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Dear Editor(s), 28 October 2015

Please find attached our revised manuscript, including a marked version here with revisions marked in track changes mode. The revisions in our manuscript were done in response to comments provided by reviewers one and two (our point by point responses documenting these revisions have already been uploaded, and we copied them below here as well). In addition, we made changes described below in response to the final comments by Associate Editor Warwick F. Vincent on 12 Oct 2015.

Comments from W.F. Vincent: Please keep in mind that the concerns raised by the referees may also be those of future readers. It will be useful to transfer some of your very helpful response comments (in condensed form) to your revised manuscript. For example, one point that seems a bit contradictory is in reponse to referee 2 who said: "Could the authors thereby combine in situ spectral UV absorption and residence time (treated separately 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. You responded: "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." But then you say: "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...." This seems to contradict your previous statement. One way to handle this (but you may have a better way) would be to condense your comments into something in the Discussion like 'Equation 3 was multiplied by residence time (Rt) to generate the results in Fig. 9. However, a precise estimate of Rt is difficult to achieve in practice given that there are inputs of water and fresh CDOM as a parcel of water moves downstream.'

Author response: We took your suggestion and added condensed versions of our responses to reviewer comments to the discussion on (1) the effects of residence time on DOM photo-degradation (including the challenges associated with this assessment), and (2) the counter-intuitive result that protection of the bottom water from UV light under stratified conditions actually leads to more DOM photo-degradation under these conditions. These revisions are on pages 20-21 in the MARKED (track changes) manuscript (attached in this document).

Sincerely,

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Author responses to Anonymous Referee #1

Reviewer: - Introduction, the introduction is well written and provides a solid background and rational for the presented study - Methods, the methods used in this study are robust and thoroughly presented - Results and discussion, the results in the text are consistent with the data presented in the tables and figures. The discussion walks the reader through the conceptual model clearly and thoroughly and is well supported with literature. - The word "significant" is used throughout the results and discussion with no p values (or alternative measures of significance) presented. The authors should add in tests of significance or consider revising the text to reflect that their differences are measured, but not tested statistically for significance.

Reviewer: Technical Corrections: - Figures 3 and 4 are tough to read with such a small font. Would it be possible for the authors to increase the size? - Page 9818, line 7, "attention" should be revised to read "attenuation".

Author Response: Thank you for the review of our manuscript.
We revised Tables 2 and 3 to more clearly indicate when measures of DOM composition were statistically, significantly different. For example, for Table 2, we used t-tests to evaluate whether means for a water type were significantly different between years (2011 vs. 2012) at $p < 0.05$. For the data shown in Table 3, we did an ANOVA comparing mean values among the three water types (soil water, pool bottom water, and pool surface water), across both years ($p < 0.01$). As now indicated in the footnote of Table 3, all water types were statistically different from one another for all variables.
In contrast to Tables 2 and 3 which evaluate mean water or DOM chemistry by water type over all dates, the data shown in Figure 5 compare DOM concentration and chemistry between surface and bottom water in each pool on two dates, with mean ± SE (of replicates from the same sample bottle). Because a single discrete sample was analyzed from each depth in each pool, no t-tests could be conducted on surface vs. bottom water values from each pool in this Figure. Nonetheless, the results in Figure 5 show that the concentration and composition of DOM in surface waters generally did not overlap with the values of DOM in the bottom water (analytical replicates). Thus, the data in Figure 5 provide an example of one date to show why surface waters as a group were significantly different than bottom waters when pools were stratified (as quantified by t-tests or ANOVA in Tables 2 and 3, respectively).

We increased the font and can request that the journal re-size Figures 3 and 4 (new versions uploaded).

We replaced the typo "attention" with attenuation on line 9818.

Author Responses to Anonymous Referee #2

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 export.

Author response: We revised the text 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 ~ 0.3 on cloudy days typical in August to ~ 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 $K_{d,\lambda}$ values were compared to $a_{CDOM\lambda}$ values obtained from the spectrophotometer after correcting for the solar zenith angle corresponding to the time of day the $K_{d,\lambda}$ values were measured.

We cited the Cory et al. paper for these methods on $K_{d,\lambda}$ to account for the time and sky conditions when $K_{d,\lambda}$ was measured, but did not revise the text to add more of this background information to the manuscript given that it is published in the Cory et al. 2014 paper.

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 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 revised the text in the methods to clarify that UV exposure means the amount of light reaching the water surface that is available to be absorbed by CDOM ("$Q_{ds0,\lambda}$" in Equation 3), where UV exposure varies by time of day, day of year, and by sunny vs. cloudy days.

We also revised the text in the discussion on residence time and light-limitation of photo-degradation in response to AE Vincent's request to condense our initial response to this reviewer *here (that is, our discussion below in response to this reviewer's comment was condensed and added to the discussion):*

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 CO_2 *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 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: We modified the text in the results to clarify that your interpretation is correct, there was very little optical scattering and absorption by POC in this very high CDOM water. Strong agreement between $K_{d,\lambda}$ *and* $a_{CDOM\lambda}$ *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 ~ 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 $K_{d,\lambda}$ and $a_{CDOM\lambda}$ in Imnavait Creek suggesting there was little scattering in the UV by organic or mineral particles. There are nearby rivers that are strongly dominated by glacial inputs of suspended sediments, and in this situation the relationship between $K_{d,\lambda}$ and $a_{CDOM\lambda}$ 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 shortened 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 $K_{d,\lambda}$ and $a_{CDOM\lambda}$ for a few samples. We removed interpretations from the text other than the most likely reason for these outliers, i.e., the measurement error associated with measuring $K_{d,\lambda}$ values in-situ in streams containing high concentrations of CDOM where the UV light is rapidly attenuated.

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 added a citation to 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 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. We added pool depth to the legend for each pool, and added text in the figure captions for Figs 3 and 4 to indicate that the sensors were placed in each pool starting 5 to 15 cm from the bottom of the pool and then at intervals ranging from 5 to 50 cm (which is also in the methods section on in-situ monitoring).

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? 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: We took the associate editor Vincent's suggestion to add condensed versions our responses to this reviewer's comments (below) to the discussion.

Original responses (condensed versions added to discussion): 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 $a_{CDOM\lambda}$ values at 305 nm between these conditions in Imnavait Creek (comparing pool surface $a_{CDOM\lambda}$ 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 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.

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 m^3 (for pool 4), to ~ 100 m^3 (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.*

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

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Abstract

We investigated how absorption of sunlight by chromophoric dissolved organic matter (CDOM) controls the degradation and export of DOM from Imnavait Creek, a beaded stream in the Alaskan Arctic. We measured concentrations of dissolved organic carbon (DOC), as well as concentrations and characteristics of CDOM and fluorescent dissolved organic matter (FDOM), during ice-free periods of 2011-2012 in the pools of Imnavait Creek and in soil waters draining to the creek. Spatial and temporal patterns in CDOM and FDOM in Imnavait Creek were analyzed in conjunction with measures of DOM degradation by sunlight and bacteria and assessments of hydrologic residence times and in-situ UV exposure. CDOM was the dominant light attenuating constituent in the UV and visible portion of the solar spectrum, with high attenuation coefficients ranging from 86 ± 12 m^{-1} at 305 nm to 3 ± 1 m^{-1} in the photosynthetically active region (PAR). High rates of light absorption and thus light attenuation by CDOM contributed to thermal stratification in the majority of pools in Imnavait Creek under

low-flow conditions. In turn, thermal stratification increased the residence time of water and DOM, and resulted in a separation of water masses distinguished by contrasting UV exposure (i.e., UV attenuation by CDOM with depth resulted in bottom waters receiving less UV than surface waters). When the pools in Imnavait Creek were stratified, DOM in the pool bottom water closely resembled soil water DOM in character, while the concentration and character of DOM in surface water was reproduced by experimental photo-degradation of bottom water. These results, in combination with water column rates of DOM degradation by sunlight and bacteria, suggest that photo-degradation is the dominant process controlling DOM fate and export in Imnavait Creek. A conceptual model is presented showing how CDOM amount and lability interact with incident UV light and water residence time to determine whether photo-degradation is "light-limited" or "substrate-limited". ~~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.~~ We suggest that degradation of DOM in CDOM-rich streams or ponds similar to Imnavait is typically light-limited under most flow conditions. Thus, 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).

1 Introduction

The decomposition of dissolved organic matter (DOM) to CO_2 and it subsequent transport to and release from surface waters is an important process in the carbon cycling of inland waters (e.g., Cole et al., 1994, 2007; Kling et al., 1991). This decomposition has been mainly attributed to bacterial respiration in the water column and sediments (e.g., Battin et al., 2009; Cole et al., 2007; Wetzel, 2001). Exposure to ultraviolet (UV) light is also a key control on the photochemical conversion of DOM to CO_2 in surface waters (e.g., Cory et al., 2007; Moran et al., 2000; Vähätalo and Wetzel, 2008), and coupled photochemical and microbial processing can enhance DOM degradation beyond the effect of bacteria or light alone (Cory et al., 2013; Judd et al., 2007; Tranvik and Bertilsson, 2001).

Recent work demonstrated that in shallow arctic lakes and streams the photo-degradation of DOM can greatly exceed bacterial respiration, accounting for up to 94% of the total DOM processed in the water column (Cory et al., 2014). The water column rate of DOM photo-degradation to CO_2 (photo-mineralization) or to partially degraded DOM (e.g., photo-stimulated bacterial respiration; Cory et al., 2013) depends on (1) the amount of UV radiation from sunlight reaching the water surface, (2) the absorption of UV light by chromophoric DOM (CDOM), and (3) the apparent quantum yield, a term quantifying the lability of DOM as moles of product formed per moles of photons absorbed by DOM. Water column rates of DOM photo-degradation increase linearly with increasing UV light reaching the water surface, or with increasing photo-lability of DOM. However, the rate of DOM photo-degradation in the water column depends non-linearly on CDOM concentrations and depth due to attenuation of light mainly by CDOM with depth in the water column (Hu et al., 2002; Miller, 1998).

As CDOM concentrations increase, the depth of UV light penetration decreases to shallower depths, but the average rate of light absorption by CDOM increases in the water column (Hu et al., 2002). Thus, while the depth of UV light penetration is low, on the order of 10 to 100 cm in the streams and small ponds in the Arctic characterized by high concentrations of CDOM (Cory et al., 2007, 2014; Gareis et al., 2010; Prairie et al., 2009; Watanabe et al., 2011), the rate of light absorption by CDOM may be high. If the light absorption rate is high enough, photo-degradation rates of DOM reach an asymptote such that increasing CDOM has no effect on photo-degradation integrated through the water column (Hu et al., 2002). At this point, where photo-degradation is insensitive to changing CDOM concentrations, the system is 'light limited' – in a light-limited system, as the amount of incident UV light increases so does the rate of photo-degradation. In contrast, in very clear waters light attenuation by CDOM is low and rates of DOM photo-degradation are limited by insufficient CDOM to absorb the available light – in these 'substrate-limited' systems, increasing the incident UV light has no effect but higher CDOM concentrations increase rates of photo-degradation. Thus, depending on the incident light available, the CDOM concentrations, and the depth of the water column, the rates of DOM degradation in surface waters may be either light-limited, substrate-limited, or co-limited by light and substrate. To our knowledge, the range of conditions and the interactions of controls on photo-degradation across the continuum of light- versus substrate-limitation have not been described or characterized.

At the scale of a stream reach, lake, or catchment, DOM degradation is related to both photochemical processing and the influence of hydrology on light exposure. Water residence times in a stream or river are generally a function of watershed and channel characteristics, but may also be influenced by surface and subsurface transient storage (e.g., (Chapra and Runkel, 1999; Neilson et al., 2010; Zarnetske et al., 2011) and thermal stratification that can isolate water masses (e.g., Merck and Neilson, 2012). While the influence of these factors on biogeochemical processes and solute concentrations has been studied (e.g., Boano and Harvey, 2014; Miller et al., 2009), the relative importance of CDOM concentration and lability, UV exposure, and water residence times on the degradation of DOM is unknown for stream or lake ecosystems.

Running waters, and especially lower-order streams, may be expected to have relatively low DOM degradation in the water column due to their high flow rates and short water residence times. Although small streams are often shallow and if unshaded by riparian vegetation may have light penetration to the bottom, the water residence time in any given reach is short and therefore there is little time for substantial photo-degradation of DOM. However, in areas of low relief, the headwater streams have longer residence times and greater light exposure through a shallow water column. In the Arctic, residence times within low gradient, first-order beaded streams are controlled by thermal stratification of the beads (pools) (Merck et al. 2012, Merck and Neilson 2012). Strong thermal stratification (up to 10 °C temperature difference within 0.5 m depth) observed in Imnavait Creek on the North Slope of Alaska was attributed to a combination of high concentrations of CDOM, low wind stress at the stream surface, underlying frozen soils, and low in-stream discharge (Merck et al. 2012). Because sunlight is rapidly attenuated in high-CDOM waters, warming by solar radiation is restricted to surface layers and can cause strong thermal stratification and density gradients (Fee et al., 1996; Houser, 2006; Kling, 1988). Merck et al. (2012) found that this stratification isolated the pool surface water from the bottom water and increased the water residence times in a reach from minutes under mixed conditions to hours or weeks when the pools were stratified. At the same time, there were distinct gradients in the concentrations of chromophoric and fluorescent fractions of dissolved organic matter (CDOM and FDOM, respectively) between pool surface and bottom waters (Merck et al. 2012). The authors suggested that these gradients in CDOM and FDOM were due to photo-degradation of DOM in the surface waters, and that stratification regulated the residence times of water and DOM and thus controlled the extent of DOM degradation in this stream.

To quantify the role of photo-degradation in producing observed DOM gradients in stratified stream pools, and to generally determine the influence of in-stream stratification, water residence times, and UV exposure on DOM degradation, we measured the lability and rates of

DOM degradation by sunlight and bacteria along with changes in CDOM and FDOM within the pools of Imnavait Creek in two summers with differing discharge and stratification patterns. We demonstrate that photo-degradation is the dominant process altering DOM chemistry and producing CO_2 in the water column of this headwater stream under all conditions, and we show how rates of photo-degradation are governed by the amount and lability of DOM (CDOM), light attenuation, patterns of stratification, and residence time. We suggest that in relatively shallow, high CDOM headwater streams, DOM photo-degradation is limited by available light instead of by available substrate (DOM) under a wide range of hydrological conditions.

2 Methods

2.1 Site description

Imnavait Creek is a headwater, beaded stream located on the North Slope of Alaska in a glacial valley formed during the Sagavanirktok glaciation in the Kuparuk River basin (68.616 °N, 149.318 °W; (Detterman et al., 1958; Hamilton, 1986). The creek primarily lies in the organic soil layer and only occasionally cuts through to the mineral soil (McNamara et al., 1998). The connected pools, or beads, were formed by the erosion and melting of large ice deposits that had underlain the creek (McNamara et al., 1998; Walker et al., 1989) .

Previous studies of Imnavait Creek found that spring snowmelt accounts for 23 to 75 % of the watershed's annual water flux(Kane et al., 2004; McNamara et al., 2008) compared to 6 to 9 % produced by the largest, single summer storm events (McNamara et al., 2008). Subsurface water paths are limited to the thawed active layer as the region is underlain with up to several hundred meters of permafrost, which effectively separates the active layer from any deep ground water (Osterkamp and Payne, 1981). Typical seasonally-thawed active layer depths at Imnavait ranged from 25 to 40 cm, occasionally extending to 100 cm (Hinzman et al., 1991). Water inputs from the riparian zone occur through both surface and diffuse subsurface flow(Kane et al., 2000). In addition to surface chutes that connect the stream pools, water travels between pools through the riparian zone with both subsurface flow through the active layer and surface flow during significant precipitation events (Merck and Neilson, 2012).

We studied a ~120 m reach of the creek consisting of a series of seven pools connected by short chutes (Fig. 1). Pools were named starting with pool 1 and proceeding downstream sequentially to pool 7. Across these 7 pools, surface areas ranged from 2 to 129 m^2, volumes ranged from 0.2 to 102 m^3, and pool depths were between ~0.21 – 2 m. Along the reach of creek studied, we collected soil water from a water track that drains from the adjacent eastern hillslope into the pools. Seventeen sites were sampled along the water track from the hill top to the valley bottom along the water track with distances between sites ranging from 30 to 190 m. Soil water was also collected from an array of 55 sites within a 150 m by 90 m grid in a riparian zone on the eastern hillslope adjacent to the study pools in Imnavait Creek (Fig. 1).

2.2 Water sample collection

Water samples were collected from the surface and bottom of the seven pools monthly from 23 June through 4 August 2011, and weekly from 27 June through 18 August 2012. Pool water was collected from the surface and bottom of each pool through MasterFlex® tubing (Cole-Parmer, Vernon Hills, IL) using a peristaltic pump (GeoPump Inc., Medina, NY). Soil water was collected from the 17 sites in the water track flowing into the pools (Fig. 1), once in June and twice each in July and August in both 2011and 2012, and from the riparian zone adjacent to the study pools monthly from June through August 2011. From the water track or riparian area, soil water was withdrawn using stainless-steel soil needles inserted into the soil, through MasterFlex® tubing, into plastic syringes. Temperature, conductivity, and pH were measured from pool and soil water at the time of collection using WTW meters (models 3210; Xylem, White Plains, NY). All pool and soil water samples were filtered in the field into high-density polyethylene bottles and kept cool and dark until analysis. Aliquots for analysis of DOM quantity and quality were filtered through pre-combusted Whatman GF/F glass fiber filters (Whatman, Clifton, NJ).

Sunlight attenuation

Light attenuation with depth was measured in pools 1, 2, 3, and 6 on 27 June 2011 and in pools 1, 2, 3,6 and 7 on 23 June 2012 using a compact optical profiling system for UV light in natural waters (UV C-OPS; Biospherical Instruments Inc., San Diego, CA) as previously described (Cory et al., 2013, 2014). The C-OPS measured downwelling cosine-corrected irradiance at 7 wavebands (305, 313, 320, 340, 380, 395, and 412 nm) and photosynthetically active radiation (PAR, 400-700 nm). Attenuation coefficients ($K_{d,\lambda}$) were calculated from the downwelling irradiance (E_{λ}) as a function of depth (z) at each waveband:

$$E_{\lambda,z} = E_{\lambda,0} e^{-K_{d,\lambda} z} \qquad (1)$$

From multiple casts in each pool (n = 2 to 5), the coefficient of variation of $K_{d,\lambda}$ ranged from 1 to 3 % in the UV and 9 % for PAR. Means ± standard error (SE) of K_d are reported.

2.3 In-situ monitoring

Temperature sensor arrays (HOBO® Water Temp Pro v2; Onset Computer Corporation, Inc., Bourne, MA) were deployed vertically in each pool (n = 1 to 5 per pool in 2011 and n=3-25 per pool in 2012) from late-June through mid-August, measuring at 5 minute intervals. The probes were wrapped with aluminum foil to prevent radiation-caused heating (Neilson et al., 2010) and placed starting 5 to 15 cm from the bottom of the pool and then at intervals ranging from 5 to 50 cm. Additional monitoring of pool 2 was conducted for one week in July 2011 and for most of July and part of August in 2012 where two sondes were deployed near the surface and bottom of the pool with oxygen, pH, specific conductance, and temperature probes (YSI 6920 V2 sonde with ROX™ optical dissolved oxygen, 6561 pH, 6560 conductivity, and 6560 temperature sensors; YSI Inc., Yellow Springs, OH) measuring at 15 minute intervals. Finally, discharge data were collected at a weir further downstream to compare and contrast the flow variability between summer 2011 and 2012 (Kane and Hinzman, 2011; Kane, 2015).

2.4 Meteorological measurements

Air temperature 1 m above the ground and precipitation were measured hourly at a meteorological station on the west-facing ridge of the Imnavait Creek basin approximately 1 km upstream of the study site using a temperature probe (model HMP45C; Campbell® Scientific, Logan, UT) and tipping bucket rain gauge, respectively (Kane and Hinzman, 2011). Global solar, UVA and UVB radiation were each measured at five minute intervals at Toolik Field Station (TFS, 11 km West of Imnavait at 68.616 °N, 149.318 °W) with pyranometers from Kipp & Zonen (CMP-6) and Yankee Environmental System, Inc. (UVB-1 and UVA-1), respectively. The global solar pyranometer measured a spectral range of 310 to 2800 nm, while UVB and UVA pyranometers measured 280-320 nm and 320-400 nm, respectively. Photosynthetically active radiation (PAR; 400-700 nm) was measured hourly using a quantum sensor by Li-Cor (LI-190S) at the same location.

2.5 DOM quantity and quality

Samples for dissolved organic carbon (DOC) concentration were acidified with trace-metal grade hydrochloric acid to approximately pH 3 after filtration through Whatman GF/F filters and stored in the dark at 4 °C until analysis using a high-temperature platinum-catalyzed combustion followed by infrared detection of CO_2 (Shimadzu TOC-V; Shimadzu, Columbia, MD).

The chromophoric and fluorescent fractions of DOM (CDOM and FDOM, respectively) were analyzed within hours to at most several days of collection. Samples were stored in the dark at 4 ºC until warmed to room temperature (20 to 25 °C) just prior to analysis. UV-Vis absorbance spectra of CDOM were collected using 1-cm path length quartz cuvettes with a spectrophotometer (USB 2000+UV-VIS; Ocean Optics, Inc., Dunedin, FL or Aqualog; Horiba Scientific). Sample absorption was measured against laboratory-grade deionized (DI) water blanks (Barnstead E-Pure and B-Pure; Barnstead Thermolyne, Dubuque, IA). The spectral slope ratio (S_R) was calculated from the absorbance spectrum of each sample as the ratio of the slope from 275 to 295 nm to the slope from 350 to 400 nm (Helms et al., 2008). CDOM absorption coefficients ($a_{CDOM,\lambda}$) were calculated as follows:

$$a_{CDOM,\lambda} = \frac{A_\lambda}{l} 2.303 \qquad (2)$$

where A is the absorbance reading at wavelength λ and l is the pathlength in meters. $SUVA_{254}$ was calculated as absorbance at 254 nm divided by the cuvette pathlength (m) and then divided by the DOC concentration (mg C L^{-1}; Weishaar et al., 2003).

Excitation-emission matrices (EEMs) were measured on all water samples with a Fluoromax-4 fluorometer or an Aqualog (Horiba Scientific, Edison, NJ) following previously described procedures (Cory et al., 2010). An aliquot of sample was placed in the 1-cm quartz cuvette for each EEM and diluted with DI if necessary to bring $A_{254} < 0.6$. EEMs were corrected for inner-filter effects and for instrument-specific excitation and emission corrections in Matlab (version 7.7) following Cory et al. (Cory et al., 2010). The fluorescence index (McKnight et al., 2001) was calculated from each corrected EEM as the ratio of emission intensity at 470 nm over the emission intensity at 520 nm at an excitation wavelength of 370 nm (Cory et al., 2010). Emission intensity at FDOM peaks A, C, and T was evaluated at excitation/emission pairs 250/450, 350/450, 275/340 (nm/nm), respectively, in Raman Units (RU; Stedmon et al., 2003).

2.6 DOM degradation

Water collected from Imnavait Creek in amber HDPE bottles in the field was used for photochemical and bacterial degradation experiments, as described in Cory et al. (2014). Briefly, dark bacterial respiration was measured from whole water samples incubated for five to seven days in the dark at 6-7 °C alongside killed controls (1% $HgCl_2$) in air-tight, pre-combusted 12-mL borosilicate exetainer vials (Labco, Inc). For DOM photo-degradation, GF/F filtered water was placed in air-tight, pre-combusted 12-mL borosilicate exetainer vials and exposed to natural sunlight at Toolik Field Station for ~12 hours alongside foil-wrapped dark controls at temperatures ranging from 10-16 °C. Bacterial re-growth experiments for photo-stimulated bacterial respiration were conducted as described in Cory et al. (2013, 2014). There were four independent replicates from each water sample for every analysis type and treatment. Membrane inlet mass spectrometry (MIMS) was used to measure bacterial or photochemical oxygen consumption relative to killed or dark controls, respectively. Bacterial or photochemical production of CO_2 during complete oxidation (mineralization) of DOM was quantified as production of dissolved inorganic carbon (DIC) relative to killed or dark controls, respectively, using a DIC analyzer (model AS-C3, Apollo SciTech, Inc.). After exposure to sunlight or bacteria, subsamples were analyzed for CDOM and FDOM as described above. Changes in DOM quality are reported as mean ± standard error (SE) of the four replications of each treatment.

We used previously reported lability and rates of DOM degradation by bacteria and sunlight in Imnavait Creek, measured from experiments described above, during our study periods in 2011 and 2012 to determine the sensitivity of DOM degradation in Imnavait Creek to photochemical and hydrological factors. The conversion of experimental measures of DOM degradation to water column rates of degradation is described for Imnavait Creek and other waters in the Arctic in Cory et al. (2013, 2014). In the current study, we quantified how rates of DOM photo-degradation in the water column varied with available light, CDOM concentrations, and lability of DOM measured in Imnavait Creek during the 2011-2012 summer seasons.

The integrated, water-column rate of DOM photo-degradation is:

$$Photo - degradation\ (mol\ C\ m^{-2}\ d^{-1}) = \int_{\lambda_{min}}^{\lambda_{max}} \phi_\lambda\, Q_{dso,\lambda}(1 - e^{-K_{d\lambda}z})\, \frac{aCDOM_\lambda}{atot_\lambda}\, d\lambda \quad (3),$$

where λ_{min} and λ_{max} are the minimum and maximum wavelengths of light contributing to the photo-degradation of DOC (280 and 700 nm, respectively). Φ_λ is the apparent quantum yield spectrum for photo-degradation of DOM (mol product mol^{-1} photons absorbed nm^{-1}; a measure of DOM lability to photo-degradation which decreases exponentially with increasing wavelength). We used previously reported spectra of DOM lability (Φ_λ) in Imnavait Creek for photo-mineralization DOC to CO_2 and photo-stimulated bacterial respiration (Cory et al. 2014). $Q_{dso,\lambda}$ is the spectrum of the UV from sunlight that reaches the water surface (accounting for reflection; Cory et al. 2014). $Q_{dso,\lambda}$ varies by location (latitude/longitude), time of day, date, and sunny vs. cloudy sky conditions, as described in Cory et al. 2014. $K_{d,\lambda}$ is the attenuation coefficient with depth (*Eqn. 1*). ~~$Q_{dso,\lambda}$ is the spectrum of UV light just below the water surface (accounting for reflection; Cory et al. 2014), and $K_{d,\lambda}$ is the attenuation coefficient with depth (*Eqn. 1*).~~ $a_{CDOM,\lambda}$ is the concentration of CDOM measured as described above (*Eqn. 2*). $a_{CDOM,\lambda}/a_{tot,\lambda,}$ is the spectrum of the ratio of absorption by CDOM to the total absorption (where $a_{tot,\lambda}$ is the total absorption in the water column due to CDOM, particles, and water). The ratio of $a_{CDOM,\lambda}/a_{tot,\lambda}$ was assumed to be 1 at all wavelengths (i.e., CDOM was the main UV-absorbing constituent in Imnavait Creek; Cory et al. 2014).

From *Eqn. 3*, it follows that as DOM lability to photo-degradation (Φ_λ) or incoming UV light ($Q_{dso,\lambda}$) increase, the depth-integrated or areal water-column rate of DOM photo-degradation increases. In addition, photo-degradation of DOM throughout the water column increases with increasing $K_{d,\lambda}$ up to a point where at high $K_{d,\lambda}$ the relationship is asymptotic (Fig. S1). This is because while increasing CDOM provides more DOM to absorb light and photo-degrade, the absorption of UV light by CDOM also controls light attenuation (i.e., $a_{CDOM,\lambda} \approx K_{d,\lambda}$; presented in the *Results* section below). Thus as light attenuation ($K_{d,\lambda}$) increases, at some point light becomes limiting and adding more CDOM (increasing K_d) results in no change in the integrated water column rate of photo-degradation (Fig. S1). In this study, we used the range of terms in *Eqn. 3* observed in Imnavait Creek (Fig. S2) to develop a conceptual model of controls on DOM photo-degradation in this and similar systems. For example, we used the range of $Q_{dso,\lambda}$ spectra for Imnavait Creek representing the average, minimum and maximum UV light reaching the surface of Imnavait Creek over the course of the day during the study period, as well as the average, minimum and maximum of $a_{CDOM\lambda}$ observed in Imnavait Creek.

3 Results

3.1 Meteorological Conditions

There was no difference in mean air temperatures between the mid-June through mid-August study periods in 2011 vs. 2012 at Imnavait Creek. However, June-August was generally sunnier and drier in 2011 compared to 2012 (Table 1). The total global solar radiation (310-2800 nm) and total UV and visible photon flux (280-700 nm) were 17 % and 24 % higher, respectively, in 2011 compared to 2012 (Table 1, Fig. S3). Precipitation was three times greater during the summer 2012 compared with 2011, and the lower precipitation in 2011 resulted in significantly lower volume of water passing the weir in 2011 versus 2012 (Table 1, Fig. S1).

3.2 Pool stratification and separation of water masses

Light attenuation coefficients ($K_{d,\lambda}$) in Imnavait Creek decreased exponentially with increasing wavelength from 88 ± 12 m^{-1} at 305 nm to 17 ± 3 m^{-1} at 412 nm to 3 ± 1 m^{-1} in the photosynthetically active region (PAR). In most pools, there was no significant difference between in-situ $K_{d,\lambda}$ values and CDOM absorption coefficients ($a_{\mathrm{CDOM},\lambda}$) collected from filtered water from the same pool at the time $K_{d,\lambda}$ was measured (as shown for 320 nm and 412 nm in Fig. 2). These results demonstrate that in most pools CDOM was the dominant light absorbing constituent in the water column (Fig. 2),. consistent with low particulate matter concentrations in this stream and previous work showing that CDOM dominates UV light absorption in these streams (Cory et al. 2014). However, in two pools sampled in June 2011, the in-situ $K_{d,\lambda}$ values at 320 nm were significantly higher than the corresponding CDOM absorption coefficients measured from filtered water (Fig. 2). This was likely due to the inherent challenges deploying an instrument to quantify $K_{d,\lambda}$ in the UVB range in high CDOM waters where 99 % of light at 320 nm is attenuated by ~ 8 cm (based on the mean $K_{d,\lambda}$ or CDOM coefficients in Fig. 2). This could be due to inadvertent mixing of sediment from the bottom during the instrument casts to measure light attenuation, or to general difficulties quantifying $K_{d,\lambda}$ in the UVB range in high CDOM waters, given that 99 % of light at 320 nm is attenuated by ~ 8 cm (based on the mean $K_{d,\lambda}$ or CDOM coefficients in Fig. 2). In addition, co-precipitation of iron and DOM during filtration may have caused these differences between in-situ $K_{d,\lambda}$ vs. CDOM coefficients given the relatively high concentrations of iron in Imnavait Creek, ranging from 4 to 21 μM total iron in the surface waters with most iron present as ferrous iron (Page et al., 2013, 2014).

Five of the seven pools (2, 3, 5, 6, 7) were repeatedly thermally stratified with a nearly 10 °C temperature difference between top and bottom waters during sunny and dry (low-flow) conditions in Imnavait Creek (Figs. 3 and 4). In contrast, pools 1 and 4 did not exhibit stratification in 2011 or 2012. During the sunnier and drier summer of 2011, pools 2, 3, 5, 6, 7 were stratified on 43 to 46 out of 50 days measured (Fig. 3), while during the wetter summer of 2012, these pools stratified only 11 out of 49 days measured (Fig. 4). Within each summer, the roles of solar radiation and precipitation were evident in the frequency and extent of stratification in each pool. For example, pools 2, 3, 5, 6, and 7 showed the greatest extent of thermal stratification once the discharge from snowmelt had receded, coinciding with the period when solar irradiance was highest (e.g., late June in 2011 and 2012; Figs. 3, 4). In addition, during both summers a portion of each stratified pool mixed nightly due to surface heat loss, followed by re-stratification with increasing solar irradiance during the day (Merck and Neilson, 2012). Following substantial precipitation events, stream flow increased and caused stratified pools to mix completely within hours of precipitation, as demonstrated for example after a rain even on 17 July 2011 (Fig. 3). After mixing, pools stratified again within four to five days (Fig. 3).

Under stratified conditions, water and DOM in the pools experienced contrasting UV exposure. For example, Pool 3 had a depth of 1.4 m from the water surface to the sediment, and on average the depth of the surface mixing layer was 50 cm (ranging from 20 – 50 cm below the water surface; Fig. 3). It follows that DOM below 50 cm was in the “bottom water”, defined as water trapped below the diel mixing depth during stratified conditions. The depth of UVB and UVA light penetration was always less than 50 cm in Imnavait Creek. For example, using the mean CDOM absorption coefficients at 320 nm and 412 nm (Fig. 2), 99 % of all incoming UVB and UVA light was absorbed within 8 ± 1 cm and 35 ± 3 cm, respectively (average ± SE; maximum depth of UVA penetration observed was 45 cm based on attenuation coefficients at 412 cm in Fig. 2). Therefore, DOM in the surface of the pools experienced UV light exposure each day while DOM trapped in pool bottom waters was protected from UV light during stratified conditions.

3.3 Stream and soil water chemistry

Both the pool water and the soil water draining into Imnavait Creek had low pH, low conductivity, and high concentrations of DOC, CDOM, and FDOM (Table 2). The pH ranged from 5.2 ± 0.1 to 5.7 ± 0.1 and the conductivity ranged from 25 ± 10 to 12 ± 2 μS cm^{-1} in soil and pool water, respectively. DOC concentrations ranged from 1412 ± 78 and 785 ± 13 μM C in pool and soil water, respectively, during summer of 2012 (Table 2). CDOM and FDOM proxies for the chemical composition of soil and pool water DOM were consistent with a terrestrial source of DOM, i.e., high molecular weight, aromatic compounds derived from degradation of plant and soil organic matter. For example, in the soil waters draining to Imnavait Creek, the spectral $S_{R,}$ a proxy for average molecular weight of DOM (Helms et al. 2008) was 0.75 ± 0.08, and the specific UV absorbance at 254 nm ($SUVA_{254}$), strongly correlated with aromatic C content, was 4.4 ± 0.1 L mg C^{-1} m^{-1}. The fluorescence index, a proxy for DOM source and aromatic C content, was 1.59 ± 0.07. Although there were some significant differences in mean values between soil and pool water DOC, CDOM and FDOM (discussed below), similar ranges of DOC, CDOM and FDOM were observed for the pool bottom waters in Imnavait Creek and for the soil water draining into the pool bottoms (Table 2).

There were no significant differences in average pH, conductivity, DOC, CDOM, or FDOM concentrations in the soil waters between 2011 and 2012 (Table 2). There was no difference in average optical character of soil water DOM between summers except for $SUVA_{254}$, which was significantly lower in the soil waters in 2012 compared to 2011 (Table 2). In contrast, there were significant differences in DOM quality between 2011 and 2012 when comparing pool bottom or surface water across years (Table 2), likely due to differences in the extent of stratification between years.

When the pools in Imnavait Creek were stratified, there were significant differences in water chemistry between pool surface and bottom water. In-situ data collected under stratified conditions in Pool 2 from 8 - 15 July 2011 showed significantly higher dissolved oxygen in the surface compared to the bottom pool water (Fig. 3). Discrete water samples collected when pools were stratified in 2011 and 2012 showed significantly higher concentrations of DOC, CDOM, and FDOM in bottom waters compared to surface waters (as shown in Fig. 5 for pools sampled on 14 July 2011). The surface waters of most pools sampled under stratified conditions had different DOM quality compared to bottom waters, as indicated by significantly lower $SUVA_{254}$, higher S_R, and lower FI (Table 3; Fig. 5). When the stream pools stratified, DOM in pool bottom water was not significantly different than soil water for most CDOM and FDOM measures or DOM quantity and quality (Table 3). In contrast, when the pools were mixed, there were no significant differences in DOC, CDOM, and FDOM between pool surface and bottom waters (e.g., as shown in Fig. 5 for pools sampled on 21 July 2012).

3.4 Photochemical degradation of DOM

Previous work showed that photo-mineralization of DOM to CO_2 accounted for the majority of DOM degradation in Imnavait Creek (24.69 ± 18.28 mmol C m^{-2} d^{-1}, mean ± SE; Cory et al. 2014). Here we show that in addition to mineralization of DOM, exposure of Imnavait Creek DOM to ~12 hours of sunlight altered the chemical quality of the remaining DOM, likely due to preferential mineralization of the aromatic fraction (Cory et al., 2007; Stubbins et al., 2010) and to partial photo-oxidation of the DOM (Cory et al., 2013, 2014). These photochemical alterations of DOM resulted in a significant loss of CDOM and FDOM at each wavelength compared to dark controls (12.1 ± 1.4 % to 27.2 ± 2.1 % less CDOM or FDOM compared to the dark control depending on CDOM wavelength or FDOM peak, Table 4). Because there was greater loss of CDOM at long wavelengths compared to shorter wavelengths, photo-degradation significantly increased the S_R by 15.8 ± 1.3 % and decreased the FI by -11.7 ± 0.8 % on average. There was an increase in peak T intensity by 4.1 ± 1.5 % for photo-exposed DOM compared to dark controls (Table 4).

Photo-degradation of DOM enhanced the respiration of bacteria fed the photo-exposed DOM (compared to DOM kept in the dark); the water column rate of photo-stimulated bacterial respiration was 3.04 ± 1.31 mmol C m^{-2} d^{-1} (Cory et al. 2014). Relative to the initial photo-exposed DOM, bacterial incubation generally increased CDOM and FDOM (from 3 ±1 to 15 ±1 %, Table 4). The exception was that following bacterial degradation of the photo-exposed DOM, there was a 12 ± 1 % loss of peak T fluorescence (Table 4). Coupled photo and bacterial degradation increased the fluorescence index by 5 ± 1 % (Table 4).

3.5 Bacterial degradation of DOM

The average areal rate of dark bacterial respiration of DOM integrated over the mean depth (0.5 m) in Imnavait Creek was 2.35 ± 0.34 mmol O_2 m^{-2} d^{-1}. Bacterial degradation resulted in significant loss of CDOM and FDOM compared to the killed control over the six day incubation period at 6 - 7 °C (-2.9 ± 1.6 % to -7.6 ± 2.4 %, Table 4). There was no detectable change in the S_R or the FI after dark bacterial degradation of DOM compared to the killed control (Table 4).

4 Discussion

4.1 Stratification in beaded streams

Stratification is likely widespread during the summer in beaded pools and small ponds across the Arctic. Stratification in tundra ponds is well documented (Boano and Harvey, 2014; Hobbie, 1980), as are the factors conducive to stratification including high light attenuation by CDOM (Cory et al., 2007, 2014; Gareis et al., 2010; Watanabe et al., 2011), adequate solar radiation, and in streams low wind stress at the surface and low enough discharge coupled with permafrost below the stream (Merck and Neilson, 2012; Merck et al., 2012; this study). For example, nearly one third of both lower-order streams and coastal plain lakes sampled in the Alaskan Arctic had average CDOM absorption coefficients at 305 nm greater than or equal to the absorption coefficients observed in the surface of Imnavait Creek (Cory et al., 2014), consistent with high CDOM absorption coefficients reported in streams and small ponds and lakes across the Arctic (Gareis et al., 2010; Watanabe et al., 2011). While fewer studies have reported in-situ $K_{d,\lambda}$ values compared to reports of CDOM absorption coefficients in arctic freshwaters, strong agreement between $K_{d,\lambda}$ and $a_{\mathrm{CDOM},\lambda}$ in this and other studies (Fig. 2; Cory et al., 2014; Gareis et al., 2010; MORRIS et al., 1995) demonstrate that CDOM was the main UV and visible (PAR) light absorbing constituent in surface waters across the Arctic. 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).

Given that there was no significant difference in the average CDOM absorption coefficients in pool surface waters between 2011 and 2012 (Table 3), or between pool bottom water temperatures or in wind stress (Table 1), differences in the extent and frequency of stratification in the pools between years were most likely due to differences in discharge (Table 1; Fig. S1). Low in-stream discharges common in 2011 were due to significantly less precipitation than in 2012. Low discharge led to low turbulence, allowing for more common thermal stratification in the pools throughout a large fraction of the open water season (Table 1, Fig. 3). The higher flows during summer 2012 resulted in approximately five-fold greater stream volume compared to 2011, which increased the turbulence that induced frequent mixing throughout the water column in the pools (Table 1; Fig. 4).

4.2 DOM composition and photo-degradation

There are three lines of evidence in support of photo-degradation as the main control on the observed differences in DOM quantity and composition between pool surface and bottom waters in Imnavait Creek under stratified conditions: (1) water column rates of photo-mineralization of DOM and photo-stimulated bacteria respiration each exceeded dark bacterial respiration (Cory et al. 2014; Table 4), (2) experimental photo-degradation of Imnavait DOM closely reproduced the depth differences in DOM concentration and composition (Table 4), and (3) depth differences in DOM concentration and composition were consistent with effects of sunlight on DOM observed in other studies.

The mean water column rate of photo-mineralization of DOM to CO_2 was about ten times faster than photo-stimulated bacterial respiration or dark bacterial respiration in Imnavait Creek (Cory et al. 2014, Table 4). Thus, although 99 % of all UVB and UVA light causing photo-mineralization of DOM was attenuated within 8 to 35 cm below the pool surface, respectively (Fig. 2), thereby confining photo-degradation of DOM to the top ~ 35 cm of the pool, photo-mineralization in this surface layer was fast enough to exceed rates of bacterial respiration occurring throughout the UV-exposed and UV-protected portions of the water column (Table 4).

The second line of evidence in support of photo-degradation as the dominant process creating differences in DOM character between surface and bottom waters was that photo-degradation experiments reproduced the magnitude and direction of depth differences in DOC, CDOM, and FDOM observed under stratified conditions (Tables 2 and 4, Fig. 5). Compared to pool bottom waters, surface waters had significantly lower CDOM and FDOM concentrations, higher S_R, and lower FI, by 9 to 55 % (Tables 2 and 4, Fig. 5). Exposure of bottom water to ~12 hours of natural sunlight resulted in a comparable loss of CDOM and FDOM, and similarly higher S_R, and lower FI (11 to 27 % loss or change in CDOM or FDOM compared to dark controls; Table 4). Thus, DOM in pool surface waters and in photo-exposed bottom waters had lower concentrations of aromatic DOM (i.e., CDOM and FDOM) with lower average molecular weight compared to DOM protected from UV in the bottom waters. Many studies have demonstrated that photo-degradation of DOM results in a loss of CDOM and FDOM Granéli et al., 1996), a decrease in aromaticity (Brooks et al., 2007; Stubbins et al., 2010), and a decrease in average molecular weight (e.g., S_R, Cory et al., 2007; Helms et al., 2008; Spencer et al., 2010), just as we observed.

It is unlikely that bacterial processing of DOM could produce similar changes to those observed between surface and bottom waters or to the results of photo-degradation experiments. Bacteria degrade stream DOM and decrease CDOM and FDOM (Cory and Kaplan, 2012), but, at the same time some bacterial processes can regenerate CDOM and FDOM (e.g., Amado et al., 2006; Moran et al., 2000), leading to a net balance between degradation and regeneration. In our experiments the dark bacterial degradation of DOM resulted in a net loss of CDOM and FDOM, but the loss was much lower compared to photo-degradation (e.g., ~ 2 to 8 % decrease over six days, Table 4). Furthermore, bacterial degradation had no detectable effect on the S_R or FI, and thus cannot explain the significant differences in S_R and FI between surface and bottom waters in Imnavait Creek (Tables 2, 3 and 4, Fig. 5).

In an earlier study of Imnavait Creek, Merck et al. (2012) found that soil water FDOM was chemically similar to pool bottom water FDOM. Cold soil water from subsurface lateral flows plunged into the pool bottom during stratified conditions, bringing in FDOM that remained relatively unchanged in composition from the FDOM in soil waters. In our study we show that, similarly, FDOM but also pH, conductivity, DOC, and CDOM are comparable in quantity or quality between soil waters and pool bottom waters (Tables 2 and 3). These results suggest that either DOM in soil waters draining into isolated pool bottoms experiences little degradation in the pool, as would be expected based on relatively slow rates of bacterial respiration in cold, acidic, low nutrient, and often anoxic water (Table 4, Fig. 3-4), or that the pathways, rates, and fate of DOM degradation in both soils and bottom waters are similar.

4.3 Synthesis of factors controlling DOM degradation

Given that photochemical processes dominate the degradation and alteration of DOM in Imnavait Creek, estimates of DOM degradation or export at a stream reach or whole catchment scale must be based on an integration of the photochemical and hydrological controls on DOM degradation. These controls include (1) the amount of surface UV available to be absorbed by CDOM ($Q_{dso,\lambda}$, *Eqn. 3*), (2) the amount of CDOM to absorb and attenuate UV light in the water column ($a_{\mathrm{CDOM},\lambda}$ and K_d; *Eqn. 3*), (3) the lability of DOM to photo-degradation, quantified as apparent quantum yields (Φ_λ; *Eqn. 3*), and (4) the residence time of DOM in the water column or in a stream reach as affected by flow rates and stratification that in turn control the total UV light exposure and amount of DOM photo-degradation. These main controls and their feedbacks are summarized in Fig. 6, which shows that as light exposure increases, DOM photo-degradation increases. Similarly, there are different pathways through which increased CDOM can affect light exposure. First, higher CDOM increases light attenuation and thus helps facilitate thermal stratification. Stratification in turn results in increased water residence times that can increase the opportunity for light exposure and photo-degradation. For example, in pool surface waters where light exposure is greatest, during the day under low-flow conditions nearly the entire upper layer is stratified (Fig. 3), which increases residence time and light exposure (right side of Fig. 6). Second, although increasing CDOM increases light attenuation, the effect on light exposure can vary (left side of Fig. 6). In general, if K_d is relatively low and light penetrates to the bottom of the water column, increasing CDOM will result in greater total light exposure of DOM in the system, and thus greater total light absorption by CDOM to drive photochemical reactions. However, if K_d is relatively high and light is extinguished well before it reaches the bottom of the water column, the system is light-limited and adding more CDOM will not increase the overall light exposure of DOM (or light absorption by CDOM). The relative importance of these scenarios can be estimated by first examining the sensitivity of various components in the photo-degradation model (*Eqn. 3*).

To investigate the sensitivity of DOM photo-degradation to the amount of surface UV, CDOM, or Φ_λ, we varied each term independently in the equation for the water column rate of DOM photo-mineralization (*Eqn. 3*), using the average, minimum, and maximum values observed in Imnavait Creek (Fig. S2). Holding surface UV and Φ_λ constant (using the average observed values) and varying CDOM across the range observed in the pool surface waters of Imnavait Creek (39 to 63 m^{-1} at 305 nm, mean of 53 ± 2; Table 2), there was little variation in water column rates of photo-mineralization (Fig. 7). This result indicates that photo-degradation of DOM in Imnavait Creek is represented by higher K_d and falls in the asymptotic range shown in Fig. S1, meaning it is limited by insufficient UV light. It follows that increasing UV light (while holding CDOM and Φ_λ constant), should significantly increase the rate of DOM photo-mineralization, as shown in Fig. 7. That is, the daily total surface UV light varied by nearly 10-fold over the course of the summer season due to differences in solar zenith angle or cloud cover (as shown for 2012 in Fig. S3), and thus there was a nearly 10-fold higher rate of photo-mineralization when using the maximum vs. minimum surface UV light available in *Eqn. 3* (Fig. 7). The greatest effect on the rate of photo-degradation occurred when holding the UV light and CDOM to their average values, and varying the lability of DOM to photo-mineralization (i.e., varying Φ_λ). In this case, with a 6 to 20-fold range in Φ_λ (depending on wavelength; Fig. S2), DOM was converted to CO_2 by sunlight ~ 13-fold faster using the maximum vs. the minimum observed Φ_λ (Fig. 7).

The second step in understanding photo-degradation for any system is to consider the integrated effects of light attenuation with flow rates, stratification, and anticipated residence time distributions. Integrating the photochemical and hydrological factors produces a continuum of conditions that can represent or classify any particular system (Fig. 8a,b). For example, as light exposure and residence times increase, the amount of DOM lost through photo-mineralization increases (Fig. 8a). However, the quantity and photo-lability (*quality*, Φ_λ) of CDOM both determine the rates and the total amount of DOM photo-degradation. In systems with high CDOM concentrations or low light exposure, photochemical processes can be light limited rather than substrate (CDOM) limited. In such systems waters are rarely photo-bleached clear before inputs from soil waters or sediments replenish the CDOM lost to photo-degradation. This is the situation in Imnavait Creek (e.g., Table 3; Fig. 8a, left side;), which applies to most arctic headwater catchments or any system that receives high inputs of organic matter (Koehler et al., 2014). Similarly, if the photo-lability (and thus the Φ_λ) of the DOM is low (the lower, dashed line on Fig. 8a), then more UV is required for photo-degradation, and the system would be again considered light-limited. This is likely the case in the lower-CDOM Kuparuk River (spectral characteristics described in Cory et al. 2014), a fourth-order stream where it is joined by Imnavait Creek, although under some situations this river may be co-limited by light and substrate. Most of the waters in the Alaskan Arctic would fall in between these examples on this conceptual diagram, based on CDOM concentrations and Φ_λ values (Cory et al. 2014). In these cases where DOM photo-degradation is light-limited, the amount of time the DOM is exposed to UV becomes more important than the mass of DOM exposed. On the other hand, if photo-lability is very high and CDOM concentrations are very low, then the system is substrate-limited and the total mass of DOM exposed is more important than the amount of time the DOM spends exposed to UV (Fig. 8a, right side). This is because when the system is substrate limited, even a short exposure to UV will result in rapid and substantial photo-degradation, and exposing greater amounts of DOM even over short residence times will increase the overall photochemical processing in the system. Similarly, as one moves further right on Fig. 8a, the DOM loss as a percentage of initial amount declines once the system has switched from light- to substrate-limitation.

Finally, the nature and controls on DOM photo-degradation of a river reach (or whole system) can be expressed as a function of light attenuation and residence times (Fig. 8b). When water is flowing quickly through a stream the residence times are very short and the water column is well mixed, DOM spends less time exposed to UV light, and even at medium to low values of CDOM and K_d the system is light-limited (Fig. 8a,b left) and DOM loss to photo-mineralization is low (Fig. 8a left). At the other extreme, low flow conditions create long residence times, and even at medium values of CDOM the system is substrate-limited (Fig. 8b, right) and again DOM photo-mineralization may become low (Fig. 8a, right).

~~The relationship between residence time and photochemical controls is plotted for measured values in Imnavait Creek in Fig. 9. Combinations of minimum and maximum values of incident UV light, CDOM, and Φ_λ were used to create a 'lowest case' and 'highest case' scenario of photo-degradation over a range of residence time from hours to 20 days. Because it was shown in Fig. 7 (left set of bars) that the natural variability in CDOM concentrations has no effect on water column rates of photo-degradation, the scenarios were created by varying incoming UV light and DOM quality (Φ_λ). For example, the minimum UV light and minimum Φ_λ values observed resulted in low rates of photo-mineralization; over a 20 day residence time less than 5% of the DOM in surface waters could be converted to CO_2 by photo-mineralization. Conversely, combining the maximum UV light and maximum Φ_λ values shows that 100% of the DOM could be converted to CO_2 by photo-mineralization at the end of about one week (Fig. 9).~~ The relationship between residence time and DOM photo-degradation in Imnavait Creek was explored by multiplying *Eqn*. 3 (representing the water column rate of DOM photodegradation as the product of UV light, CDOM, and Φ_λ) by residence time to generate the results in Fig. 9. Combinations of minimum and maximum values of incident UV light, CDOM, and Φ_λ were used to create a 'lowest case' and 'highest case' scenario of photo-degradation over a range of residence time from hours to 20 days. Thus, Fig. 9 shows cumulative DOM loss as a function of residence for a range of conditions (i.e., UV light availability, CDOM, and Φ_λ) generated using a

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'lowest case' and 'highest case' scenario of photo-degradation. Because it was shown in Fig. 7 (left set of bars) that the natural variability in CDOM concentrations has no effect on water column rates of photo-degradation, the scenarios were created by varying incoming UV light and DOM quality (Φ_λ). For example, the minimum UV light and minimum Φ_λ values observed resulted in low rates of photo-mineralization; over a 20 day residence time less than 5% of the DOM in surface waters could be converted to CO_2 by photo-mineralization. Conversely, combining the maximum UV light and maximum Φ_λ values shows that 100% of the DOM could be converted to CO_2 by photo-mineralization at the end of about one week (Fig. 9). However, a precise estimate of residence time is difficult to achieve in practice given that there are inputs of water and "fresh" (labile) CDOM as a parcel of water moves downstream; accounting for these inputs is needed to quantify the total, integrated amount of DOM broken down by light as a function of residence time in a stream.

~~In all surface waters there is a variety of combinations of photochemical and hydrological controls that vary in space and time, and that define the "range" of DOM photo-degradation rates. For example, in Imnavait Creek longer residence times occur during times of low flow and stratification, but this stratification serves to protect DOM from UV light by isolating water masses in pool bottoms (e.g., Table 3, Fig. 5). Although exposure of surface waters to UV light did create chemical differences in DOM between surface and bottom waters, overall there was a relatively narrow range of CDOM concentrations at all locations and times in Imnavait Creek.~~ In all surface waters there is a variety of combinations of photochemical and hydrological controls that vary in space and time, and that define the "range" of DOM photo-degradation rates. For example, in Imnavait Creek longer residence times occur during times of low flow and stratification, and this stratification serves to protect DOM from UV light by isolating water masses in pool bottoms (e.g., Table 3, Fig. 5). The volume of water sequestered in the pool bottoms (below the mixing depth) under stratified conditions was on average about 70% of the total pool volume (Figs. 3, 4; Merck et al. 2012). Thus, under stratified conditions, the majority of the pool volume was sequestered in the bottom, below the depth of UV light penetration (8 – 45 cm see results section 3.2). However, 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 $a_{CDOM\lambda}$ values at 305 nm between these conditions in Imnavait Creek (comparing pool surface $a_{CDOM\lambda}$ 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; Fig. 9). Therefore, although most water was sequestered in the pool bottoms under stratified conditions, more DOM is lost due to photo-degradation under these conditions. This is because there is enough light-absorbing DOM that is labile to photo-degradation even in the pool surface waters under all conditions that DOM photo-degradation is not limited by substrate (DOM supply). 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.

Rates of photo-mineralization varied little over this narrow range of CDOM (Fig. 7, left), and because CDOM was very high photochemical reactions were light-limited (Fig. 8b). In addition, the consistently high CDOM concentrations observed across space (pool to pool) and averaged over time (2011 to 2012) in Imnavait Creek (Tables 2 and 3, Fig. 5) suggests that CDOM lost to photo-mineralization under any photochemical or hydrological conditions is rapidly replenished from riparian soil waters over relatively short time periods (see also Merck et al. 2012). ~~In other words, i~~It is likely that stream reaches with high CDOM concentrations (substrate rich) and residence times in the range observed in Imnavait Creek are similarly always light-limited (Fig. 8). Increased residence times, or lower CDOM concentrations such as those observed in the Kuparuk River, will move a system from light-limitation toward co-limitation by light and substrate (Fig. 8), again depending on the combination of photochemical and hydrological properties and their variability in space and time.

5 Conclusions

Results from this study demonstrate that in Imnavait Creek photo-degradation dominates over bacterial degradation of DOM, and photo-degradation can create substantial differences in DOM chemistry between water masses isolated during stratification. The amount and lability of CDOM and the light attention by CDOM form a critical control point in DOM degradation – higher CDOM attenuates light faster with depth but results in no change or an increase in the overall rate of light absorption in the water column. With increasing CDOM and thus increasing rates of light-absorption, photo-degradation rates in the water column are more likely to be light-limited and rates will increase with incident UV light or residence time. Given that higher light attenuation by CDOM traps heat in surface waters and creates stratification, which lengthens residence times and thus the time-integrated light exposure of DOM, low-flow conditions in Imnavait Creek likely maximize the conditions for photo-degradation of DOM.

On the other hand, if CDOM concentrations are very low, then the system is substrate-limited and the total mass of DOM exposed is more important than the amount of time the DOM spends exposed to UV (Fig. 8a, right side). This is because when the system is substrate limited, even a short exposure to UV will result in rapid and substantial photo-degradation, and exposing greater amounts of DOM even over short residence times will increase the overall photochemical processing in the system. In addition, in our conceptual model the lability of DOM to photo-degradation acts as a control on processing rates independent of whether a system is light- or substrate limited (Fig. 8a). Finally, at the scale of a stream reach or catchment, the balance between light- vs. substrate-limitation of DOM degradation varies with changes in water residence times, the incident UV light, and photo-lability of DOM. Our analyses indicate that the hydrological and photochemical conditions in Imnavait Creek create light-limitation for DOM photo-degradation, and we suggest that photo-degradation in most streams and ponds with high CDOM is similarly light-limited.

Author contributions

GWK, BTN and RMC designed the field sampling plan and all authors contributed to the field work and data analysis. RMC, GWK and BTN prepared the manuscript with contributions KHH.

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Table 1. Meteorological conditions at Toolik Field Station during study periods

Period	[a]Global Solar Radiation	[a]UV+Visible Photon Flux	[b]Air Temperature (1 m)	[a]Precipitation	[c]Total discharge at weir
	kW m^{-2}	mol photons m^{-2}	°C	mm	m^3
2011	12	2111	9	63	$41x10^3$
2012	10	1600	10	189	$233x10^3$

[a]Sum of daily average values from 23-June through 18-August in each year (sampling periods in 2011 and 2012).
[b]Daily average value from 23-June through 18-August. [c] Sum discharge passing the weir at Imnavait from 28-Jun to 18-August.

~~**Table 2.** Annual average hydrologic and chemical characteristics of soil and stream water samples from Imnavait Creek.~~

		~~Soil Water~~		~~Pool Bottom Water~~		~~Pool Surface Water~~	
		~~2011~~	~~2012~~	~~2011~~	~~2012~~	~~2011~~	~~2012~~
~~Water Temp~~	~~°C~~			~~11 ± <1~~	~~11 ± <1~~	~~14 ± 1~~	~~11 ± 1~~
~~pH~~		~~5.2 ± 0.4~~	~~5.2 ± 0.1~~	~~5.5 ± 0.1~~	~~5.6 ± 0.1~~	~~5.7 ± 0.1~~	~~5.7 ± 0.1~~
~~Conductivity~~	~~μs cm^{-1}~~	~~26 ± 1~~	~~25 ± 2~~	~~42 ± 10~~	~~17 ± 3~~	~~13 ± <1~~	~~12 ± <1~~
~~DOC~~	~~μM C~~	~~1357 ± 110~~	~~1412 ± 78~~	~~1252 ± 85~~	~~1100 ± 17~~	~~785 ± 13~~	~~1028 ± 21~~
~~a_{305}~~	~~m^{-1}~~	~~96 ± 10~~	~~87 ± 7~~	~~118 ± 19~~	~~61 ± 2~~	~~53 ± 2~~	~~53 ± 1~~
~~S_R~~		~~0.75 ± 0.01~~	~~0.74 ± 0.01~~	~~0.70 ± 0.02~~	~~0.75 ± 0.01~~	~~0.78 ± 0.02~~	~~0.76 ± <0.01~~
~~SUVA$_{254}$~~	~~(L mg C^{-1} m^{-1})~~	~~4.4 ± 0.1^{A}~~	~~4.1 ± 0.1^{B}~~	~~5.2 ± 0.5~~	~~3.9 ± 0.1~~	~~4.5 ± 0.1~~	~~3.7 ± <0.1~~
~~Peak A~~	~~RU~~	~~3.3 ± 0.2~~	~~2.9 ± 0.2~~	~~3.5 ± 0.1~~	~~2.8 ± <0.1~~	~~2.5 ± <0.1~~	~~2.7 ± 0.1~~
~~FI~~		~~1.59 ± 0.01~~	~~1.60 ± 0.01~~	~~1.55 ± 0.01~~	~~1.57 ± 0.01~~	~~1.51 ± 0.01~~	~~1.55 ± <0.01~~

~~All values are seasonal averages across all dates in 2011 or 2012 shown with standard error in parentheses.~~

Table 2. Annual average hydrologic and chemical characteristics of soil and stream water samples from Imnavait Creek.

		Soil Water		**Pool Bottom Water**		**Pool Surface Water**	
		2011	**2012**	**2011**	**2012**	**2011**	**2012**
Water Temp	°C			11 ± <1	11 ± <1	14 ± 1^{A}	11 ± 1^{B}
pH		5.2 ± 0.4	5.2 ± 0.1	5.5 ± 0.1	5.6 ± 0.1	5.7 ± 0.1	5.7 ± 0.1
Conductivity	μs cm^{-1}	26 ± 1	25 ± 2	42 ± 10^{A}	17 ± 3^{B}	13 ± <1	12 ± <1
DOC	μM C	1357 ± 110	1412 ± 78	1252 ± 85^{A}	1100 ± 17^{B}	785 ± 13^{A}	1028 ± 21^{B}
a_{305}	m^{-1}	96 ± 10	87 ± 7	118 ± 19^{A}	61 ± 2^{B}	53 ± 2	53 ± 1
S_R		0.75 ± 0.01	0.74 ± 0.01	0.70 ± 0.02^{A}	0.75 ± 0.01^{B}	0.78 ± 0.02	0.76 ± <0.01

$SUVA_{254}$	(L mg C^{-1} m^{-1})	4.4 ± 0.1^{A}	4.1 ± 0.1^{B}	5.2 ± 0.5^{A}	3.9 ± 0.1^{B}	4.5 ± 0.1^{A}	3.7 ± <0.1^{B}
Peak A	RU	3.3 ± 0.2	2.9 ± 0.2	3.5 ± 0.1^{A}	2.8 ± <0.1^{B}	2.5 ± <0.1^{A}	2.7 ± 0.1^{B}
FI		1.59 ± 0.01	1.60 ± 0.01	1.55 ± 0.01^{A}	1.57 ± 0.01^{B}	1.51 ± 0.01^{A}	1.55 ± <0.01^{B}

All values are seasonal averages ± standard error across all dates in 2011 or 2012. Letters indicate significant difference ($p < 0.05$) in mean values between years (2011 vs. 2012) for each water type (soil waters, pool bottom waters, and pool surface waters).

Table 3. DOM in soil waters compared to pool water in Imnavait Creek under stratified conditions

		Soil Water	**Pool Bottom Water**	**Pool Surface Water**
DOC	µM C	1382 ± 69	1188 ± 56	815 ± 12
a_{305}	m^{-1}	92 ± 6	100 ± 13	50 ± 1
S_R		0.75 ± 0.01	0.71 ± 0.01	0.77 ± 0.01
$SUVA_{254}$	(L mg C^{-1} m^{-1})	4.4 ± 0.1	4.9 ±0.3	4.2 ± 0.1
Peak A	RU	3.1 ± 0.2	3.2 ± 0.1	2.38 ± 0.05
FI		1.60 ± 0.01	1.57 ± 0.01	1.52 ± 0.01

All values shown as average ± standard error; calculated in the pool surface or bottom across all dates in 2011 and 2012 when pools were stratified (2011: 27 Jun, 29 Jun, 14 Jul, 4 Aug; 2012: 23 Jun, 30 Jun).
Soil water values were calculated as average over both years (2011-2012).

Table 3. DOM in soil waters compared to pool water in Imnavait Creek under stratified conditions

		Soil Water	**Pool Bottom Water**	**Pool Surface Water**
DOC	µM C	1382 ± 69	1188 ± 56	815 ± 12
$\boldsymbol{a_{305}}$	m^{-1}	92 ± 6	100 ± 13	50 ± 1
$\mathbf{S_R}$		0.75 ± 0.01	0.71 ± 0.01	0.77 ± 0.01
$\mathbf{SUVA_{254}}$	($L\ mg\ C^{-1}\ m^{-1}$)	4.4 ± 0.1	4.9 ±0.3	4.2 ± 0.1
Peak A	RU	3.1 ± 0.2	3.2 ± 0.1	2.38 ± 0.05
FI		1.60 ± 0.01	1.57 ± 0.01	1.52 ± 0.01

All values shown as average ± standard error; calculated in the pool surface or bottom across all dates in 2011 and 2012 when pools were stratified (2011: 27-Jun, 29-Jun, 14-Jul, 4-Aug; 2012: 23-Jun, 30-Jun). Soil water means were calculated from over both years (2011-2012). All water types were statistically different from one another for all variables (ANOVA $p < 0.01$).

Table 4. Effect of sunlight and bacteria on CDOM, FDOM and DOM mineralization.

Process	a_{305}	S_R	$SUVA_{254}$	FI	Peak A	Peak C	Peak T	Mineralization rate
	m^{-1}		*L mg C*$^{-1}$ *m*$^{-1}$		*RU*	*RU*	*RU*	(mmol C m^{-2} d^{-1})
[a] Photo-degradation	-12.4 ± 1.8	15.8 ± 1.3	-4.9 ± 0.01	-11.7 ± 0.8	-12.1 ± 1.4	-27.2 ± 2.1	4.1 ± 1.5	24.7 ± 18.3
[b] Bacterial degradation	-2.9 ± 1.6	ND	5.0 ± 0.03	ND	-7.6 ± 2.4	-3.6 ± 1.5	-2.5 ± 8.2	2.35 ± 0.34
[c] Photo + bacterial degradation	3 ± 1	1 ± 1	NM	5 ± 1	7 ± 1	15 ± 1	-12 ± 1	3.04 ± 1.31

DOM degradation quantified as percent change in CDOM or FDOM of Imnavait Creek waters after [a]exposure to 12 h sunlight compared to dark control (photo-degradation), [b] after seven days of incubation of whole waters at 6-7 °C compared to killed control (bacterial degradation), or [c] after 12 h sunlight followed by seven days of incubation with natural bacterial community in stream water at 6-7 °C relative to killed controls (here the percent change is relative to the initial photo-exposed water). Data shown as average ± standard error of three photochemical experiments, two bacterial incubations, and one coupled photo-bacterial incubation. Within each of the bacterial or photo + bacterial experiments there were four replicates per treatment (light, dark, live or killed controls). ND = none detected based on no significant difference compared to killed controls. NM = not measured.

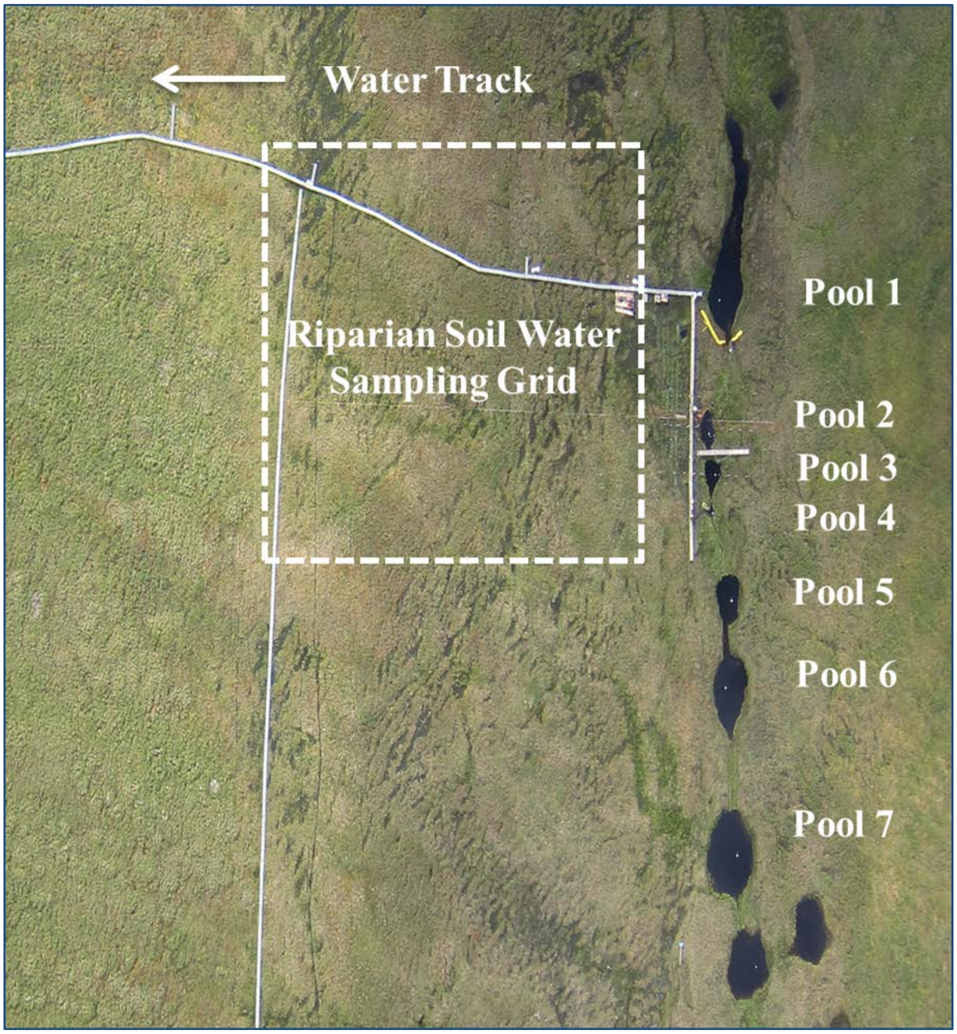

Fig. 1. Study area showing the 120 m reach of Imnavait Creek containing seven consecutive pools, and the locations of soil water collection (riparian zone and water track; only the bottom portion of the water track is shown in this image). Also visible in this areal image as white solid lines are boardwalks installed to access sampling sites.

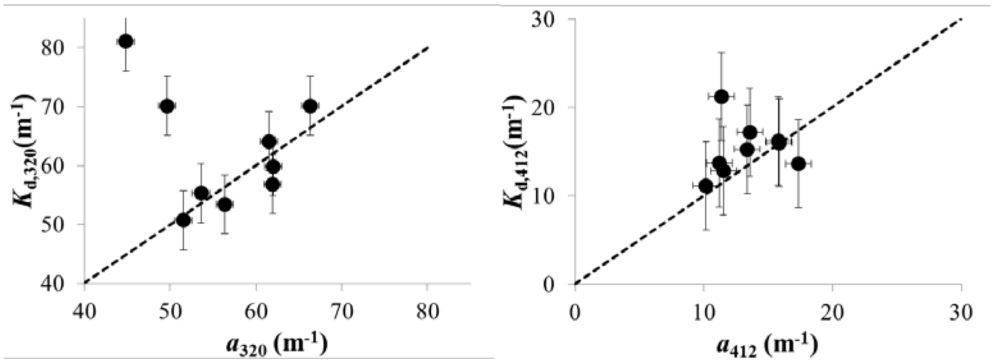

Fig. 2. $K_{d,\lambda}$ vs. $a_{\text{CDOM},\lambda}$ at 320 nm (left) and 412 nm (right) plotted vs. 1:1 line (dotted line). $a_{\text{CDOM},\lambda}$ measured on the laboratory spectrophotometer was corrected for the average cosine of downwelling radiation for the time of day (i.e., zenith angle) that the in-situ $K_{d,\lambda}$ values were measured in Imnavait Creek. Thus $a_{\text{CDOM},\lambda}$ values in this figure are not directly comparable to the values presented in Tables 2 and 3.

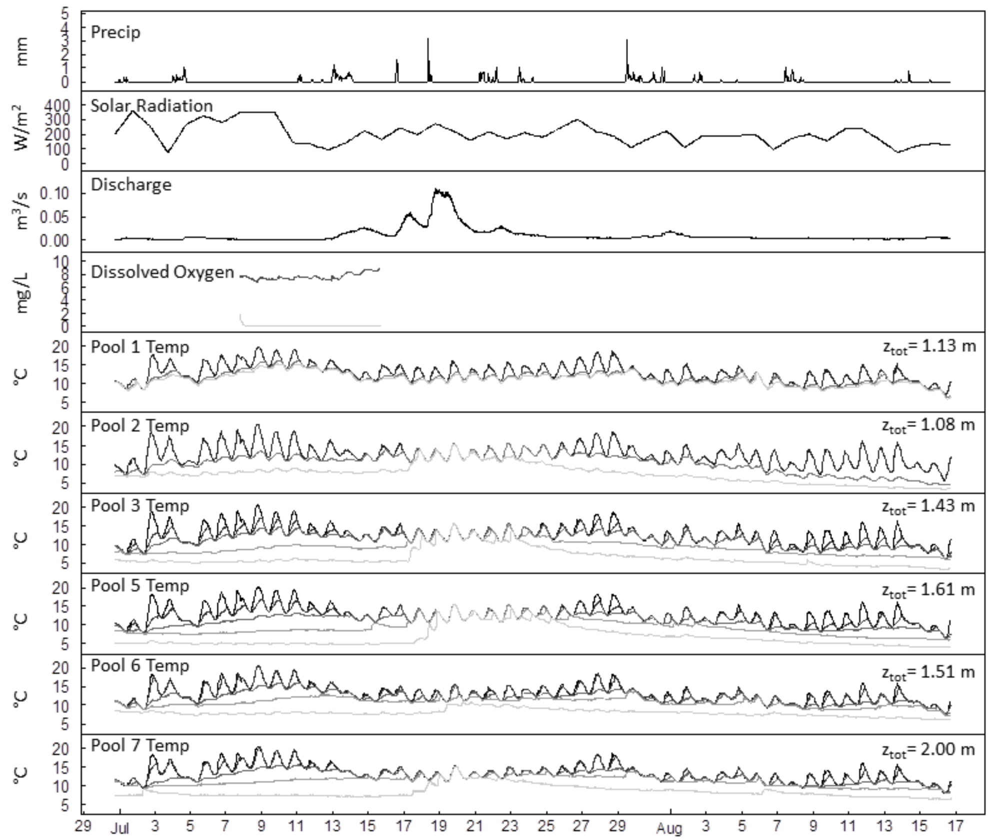

Fig. 3. Imnavait Creek precipitation, solar radiation, discharge (at location downstream of study reach), dissolved oxygen in pool 2 top and bottom, and vertical arrays (VA) of temperature sensors within each study pool (P) in summer 2011. The darkest lines represent the sensor at the top of the water column; subsequent lines become lighter with depth of each sensor. The sensors were placed in each pool starting 5 to 15 cm from the bottom of the pool and then at intervals ranging from 5 to 50 cm over the depth of each pool (z_{tot}) as indicated in the figure.

Comment [RMC1]: Revised Figure replaces former Fig 3.

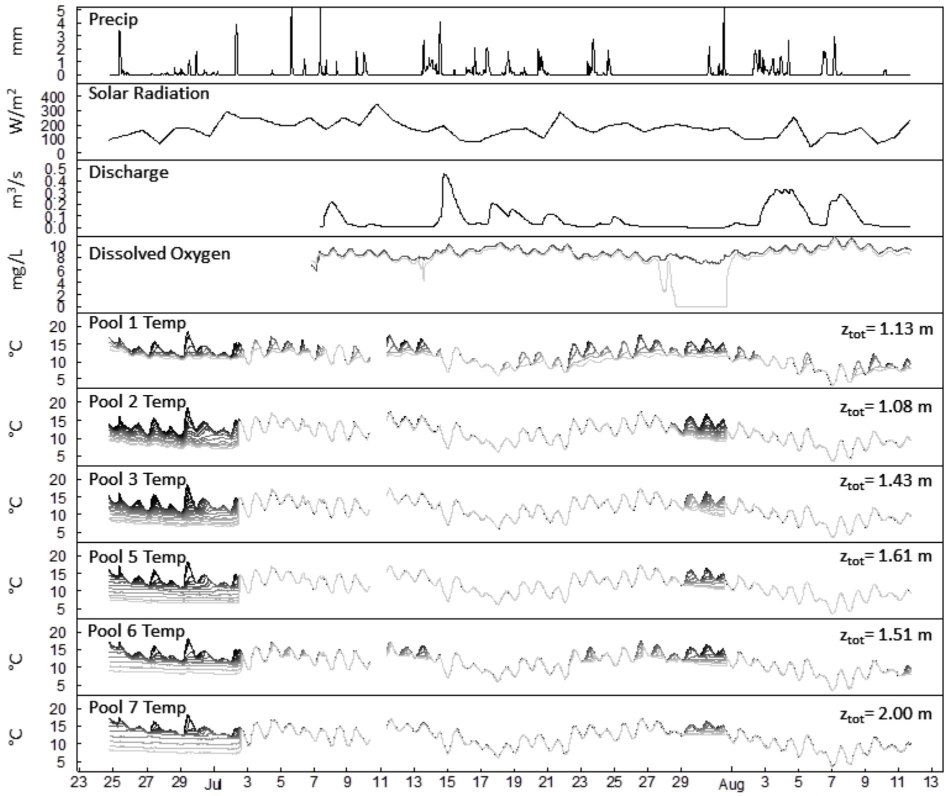

Fig. 4. Imnavait Creek precipitation, solar radiation, discharge (at location downstream of study reach), dissolved oxygen in pool 2 top and bottom, and vertical arrays (VA) of temperature sensors within each study pool (P) in summer 2012. The darkest lines represent the sensor at the top of the water column; subsequent lines become lighter with depth of each sensor. The sensors were placed in each pool starting 5 to 15 cm from the bottom of the pool and then at intervals ranging from 5 to 50 cm over the depth of each pool (z_{tot}) as indicated in the figure.

Comment [RMC2]: Revised figure replaces former Fig 4.

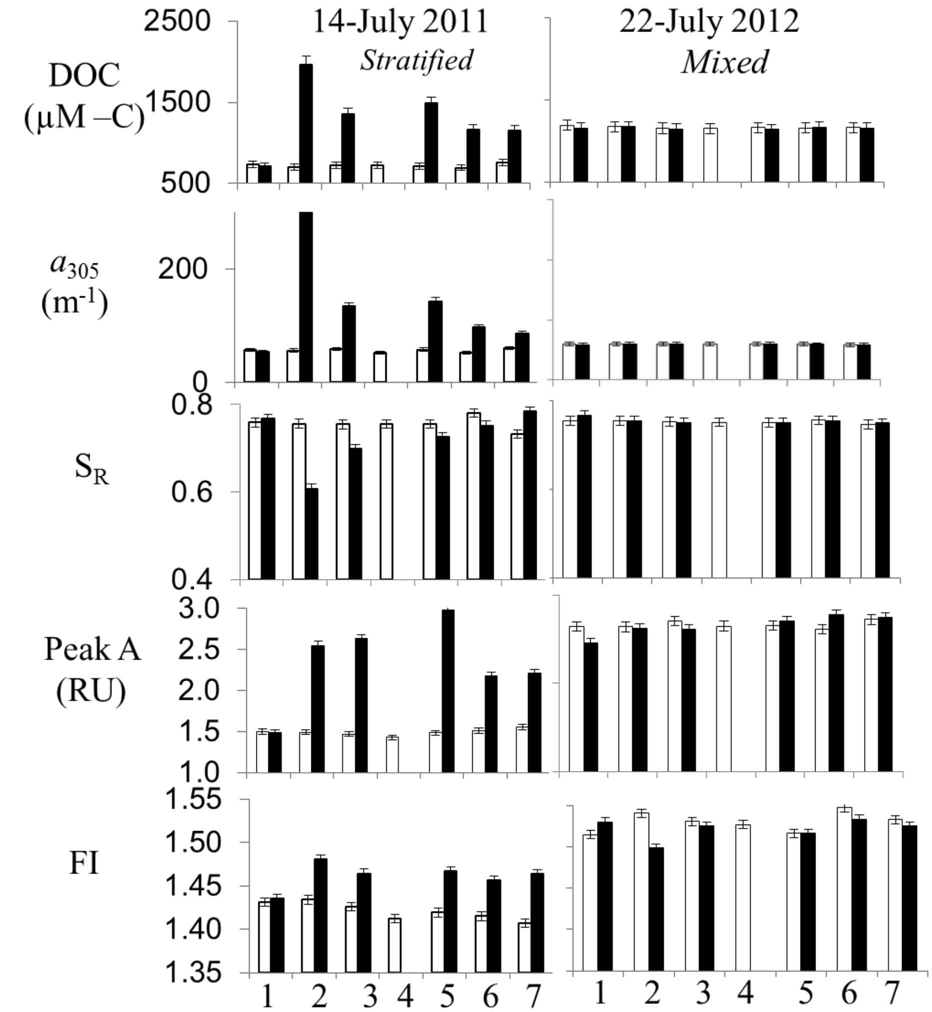

Fig. 5. Concentration and quality of DOM in the surface (open bars) and bottom waters (filled bars) in pools 1-7 In Imnavait Creek under stratified (left) and mixed (right) conditions in 2011 and 2012, respectively. CDOM and FDOM concentrations shown as absorption coefficients at 305 nm (a_{305}) and emission intensities at Peak A (Raman Units; RU), respectively. DOM quality shown as slope ratio (S_R) and fluorescence index (FI); CDOM and FDOM proxies for DOM described in text.

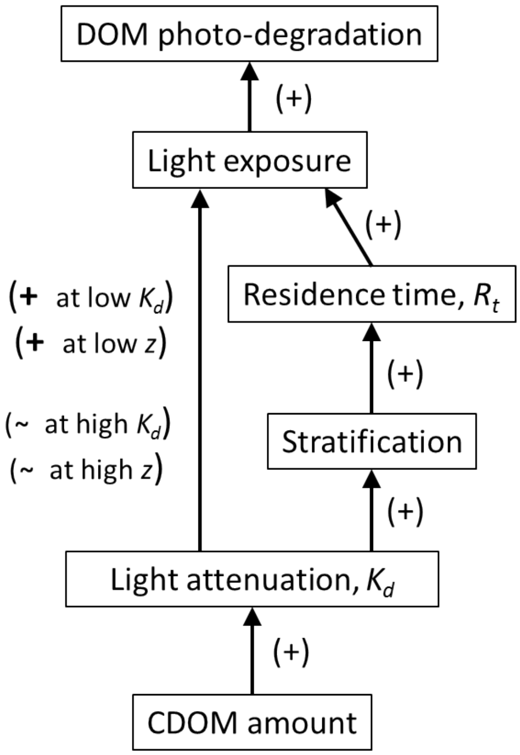

Fig. 6. Conceptual diagram illustrating the controls on DOM photo-degradation. As CDOM increases it absorbs more light at the surface and strengthens stratification, which increases residence times, length of light exposure, and thus DOC photo-degradation (right side). Similarly, as CDOM and thus light attenuation increase the total amount of light exposure and light absorption increases in situations where there is low K_d or shallow water column depth z. However, as K_d or shallow water column depth increase the system becomes light limited, and further increases in CDOM result in no change in DOM photo-degradation (asymptote of Fig. S1).

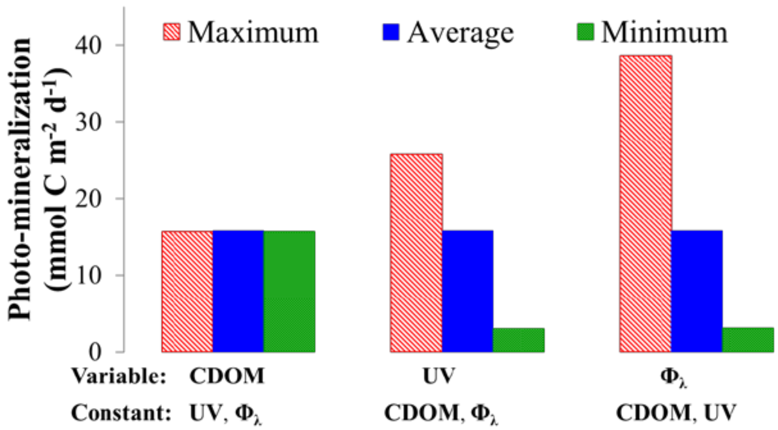

Fig. 7. Effect of CDOM, incident UV, and Φ_λ (apparent quantum yield) on water column rates of photo-mineralization of DOM to CO_2 in Imnavait Creek. For each scenario, two variables from *Eqn. 3* were held constant, and one was varied using the average, minimum, and maximum values observed over the study period at Imnavait Creek (2011-2012). UV = daily total UV reaching water surface at Imnavait Creek (dependent on solar zenith angle and cloud cover).

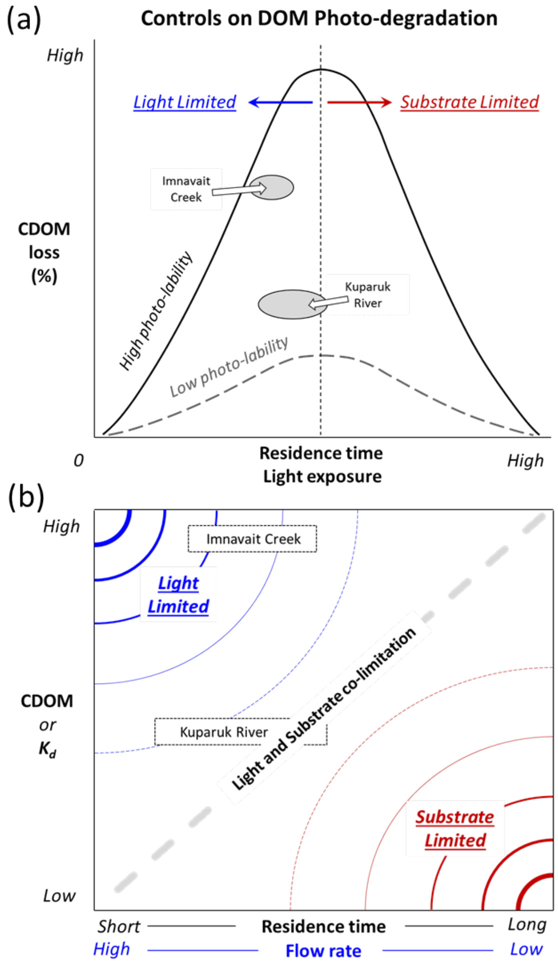

Fig. 8. Controls on DOC photo-degradation. **(a)** As residence time or light exposure increase, so does DOC photo-degradation (% loss of the initial pool of CDOM, without replacement). The CDOM loss for any given light exposure is greater for higher photo-labile DOC (solid line) than it is for lower photo-labile DOC (dashed line). At low light exposure levels photo-degradation is "light-limited", but after sufficient CDOM is lost the process switches to be "substrate-limited" (insufficient CDOM). **(b)** This shows the light- vs. substrate- limitation in terms of CDOM concentrations or light attenuation (K_d), Y-axis, and the water residence time or flow rate (X-axis). At high CDOM and short residence time there is insufficient light available for photo-degradation (upper left), while at low CDOM concentrations and long residence times there is abundant light yet insufficient CDOM. The range of conditions for DOC photo-degradation in Imnavait Creek is likely always light-limited, while in the Kuparuk River conditions may be substrate-limited at times.

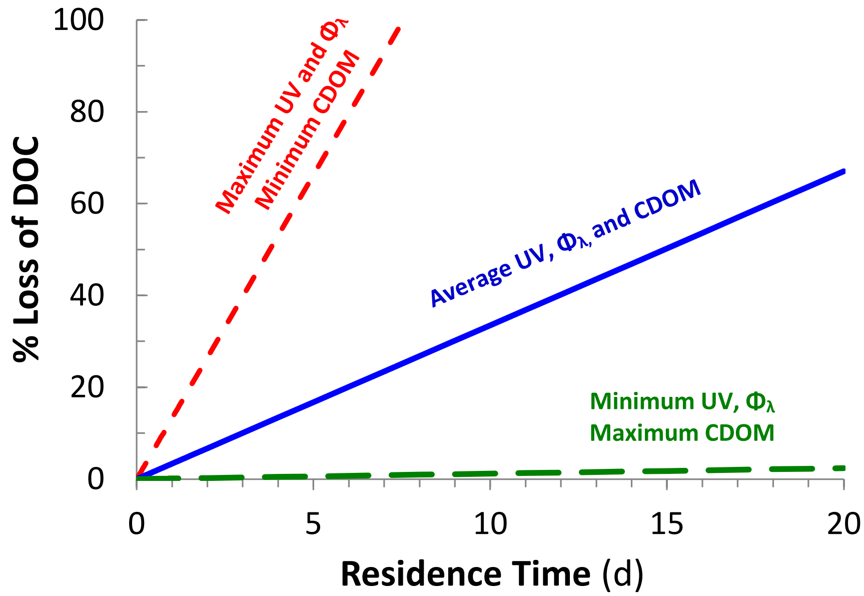

Fig. 9. Cumulative percent of DOC loss in Imnavait Creek lost through photo-mineralization as calculated from *Eqn. 3* (removal of DOC as mol C m^{-2} d^{-1} over the mean depth in Imnavait Creek; 0.5 m) in Imnavait Creek using combinations of the range of surface UV light exposure, CDOM concentrations, and apparent quantum yields (Φ_λ) measured in this study for up to a 20 day residence time. For each scenario, the initial DOC concentration was set to 943 µM C, the average surface water DOC concentration over both 2011 and 2012 (Table 2). Calculations do not include (1) the effect of DOC loss on changing light attenuation (K_d) over the residence time (i.e., CDOM and thus $K_{d,\lambda}$ remain constant over the residence time for each scenario), or (2) the effect of UV light exposure on Φ_λ over time (Φ_λ, or DOM lability, remained constant over the residence time for each scenario).

Supporting Information – Figures and Data

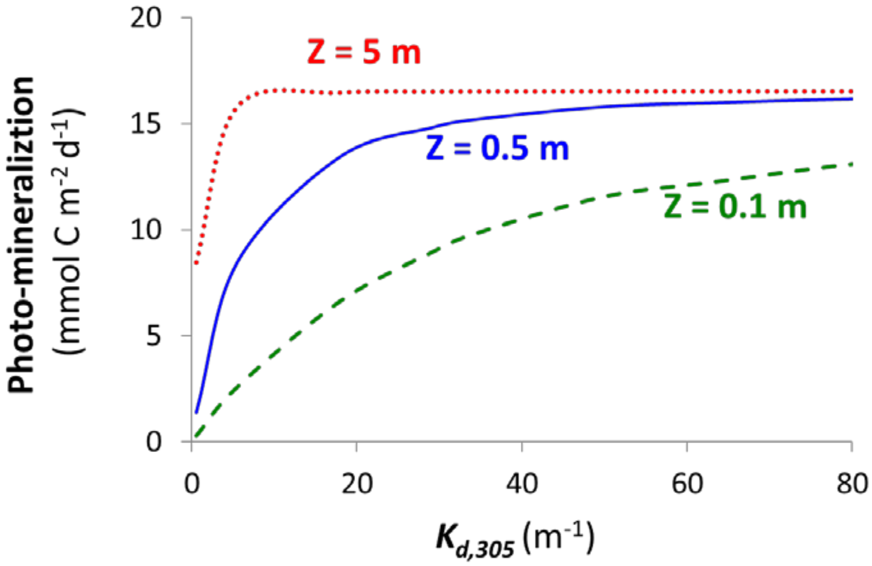

Fig. S1. The dependence of water column rates of photo-mineralization as a function of K_d, which increases with increasing CDOM. Three situations with varying depth (z) of the water column are shown. In all but the shallowest water columns, the photo-mineralization rate asymptotes at relatively low K_d values – the range of K_d at 305 nm measured in Imnavait Creek was 39 to 63 m^{-1}.

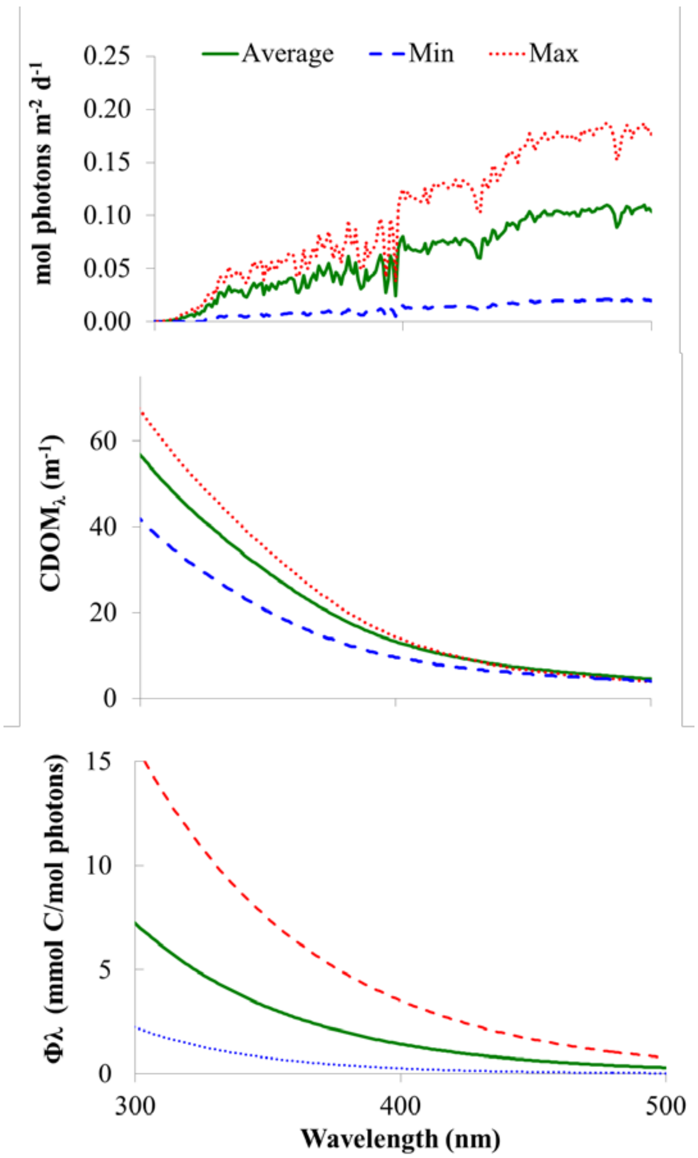

Fig. S2. Average, minimum, and maximum spectra of incident UV light (daily photon flux), CDOM, and apparent quantum yield of photo-mineralization measured in Imnavait Creek.

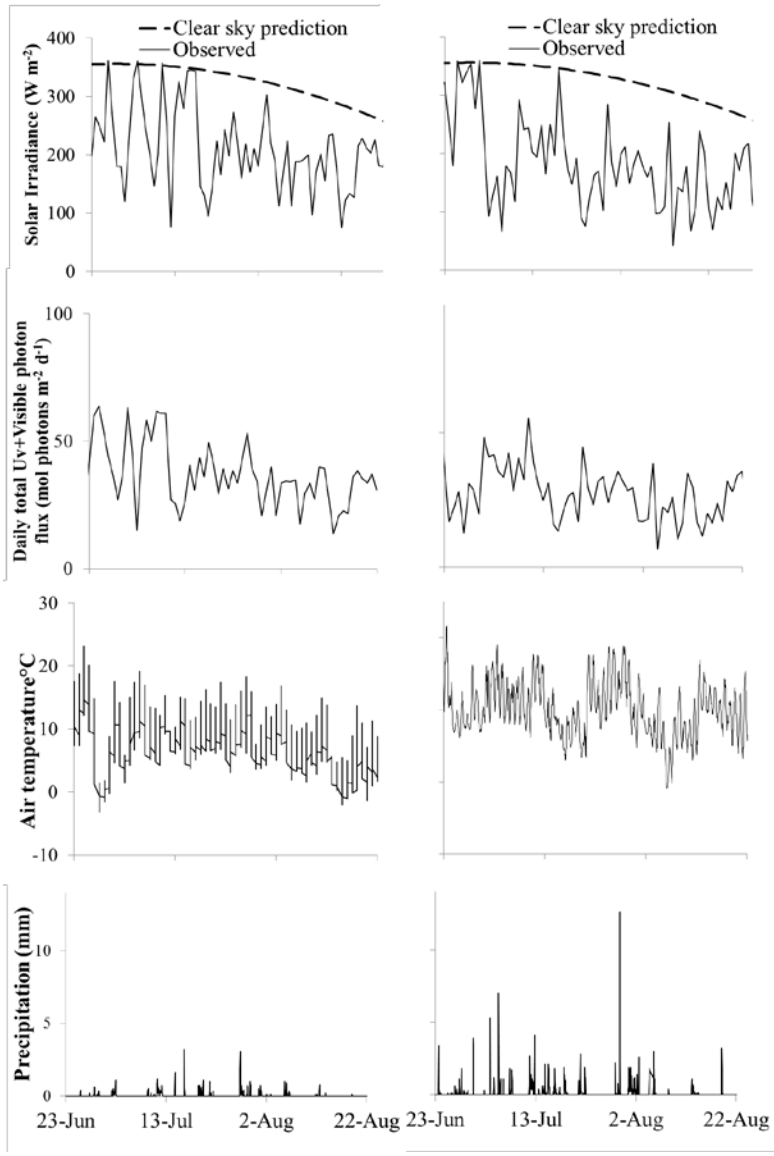

Fig. S3. UV and climate data at Imnavait Creek for 2011 (left) and 2012 (right) during the study periods. (A) Predicted and observed mean daily global solar irradiance. (B) Daily total sum of UV+ Visible photon flux reaching water surface. (C) Air temperature measured 1m above ground at Imnavait Creek. (D) Precipitation.