand why DOC in some waters is more or less labile to degradation by bacteria or light. The approach in this study was to measure the biologically or photochemically degradable DOC in relatively short-term laboratory incubations where DOC collected from lakes, rivers or wetlands was incubated with bacteria or exposed to simulated sunlight. The authors reported relationships between the loss of DOC during the experiment and initial DOC quality

(e.g., amount or type of absorbing or fluorescing constituents) and lability to bacterial or photochemical degradation, and then inferred what these relationships may mean for landscape level importance of autochthonous or allochthonous DOC degradation.

However, there is a critical flaw with the photochemistry approach (described below) that probably invalidates most of the conclusions on the photochemical lability of DOC. At least it is impossible to evaluate lability of DOC to photodegradation until the photochemical approach is corrected. Until this problem is addressed, the photochemical component of this manuscript should be removed.

Specific comments: 1. The authors want to quantify the lability of DOC to photo-degradation as the loss of DOC after exposure to light, and relate this lability to the initial composition of the DOC (e.g., as CDOM or FDOM proxies for DOC chemical composition). The amount of DOC lost upon exposure of a water sample to light in a glass tube depends on (1) the light available (the term described as "light dose" by the authors), (2) the rate of light absorption by CDOM, and (3) the lability of the DOC to be broken down by light. The authors want to uniquely quantify the third aspect, but instead they have quantified the net effect of (1), (2), and (3). Quantifying the lability of DOC to photo-degradation requires correcting for any differences in the light dose and the rate of light absorption by the DOC. Otherwise, one gets a trivial answer: the more light, the more DOC was photo-degraded, or the more light-absorbing DOC, the more DOC was photo-degraded (e.g., Fig. 2 bottom left panel, and Fig. 3 - wetlands or rivers have more light-absorbing DOC and so have more photo-degradation during an experiment). The authors did remove the effect of light dose (factor #1 above) from their results because they used a solar simulator at a "fixed" dose ($\sim$ 130 W m-2). However, it is unclear why they concluded that there was no effect of light dose on the results based on Fig. A2, which is the photochemically degradable DOC in a sample (pd DOC) normalized to a constant light dose (130 W m-2). Of course there is a 1:1 correlation between all "uncorrected" pd DOC values and the values divided by the same constant (130 W m-2). It is not variability in the light dose that is the prob-

lem, but instead the fact there was a wide range of rates of light absorption by DOC (factor #2 above) between the lakes, rivers and wetland waters (e.g., a wide range of initial CDOM concentrations). This Figure A2 and their discussion of their corrections (page 6680) makes it clear that these photochemical fundamentals have been misunderstood. Because this fundamental issue arises in many published papers, I will try to explain the issue in another way. Simply put, the problem is that in lower initial CDOM samples (lower initial absorbance values such as in clear lake waters), there was more light available to be absorbed by CDOM in the glass tubes assuming a pathlength of 24 mm (the pathlength provided by the authors on page 6680), compared to a water sample with higher initial CDOM concentration (see "Ez" as the mol photons m-2 d-1 nm-1 available to be absorbed by CDOM at a depth, z, of 24 mm in the tube in my Fig. 1 below, which is based on my estimates of their data). This is because light decays exponentially through a medium depending on the absorbance of the medium (basic photochemistry, reviewed in many articles extensively for DOC, e.g., Hu et al. 2002). Thus, during an experiment, a low CDOM sample will have more light on average available to be absorbed by the CDOM to initiate photodegradation reactions over the course of the experiment, compared to a high CDOM sample where less light is available on average throughout the tube. Reviewer Fig. 1: The light available to be absorbed at the bottom of the experimental tube depends on the concentration of CDOM in the tube. With more CDOM, there is less light that makes it through to the bottom of the tube. I used the pathlength provided by the reviewers (24 mm) and estimated the high and low CDOM based on the values provided in the paper (such as Fig. 7 and A1).

Here is one example (of many) of how the incorrect photochemistry approach influences the interpretation of the photochemical data. The authors use differences in loss of DOC fluorescence (FDOM) between water types and sites to suggest that the relationship between biologically and photochemically degradable DOC exhibited a "complete decoupling in clear-water environments to strong coupling in browner streams. . . ." This is most likely NOT related to differences in the lability of the DOC to pho-

todegradation, but instead the net effect of #2-3 above: the amount of CDOM actually exposed to light and the photo-lability of the DOC in the glass reaction tubes. Without correcting for differences in the rate of light absorption in the tubes, the results will be strongly biased by the amount of CDOM in the tube (controlling the exponential decay of light in the tube). This problem likely explains any relationship in this study between photochemically-degradable DOC and CDOM or FDOM.

Interactive comment on Biogeosciences Discuss., 11, 6673, 2014.

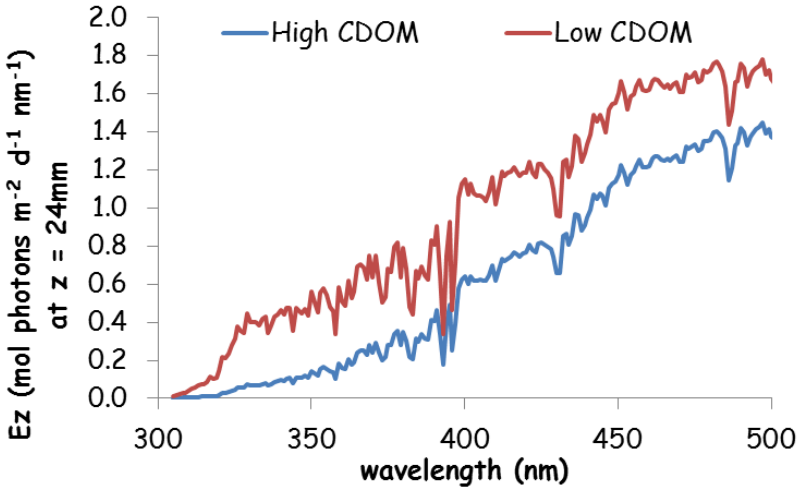

Fig. 1. Light available to be absorbed by CDOM