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Interactive comment on "Controls on dissolved organic matter (DOM) degradation in a headwater stream: the influence of photochemical and hydrological conditions in determining light-limitation or substrate-limitation of photo-degradation" *by* R. M. Cory et al.

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Author Response: Thank you for the review of our manuscript.

Reviewer: P9795, Line 26: "We suggest that degradation, and thus export, of DOM in CDOM-rich streams or ponds similar to Imnavait is typically light-limited under most flow conditions." This does not sound logically correct to me: if degradation reduces DOM export, then a factor that limits degradation should favor rather than limit DOM

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export.

Author response: We will revise the text here and in the abstract to clarify that because DOM degradation is light-limited in Imnavait Creek, export of DOM from this stream will be less under conditions that increase the light available for DOM photo-degradation (i.e., low flows, sunny days).

Reviewer: P9081, Line 2: Optical measurements were at what time of day (zenith angle, used later as an important correction for a) and under what sky conditions (OVC, scattered, clear skies)?

Author response: In-situ attenuation coefficients were measured between 10 -11 am Alaska Standard Time on 28 June 2011 and between 11 am - 2:30pm on 23 June 2012. Conditions were mostly sunny (28 June 2011) or sunny (23 June 2012). Specifically, the cloudiness factor for these dates was 0.7 and 1, respectively on these dates, as calculated in Cory et al. 2014 to estimate the amount of direct vs. indirect light reaching the water surface export of DOM. The cloudiness factor was calculated as the ratio of mean measured to mean modeled (SMARTS) solar irradiance at Toolik Field Station, and was found to range from $\sim$ 0.3 on cloudy days typical in August to $\sim$ 1 for the clear skies characteristic of May-June at the field station near Imnavait Creek (Fig. S6 in Cory et al. 2014). As described in Cory et al. 2014, in-situ Kd,λ values were compared to aCDOMλ values obtained from the spectrophotometer after correcting for the solar zenith angle corresponding to the time of day the Kd,λ values were measured. We can add more of this background information to the manuscript if the editor and reviewers believe it is necessary.

Reviewer: The term UV exposure is used but not fully defined (e.g. P9797, Line 25). It would be interesting to distinguish exposure rate (spectrally integrated mol photons absorbed by CDOM m-2? s-1 and cumulative exposure or dose (exposure rate integrated over the time for a parcel of water to travel through a defined reach). Could the authors thereby combine in situ spectral UV absorption and residence time (treated separately

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in much of the Discussion) into a single equation = cumulative UV exposure or absorption. In this way 'light-limitation' could occur through a) low surface irradiance and light limitation at all depths; b) complete absorption of irradiance in the surface waters and light limitation at depth; or c) insufficient time (cumulative exposure) for complete photochemical breakdown.

Author response: We will revise the text to clarify that UV exposure means the amount of light reaching the water surface that is available to be absorbed by CDOM ("Qds0, λ" in Equation 3), where UV exposure varies by time of day, day of year, and by sunny vs. cloudy days.

Yes, the reviewer is correct that in a general sense the overall "light limitation" is a function of "exposure rate" and the "length of exposure" or residence time. This is what we are showing in our conceptual diagram in Fig. 8, and we have quantified this in our Fig. 9. Our equation 3 (a standard equation in photochemical studies) describes how much light is available at the water surface (UV exposure), how much light is absorbed by CDOM, and then per light absorbed how much DOM is degraded (for example, the mol of CO2 produced per mol of light absorbed, which is the apparent quantum yield). This amount of "UV light exposure" and "DOC degradation" (from equation 3) is then multiplied by the residence time (which is what it seems the reviewer is requesting), and the results are presented in Fig. 9. In this figure the DOC loss is shown as a function of residence time; thus, at any given residence time the various lines (for different conditions of light availability, CDOM amount, and apparent quantum yields) give the cumulative loss of DOC. It appears that this is what the reviewer is asking for, an independent treatment of in-situ absorption and degradation (the three lines of different slopes in Fig. 9) and of residence time (the Y-axis in Fig. 9). We experimented with adding a third axis to our conceptual diagram to illustrate the relationships between (a) light at the surface, (b) light absorption and limitation at depth, and (c) residence time (as mentioned by the reviewer), but found that the figure became very complicated and lost its simplicity at conveying our ideas. Also, we would need a fourth axis to

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convey the factor of DOM lability (represented in the apparent quantum yield) that we show is important as well – therefore, we believe that the most simple and effective way to present this information is the combination of Figs. 8 and 9.

Beyond what is presented in a figure, it might be convenient to have a single equation highlighting light exposure and residence time – this equation would multiply equation 3 by Rt, residence time. However, the situation as we present it in the manuscript is more complicated. For example, Rt as a concept is simple (the stock divided by the input or output rate at steady state), but it can be extremely difficult to calculate in practice and a discussion of those calculations is beyond this manuscript. Furthermore, both our current approach and the approach suggested by the reviewer do not consider inputs of water (and CDOM) as a parcel of water moves downstream. Considering the input of water containing "fresh" (labile) CDOM is needed to quantify the total, integrated amount of light absorbed by CDOM as a parcel of water moves downstream over time. However, this as well is beyond the scope of the current study.

Reviewer: Fig. 2. It is interesting that Kd and the absorption coefficients (zenith angle adjusted) were so close – so no optical scattering in this environment? Or masked by the effects of having such high aCDOM. What was the range of suspended sediment concentrations and POC in this water?

Author response: Your interpretation is correct, there was very little optical scattering and very high CDOM in this environment – we can clarify this in the manuscript. Strong agreement between Kd,λ and aCDOMλ values here are consistent with agreement reported for a wider range of surface waters in the Arctic by Cory et al. 2014 and Gareis et al. 2010, for example (as noted in the manuscript on pg 9811, first paragraph). We did not collect samples for POC analysis from Imnavait Creek for this study because POC is on average $\sim$ 20-fold less than DOC concentrations in streams like Imnavait Creek near Toolik Lake (Kling et al. 2000). Relatively low POC concentrations (relative to DOC) are consistent with the strong agreement between Kd,λ and aCDOMλ in Imnavait Creek suggesting there was little scattering in the UV by organic or mineral

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particles. There are nearby rivers that are strongly dominated by glacial inputs of suspended sediments, and in this situation the relationship between Kd,λ and aCDOMλ weakens (see Cory et al. 2014).

Reviewer: P9806, Line 18 onwards: There is a long speculative section to discuss the outlier points in this graph – this could be contracted, transferred to the discussion or deleted. Also, could these outliers simply be the result of absorption and scattering by naturally suspended sediments on those dates?

Author response: We will shorten this section, which was included to speculate on the reasons other than scattering by sediment (see response to above comment), to explain the poor agreement between Kd,λ and aCDOMλ for a few samples. As currently described in the manuscript, the most likely reason for these outliers is the measurement error associated with measuring Kd,λ values in-situ in streams containing high concentrations of CDOM where the UV light is rapidly attenuated. We will remove other interpretations from the text.

Reviewer: P9811, Line 10: 'Because UV and PAR account for approximately 51% of the energy within the shortwave radiation portion of the spectrum (300–2500 nm), absorption of sunlight by CDOM contributes to the frequency and extent of stratification by restricting warming to the surface layers (Merck and Neilson, 2012).' See also: Caplanne S & Laurion I (2008) Effect of chromophoric dissolved organic matter on epilimnetic stratification in lakes. Aquatic Sciences 70 (2), 123-133.

Author response: We will revise the text to cite the work of Caplanne and Laurion (2008) on the role of CDOM in lake stratification, which showed that as CDOM absorption coefficient increased, UVA and especially visible light played an increasing role in stratification compared to low CDOM lake.

Reviewer: Figs 3 and 4: The axis labels need to be checked- _C, m3/s. Also PxVA or 'vertical array' is not a variable – the pond labels could be, for example for Pond 5: P5T (_C). For these figures, it would be helpful to know what the measurement depths were

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for each pond. If this would make the caption too long, each probe depth for each pond could be spelled out in the Methods (at the moment it is only given as a broad range).

Author response: We revised the figure to fix the axes as suggested (revised versions uploaded as png attachments), and we will add depths for each pond in the Methods section.

Reviewer: P9817, Line 14: 'but this stratification serves to protect DOM from UV light by isolating water masses in pool bottoms (e.g., Table 3, Fig. 5).' How does the river flow during these conditions – is water flowing across the surface of the stratified pond? In which case, stratification is reducing the 'light limitation' of the flowing water because its mean depth is shallower than under conditions of full water column mixing?

Author response: You are correct that under stratified conditions water moves across the surface of the ponds. These conditions increase the residence time of the pool bottom water because these waters are stagnant until the next mixing event. The effect of stratification on the light exposure of DOM in the bottom waters is low because, as stated on p.9807 lines 20-26, the depth of the UVB and UVA light penetration is always less than the diel mixing depth when stratified, meaning that DOM in the bottom of the pools is protected from UV light under stratified conditions.

It is also important to note that the depth of light penetration into the ponds does not differ between stratified (low flow) or mixed (high flow) conditions as shown by the limited differences in aCDOMλ values at 305 nm between these conditions in Imnavait Creek (comparing pool surface aCDOMλ values in 2011 vs. 2012, Table 3). Thus, the amount of CDOM exposed to light, or the rate of light absorption, does not differ between stratified vs. mixed conditions (for a given amount of sunlight under given sky conditions). The only difference is the amount of time for the photo-degradation to occur (greater photo-degradation under longer residence times associated with low-flow, stratified conditions; Figure 9).

Of course it is more complicated than that because during peak radiation nearly the

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entire water column can become stratified, thus increasing the residence time in the surface waters until there is cooling at night and downward mixing (although not all the way to the bottom). Such complex dynamics require a model to characterize and understand, and while interesting it is beyond the scope of the current paper.

Reviewer: What is the volume of the water sequestered at the bottom of a typical pool relative to the river flow – i.e. equivalent to how many seconds, minutes hours, days of average flow? Is it a major or minor component?

Author response: The volume of water sequestered in the pool bottoms (below the mixing depth) under stratified conditions varies, but on average was about 70% of the total pool volume. Pool volumes ranged from < 1 m3 (for pool 4), to $\sim$ 100 m3 (pool 7), and active volumes (defined as the volume of the pool undergoing mixing), were around 30% of pool volume under stratified conditions (compared to 100% of the pool volume mixing under mixed conditions). This means that under stratified conditions, the majority of the pool volume was sequestered in the bottom, below the depth of UV light penetration (surface mixing layer depth was on average 50 cm, compared to depth of UVB and UVA light penetration of 8 – 45 cm as discussed on pg. 9807 lines 20-30).

Although most water was sequestered in the pool bottoms under stratified conditions, more DOM is actually lost due to photo-degradation under these conditions. This finding may seem counter-intuitive at first, considering that most of the DOC was protected from photo-degradation when it was sequestered in pool bottoms under stratified conditions. However, as we demonstrated in this paper, there was enough light-absorbing DOM that is labile to photo-degradation even in the pool surface waters under all conditions that DOM photo-degradation was never limited by substrate (DOM supply). This means that the amount of water and DOM sequestered in the bottom waters does not influence the amount of DOM that can be degraded by light in this system.

Interactive comment on Biogeosciences Discuss., 12, 9793, 2015.

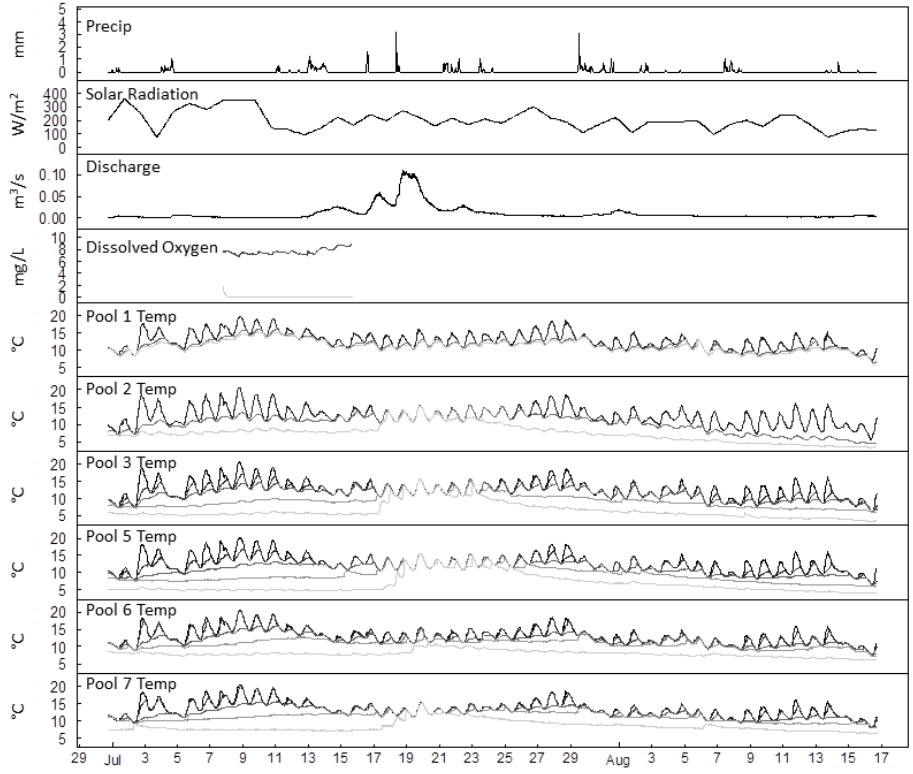

Fig. 1.

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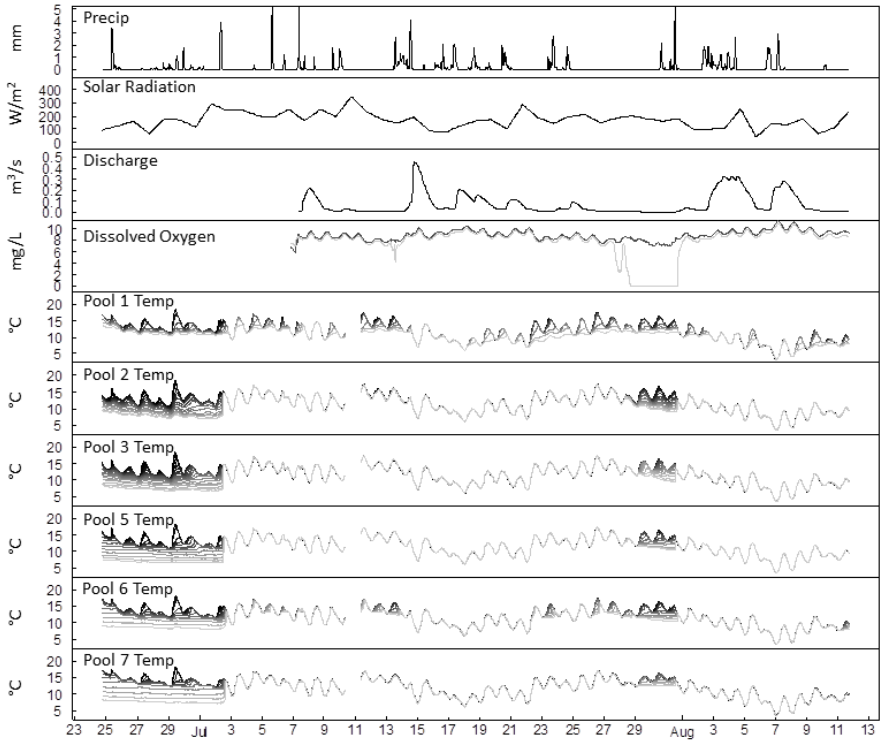

Fig. 2.

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