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Interactive comment on "Biologically labile photoproducts from riverine non-labile dissolved organic carbon in the coastal waters" *by* V. Kasurinen et al.

Anonymous Referee #1

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General Comments:

I commend the authors for tackling BLP experiments from a wide variety of rivers, an important task in fully understanding the role of photochemistry in the global carbon cycle. Not knowing the exact nature of these compounds means that the quantification of BLPs certainly isn't trivial and the authors have done nice job by looking at both bacterial production (BP) and bacterial respiration (BR). That said, I feel like the authors have left out key information that does not allow me to fully understand or believe their results, especially in regards to their methods for determining apparent quantum yield spectra.

In order to produce accurate AQY estimates, we need correct information for both the numerator and the denominator of the AQY (Equation 1). Until molecular level information becomes available that identify all the specific absorbing compounds responsible for specific photoproducts, we remain limited by using overall solution absorption coefficients to determine the rate of photon absorption, the denominator, for all products. However, this still means that accurate quantification of absorbed photon doses within sample containers is critical for any AQY experiment. The authors here have irradiated their samples in quartz flasks in a water bath, with dark control flasks wrapped in tin foil in the same water bath. First, I am not sure the best method for quantifying absorbed photon doses in a sphere. The authors only briefly mention that this was done following the methods of Aarnos et al. (2012). In the Aarnos et al. paper, the authors only describe how they determined CDOM absorption coefficients (which is standard) and say that absorbed photons was quantified following equations in supplementary material (text S1 in Aarnos et al.). However, when I tried to look at the supplementary material for Aarnos et al. (2012), I could not find this information. The text S1 referenced in the Aarnos et al. paper gives a table with measured and modeled photomineralization rates of DOC. This tells me nothing about how they calculated photon absorption rates.

Even if the math the authors use to calculate absorb photons is correct, I am still worried that they are missing elements critical to this calculation. Since this is not discussed, I can only guess at things that were/were not considered in this study. For example, having their darks in the water bath during irradiations means they are adding a hard reflector (tin foil) to the system, which will certainly change photon doses when compared with their absence. Were darks placed in the same spot every time? Were darks present during the light measurements that were used to calculate absorbed photon doses? Were light measurements performed above or in the water bath and at different locations? Having worked with CPS solar simulators, the light is not entirely uniform throughout and this needs to be accounted for. Absorbed photon calculations must include accurate pathlength information, but when light hits a curved surface it will bend and focus the light, so what is the pathlength inside a quartz sphere? I am

hoping the authors can tell me in the next iteration so I can learn something. And, this will certainly be affected by the differences in refractive indices between fresh water (the water bath) and their salty samples (salinity in this study $\sim$ 15). It might be small but may also artificially increase the pathlength and I am not sure how the authors account for this. And finally, maybe because I am not familiar with these calculations, I would love to see something to verify these photon dose calculations are correct (i.e. actinometry).

My second major issue is with the AQY calculation itself. To me, apparent quantum yields as reported here should reflect spectral information. This can either be done with monochromatic (irradiate at single wavelengths throughout the solar spectrum) or polychromatic (irradiate with a variety of polychromatic light fields with various long bandpass cutoff filters throughout the solar spectrum) methods. Here, the authors have chosen polychromatic light, but used only ONE light field. In this way ALL spectral information is lost. It is fine to divide their BP or BR rates by absorbed photons (assuming it is correct), but I am opposed to them calling this a spectral AQY. The authors should call it a broadband (e.g. Fichot and Benner 2014) AQY or a pseudo-AQY or anything but a spectral AQY. I have such a strong objection to this because it is very misleading to the community; especially to research groups that are not familiar with AQY determinations and blindly follow a published method that includes only one light treatment (and likely less time required to do the experiment). Furthermore, since there is only one light treatment, this means there is only one point the authors can use to model the AQY spectrum (see common methods for polychromatic determinations, e.g. Johannessen and Miller, 2001; Koehler et al., 2014; Zhang et al., 2006). Mathematically you can't define an exponential line using one data point. Or even two data points. Here the authors model one point with exponential Equation 2 and solve for TWO variables! How is this at all constrained? It doesn't matter that these model equations give BP/BR rates that are in agreement with what has been measured in previous studies, it is just plain wrong. The authors should therefore either do more light treatments (giving multiple points for an exponential equation) or drop this equation entirely. Since I

am assuming the authors are not going to be able to repeat these experiments, it will probably have to be the latter option.

Specific comments:

Abstract

Lines 11&15: please drop 'spectral' and call it 'broadband' or something else (as stated above), and change numbers to reflect this.

Intro

Line 22: "BLPs are linearly related to CDOM photobleaching." Is this true everywhere, all the time? At what wavelengths? Modeling fading isn't trivial either.

Page 8202 lines 3-5: How is the light-dark difference to determine BLPs different from other studies? I thought this was common practice. Or has no one determined BGE for BLPs before?

8202 line 20: How do you get a unit of Mt C for CDOM? CDOM is an optical property with units of m-1; it does not mean carbon. Is there some sort of relationship used to get to [DOC]? If so, say this.

Materials/methods

2.1 Materials

a) The use of detergent (a carbon source surely) for bottle cleaning worries me. How did you verify that all detergent was removed? Could this change or alter DOC/CDOM concentrations? Maybe I'm just being paranoid but, any left over could be a carbon source for these microbial communities and would seriously alter the results of this study.

b) Artificial seawater preparation. Although the formula from Kester et al. (1967) was followed to make artificial seawater, there are no details on how (or if) these salts were

cleaned. Commercially available salts can be very dirty (contaminated with organic carbon and trace metals) and should at least be baked in a muffle furnace (e.g. Nelson et al., 2007) to lower carbon contamination here. If this was not done it should at least be noted since it could affect both their light and dark results.

2.2 Experimental

2.2.2 Please see general comment above for major issues with this section

8204 line 21: How was this irradiation time selected? I'd like to see a comparison to a 'real world' photon flux. And does this group have any information on how BR/BP changes with different photon doses? 44-46 hours in a Suntest (causing 50% CDOM fading at 300 nm here), must be a rather large photon flux. In another study with similar irradiation conditions (round quartz flasks, sealed with no head space, irradiated with a 1000 W Oriel xenon lamp; Xie et al., 2004), CDOM absorption also decreased by $\sim$50-55% in two river samples from the Southeastern USA after 46 h of irradiation. On the other hand, oxygen concentrations also decreased by 86% in both rivers, but exponentially. This was reflected in the rates of DIC photoproduction in this study, which were faster during the early (e.g. 2 – 4 h) stages of the experiment. For a "true" AQY calculation, initial rates are a requirement, but after 46 h, the rate of photoproduction can be significantly slower than at the beginning of the experiment, even when correcting for CDOM photobleaching ((Xie et al., 2004), rates of DIC production normalized to average ag(320) were 0.29 μM m h-1 for the first 4 h and 0.14 μM m h-1 after 46 h). This point is at least worthy of discussion so other researchers consider these points in their experiments because BLP production rates may not be the same over time. Reader and Miller (2014) do a nice job showing and discussing the effects of different irradiation times on the photoproduction of BLPs, and it is pretty clear that some BLPs are both biolabile and photolabile, and selection of photon dose is critical to interpreting the results.

Section 2.2.6

Why stop at 12 d if max biomass has not been reached? After 46 h of irradiation, I can imagine that there is a significant buildup of H2O2 in all irradiated solutions. Microbes will have to devote some of their metabolic energy at the beginning of the bioassays to deal with external H2O2 stress (perhaps reflected in the low respiration at the beginning of the BR curves, fig. 3), enzymes which coincidently give O2 back. Could you be underestimating BR if the bioassay was stopped early in solutions with significant oxidative stress (i.e. the St. Lawrence and the Mekong)?

Section 2.4

Again please call "broadband" or something similar and lose the model, as stated in the general comment above.

Section 2.5 Please add an equation to describe the Q calculation. At first it sounds like a product of solar radiation and CDOM in the water column but then (starting line 6 pg. 8208) is sounds like you're multiplying solar ration by global radiation? Please clarify.

8208 line 6: integrating out to 750 nm is not appropriate because the majority of photochemistry (for all products I know of) comes from wavelengths < 400 nm. Otherwise we'd all get a sunburn indoors. Some groups (e.g. Simon Belanger/ Huixiang Xie) integrate out to 600 nm, but I don't think there's any measureable photochemistry beyond 500 nm. Changing this may lower the results of their BLP photoproduction model, maybe not significantly but it is worth doing.

Results

Section 3.5: Again, I think these results need to be reworked to reflected broadband calculations.

Section 4.4.1

8213 line 23: Have you also considered that the high r2 value is due to the fact that you have one point with a large delta (aÂňg) and a large BR? How does this change without this point?

8214 lines 1-4: This is a dangerous statement. I like that this study uses rivers from all over the world, but to say that their correlation between BLPs and CDOM loss is a useful BLP proxy is very misleading. This relationship is from 7 samples, and includes one rather high point in figure 2, driving the whole correlation. How does this change for other times of year? With more samples? With a different irradiation time? I think the claim made here needs to be softened quite a bit to reflect the way this relationship could (and certainly does) change. Same goes for the conclusions (8217 lines 7-9) of this paper.

8214 lines 7-10: Because you used reference fluxes for the Mississippi, Lena and St. Lawrence and calculated the flux for the rest, I'd like to know what kind of numbers this calculation gives for these three rivers. Is it even close?

Section 4.1.2. Please note when you are comparing to spectral AQY and broadband AQY experiments.

Table 5 (as per general comment), should not be included.

Technical corrections:

8204 line 13: what is the 2.2.1 in reference to? 8213 line 17: BLPs and again on pg. 8215

Please check all references, I found these but there may be others: 8213 Line 27: Wagner et al. (2015) ref. not found in references section White et al. (2010) is in reference list but not in text.

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