Diurnal cycles in the degradation of fluvial carbon from a peat headwater stream

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Abstract

In-stream processing of allochthonous dissolved organic carbon (DOC) and particulate organic carbon (POC) in peat-sourced headwaters has been shown to be significant flux pathways in the terrestrial carbon cycle, through photo- and bio-degradation, with both DOC and POC evolving into carbon dioxide (CO_2).

This study reports a series of 70-hour, in-situ experiments investigating rates of degradation in unfiltered surface water from a headwater stream in the River Tees, North Pennines, UK. Half the samples were exposed to the normal day/night cycle; half were continuously dark. The study found that the DOC concentration of samples in the daylight declined by 64% over the 70 hours, compared with 6% decline for the samples kept in the dark. For POC, the loss in the light was 13%. The average initial rate of loss of DOC in the light during the first day of the experiment was 3.36 mg C/l/hour, and the average rate of photo-induced loss over the whole 70 hours was 1.25 mg C/l/hour. Scaling up these losses, the estimate of total organic carbon loss from UK rivers to the atmosphere is 9.4 Tg CO_2/yr which is 0.94% of the estimate from the 2013 IPCC report.

Initial rate kinetics in the light were as high as 3rd order, but the study could show that no single rate law could describe the whole diurnal degradation cycle and that separate rate

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laws were required for dark and light processes. The comparison of dark and light processes showed no evidence of any priming effect.

Keywords: DOC, POC, in-stream, upland, river, UK

Introduction

Peatlands, as highly organic soils, are an important, if not the most important, source of dissolved (DOC) and particulate (POC) organic carbon to rivers (Aitkenhead et al. 2007; Rothwell et al. 2008; Tipping et al. 2010). Both DOC and POC are important components of the fluvial carbon cycle, facilitate the transport of pollutants (Rothwell et al. 2007); contribute to the nutrients supply and energy sources in the river (Marschner and Kalbitz, 2003; Tipping et al. 2010); and the cost of water treatment (Evans et al. 2012). Across the northern hemisphere there have been widespread reports of increasing concentrations of DOC in river water in recent years (Evans et al. 2005; Freeman et al. 2001); and widespread erosion in UK peatlands has led to an increase in POC fluxes into some headwaters (Evans et al. 2006; Pawson et al. 2008).

The fluxes of DOC and POC from World rivers have been measured and modelled (e.g. Harrison et al. 2005), but these studies have calculated flux of organic components at the outlet of the catchments rather than the flux from the terrestrial sources (e.g. peat soils) and thus do not take into account any changes that have occurred along the path of the river, such as in-stream processing of DOC and outgassing of dissolved inorganic carbon (DIC; Worrall et al. 2012) and so are poor estimates of how much carbon is being lost from terrestrial environments and how much carbon is contributed from rivers to the atmosphere. In-stream processing of DOC includes processes that can both decrease and increase the DOC concentration of the stream including interaction with POC and the autochthonous production of DOC (Figure 1).

47 The extent to which the processing of DOC and POC contribute to the release of
48 atmospheric greenhouse gas depends upon the rates of processes that degrade and convert
49 DOC to greenhouse gases. A range of studies have examined the changes in DOC
50 concentration that occur in a range of environments. Graneli et al. (1996) found a rate of loss
51 of 0.0009-0.4 mg C/l/day and Hudson et al. (2003) found a DOC loss of 0.43%/day, both in
52 lake water. Gennings et al. (2001) states that 40-70% of annual inputs into boreal lakes is
53 evaded to the atmosphere. At a global scale, Cole et al. (2007) estimated that 1.9 Pg C/yr
54 enters rivers of which 0.8 Pg C/yr (42% of the input) is returned to the atmosphere. Battin et
55 al. (2009) suggested a lower removal rate of 21%, and Raymond et al. (2013) estimated a
56 value of CO_2 lost from global rivers of 1.8 Pg C/yr and 0.32 Pg C/yr from lakes and
57 reservoirs.

58 Lakes and reservoirs have residence times of weeks to years, which is far longer than
59 the residence times of rivers and especially for rivers in the UK – in-stream residence time in
60 the UK and median flow is only 26.7 hours (Worrall et al. 2014a). Also, due to the long
61 residence times, the DOC will be "old", having been in the fluvial network for a longer time.
62 "Young" DOC is readily biodegradable (Marschner and Kalbitz, 2003), and "old" DOC is
63 more refractory (Southwell et al. 2011). Preferential degradation of "young" DOC means
64 that large rivers, reservoirs, lakes and the sea will have larger proportions of "old", less
65 degradable DOC, and so the rates of degradation of DOC would be lower than in smaller
66 rivers and their headwaters (Raymond and Bauer, 2001). For the UK, Worrall et al. (2007)
67 estimated the first national scale flux of total fluvial carbon and estimated the average annual
68 total fluvial C flux from the terrestrial source in the UK was 2.5 Tg C/yr (10.34 Mg
69 $C/km^2/yr$) with a flux of DOC from the terrestrial source of 1.37 Tg C yr^{-1} with 29% removal
70 of DOC in stream. Worrall et al. (2012) used empirical and structural modelling of the DOC
71 export from over 194 catchments across the UK; across 7 years; and found a net watershed

loss of DOC up to 78% (equivalent to between 9.0 and 12.7 Mg C/km^2 of UK land area/yr). Worrall et al. (2014b) was able to update POC fluxes for the UK and found that the total fluvial flux of carbon from the terrestrial source was 5.0 Tg C/yr (22.2 Mg C/km^2/yr) with 3.2 Tg C/yr lost to the atmosphere – equivalent to 13.9 Mg C/km^2/yr or a total loss rate of 63% and including a 20% net loss of POC across watersheds. Moody et al. (2013) performed experimental observations of the fate of DOC and POC in "young", fresh, peat stream water from the River Tees, northern England, and found an average 73% loss of the DOC over 10 days, with the majority of the loss occurring in the first two days, and between 38 and 87% removal of peat-derived POC. If the majority of degradation and loss of DOC and POC is occurring over a period of 2 days and the residence time of UK rivers is of the order of 1 day then degradation processes need to be considered on the order of hours and not days. As photodegradation, by definition, requires light, the DOC concentration in a stream is likely to exhibit a diurnal cycle of degradation which would not readily observed if daily timescales were considered (Worrall et al. 2013). Therefore, the aim of this study is to consider fluvial carbon dynamics over periods of hours and not days.

Materials and Methods

This study adapts the method to Moody et al. (2013) to conduct in-situ degradation measurements of DOC from the headwater of the River Tees in North-East England over periods of up to 70 hours.

Study Site

This study used one of the four sites used in Moody et al. (2013), the source water site, Cottage Hill Sike (Figure 2, CHS; UK national grid ref: NY 744 327). The site is within the Moor House National Nature Reserve (NNR), the most extensively studied of all UK

97 peatlands (Billett et al. 2010), and has a catchment area of 0.2 km^2, with 100% peat cover.
98 The Moor House NNR is part of the Environmental Change Network (ECN) monitoring
99 programme which means that DOC concentration has been monitored in the stream water
100 weekly since 1993 (Worrall et al. 2009).
101
102 ***Degradation measurements***
103 The degradation measurements were made outside of the laboratory in ambient light and
104 temperature conditions (rather than indoors under artificially controlled conditions). The
105 study considered two treatments, one in which degradation experiments were always exposed
106 to ambient light (thus experiencing both night and day time conditions); and one in which all
107 experiments were exposed to ambient temperature but were covered and therefore always in
108 darkness. These treatments, henceforward referred to as light (always in ambient conditions
109 and therefore experienced both light and dark conditions over a diurnal cycle) and dark
110 (never in the light), were employed so as to distinguish between components of degradation
111 (i.e. the difference between light and dark degradation rates is the photo-induced
112 degradation). Experiments were conducted each month over the course of a year so that, a
113 priori, samples were taken across a range of both meteorological conditions and DOC
114 concentrations and compositions. So as not to exclude particulates, the samples were not pre-
115 filtered, and therefore this study could consider the net fate of DOC and could include
116 production from POC or adsorption by it.
117 Water samples were taken on a monthly basis, except January when samples were not
118 obtained from the site as poor weather conditions prevented access to Moor House NNR.
119 Each degradation experiment spanned approximately 70 hours with sacrificial sampling
120 taking place at hour 0, 1, 2, 8, and then at dawn and dusk on day 2, 3 and 4, with light and
121 dark treatments on each month. Fixed numbers of hours since the start of the experiment

were not used in the experiment because change in day length would mean that samples in daylight one month maybe in darkness in a subsequent month, and thus samples were taken relative to dawn and dusk for each period of experimentation each month. Replicates were included within each degradation experiment and over the course of the year each combination of factors was replicated. No hour 0 samples were replicated, but 47% of all other measurements were replicated (187 of 398 samples). Replication was limited by practical constraints of the amount of equipment available and the time taken to process DOC analysis to ensure the short timescales at the beginning of the experiment.

The sampled stream water was poured into acid-washed, quartz glass tubes, stoppered with a rubber bung at the bottom, and loosely stoppered at the top. Quartz glass allows all light wavelengths to pass through it. Dark samples were wrapped in foil to prevent exposure to light. All samples were put outside in trays, with all tubes lying at an angle to prevent rainfall entering and the sample evaporating or pouring out. The angling of the tubes also stopped the light samples being shaded by the top bung and exposed a larger surface area of water to light. The samples were moved to different positions daily to avoid any bias in shading from nearby trees. A data logger with a PAR (photosynthetically active radiation) meter and thermocouple recorded the radiation levels and air temperature at 15-minute intervals throughout the 70-hour period of each month's experiment. Radiation and temperature conditions were summarised as the average conditions over the period for each sample and PAR measurements were summed to give the total radiation experienced by any one sample. The radiation measurements were treated in this way because a sample after 70 hours may have experienced the same average radiation as a sample after 1 day but will have received a larger total radiation dose.

The first day of the experiment was conducted at the field site so the samples were exposed to the same light and temperature conditions as the river. At dusk all tubes were

147 taken to the laboratory and placed outside so they would continue to experience natural light
148 and temperatures with ongoing monitoring of these conditions.

149 The quartz glass tubes had a diameter 55 mm and filled to give a water depth of
150 approximately 150 mm. An examination of the flow stage records for the sample stream
151 showed that 150 mm was the 46.5th percentile flow depth, i.e. 150 mm represented almost
152 median flow depth in the source stream. Light attenuation can be considerable in coloured
153 waters, and Bukaveckas and Robbins-Forbes (2000) have related light attenuation to DOC in
154 74 Adirondack lakes. Taking the best-fit equation from Bukaveckas and Robbins-Forbes
155 (2000) the half-depth of light attenuation could be calculated for the study catchment at the
156 source water in the Cottage Hill Sike and for the measured DOC concentrations (1993 -2010
157 – see below for further details) the inter-quartile range of half depth of light attenuation was
158 150 to 340 mm, i.e. the quartz tubes selected represented 100% of the light penetration 25%
159 of time but 62.5% of the light penetration 75% of the time. Furthermore, at the tidal limit of
160 the study catchment (only a median water transit time of 35 hours from Cottage Hill Sike –
161 Worrall et al. 2014a) the half-depth of light attenuation has an interquartile range of 62 to 102
162 mm but examining the flow stage duration for the tidal limit shows that even 62 mm water
163 depth was only exceeded on 17% of days and 102 mm was exceeded on only 7% of days, i.e.
164 there was almost full light penetration most of the time. Of course, such a light penetration
165 calculation estimates the light conditions experienced by the base of the quartz tube while
166 DOC molecules will move up and down the water column in the quartz tube on convective
167 currents and so experience a range of light conditions greater than those estimated above.
168
169 ***Sample analysis***
170 To achieve the temporal resolution required for this study samples for DOC analysis from
171 degradation experiments were filtered to 0.45 μm, and then "fixed" with concentrated

sulphuric acid. This technique was used because addition of concentrated sulphuric acid is the first step in the analysis of DOC concentration measured using the wet oxidation method described in Bartlett and Ross, (1988). The measurement of DOC concentration was calibrated using standards of oxalic acid of known concentrations, and only calibration curves with an r^2 of 0.95 or above were used. The Bartlett and Ross method is accurate between 2 and 60 mg/l DOC and samples were diluted with deionised water so as to be within this range. At each sampling time a duplicate sample was filtered to 0.45 μm, and used for further analysis. Absorbance at 400 nm was measured a basic (visible) colour reading and the specific absorbance was taken as the absorbance at 400 nm divided by the DOC concentration of the sample. All optical measurements were performed using a UV–Vis spectrophotometer, with a 1 cm cuvette. Blanks of deionised water were used.

Suspended sediment (SS) concentration in each monthly experiment was measured in samples at the beginning, middle and end of each experiment. Samples were filtered through pre-weighed, 0.45 μm, glass fibre filters; dried to 105 °C and the filter paper re-weighed to give the concentration of suspended sediment. The filter papers were then put in a furnace for 4 hours at 550 °C, and then re-weighed. The mass lost in the furnace equates to the mass of particulate organic matter (POM), and 47.5% of this was assumed to be particulate organic carbon (Moody et al. 2013; Worrall et al. 2003).

Conductivity, pH and water temperature of water samples as it left each quartz glass vial were measured by electrode methods to provide covariate information in ANCOVAs. Cations such as Fe and Al were not included in the analysis. However, the stream water at Cottage Hill Sike is regularly sampled as part of the monitoring programme of the Environmental Change Network (www.ecn.ac.uk – Sykes and Lane, 1996.).

Statistical methodology

197 The design of the experiment incorporated three factors: month, sample time and treatment.
198 The month factor had 11 levels (one for each calendar month sampled except for January
199 when weather prevented sampling); sample time had 10 levels (with average hours since start
200 of experiment as: 0, 1, 2, 4.37, 9, 21.96, 30.96, 45.09, 54.48, and 68.87); and treatment had
201 two levels (light and dark). The sample times are the averaged values (each has a standard
202 error) that represent the samples taken on the first day (average hours 0, 1, 2, 4.37, 9), dawn
203 and dusk on day 2 (average hours 21.96 and 30.96), dawn and dusk on day 3 (hours 45.09
204 and 54.48) and dawn on day 4 (average hour 68.87, henceforward referred to as t_{70}).

205 A similar analysis progression was used to Moody et al. (2013) as the experimental
206 design was similar and this allowed comparisons to be made between the two studies. An
207 analysis of variance (ANOVA) was used to assess the significance of all three factors and
208 where possible the interactions between the factors were also determined. Furthermore, the
209 analysis was repeated including covariates (ANCOVA). The covariates used were: pH,
210 conductivity, specific absorbance; and light and temperature variables. The ANOVA and
211 ANCOVA were performed separately so as to explore what effects existed and whether they
212 could be explained by the available covariates. The concentrations of DOC were analysed in
213 both absolute and relative terms where the relative value for each sample in an experiment
214 was expressed as the ratio of the measured value to measurement at hour 0 (t_0) for that
215 experimental run. The magnitude of the effects and interactions of each significant factor and
216 interaction were calculated using the method of Olejnik and Algina (2003). Main effects
217 plots use the least squares means which are marginal means corrected for the influence of all
218 other factors, interactions and covariates, to visualise the data.

219 Guided by the results of the ANOVA and ANCOVA, stepwise linear regression was
220 used to develop empirical models. Variables whose effect was significant at least at 95%
221 probability of not being zero were included in the developed model with the further caveat

that final models were also chosen so as to be physically interpretable. The month factor was transformed into the sinusoidal function: $\left(sin\left(\frac{m\pi}{6}\right) + cos\left(\frac{m\pi}{6}\right)\right)$, where m is the month number (January = 1 to December = 12). Some of the variables were transformed for the sake of physical-interpretability, e.g. reciprocal of the absolute temperature.

The change in DOC concentration and rate of degradation of DOC were considered relative to the individual treatments; i.e. (i) the rate of degradation in the light (total degradation); (ii) the rate of degradation in the dark (biodegradation); and (iii) the difference between the two treatments which was taken as the rate of photic processes.

To perform an initial rate analysis, the rates of DOC degradation were also calculated for the very first hour of each experiment. Worrall et al. (2013) proposed a simple kinetic model for the loss of DOC based upon two zero-order decay processes, one for daylight hours and one for night time. To test this approach the rate of change for the whole days and nights in the first 48 hours of the experiments were calculated, The rates were calculated for day 1 (between t_0 and dusk on day 1), night 1 (between dusk on day 1 and dawn on day 2), day 2 (between dawn and dusk on day 2) and night 2 (between dusk on day 2 and dawn on day 3) of each experiment. These rates then underwent the same ANOVA, ANCOVA and regression process as the DOC concentrations, with the sample time factor being replaced by a "stage" factor with four levels (day 1, night 1, day 2 and night 2).

Priming effect

One aspect of DOC and POC degradation not extensively studied is "priming", that is the extent to which a treatment causes a greater capacity to respond to a second stimulus (Bianchi, 2011). Priming of DOC turnover has been studied under elevated CO_2 conditions in peat cores, where the microbial breakdown of labile soil carbon led to the production of "priming compounds" that are rapidly cycled by microbes causing more carbon to be lost as

CO_2 (Freeman et al. 2004). In this study it is hypothesized that "priming" could be expected to lead to increased rate of breakdown of DOC and POC during the night as a result of exposure to daylight during the day. The presence of a priming effect was tested in two ways. Firstly, if there were priming then there should be a difference between the night time rates measured in samples that have been exposed to light from the night time rate for those samples that have always been in the dark. An ANOVA was performed on the night time rates, using treatment and month as factors with the hypothesis that night time rates would be significantly higher for light treatments. Secondly, the ratio of the night time rate in the light to that in the dark treatments would be one if there was no priming effect; therefore, a single value t-test was used to test whether the ratios of night time rates were different from one.

Apparent quantum yields and activation energies

The apparent quantum yields (AQYs – the extent of reaction per unit concentration of incident photons) were estimated for the photo-induced DOC loss using the change in DOC concentrations, the cumulative light exposure and the number of hours since the beginning of the experiment. The results are presented as a range, due to some instances of photo-production and therefore negative yields. ANOVA and regression analysis were applied to the AQY values, using month and time as factors.

The activation energy was calculated to show the effect of temperature on the rate of degradation in the light, using the universal gas constant, 0.692 J/K/g C.

Results

In total 398 individual experiments with complete covariate information and within the context of the factorial design were conducted and analysed. Summary of the water chemistry over the 70 hours of the study period in light conditions are given in Table 1.

DOC concentrations

For nearly every month of measurement the DOC concentration in both treatments decreased. The average DOC concentration over time showed a steep initial decline, although the rate of decline was still not zero even after 70 hours (Figure 3). The average decline in DOC concentration across all months for samples in daylight was from 42 to 17 mg C/l after 70 hours: when concentrations were judged relative to the DOC_0 concentration (DOC concentration at t_0) then the average decline over 70 hours was 64%. For experiments only in the dark the average decline over a 70-hour period was 6%. The average difference across all times between samples in light and dark was 15 mg C/l with DOC_{70} concentrations (DOC concentrations at t_{70}) of samples kept in the light being on average 58% lower than those kept in the dark when judged relative to the DOC concentration at t_0.

Of all the experiments run, there were 61 experiments (out of a total of 398 experiments) where an increase in DOC concentration was observed relative to the initial DOC concentration. In six of the cases there was a higher DOC_{70} concentration than DOC_0. Given that no raw water samples were filtered prior to inclusion in the experiment it was possible that particles or the microbial population within the sample generated DOC over the course of the experiments. Experiments where there was an increase in DOC over the course of the experiment were not removed from the analysis, as the study was interested in the conversion of POC to DOC and the average fate of DOC.

ANOVA on DOC concentrations

The Anderson–Darling test showed that neither the distribution of DOC concentration nor relative DOC concentration for the experiments conducted in the light, nor those in the dark, met the condition of normality, therefore all subsequent ANOVA were performed on log-

297 transformed data: re-application of the Anderson-Darling test proved that no further
298 transformation was necessary.

299 When the relative concentration data for both treatments (light and dark) were
300 considered without covariates, all single factors were found to be significant (Table 2). The
301 least important single factor was time (explaining only 7% of the variance in the original
302 dataset). The most important factor was treatment, explaining 28% of the original variance.

303 One of the reasons for using relative DOC concentration was to minimize the
304 difference between months. To show that this has been effective, the same ANOVA was
305 carried out on the raw DOC values, and this found that the variance explained by the month
306 factor was substantially smaller when the relative concentrations were used. Even using the
307 relative DOC concentrations there was still a significant effect due to month, this may reflect
308 the importance of the t_0 DOC concentration for the degradation rate (with faster degradation
309 rates associated with higher initial concentrations) rather than a seasonal cycle in degradation
310 behaviour *per se*, which also explains the significant interactions between the month factor
311 and the sample time and the treatment factors. Overall the ANOVA of the relative DOC
312 concentration explained 68% of the variance in the original data. The error term represented
313 15% of the variance. This error term represents the unexplained variance in the model, which
314 was not only due to sampling or measurement error but also variables, factors or their
315 interactions that were not or could not be included in the ANOVA. One possible variable
316 that could not be included is the river discharge at the start of each experiment – this data is
317 not readily available for Cottage Hill Sike.

318 Including covariates in the ANOVA (ANCOVA) showed the most important
319 covariate was the t_0 relative absorbance, followed by DOC_0 concentration. This suggests that
320 degradation rate was concentration and composition dependent.

Guided by the results of the DOC ANOVA and ANCOVA it was possible to give the best-fit equation for the change in the DOC concentration (ΔDOC) in light conditions:

$$\Delta DOC = -1548.23 Abs_0 + 16.38 lnDOC_0 + 2.31 lnt - 39.45$$

(454.5) (2.8) (0.5) (11.4)

n=180, r^2=0.36 (Eq. 1)

where Abs_0 is the specific absorbance at t_0, DOC_0 is the DOC concentration at t_0 (mg C/l), and *t* is the time since the start of the experiment (hours). Only variables that were found to be significantly different from zero at least at a probability of 95% were included. The values in brackets give the standard errors on the coefficients and the constant term. This equation showed that the initial DOC concentrations and composition are significant in determining the change in DOC.

In Moody et al. (2013) the equation for the change in DOC (*ln*ΔDOC – Eq. viii) found the DOC_0 concentration, time since the start of the experiment (in days) and the month of the experiment to be significant, although that equation was derived for four sites used in that study that were situated down the River Tees from the source to the tidal limit. The equation in this study (Eq. 1) found similar factors to be significant, showing that these factors are consistent across different time scales and in two separate experiments.

The r^2 in Moody et al. (2013) was 0.76, whereas the r^2 of Eq. 1 in this study was lower, 0.36, suggesting that the change in DOC concentration is harder to model for the CHS samples alone. This may be because the regression analysis is trying to fit a single straight line through the data, when CHS may benefit from using two lines, one for the initial rapid decrease during the first day and one for the remaining time of the experiment. Analysing the change in DOC concentrations for two sections separately found an r^2 of 0.47 for the first 10

hours (Eq. 2), and 0.33 for the last 60 hours of the experiment (Eq. 3). The equations had three factors in common: the initial DOC concentration, the ∑PAR and $^{1}/_{\sum T}$, however the parameter estimates suggest that both of these latter two parameters were more influential in the first 10 hours. It is interesting to note that neither equation found time of the experiment to be a significant parameter, however both the ∑PAR and cumulative temperature factors will reflect changes in both time and month.

CHS, between t_0 and t_{10}:

$$\Delta DOC = 29.56 lnDOC_0 + 0.19 \sum PAR + \frac{10758}{T} + 4.50\left(sin\left(\frac{\pi m}{6}\right) + cos\left(\frac{\pi m}{6}\right)\right) - 137.04$$

(4.1) (0.06) (6277) (1.2) (29.5)

n=76, r^2=0.47 (Eq. 2)

CHS, between t_{10} and t_{70}:

$$\Delta DOC = 16.75 lnDOC_0 + 0.03 \sum PAR + \frac{14051}{T} - 75.16$$

(3.2) (0.008) (3135) (15.2)

n=96, r^2=0.33 (Eq. 3)

where $\sum PAR$ is the cumulative photosynthetically active radiation experienced by the sample (W/m^2), T is the cumulative temperature (K), m is the month number and all other terms are as described above.

ANOVA on photo-induced degradation

366 The difference between the dark and light concentrations in each experiment was taken as the
367 estimate of the impact of photic processes (Figure 4). The extent of photo-induced
368 degradation could be estimated in 202 cases and the loss due to photo-induced degradation
369 varied from 31 mg C/l to -44 mg C/l (i.e. similar to the above there were 18 occasions where
370 the DOC concentration was observed to increase, implying photo-induced production). Of
371 the 18 occasions where an increase was observed, only four were higher than 10 mg C/l,
372 showing the majority of cases have higher dark DOC than light DOC, or a very small
373 difference between the two. The average difference in DOC concentration that can be
374 ascribed to photo-induced degradation over the 70 hours was -15 mg C/l.

375 The ANOVA shows that all single factors and all interactions were significant (Table
376 3). Two covariates were found to be a significant: the PAR and temperature variables. The
377 month factor, although significant and explaining the highest proportions of the variance in
378 the ANOVA was no longer significant in the ANCOVA. The other significant factor, time,
379 and the significant interaction (time*month) all explain 17% and 11%, respectively, of the
380 variance in the ANOVA.

381 Given the results of the ANOVA it was possible to identify the best-fit equation for
382 the loss due to photo-induced degradation:

383

$$\Delta DOC_{photo} = -3.66\left(sin\left(\frac{\pi m}{6}\right) + cos\left(\frac{\pi m}{6}\right)\right) - 4.60lnt - 4.59lnDOC_0 - \frac{2688}{T} + 17.96$$

384 (1.02) (1.32) (3.18) (2041) (13.13)

385 n=191, r^2=0.21 (Eq. 4)

386

387 where ΔDOC_{photo} is the difference between the dark and light DOC concentrations (mg C/l).
388 The apparent quantum yields (AQYs) were estimated for the photo-induced DOC loss and
389 was found to vary between 82 and -56 mmol C/mol photons; this range is much larger than

the range found in Moody et al. (2013) of 9.6 to -1.7 mmol C/mol photons, and the literature values cited therein (Osburn et al. 2009). The ANOVA on the AQYs found that there were significant differences between the month and time factors, and the interaction of month*time. A regression analysis showed that both month and time were significant:

$$AQY = -3.06\left(sin\left(\frac{\pi m}{6}\right) + cos\left(\frac{\pi m}{6}\right)\right) + 2.81lnt - 12.20$$

(1.09) (0.72) (2.09)

n=173, r^2=0.12 (Eq. 5)

The seasonal cycle exhibited a similar pattern to that described in Moody et al. (2013), with a peak in December and a minimum between February and June, showing the DOC in December was more photodegradable than the DOC in June. The AQY varied with time, having the smallest yields at the beginning of the experiment (Figure 5), showing that exposure to light had the greatest effect on the DOC when it was freshest, early on in the experiment.

The regression analysis on ΔDOC_{photo} (Eq. 4) showed that the DOC loss due to photo-induced degradation could be calculated from the seasonal cycle, sample time, DOC_0 and temperature; all variables that can be easily measured, and therefore the equation is easily physically interpretable and easy to apply to other data sets.

Comparing this equation to that derived in Moody et al. (2013) showed that there are few factors in common, as Eq. ix in Moody et al (2013) found that the t_0 DOC concentration and absorbance at 400 nm were significant in modelling the change in photo-induced DOC.

Rate of degradation in the light

For samples in the light, the degradation rate varied from 37 mg C/l/hour to -5 mg C/l/hour (Figure 6); i.e. increases or no change in DOC concentrations were observed in 3 cases out of 91, showing that the majority of cases have a positive rate of degradation. The average rate of degradation in the light for samples from CHS was 2 mg C/l/hour.

The ANOVA of the rate of degradation for samples in the light showed that only the time factor was significant (Table 4). When included, no covariates were found to be significant, which means that the rate of degradation is not dependent on anything other than time of the experiment. Guided by the results of the ANOVA, the best-fit equation for degradation rate in the light treatment was calculated:

$$lnrate_{light} = 0.08 - 0.79lnt + \frac{277}{T} + 0.00024\sum PAR$$

(0.8) (0.1) (228) (0.0005)

n=141, r^2=0.57 (Eq. 6)

where $rate_{light}$ is the rate of DOC change in the light treatment, and all other terms are as described above.

The regression analysis showed that the cumulative light exposure and inverse temperature, along with the time since the start of the experiment, were significant in determining the rate of DOC degradation, suggesting that the DOC degradation was influenced by environmental factors, such as the temperature and weather during the experiments.

Moody et al. (2013; Eq. x) found the rate of degradation in the light to be dependent on the DOC_0, time since the start of the experiment and the inverse temperature. This shows that the temperature and time since the start of the experiment are consistently significant in

436 modelling the rate of DOC degradation in the light over the two time scales considered by
437 this study and by Moody et al. (2013).

438 As the reciprocal of absolute temperature was significant in the regression equation
439 (Eq. 6), it was possible to estimate the activation energy of the degradation to be 0.19 ± 0.16
440 kJ/g C. This is considerably lower than the value found by Moody et al. (2013) of 2.6 ± 1.2
441 kJ/g C, suggesting that the degradation for DOC from CHS is much less sensitive to changes
442 in temperature than the average of the four sites used in Moody et al (2013).

443

444 ***Rate of degradation in the dark***

445 It was possible to calculate the rate of degradation in the dark in 91 experiments, which
446 ranged from a decrease of 28 mg C/l/hour to -5 mg C/l/hour, (in 8 cases, an increase or no
447 change in DOC concentration was observed). The median value for the rates of dark
448 degradation was 0.005 mg C/l/hour, i.e. the majority of the rates were negligible (Figure 6).
449 For the rate of degradation in the dark, the ANOVA and ANCOVA show that no factors or
450 covariates were significant (Table 4); even so regression was attempted, but no significant
451 variables were found. There were no significant differences between the rates at different
452 times during the experiment. Moody et al. (2013) found that the rate of degradation in the
453 dark could be modelled from the DOC_0, time since the start of the experiment, month of the
454 experiment and inverse temperature (Eq. xi), but applying that equation to the data in this
455 study found none of the same variables to be significant.

456

457 ***The rate of photo-induced degradation***

458 The rate of the photo-induced degradation could be calculated from 91 experiments and
459 varied from 36 mg C/l/hour to -13 mg C/l/hour, (in 10 cases an increase or no change was
460 observed). The average rate of photo-induced degradation was 1 mg C/l/hour. Time was

found to be significant (Table 4) in an ANOVA and when included no covariates were found to be significant. Guided by the ANOVA, a regression was calculated:

$$lnrate_{photo} = 1.8 - 1.12lnt$$

(0.2) (0.1)

n= 59, r^2=0.7 (Eq. 7)

where $rate_{photo}$ is the rate of photo-induced degradation (mg C/l/hour) and t is the time in hours since the beginning of the experiment.

The regression shows that the only factor affecting the rate of photo-induced degradation is the time since the start of the experiment. The same equation in Moody et al. (2013) found that DOC_0, time since the start of the experiment, month of the experiment and cumulative PAR to be significant (Eq. xii), making those more complicated than the equation found in this section. Also the equation in Moody et al. (2013) has a much lower r^2 than these equations, once again showing the benefit of the sub-daily sampling times.

Rate of degradation during each day and night

The rates in each stage varied from 10 mg C/l/hour in the light during day 1 (between t_0 and dusk on day 1) to -2 mg C/l/hour in the dark during night 1 (between dusk on day 1 and dawn on day 2).

The ANOVA found all three factors significant (Table 5), as well as three interactions: treatment*stage, treatment*month, and stage*month. Stage explains the largest proportion of the variance (27%) followed by the interaction of stage*month (14%), showing that the rates of DOC degradation differ significantly between the four stages of the experiment and between months. However, there was no clear seasonal cycle to the rates

during each stage. The relationship between treatment and stage showed the significant differences between the average rates per stage for treatments, with the night rates being not significantly different from zero (Figure 7). There were no significant covariates.

The rates of degradation in the light treatment during the first two days and nights were modelled using ANOVA, and it was found that the stage of the experiment was significant, and no month factor or DOC_0 concentration was significant, i.e. it would be reasonable to use single zero-order rates for day 1, day 2, night 1 and night 2 without correction and that would account for 45% of the original variance. This is a large proportion of the variation accounted for by the rate at each stage, comparable to the results of the more sophisticated ANCOVA above. The rates of degradation are interesting as they represent the rate of change in the newest, freshest material in the river system.

Initial rates of degradation

The initial rates of DOC degradation (during the first hour of the experiment) varied from 38 to -8 mg C/l/hour. The average rate in the light treatment was 12 mg C/l/hour, and in the dark treatment was 4 mg C/l/hour.

An ANOVA on the rates of degradation during the first hour of the experiment had two factors, treatment and month. The ANOVA found all factors and interactions were significant (Table 6). The month factor explained the largest proportion of the variance (38%), closely followed by the interaction of month*treatment, showing that the initial rates of DOC degradation differ significantly between the treatments and between months. Again, there was no clear seasonal cycle to the monthly initial rates. Once covariates were added, the DOC_0 concentration was significant, and the month factor was no longer significant. This shows that the initial rate of DOC degradation is dependent in the initial concentration of

DOC, and the monthly differences found in the ANOVA are likely due to the monthly differences in the DOC_0 concentration.

Guided by the results of the ANCOVA, the following rate equation could be derived for the light treatment:

$$lnrate_0 = 2.3lnDOC_0 + 0.6cos\left(\frac{\pi m}{6}\right) - 6.3$$

(0.7) (0.3) (2.6)

n= 18, r^2=0.5 (Eq. 8)

where $rate_0$ is the initial rate of DOC change (mg C/l/hour), DOC_0 is the initial DOC concentration and *m* is month number (1 = January, 12 = December).

This regression shows that the factors affecting the initial rate are the initial DOC concentration and a seasonal factor. This method of analysis would suggest that at CHS in the light, the initial important reaction is of the order 2.3 ±0.7 which is not significantly different from second or third order. However it is most likely to be fractional or mixed order because of the number of potential processes contributing.

Priming

The average night time rates for the two treatments were -0.2 ± 0.13 mg C/l/hour in the dark treatment and 0.1 ± 0.07 mg C/l/hour in the light treatment. An ANOVA based on the night time rates, using treatment and month as factors, found no significant differences in the rate of degradation. Secondly, a single sample t-test was used which showed that the mean ratio was 2.15 (95% ci = 0.31 – 3.98) i.e. not significantly different from 1 at the 95% probability. Therefore it was concluded that there was no priming effect.

533 ***POC concentrations***

534 The suspended sediment concentrations were measured in each of the 11 months at the
535 beginning, middle and end of the experiments. Six months of these suspended sediment
536 measurements were analysed further to calculate the particulate organic matter (POM)
537 concentrations, resulting in 62 POM measurements. Extrapolating from the six months of
538 data, the percentage of POM, and therefore POC, was calculated, and applied to the whole
539 suspended sediment data set, resulting in a year of calculated POC concentrations.

540 The average change in POC concentration across all months for samples in the
541 daylight was from 7 to 6 mg C/l after 70 hours; this is a decrease of 13%. The POC
542 concentration in samples kept in the dark increased between t_0 and t_{70} (average increase of
543 45%). Again, the change at CHS in the light is the most interesting number as the POC at
544 CHS will be the newest material into the river and so the change in its concentration
545 treatment represents the most realistic scenario.

546 The Anderson-Darling test showed that the distribution of POC concentration did not
547 meet the conditions of normality, and so the data was log transformed. An ANOVA on POC
548 concentrations found that time and month were significant single factors, as was the
549 interaction between them (Table 7). Month explained the highest proportion of the original
550 variance (26%). An ANCOVA found no covariates were significant, and although a
551 regression was attempted, no significant equation could be calculated, even using only the
552 daylight samples.

553

554 **Discussion**

555 Moody et al. (2013) found 73% DOC removal over 10 days. If this rate of loss were
556 constant, it would relate to a 21% loss in 70 hours. This is a lower estimate than found in this
557 study (64%), although the former experiment was conducted over 10 days rather than 70

558 hours, and presuming a constant rate of loss is unrealistic, especially as the majority of the
559 decline occurred in the first two days of the experiments. Ten days is much longer than the
560 residence times of most British rivers across a wide range of flows, and so will not provide a
561 reliable estimate of the in-river loss of DOC. The more frequent sampling of this study
562 enabled sub-daily rates to be calculated, and therefore the day/night rates could be compared.
563 This led to the diurnal cycle that would not be observed in experiments where samples were
564 only taken daily which could lead to over/under estimates of DOC losses though degradation.
565 For Moody et al. (2013), the rates of loss in the light and dark in the first day were
566 calculated as 72 mg C/l/day and 49 mg C/l/day respectively. However, this was the total loss
567 of DOC between the beginning of the experiment and day 1 (approximately 24 hours),
568 whereas in this study, the value was for the first stage of light of the experiment, between the
569 beginning of the experiment and dusk on day 1. A rate of loss in the first hour for Moody et
570 al. (2013) was calculated by dividing the rate for the whole first day by 24, resulting in a loss
571 of 3 mg/l/hour in the light and 2 mg /l/hour in the dark. This method for calculating the rates
572 had certain drawbacks, as it assumed a constant rate of loss over the 24 hours and resulted in
573 initial rates much lower than those measured in this study (12 mg C/l/hour in the light and 4
574 mg C/l/hour in the dark). It could be assumed that of the first 24 hours, 12 of them were the
575 hours of darkness, when the rate of DOC decline in the light treatment was negligible in this
576 study, and so the total DOC loss in Moody et al. (2013) actually took place in the 12 hours of
577 daylight, resulting in the rate in the light being 6 mg C/l/hour, more comparable rate to this
578 study. The rate of DOC decline in the dark treatment would not be as affected by the change
579 between daylight and darkness, and so the estimate for the decline in the first hour may be
580 fairly accurate, as it is similar to the value for the rate in the dark from this study. Removal
581 rates reported in the literature for similar environments range from 21% (Battin et al. 2009) to

582 70% (Gennings et al. 2001), so the loss of 64% from this study is not unprecedented,
583 however it is towards to higher end of the literature ranges.

584 To scale up the DOC loss from the Tees to the whole UK, the UK DOC export
585 estimate for peat-covered catchments of 555-1263 Gg C/yr (Worrall et al. 2012) and the
586 estimate of the POC flux from the UK of 312-2178 Gg C/yr (Worrall et al. 2014b) were used,
587 in conjunction with the 13% loss of POC and the 64% loss of DOC loss from this study.
588 Applying the 64% loss of DOC to this would suggest the DOC flux at the source would have
589 been 1542-3508 Gg C/yr. Loss of DOC to the atmosphere would be 987-2245 Gg C/yr, or
590 3619-8231 Gg CO_{2eq}/yr (14.86-33.79 Mg CO_{2eq}/km^2/yr from the UK). The 13% loss of POC
591 observed in this study would equate to a POC flux at the source of 359-2503 Gg C/yr, and
592 loss of POC to the atmosphere would be 47-325 Gg C/yr, or 171-1194 Gg CO_{2eq}/yr (0.70-
593 4.90 Mg CO_{2eq}/km^2/yr from the UK). These CO_2 emission values assume that 100% of the
594 DOC and POC lost from a catchment is lost to the atmosphere.

595 The total CO_2 emissions from the UK in 2012 were 580.5 Tg CO_{2eq} (Department of
596 Energy and Climate Change, 2014). The upper estimate from DOC loss of 8.2 Tg CO_2/yr
597 from rivers in the UK is 1.4% of the UK total emissions, and larger than the CO_2 emissions
598 from the public sector (8 Tg), although it is still much lower than the emissions from the
599 energy supply (204 Tg) and transport (122 Tg) sectors (Department of Energy and Climate
600 Change, 2012). The maximum CO_2 from POC losses equates to 1.2 Tg CO_2/yr, and is
601 therefore a smaller flux than from any individual sector; however it increases the total
602 greenhouse gas contribution from UK rivers to 9.4 Tg CO_2/yr.

603 Recent estimates of the global CO_2 emissions from inland waters are 1.8 Pg/yr (1.5-
604 2.1 Pg/yr) from streams and rivers and 0.3 Pg/yr (0.06-0.84 Pg/yr) from lakes and reservoirs
605 (Raymond et al. 2013). The total inland water CO_2 flux from Raymond et al. (2013) is larger
606 than the estimates from the fifth assessment by the IPCC (IPCC, 2013) that has a flux of 1 Pg

607 C/yr degassing from freshwater lakes/reservoirs. The UK is the 80th largest country in the
608 world, covering 0.16% of the Earth's land area (CIA, 2010). The estimate of total organic
609 carbon loss of 9.4 Tg CO_2/yr from this study for UK is 0.52% of the total CO_2 emissions
610 from inland waters from Raymond et al. (2013), or 0.94% of the estimate from the 2013
611 IPCC (2013), meaning that the UK inland water CO_2 emissions account for a larger
612 proportion of the global CO_2 water emissions that the total land area suggests it should. This
613 could be that the total inland water CO_2 flux from the UK is higher than expected due to the
614 disproportionately high contribution of low-order streams to the CO_2 flux found by Raymond
615 et al. (2013). The rivers of the UK are generally small and organic-rich, compared with
616 world rivers, and the majority of DOC and POC losses measured in this study were from low-
617 order streams, potentially resulting in over-estimates of loss as CO_2. The higher than
618 expected contribution from the UK inland waters to the global CO_2 flux than the land area of
619 the UK suggests it should be could also be due to the high percentage of land covered by
620 deep peat in the UK. This is linked to high and increasing DOC fluxes, and therefore high
621 losses of organic carbon as CO_2, especially in low-order streams.

622 This study shows the importance of the diurnal cycle in flux calculations. Previous
623 estimates of flux that do not account for the diurnal cycle of in-stream processing are prone to
624 under/over estimation, due to the times of day at which the majority of samples are taken.
625 Residence times of rivers are rarely an exact multiple of 24, and so estimates of fluxes based
626 on measurements during the day and extrapolated to represent the whole 24 hours will
627 overestimate the flux, as the night time flux is unlikely to be the same as the flux during
628 daylight. Worrall et al. (2013) developed a 'correction factor' dependent on the residence
629 time of the water body and the day:night ratio of the biogeochemical process being
630 investigated. They applied their model to the flux on the River Tees and found that fluxes
631 could have been overestimated by between 5 and 25%. Using their model and the median

first day and first night rates found in this study for the CHS L treatment, it was calculated that sampling at 9am would have underestimated the flux of DOC by 46%, compared to sampling at every hour on every day. This demonstrates the need to take the diurnal cycle into account when scaling up fluxes.

In this study, as Moody et al. (2013), the DOC concentration does not become zero during the experiment, suggesting that something other than time is limiting the DOC degradation. A number of factors could be limiting the degradation, for example, the nutrient concentration of the river water or autochthonous production of DOC that means over all concentration does not decrease but reaches a position of quasi-equilibrium.

Conclusion

This study found the average loss of DOC in light conditions was 64% over 70 hours with the majority of the loss occurring within the first 10 hours of daylight. The study found a strong diurnal cycle, with the average rates of headwater DOC degradation during the daylight being approximately 30 times higher than those during the night for the same treatment. The analysis of the initial rates of DOC degradation in the light found that that a 2^{nd} order, or a mixed order reaction best explains the process.

Acknowledgements

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751 Worrall F, Burt TP, Howden NJK (2014b) The fluvial flux of particulate organic matter from
752 the UK: Quantifying in-stream losses and carbon sinks. Journal of Hydrology 519:611-
753 625.

754 Table 1. Mean and coefficient of variation (CV - %) for al months of data from Cottage Hill
755 Sike (CHS) for the range of times considered in the study.
756

Determinant	Cottage Hill Sike (CHS)			
	t_0		t_{70}	
	Mean	CV (%)	Mean	CV (%)
POC (mg C/l)	2.86	31	3.23	14
Conductivity (μS/cm)	35.87	25	78.23	61
pH	4.57	14	6.34	5
DOC (mg C/l)	41.75	30	16.52	85
Abs_{400}	0.16	39	0.17	45

757
758

759 Table 2. Results of ANOVA for relative DOC concentrations for all experiments across both
760 daylight and dark treatments.
761

	Without covariates		With covariates	
Factor (or covariate)	p	ω^2	p	ω^2
Abs_{400}/DOC_0	na		<0.0001	4.94
DOC_0	na		0.0161	0.67
treatment	<0.0001	27.93	<0.0001	33.31
time	<0.0001	6.67	<0.0001	3.65
month	<0.0001	10.62	ns	-
treatment*time	<0.0001	6.20	<0.0001	4.42
treatment*month	<0.0001	13.48	ns	-
time*month	0.0070	2.65	ns	-
Error		15.19		3.47

762
763

764 Table 3. Results of ANOVA for the difference in DOC concentrations between light and
765 dark treatments, attributed to photo-induced degradation.
766

	Without covariates		With covariates	
Factor (or covariate)	p	ω^2	p	ω^2
1/T	na	-	0.0003	6.10
∑PAR	na	-	0.0059	3.35
time	<0.0001	16.60	0.002	12.10
month	<0.0001	36.59	ns	-
time*month	0.0008	10.83	ns	-
Error		21.87		1.98

767
768

769 Table 4. The results of ANOVA of the degradation rates of DOC

		Without covariates		
Variable	Factor	p	ω^2	Error
Light rate	time	<0.0001	35.21	5.98
Dark rate	-	ns	-	-
Photo rate	time	0.0206	11.19	8.00

770

771

772 Table 5. The results of the ANOVA on the rates of degradation in each stage.

	Without covariates	
Factor	p	ω^2
treatment	<0.0001	6.87
stage	<0.0001	27.15
month	0.0383	2.06
treatment*stage	<0.0001	11.76
treatment*month	0.0183	2.59
stage*month	<0.0001	13.91
Error		12.17

773

774 Table 6. The results of the ANOVA on the rates of degradation in the first hour.

775

Factor (or covariate)	Without covariates		With covariates	
	p	ω^2	p	ω^2
DOC_0	na	-	<0.0001	30.23
treatment	<0.0001	10.94	0.0065	9.84
month	<0.0001	38.29	ns	-
treatment*month	<0.0001	34.20	ns	-
Error		8.25		3.32

776

777

778 Table 7. The results of ANOVA of the POC concentrations.

779

	Without covariates	
Factor	p	ω^2
time	0.0016	4.70
month	<0.0001	25.96
time*month	<0.0001	19.12
Error		24.32

780

781

Fig 1. Schematic diagram of the DOC processing within a peat-sourced stream, adapted from Moody et al. (2013).

Fig 2. Location of the site and study catchment.

Fig 3. The main effects plot of relative DOC concentration change for light and dark treatments over the course of the experiment. Error bars give the standard error.

Fig 4. The main effects plot of the change in loss due to photo-induced degradation over the course of the experiment. Error bars give the standard error.

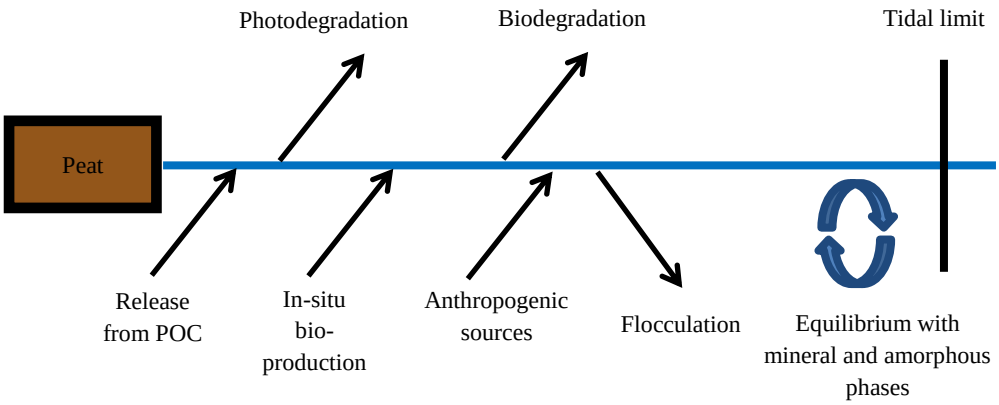
Fig 5. Main effects plot of the apparent quantum yield (AQY) over time in the experiment. Error bars give the standard error.

Fig 6. Main effects plot of rate of DOC loss in light and dark treatments over time in the experiment. Error bars give the standard error.

Fig 7. The main effects plot of average rates of DOC degradation per stage of the experiment for both treatments. Error bars give the standard error.

803 **Fig 1.**

804



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808 **Fig 2.**

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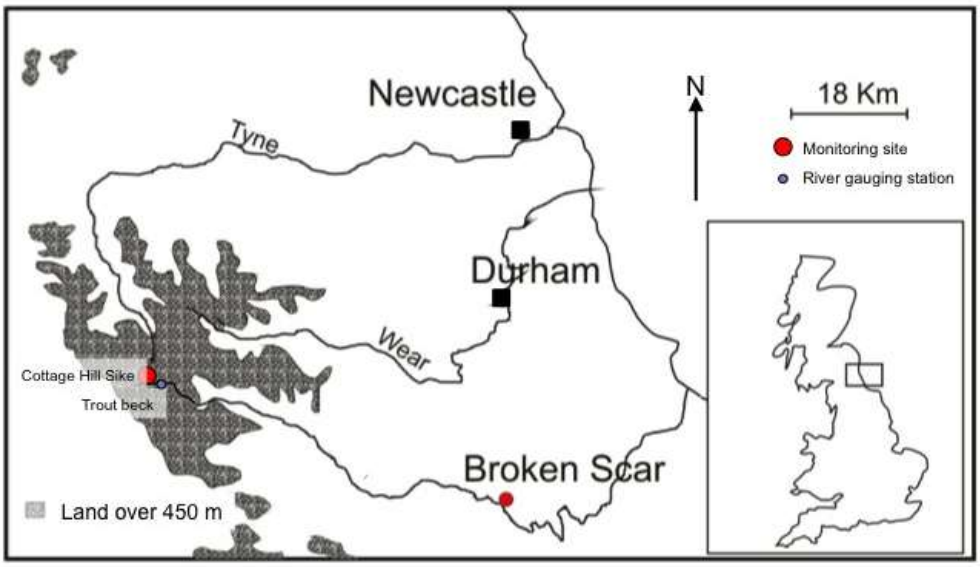

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812 **Fig 3.**

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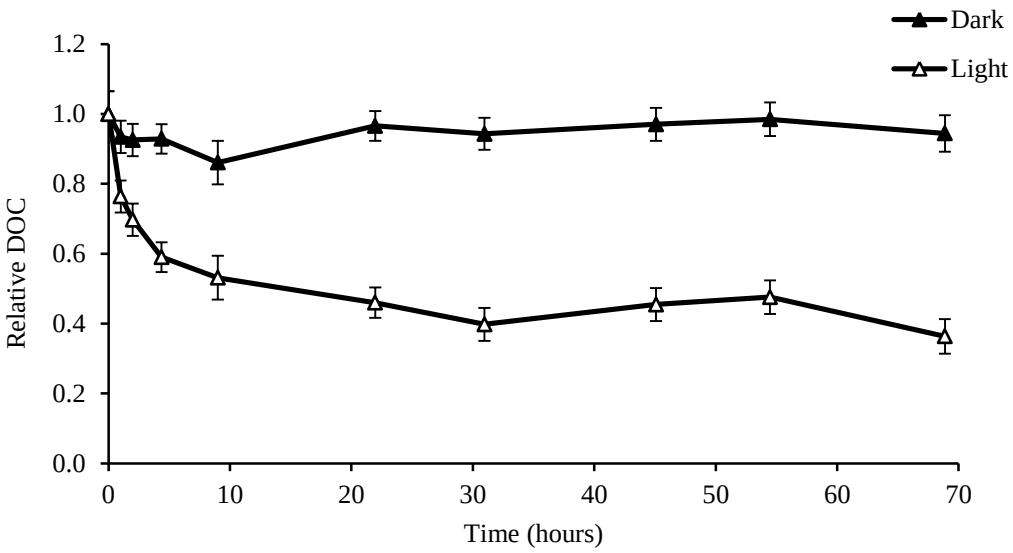

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817 **Fig 4.**

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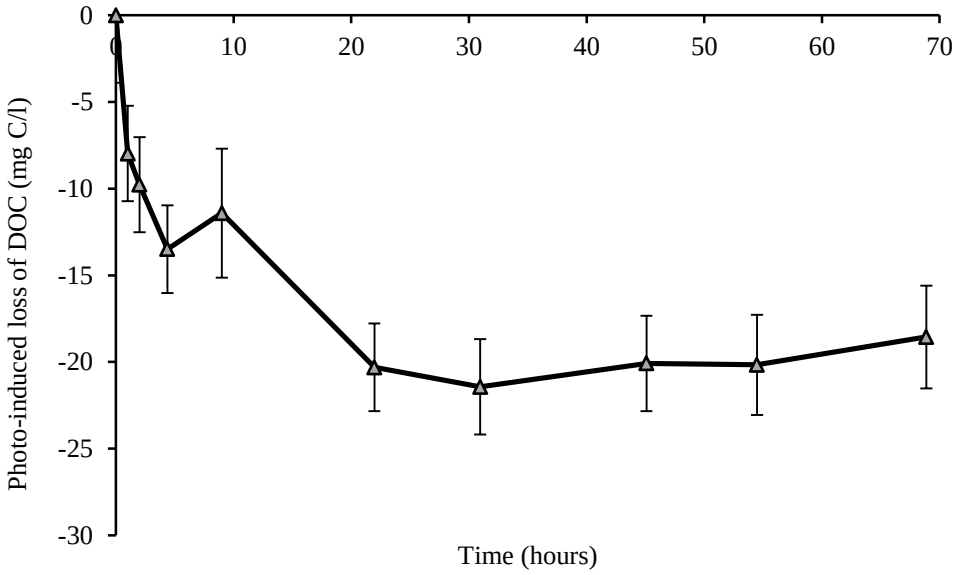

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821 **Fig 5.**

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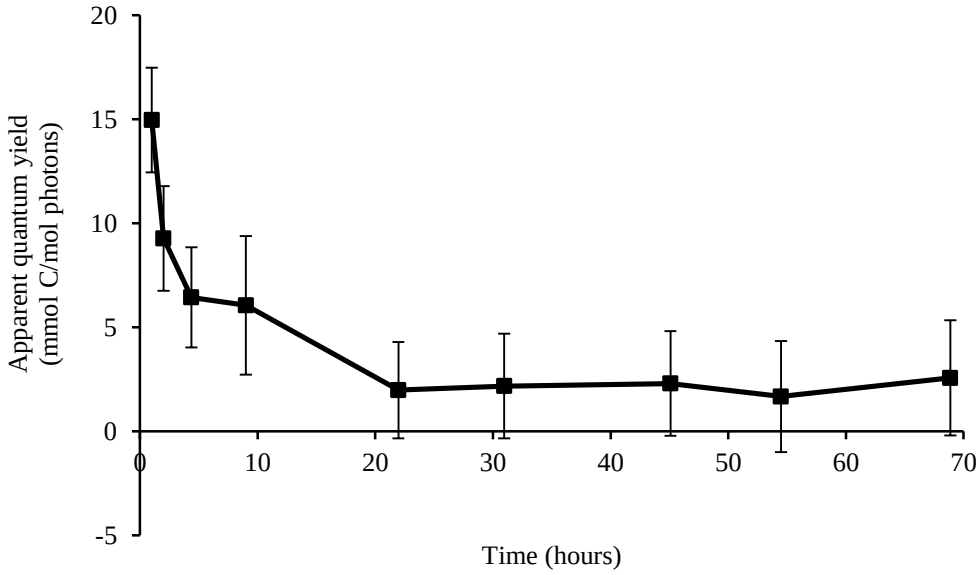

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826 **Fig 6.**

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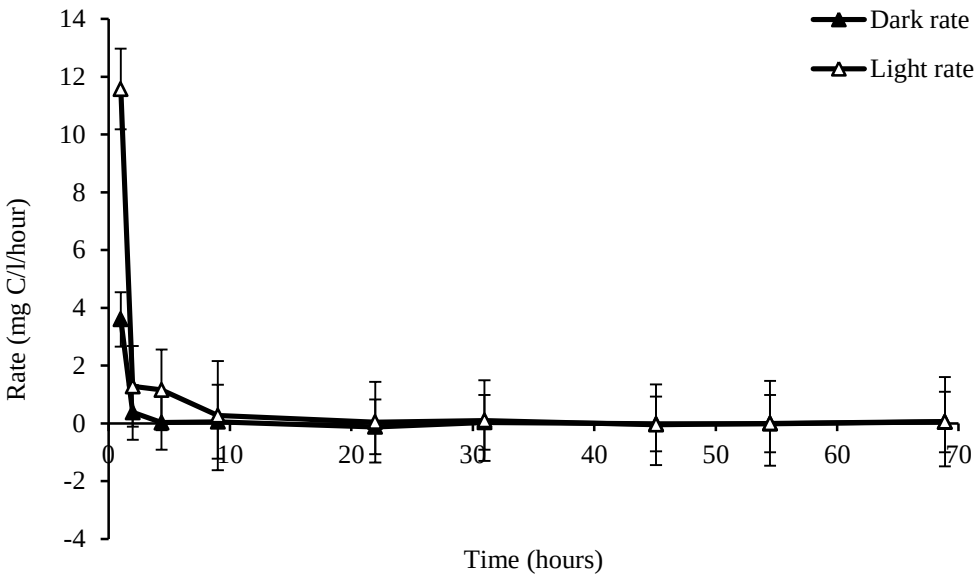

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830 **Fig 7.**

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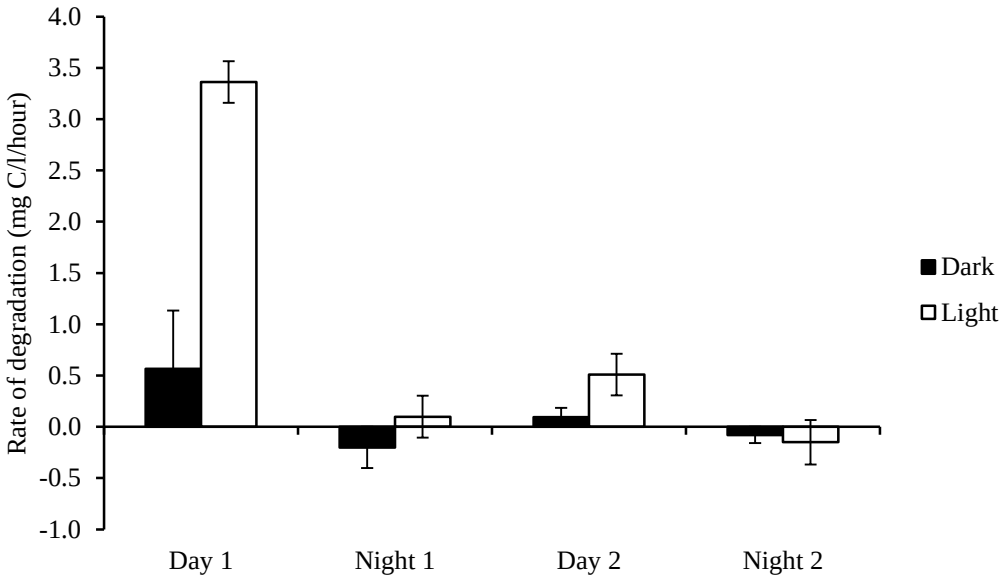

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