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Moody, C.S.; Worrall, F.; Evans, C.D.; Jones, T.G.. 2013. **The rate of loss of dissolved organic carbon (DOC) through a catchment.**

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# THE RATE OF LOSS OF DISSOLVED ORGANIC CARBON (DOC) THROUGH A CATCHMENT

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## Abstract

Given observed trends in the concentration of DOC in surface waters in northern hemisphere the degradation of DOC to CO<sub>2</sub> could represent a major and increasing source of greenhouse gas to the atmosphere. However, studies of DOC turnover in rivers have been predominantly based upon mass balance studies and empirical studies have focused upon lakes and estuaries which have far longer residence times than would be the case for transit via rivers. The study measured DOC loss in unfiltered river water samples across an 818 km<sup>2</sup> catchment every month for a year and considered total loss, photo and aphotic degradation as well as the rates of each process. The study found:

- i) Rate of total DOC change in daylight varied from loss of 30.1 mg C/l/day to an increase of 3.5 mg C/l/day: the average loss was 73% over 10 days.
- ii) Rate of change due to photic processes varied from decrease of 19.4 mg C/l/day to an increase of 6 mg C/l/day, i.e. net photo-induced production was possible.
- iii) Activation energy of the degradation was estimated as  $2.6 \pm 1.2$  kJ/gC.
- iv) The apparent quantum yield varied from 9.6 and -1.7 mmol C/mol photons.

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- v) Coupling models of total loss of DOC with estimates of in-stream residence times showed that annual loss rates of DOC across the 818 km<sup>2</sup> catchment would be between 48 and 69%, in line with estimates from mass balance studies, implying that in-stream DOC degradation represents a large, indirect source of CO<sub>2</sub> emissions from peats and other organic soils.
- vi) Annual rate of removal was increasing in line with increasing loss of DOC at source, implying that observed DOC trends are leading to increased CO<sub>2</sub> emissions.

## Introduction

The flux of dissolved organic carbon (DOC) from the terrestrial biosphere to the world's oceans has now been widely recognised as an important component of terrestrial carbon budgets particularly from highly organic soils, e.g. peats (Aitkenhead et al., 2007). Several attempts have been made to estimate the flux of DOC from the terrestrial biosphere. Meybeck (1993) estimated that the global river flux of DOC was 200 Mtonnes C/yr. Ludwig et al (1996) used a spatially-explicit model of global fluvial C fluxes to obtain an estimate of 400 Mtonnes C/yr, with a split of approximately 40:20:20 for DOC:POC:DIC. Harrison et al. (2005) estimated global river flux of DOC as 170 Mtonnes C/yr. For individual environments the export of DOC varies considerably: for lowland arable environments estimates of 0.9 and 1.9 tonnes C/km<sup>2</sup>/yr have been reported (Royer and David (2005), Dalzell et al. (2007)); for lowland grassland 0.8 and 5.5 tonnes C/km<sup>2</sup>/yr (Don and Schulze, 2008); and for forested sites of between 1.5 and 5.3 tonnes C/km<sup>2</sup>/yr (Hope et al., 1997). Worrall et al. (2012) gathered information from 33 peat-covered catchments (all less than 40 km<sup>2</sup>) from across the UK and found DOC export varied from 10.3 to 95.6 tonnes C/km<sup>2</sup>/yr. Most studies calculate flux of DOC at the outlet of catchments, which may range from < 1 km<sup>2</sup> to 818 km<sup>2</sup>. In general the rivers can be considered conduits rather than sources of DOC, since in-stream

(autochthonous) production is commonly low in peat streams relative to the soil source (Eatherall et al., 2000). By calculating the flux at the river output, the calculation ignores any processing that may have occurred prior to that point. Loss of DIC through degassing of CO<sub>2</sub> from lakes, reservoirs and streams can represent an exceptionally high loss of terrestrial C. Kempe (1982, 1984) recognised that many surface freshwater bodies were saturated with respect to CO<sub>2</sub> and would therefore be sources of CO<sub>2</sub> to the atmosphere. Not only is dissolved CO<sub>2</sub> lost in transit within the river system, but DOC will also be mineralised within the river system from its source to the river outlet (Richey et al. 2002): there will also be the possibility of autochthonous production of DOC within the river network although in peat covered catchments it is generally found to be not as great as the amount of allochthonous DOC (Eatherall et al., 2000). Therefore measuring DOC flux solely at the river outlet provides a likely underestimate of the loss of carbon (and therefore greenhouse gas emissions) from the terrestrial biosphere. Cole et al. (2007) have estimated that at a global scale 1.9 Pg C/yr enters rivers of which 0.8 Pg C/yr (42% of the input) is returned to the atmosphere, while Battin et al. (2009) suggested a lower limit of 21% removal of DOC in-stream. The IPCC now include an estimate of global DOC flux (Solomon et al., 2007) but do not yet consider any losses of DOC in-stream and so this flux value has no direct impact upon atmospheric greenhouse gases.

In-stream processing of DOC and POC is often referred to or invoked as an explanation or implication of the research in the literature, but is rarely quantified. Within streams there are a range of processes that could remove, degrade or add DOC to the flux (Fig. 1). The concept of the river spiralling and the continuum (Newbold et al., 1982) deals with the fate of all carbon (and nutrients) within a river system, but does not address the fate of individual components of the total carbon flux. However, in-stream fauna can utilise DOC and biodegradation interacts with light to speed up degradation (Moran and Zepp, 1997). The

stream fauna and flora have the potential for autochthonous DOC production and autochthonous DOC has been reported as less prone to biodegradation and less prone to photosensitisation to biodegradation, i.e. they are resistant to biodegradation and the action of light does not make them biodegradable (Obernosterer and Benner, 2004). Sunlight and especially ultraviolet radiation will oxidise DOC to CO<sub>2</sub> and CO as well as lower weight molecular organic compounds. Rates of photodecomposition in the field are generally reported for long residence time systems, e.g. lakes (Kopacek et al., 2003) or estuaries (Moran et al., 2000): rates of approximately,  $9 \times 10^{-3} - 0.4$  mg C/l/day have been reported in lakes (e.g. Graneli et al., 1996). Photodecomposition can be catalysed by the presence of other chemical species, especially Fe, and cannot be considered independent of biodegradation (e.g. Anesio et al., 2005). Flocculation with Fe and Al can remove DOC from solution (Sharp et al., 2006) or at least facilitate photoaggregation (Maurice et al., 2002). Peat-hosted streams, which are such significant sources of DOC (Aitkenhead et al., 2007), tend to be acidic, and although generally low in ionic strength this can permit Fe and Al to be mobilised, with a consequential potential for flocculation and as stream pH rises through a catchment causing Fe and Al-oxyhydroxides to precipitate out of solution; McKnight et al. (1992) showed that such mixing of streams resulted in an average 40% removal of DOC. Equally, the solubility of DOC increases with increasing pH (Lumsden et al., 2001; Evans et al., 2012) and so DOC could desorb from POC if stream pH increased across a catchment. The work that has been done has mostly concentrated on 'old' DOC and biodegradation, and has looked at the efflux of CO<sub>2</sub> rather than the decrease in DOC concentrations (e.g. Algesten et al., 2004) and in systems where the residence time of the water would be months (e.g. lakes), rather than hours and days as is the case in rivers.

Several attempts have been made to quantify the loss of DOC across a catchment. Worrall et al. (2006) used a mass balance approach to calculate the DOC export at a range of

scales to show an average net loss of 40% of DOC from source to outlet across an 818 km<sup>2</sup> catchment. Worrall et al. (2007) used nationally-collected monitoring data for biochemical oxygen demand (BOD) as a measure of DOC turnover and found an average 31% loss across the UK fluvial network – equivalent to an additional release of 1 tonne C/km<sup>2</sup>/yr across the entire UK land surface. However, in basing their approach upon BOD data a fixed fluvial residence time of 5 days was assumed – a long residence time for the short, relatively-unimpounded rivers of the UK (although in the peatland areas surface water storage in reservoirs is more common). What is more, BOD tends to be measured low down in the fluvial network and away from sources of fresh more readily degraded DOC. Alternatively, Worrall et al. (2012) used empirical and structural modelling of the DOC export from over 194 catchments across the UK, across 7 years and in comparison to the soil, land-use and hydro-climatic characteristics of each catchment to assess net watershed losses. A net watershed loss of DOC up to 78% was found, equivalent to between 9.0 and 12.7 tonnes C/km<sup>2</sup> of UK land area/yr. These figures are comparatively large when compared to other studies and did not include actual DOC measurements. Wickland et al. (2007) observed measured 6-15% conversion of pore-water DOC to CO<sub>2</sub>, and 10-90% conversion of the vegetation-derived DOC, during one-month dark incubations, and del Georgio and Pace (2008) measured rates of loss as low as 0.4%/day, but again for dark incubations of fluvial DOC. The latter study was also for samples from near the tidal limit of the Hudson River, i.e. samples that would already have been in the river for many days. Jonsson et al. (2007) estimated that around 50% of terrestrially-derived organic carbon was mineralised but for a lake catchment where residence times would be long relative to the UK. Dawson et al. (2001) did consider a short river reach (2 km) in a peat headwater and estimated that 12-18% of DOC was removed. Wallin et al. (2013) considered a 67km<sup>2</sup> boreal catchment and found that CO<sub>2</sub> evasion from the streams represented 53% of the flux of carbon in the streams, some of

this CO<sub>2</sub> evasion would be due to rapid turnover of DOC in low order streams. So the objectives of this study were to: measure the loss of DOC from source to sea along a short residence time river system (rather than in a long residence-time lake which receive DOC that may be several days old and so already refractory); assess the controls on DOC degradation and loss; and thus estimate the extent of loss of DOC across a catchment.

## **Approach and Methodology**

This study conducted in situ degradation measurements of DOC from the headwater to the former tidal limit of a major UK river, the Tees, whose headwaters are peat-covered and where DOC fluxes have been extensively studied (e.g. Worrall et al., 2008). The in-situ experiments were conducted so that it was possible to measure total loss of DOC; loss of DOC in darkness (and therefore by difference the loss due to photolytic processes); and the rate of each of these processes. Results from degradation experiments were used to construct empirical rate laws that were combined with a time series of headwater DOC concentration and estimates of in-stream residence times so that estimates of total DOC loss from the catchment could be made.

## ***Study sites***

This study considers four sites along the River Tees, northern England (Figure 2 – Table 1). The River Tees flows 132 km from its source at Moor House National Nature Reserve, before draining in to the North Sea, although the estuary is cut off by a total exclusion tidal barrage. Four sites were chosen from upstream of the barrage that differed by almost orders of magnitude in their upstream catchment area, each of which was co-located with a river flow gauging station. The two lowest order stream sites (CHS and TB – Table 1) are within the Moor House National Nature Reserve (NNR), the most extensively studied of all UK

peatlands (Billett et al., 2010), with 100% and 90% deep peat cover within their respective catchments. The Moor House NNR is part of the Environmental Change Network (ECN) monitoring programme which means that DOC concentration has been monitored in the streamwater at these sites weekly since 1993 (Worrall et al., 2009). Equally, the most downstream site (Broken Scar, DBS) is co-located with a water treatment works where water colour (not DOC concentration) has been measured daily since 1970 (Worrall et al., 2008).

### ***Degradation measurement***

The degradation measurements were made outside of the laboratory in ambient light and temperature conditions (rather than indoors under artificially controlled conditions). The study considered degradation in light and dark so as to distinguish between possible components of degradation (eg. photo-induced degradation), and measured degradation over timescales relevant to river residence times. Experiments were conducted each month on each site over the course of a year in order to experience a range of both meteorological conditions and DOC concentrations and compositions. The samples were not pre-filtered to exclude particulates, because this meant that the study considered the net fate of DOC and could include production from POC or adsorption by it.

Water samples were taken on a monthly basis from the 4 sites on the River Tees (Table 1). December and January samples were only obtained from two sites; poor weather conditions prevented the two sites within the Moor House NNR from being visited. Each degradation experiment spanned 10 days with sacrificial sampling taking place on day 0, 1, 2, 5 and 10, and light and dark treatments for each site. Replicates were included within each degradation experiment and over the course of the year all combination of factors were replicated. No day 0 samples were replicated, but 44% of all other measurements were replicates (285 of 646 samples). Replication was limited by practical constraints of the



number of quartz tubes available and the time taken to process DOC analysis. The water was then poured in to 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 10 day 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 a sample. These were treated in this way because a sample after 10 days may have experienced the same average radiation as a sample after 1 day but will have received a larger total radiation dose. By including radiation and temperature variables it was possible to estimate the apparent quantum yield and the activation energy for DOC photodegradation.

### ***Sample analysis***

Upon each day of sampling the respective quartz tube for each site, each treatment and replicates, where appropriate, were sacrificially sampled and sub-samples frozen for subsequent analysis for DOC concentration: it is assumed that the freezing and thawing of samples did not alter DOC concentrations. Samples for DOC analysis were defrosted and filtered to 0.45  $\mu\text{m}$  and the DOC concentration measured using the wet oxidation method

described in Bartlett and Ross (1988). DOC concentrations were calibrated using standards of oxalic acid with 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 so as to be within this range. Samples with a higher DOC concentration were diluted using deionised water which was also used as a blank. Absorbance at 400, 465 and 665 nm was measured and the 'E4:E6' ratio (abs at 465 nm/ abs at 665 nm) recorded. Absorbance at 400 nm is a basic (visible) colour reading and the specific visible light absorbance was taken as the absorbance at 400nm divided by the DOC concentration of the sample. The E4/E6 ratio is a measure of DOC composition, with higher ratios indicating a greater degree of humification (Thurman, 1985). All optical measurements were performed using a UV-Vis spectrophotometer, with a 1 cm cuvette. Blanks of deionised water were used.

Suspended sediment concentration in each monthly experiment was measured in samples on day 0 and day 10. Samples were filtered through pre-weighed, 0.45  $\mu$ m glass fibre filters; dried to 105°C and the filter paper re-weighed to give the concentration of particulate matter. The composition of the particulate matter was not analysed and particulate concentrations were only measured in a sample of 50 ml volume.

A number of additional water analyses were performed in order to provide covariate information. Alkalinity or acidity was measured by titration on day 0 and day 10. An acidity or alkalinity titration was carried out (in the field on day 0), titrating 20 ml of river water against either 0.1 M sodium hydroxide (NaOH) or 0.005 M hydrochloric acid (HCl), using five drops of phenolphthalein or bromophenol blue, respectively, as chemical indicators of pH change. Three titrations were carried out for each site and treatment, and the average volume of acid/alkali used was recorded. Conductivity, pH, and water temperature of samples as it left each quartz glass vial were measured by electrode methods. Ion Chromatography

was used to measure the concentrations of certain anions: fluoride, bromide, chloride, nitrate, phosphate and sulphate. 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](http://www.ecn.ac.uk) – Sykes and Lane, 1996).

The concentrations of DOC and the specific absorbance were analysed in both absolute and relative terms where the relative value for each sample in an experiment was expressed as the ratio of the measured value to measurement on day 0 for the same experimental run.

### *Statistical methodology*

The design of the experiment incorporates four factors: month, sample day, site and treatment. Each factor has a number of levels: month has 12 levels (one for each calendar month); sample day has 5 levels (days 0, 1, 2, 5 and 10); site has 4 levels (CHS, TB, MIT and DBS); and treatment has 2 levels (light and dark).

An analysis of variance (ANOVA) was used to assess the significance of all four factors and where possible the interactions between the factors were also determined. Furthermore, the analysis was repeated including covariates (ANCOVA). The covariates were: pH, conductivity, absorbance at 400 nm, E4:E6 ratio; anion concentrations; and light and temperature variables. The instantaneous river flow at the time of sampling was not available to the study. The ANOVA and ANCOVA were performed separately so as to explore what effects existed and whether they could be explained by the available covariates. The magnitude of the effects, in this case generalized  $\omega^2$  (Olejnik and Algina, 2003), of each significant factor and interaction were calculated. Post-hoc testing of the results was made for pairwise comparisons between factor levels using the Tukey test in order to assess where significant differences lay. There are several assumptions associated with using the ANOVA

approach. Firstly, the Levene test was used to assess homogeneity of variance with respect to the factors in ANOVA; if this test failed then data were log-transformed. It should be noted that ANOVA is robust against the assumptions of homogeneity of variance and normality of the data. Secondly, the Anderson-Darling test was used to ensure that the data were normally distributed; if not the data were log-transformed. Thirdly, to avoid type I errors all probability values are given even if significance was assessed at the 95% level.

### ***Empirical Modelling***

The statistical analysis was used to direct the development of empirical models of DOC loss. Multiple linear regression was used to develop the empirical model based upon terms identified from the ANOVA and including interaction terms. Only variables whose effect was significant at least at 95% 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 ( $\sin\left(\frac{m\pi}{6}\right) + \cos\left(\frac{m\pi}{6}\right)$ ) 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. When statistically significant multiple regression equations were derived a partial regression analysis was performed to assess the importance of each significant term.

The modelling of net catchment losses required an estimate of the in-stream residence, and therefore this study used the approach of Worrall et al. (2013) in order to calculate the in-stream residence time from source to a monitoring point lower in the catchment.

Flow records were available from 5 gauging stations throughout the River Tees catchment and the record from the gauge furthest upstream and within a peat covered catchment was used (Trout Beck – Figure 2). So as to coincide with available stream DOC

monitoring records, flows from 1994 to 2009 were considered. The in-stream residence time can be defined as the time that river water takes to transit from the point it entered the river to the point of interest (i.e. the point of monitoring):

$$t_r = \int_{x_e}^{x_m} \frac{l}{v} dx \quad (i)$$

where:  $t_r$  = the in-stream residence time;  $v$  = the cross-sectional average river velocity;  $x_m$  = the distance of the monitoring along the river from its source above the Trout Beck gauging station; and  $x_e$  = the expected length of the river for the monitoring point  $m$ , i.e. the length along the river at which all water at monitoring point can be assumed to have entered.

The mean velocity of a river at any point can be estimated from Manning's equation (Manning, 1891):

$$v = \left(\frac{1}{n}\right) \left(\frac{A}{p}\right)^{\frac{2}{3}} S^{\frac{1}{2}} \quad (ii)$$

where:  $A$  = cross-sectional area of the river at point  $x$ ;  $p$  = the wetted perimeter;  $s$  = the water surface slope; and  $n$  = the Manning's  $n$  coefficient. If equation (ii) is expressed in terms of  $x$ , i.e. distance along the river, then equation (i) can be solved.

It is common for the longitudinal slope profile of a river to be expressed as an exponential function of river length using the Putzinger equation (Putzinger 1919):

$$S_x = S_0 e^{-\phi x} \quad (iii)$$

Where:  $S_x$  = the bed slope at point x;  $S_0$  = the bed slope at source; and  $\phi$  = an empirical constant. It was assumed that bed slope was an approximation for the water surface slope in equation (ix).

If it is assumed that the river has a rectangular cross-sectional area then:

$$\frac{A}{P} = \frac{dw}{(2d+w)} \quad (\text{iv})$$

Where: d = river depth and w = river width. For a rectangular cross-section, the width of the river does not vary with discharge and so it is only necessary to find an expression for river depth change with river length. A rectangular section is the simplest possible section that we could consider and if justified it would be possible to replace this with a more complex representation of the channel cross-section. Dangerfield (1999) lists the bankfull width of 124 UK rivers and these data were augmented with observations from the 5 gauging stations on the River Tees (Figure 2); the River Tees was not part of the original data set from Dangerfield (1999). The data set of Dangerfield (1999) does not consider catchments less than 13 km<sup>2</sup>; this can only be marginally improved with data from the Tees to 11.4 km<sup>2</sup> (Table 1) The evidence shows a significant linear correlation between river length and river width for catchments up to 11.4 km<sup>2</sup> (5 km river length) but this equation suggested that rivers would be over 7m wide at source. In order to correct for this overestimation in small catchments, the following was assumed based upon observations of width from the test catchment used in this study:

For catchment area (C) > 11 km<sup>2</sup>

$$w = 0.055C + 7.8 \quad r^2 = 0.61, n = 129 \quad (\text{v})$$

For catchment area (C) < 11 km<sup>2</sup>

$$w = 0.68C + w_0 \quad (\text{vi})$$

Where: C = catchment area (km<sup>2</sup>); and w<sub>0</sub> = river width at source (m). A river will have finite width at source and as a default a value of 0.1 m was assumed here.

River depth varies with flow and we propose the following form of equation based upon observed depth frequency curves:

$$^f d_x = ^f d_m - \beta e^{\left(\frac{x}{\gamma}\right)^\delta} \quad (\text{vii})$$

where: <sup>f</sup>d<sub>x</sub> = depth at exceedance flow f (e.g. 10% exceedance) at river length x (m); <sup>f</sup>d<sub>m</sub> = depth of the river at the monitoring point m for exceedance flow f; and β, γ, δ = empirical constants where β approximates to <sup>f</sup>d<sub>m</sub> - <sup>f</sup>d<sub>0</sub>.

The above approach was calibrated for the River Tees given data readily available for gauging stations in the UK as reported within the National River Flow Archive ([www.nrfa.ac.uk](http://www.nrfa.ac.uk)) and the Flood Studies Report (NERC, 1975 - Table 2). The calibration of the above equations for the River Tees is discussed in Worrall et al. (2013). For Equation (iii) r<sup>2</sup> = 0.93 and for Equation (vii) the root mean square error was 0.02%, i.e. the fit of this approach was excellent and limited any error in transit time prediction. The source of most of the DOC within the River Tees is in the headwaters associated with peat soils (Aitkenhead et al., 2007). A soil map of the Tees catchment shows that peat soils end at 10 km from the source along the main river length, approximately at the location of the Trout Beck gauging

station, and so the in-stream residence time at this point was calculated using an intermediate river length of 5 km, i.e. on average DOC enters halfway between the beginning of the stream and 10 km downstream

Monitoring of stream water DOC concentration in the catchment headwaters was weekly, and so observed concentrations were paired with the flow measurement for the same time at the Trout beck, and then in-stream residence time calculated for that flow. Given the in-stream residence time for a given initial concentration of DOC it was possible to calculate the export from the DOC source and the expected loss to tidal limit of the study river, i.e. the point at which the river enters the estuary.

## **Results and Discussion**

It was possible to generate a sample size of 690 DOC concentrations with complete covariate information and within the context of the factorial design. Summary of the water chemistry at the two sites at the extremes of the study catchment over the 10 days of the study period in daylight conditions is given in Table 3. The Fe and Al concentrations for the headwater stream are below those reported for photoaggregation by Maurice et al. (2002).

### ***DOC concentrations***

For nearly every month of measurement the DOC concentration in both treatments decreased. The average DOC concentration over time over all sites showed a steep initial decline, although the rate of decline was still not zero after 10 days (Figure 3) suggesting that further decreases would have occurred in the experiments had continued for longer. The average decline in DOC concentration across all months for all sites for samples in daylight was from 51 to 14 mg C/l after 10 days: when concentrations were judged relative to the day 0 concentration at each site then the average decline over 10 days was 76%. For experiments



only in the dark the average decline over a 10 day period was 47%. The average difference across all sites and all times between samples in light and dark was 11.8 mg C/l with day 10 DOC concentrations of samples kept in the light being on average 29% lower than those kept in the dark when judged relative to the DOC concentration on day 0. Larson et al. (2007) compared DOC concentrations in samples of stream water kept in light and dark conditions for 24 hours of normal sunlight and found an average decrease between 5 and 10%.

Of all the experiments run, there were 66 samples (out of a total of 690 samples) where an increase in DOC concentration was observed. In 14 of the cases there was a higher day 10 DOC concentration than day 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. Samples where there was an increase in DOC over the course of the experiment were not removed from the analysis.

#### *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 and those in the dark met the condition of normality, but therefore all subsequent ANOVA were performed on log-transformed data which did exhibit a normal distribution. Conversely, the Anderson-Darling test of the photo-induced degradation data (i.e. the difference in concentration between experiments performed in the light and dark) was normally distributed and so this not transformed further.

When the relative concentration data for all treatments (daylight and dark) were considered without covariates, all single factors were found to be significant (Table 4). The least important single factor was Site (explaining only 0.4% of the variance in the original dataset). One of the reasons for using relative DOC concentration was to minimise the

difference between sites, and so this result indicates that this was largely effective. Post-hoc testing showed that the difference between sites was largely associated with the difference between the CHS and MIT, but not between CHS and DBS. There were no significant interactions between the Site factor and any other factor. The most important factor was Day, i.e. the time over the experiment with all days being significantly different from each other. The second most important factor was the difference between treatments, with the relative DOC concentration in the light being 48% lower than those kept in the dark. Indeed the most important interaction was that between Day and Treatment factors which reflects the difference in the curves illustrated in Fig. 3. There was a significant effect due to month but this may reflect the importance of the Day0 concentration for the degradation rate (with faster degradation rates associated with higher initial concentrations) rather than a seasonal cycle in degradation behaviour per se, which also explains the significant interactions between the Month factor and the Day and the Treatment factors. Overall the ANOVA of the relative DOC concentration explains 62.7% of the variance in the original data, i.e. the error term represents 37.3% of the variance. This error term represents the unexplained variance which was not only due to sampling or measurement error but also variables, factors or their interactions that were not or could not be included: inclusion of covariates should decrease this term.

Inclusion of covariates into the ANOVA did increase the proportion of the variance explained, by 4% (Table 4). However inclusion of covariates did not make any of the factors or interactions insignificant; on the contrary, inclusions of significant covariates increased the importance of the differences between sites even when relative DOC concentration was being tested. The most important covariate was the specific absorbance, which significantly declined with increasing DOC concentration. The second most important covariate was the day0 concentration, where relative concentration declined faster with increasing day0

concentration. This suggests that degradation rate was concentration dependent. No other covariates were found to be significant. No other covariates were found to be significant in this analysis.

Guided by the results of the results of the ANOVA it was possible to give the best-fit equation for the change in the DOC concentration ( $\Delta\text{DOC}$ ):

$$\ln(\Delta\text{DOC}) = 1.05\ln(\text{day}_0) + 0.28\ln t - 0.29\left(\sin\left(\frac{\pi m}{6}\right) + \cos\left(\frac{\pi m}{6}\right)\right) - 1.15 \quad (\text{viii})$$

$$r^2 = 0.76, n = 264$$

$$(0.04) \quad (0.04) \quad (0.05) \quad (0.18)$$

where:  $\text{day}_0$  = the DOC concentration on day zero of each experiment (mg C/l);  $t$  = time since the start of the experiment (days);  $m$  = month number (January = 1 to December = 12). Only variables that were found to be significant 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. The partial regression analysis shows that the most important variable is  $\ln(\text{day}_0)$  (partial regression coefficient = 0.66) with the other terms of approximately equal importance.

#### ***ANOVA on Photo- induced degradation***

The difference between the dark and light concentrations in each experiment was taken as the estimate of the impact of photic processes. The extent of photo- induced degradation could be estimated in 313 cases and the loss due to photo-induced degradation varied from 48 mg C/l and -11 mg C/l (i.e. as above in some experiments the DOC concentration was observed to increase, implying photo-induced production). The ANOVA shows that all single factors were significant but that there were no significant interactions

between those factors (Table 5). Only one variable, and no others, was found to be a significant covariate - the day<sub>0</sub> concentration. The Month factor, although significant, shows no clear seasonal cycle which may imply that hydroclimatic conditions on the day of sampling (e.g. riverflow) are more important than the season of the year. The Day factor showed a significant maximum in the difference due to photo-induced degradation after 2 days (Figure 4, also apparent in Figure 3) which then declines to the 10 day period.

Given the results of the ANOVA it was possible to identify the best-fit equation for the loss due to photo-induced degradation ( $\Delta\text{DOC}_{\text{photo}}$ ):

$$\Delta\text{DOC}_{\text{photo}} = 35.2 + 0.47[\text{DOC}] - 13.4\ln[\text{DOC}] - 933 \frac{\text{Abs}_{400}}{[\text{DOC}]} \quad (\text{ix})$$

$$r^2 = 0.52, n=313$$

$$(9.0) \quad (0.06) \quad (3.0) \quad (255)$$

Where: [DOC] = the DOC concentration (mg C/l); and Abs<sub>400</sub> – absorbance at 400nm. The most important term in Equation (ix) is ln[DOC] with a partial regression coefficient = 0.69, followed by Abs400/[DOC] with the least important term being [DOC] having a partial regression coefficient = 0.035.

It should be noted that neither temperature nor PAR variables were found to be significant covariates in any of the above approaches. However, it was possible to estimate the apparent quantum yield (AQY) in 158 of the experiments and this was found to vary between 9.6 and -1.7 mmol C/mol photons (again there were periods of photo-induced production as opposed to photo-induced degradation) – on an energy basis this equates to a maximum AQY of 1.9 mg CO<sub>2</sub>/kJ. Most values of AQY in the literature are defined for single wavelengths (eg. Boyle et al., 2009) or for inappropriate end-products making them less transferrable to this study (eg. Stubbins et al., 2010). Osborn et al. (2009) measured AQY

for DOC values between 1 and 3 mmol C/mol photons, for samples at the mouth of the Mackenzie River ( $> 180,0000 \text{ km}^2$ ). Soumis et al. (2007) give photoreactivity of DOC in sterile lake water as between 15.5 and 35.8 mg  $\text{CO}_2/\text{kJ}$ . This larger photoreactivity may be due to the experiment being performed in sterile containers that remove any biotic process and so photic processes are the only process operating. The ANOVA of the AQY showed significant effects due to Day, Month and with  $\text{day}_0$  as a covariate. Month was the most important factor with a peak in December and a minimum between February and June. This suggests that some months were associated with proportionately more photo-induced production than other months. This seasonal cycle could appear to be the inverse of the day length or solar declination, both of which would have peaked in June rather than December when the days are shortest and the sun's declination to the horizon at its lowest. It should be remembered that AQY is a measure of the photo-induced degradability and not the amount of photo-induced degradation, i.e. the DOC in December was more photodegradable.

### ***Rate of Degradation***

The rate of degradation of DOC was considered relative to the individual treatments, i.e. i) the rate of degradation in the light (i.e. total degradation); ii) the rate of degradation in the dark; and iii) the difference between the two treatments which was taken as the rate of photic processes. For samples in the light, the degradation rate varied from 30.1 mg C/l/day to -3.5 mg C/l/day, i.e. increases or no change in DOC concentrations were observed in 60 cases.

### ***Rate of Degradation in the light***

The ANOVA of the rate of degradation for samples in the light showed that all factors were significant (Table 6). When no covariates were included then all 3 factors were found to be significant (obviously no treatment factor was included because only experiments in the

light were being considered). Once covariates were included then neither Site nor Month factors were found to be significant. The lack of significance for the Site factor means that this study found that the different parts of the river did not have inherently different degradation rates. Equally, the lack of a significant difference between months of sampling suggests that there is no seasonal cycle in degradability. When covariates were included then both  $\ln(\text{day}_0)$  and  $1/\text{Temp}$  were found to be significant and no others, although collectively they explained only 8% of the original variance. Given the results of the ANOVA the best fit equation for degradation rate in daylight was:

$$\ln(\text{rate}_{\text{light}}) = 13.5 + 0.74\ln(\text{day}_0) - 1.28\ln t - \frac{3824}{T} \quad (\text{xi})$$

$$r^2 = 0.61, n = 167$$

$$(5.7) \quad (0.12) \quad (0.1) \quad (1567)$$

Where: T = absolute temperature of the experiment (K). The residuals of equation (xi) were normally distributed. The most important term in Equation (xi) is  $\ln(\text{day}_0)$  with a partial regression coefficient = 0.51 and the least important term being  $1/T$  with a partial regression coefficient = 0.035. Although the visual inspection of the residuals of equation (x) show no obvious changes, the main effects plot of  $\ln(\text{rate}_{\text{light}})$  vs t (Figure 5) would suggest that, although a straight line fit was significant, a combination of two straight lines would be better, with one fast rate equation covering the period up to approximately 4-5 days and one after 5 days. The significance of the reciprocal of absolute temperature in equation (xi) means that it was possible to estimate the activation energy of the degradation given a value of the universal gas constant as 0.692Jj/K/gC and in which case this would be  $2.6 \pm 1.2$  kJ/gC.

#### ***Rate of degradation in the dark***

It was possible to calculate the rate of degradation in the dark in 258 experiments, which ranged from a decrease of 19.4 mg C/l/day to -6 mg C/l/day, i.e. increase or no change in DOC concentrations were observed in 77 cases. For the rate of degradation in the dark the ANOVA shows that all factors were significant (Table 7). Once covariates were included then site was found not to be significant, however, unlike when considering the rate of the reaction in the light there was still a significant role for the month factor, i.e. there was a seasonal cycle in aphotic degradability. The main effects plot of the month factor shows that degradability peaked in July and October at 6.11 mg C/l/day, and was at a minimum in November at 0.28 mg C/l/day (Figure 6). There is a superficial similarity between the rate of degradation and the annual average temperature during each month's experiment but the temperature did not show the local maxima in July and October. When covariates were included then both  $\ln(\text{day}_0)$  and  $1/\text{Temp}$  were again found to be significant: no others were found to be significant

Given the results of the ANOVA the best fit equation for degradation rate in darkness was:

$$\ln(\text{rate}_{\text{dark}}) = 0.71\ln(\text{day}_0) - 0.71t - 0.42\sin\left(\frac{\pi t}{6}\right) - 0.59\cos\left(\frac{\pi t}{6}\right) + \frac{3267}{T} \quad (\text{xii})$$

$$r^2 = 0.45, n = 178$$

$$(0.11) \quad (0.10) \quad (0.17) \quad (0.20) \quad (2783)$$

where all terms are defined as above. The residuals of equation (xii) were normally distributed. The most important term in Equation (xii) is  $\ln(\text{day})$  with a partial regression coefficient = 0.29 and the least important term being  $1/T$  with a partial regression coefficient = 0.008. As above the main effects plot of  $\ln(\text{rate}_{\text{dark}})$  vs.  $t$  suggests that a more complex rate law than a single rate law. Again it was possible to estimate the activation energy of the

degradation and in which case this would be  $2.3 \pm 1.8$  kJ/gC, i.e. not significantly different from the estimate based on the degradation rate in the light. It is difficult to find studies that measure activation energy in comparative systems, but Alperin et al. (1995) give a value of 6.7 kJ/gC for DOC in marine sediments; a higher value may be expected for DOC that is likely to have been older and more recalcitrant than that found in rivers.

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

The rate of the photo-induced degradation could be calculated from 168 experiments and varied from 27.3 mg C/l/day to -4.3 mg C/l/day, i.e. in 39 cases an increase was observed. All 3 factors were found to be significant but again the Site factor was not found to be significant when covariates were included (Table 8). As before the Day factor was found to be the most important, though there was a significant seasonal cycle where the rate peaked in September at 7.7 mg C/l/day with a minimum in June at 1.1 mg C/l/day. The covariates found to be significant were not only Day 0 but also cumulative PAR.

$$\ln(\text{rate}_{\text{photo}}) = 31.4 - 10.51\ln(\text{day}_0) - 2.02\text{Int} + 9.1\sin\left(\frac{\pi m}{6}\right) - 0.005 \frac{\sum \text{PAR}}{t} \quad (\text{xiii})$$

$$r^2 = 0.29, n = 94$$

$$(14.8) \quad (4.5) \quad (2.0) \quad (3.9) \quad (0.003)$$

Where all terms are defined as above. The significant effect of the term in  $\frac{\sum \text{PAR}}{t}$  does suggest that we could measure significant AQY. The most important term in Equation (xiii) WAS Int (partial regression coefficient = 0.39) with no other term having a partial regression coefficient greater than 0.07. By using partial regression it was possible to examine the relationship between  $\ln(\text{rate}_{\text{photo}})$  and  $\frac{\sum \text{PAR}}{t}$ , which does suggest that the rate of photo-induced



degradation declined with increasing  $\Sigma$ PAR. This implies that there was a progressive decrease in the sensitivity of remaining DOC to photo-induced degradation, i.e. that photobleaching had occurred, and that this was associated not only with time but also with increased light intensity.

### ***Empirical modelling***

The estimated in-stream residence time for water between Trout Beck and the tidal limit varied from 12.9 to 127.2 hours. Between 1994 and 2009 the annual flux of DOC at Cottage Hill Sike varied from 14.7 to 33.3 tonnes C/km<sup>2</sup>/yr. For each measurement of DOC concentration at Cottage Hill Sike the flow measurement at the Trout Beck gauging station was used to calculate the in-stream residence time. Given an initial concentration and an estimate of the in-stream residence time it was possible to calculate the loss of DOC and the export that would represent. Based on the in-stream residence time and equation (viii), then the equivalent flux at the tidal limit would be between 5.4 and 12.6 tonnes C/km<sup>2</sup>/yr which gives an equivalent removal rate of 7.7 and 21.4 tonnes C/km<sup>2</sup>/yr which is a removal rate of between 48 and 69% (Figure 7). There was a significant trend in the DOC flux from Cottage Hill Sike, which increased at average rate across the whole period of 0.59 tonnes C/km<sup>2</sup>/yr<sup>2</sup> (3.0 % /yr<sup>2</sup>) but no significant trend was observed for the flux at Broken Scar over the same period. Therefore, it is perhaps not surprising that there was a significant increase in the predicted removal rate – 0.52 tonnes C/km<sup>2</sup>/yr<sup>2</sup> (5.0 %/yr<sup>2</sup>). The increase in the predicted removal rate is in line with the increase observed for the flux of DOC at source, and so therefore the observations of DOC degradation for this catchment imply that the river is capable of removing most or all of the increase in DOC export from the source, before it reaches the sea. This in turn implies that observed increases in DOC flux from peat soils across the northern hemisphere could translate into large increases in loss of CO<sub>2</sub> to the

atmosphere. However, in this case this would assume no other changes in sources in the rest of the catchment such as no changes in urban or agricultural sources.

### ***Limitations and Implications***

One particular process that this study has not quantified is the processing of the particulates. We deliberately did not filter the samples prior to experiment, to allow for the possibility of interaction between particulates and DOC, but because of the small volume of samples it was not possible to test the composition of the particulates over the course of the experiments. However, suspended sediment concentrations were measured in samples at day 0 and day 10, meaning that it was possible to assess the change in particulate concentration over a 10 day period in 35 cases. Over these 35 cases no increases in suspended sediment concentration were observed, with removal rates ranging from 0.2 to 15.6 mg C/l/day. Without compositional information it is difficult to infer the extent to which the particulate carbon content has changed. However, for the CHS there is no mineral soil in the catchment and so any suspended sediment can be assumed to be organic. There were 9 cases where it was possible to compare the day 0 and day 10 samples at CHS, and this gave a loss of POC between 7.5 to 29.4 mg C/l/day (assuming a carbon content of 45%), which is a removal rate of between 38 and 87% over 10 days. Of course this assumes that our experimental set up mimics the settling out of POC into a streambed, and the analysis does not indicate whether the POC was converted to directly to CO<sub>2</sub> or to DOC. Nevertheless, the absence of any evidence of increasing particulate concentrations in any of the experiments argues strongly that the widespread reductions in DOC observed were not due to flocculation or precipitation.

Based on BOD measurements from rivers across England and Wales, Worrall et al. (2007) estimated an average 29% removal of DOC, although this estimate was based upon an assumption of a fixed 5 day residence time. Worrall et al. (2006) working on the River Tees

calculated the DOC export at a range of scales to show an average net loss of 40% of DOC from source to outlet. Worrall et al. (2012) developed an empirical model of net watershed loss based upon data from 169 catchments and applying the method to the Tees catchment suggests a removal rate of 58%. Therefore, the estimates of removal rates are not dissimilar to previous less detailed estimations, and indeed not dissimilar to estimates of global in-stream removal (42% - Cole et al., 2007).

Worrall et al. (2012) estimated the flux of DOC from the UK was  $909 \pm 354$  ktonnes C/yr ( $2.2 - 5.2$  tonnes C/km<sup>2</sup>/yr), so applying the removal rates measured in this study suggests that the flux of DOC at source in the UK would have been between 1067 and 4074 ktonnes C/yr ( $4.4 - 16.7$  tonnes C/km<sup>2</sup>/yr). Rates of DOC loss through the UK's fluvial network would be between 512 and 2811 ktonnes C/yr ( $2.1 - 11.5$  tonnes C/km<sup>2</sup>/yr), which represents a greenhouse gas emission of between 1880 and 10320 ktonnes CO<sub>2eq</sub>/yr. Even the lower of these estimates would represent 1% of the UK's national total GHG budget.

Although this study has been able to develop empirical rate law for the loss of DOC, it is clear from this study that if we are to further understand the turnover of DOC in the rivers then it will be necessary to consider changes on hourly timescales rather than daily, and to better constrain in-stream residence times across regions. The study suggests that there is a strong influence of radiation on the loss of DOC which would create a strong diurnal cycle in the loss or processing of DOC, which in the short residence times of rivers has two implications: firstly, that without a good knowledge of in-stream residence time it will be difficult to judge how much DOC is lost. Second, a strong diurnal cycle in northern latitudes also implies that there should be a strong annual cycle in loss of DOC, even with a fixed in-stream residence time. The study suggests that there at least two broad types of DOC, with one rapidly turning over into the other, at the same time as the particulate organic matter is

itself turning over producing DOC. The interplay of at least these three processes means that we need to consider each of these on sub-daily timescales.

## **Conclusions**

The study has found that for peat-derived DOC in the river network the average loss of DOC in light conditions was 73% over a 10 day period, but with the majority of the loss occurring in the first 2 days. When extrapolated across a catchment the annualised removal rate was between 48 and 69% of the flux of DOC at its soil source. These measured removal rates are for DOC close to its source in rivers with residence times of only several days, and not for longer residence times systems or for the relative old DOC found downstream in a larger river networks. The results suggest that rivers could be sources of CO<sub>2</sub> equivalent to several percent of a national GHG inventory.

## **Acknowledgements**

The work was supported by DEFRA project SP1205-2011, with additional support for CSM from Natural England.

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Figure 1. Schematic diagram of the DOC processing within a peat-sourced stream

Figure 2. Location of the study catchment with monitoring sampling points and river flow gauging stations used within the study.

Figure 3. The main effects plot of DOC concentration change for light and dark over the period allowed in the study. Error bar is given as the standard error but smaller than symbol size.

Figure 4. The main effects plot of the change in loss due to photo-induced degradation over the course of the experiment. Error bar is given as the standard error.

Figure 5. Main effects plot of rate of DOC loss in light conditions over time in the experiment. Error bar is given as the standard error.

Figure 6. Main effects plot of the seasonal cycle in the rate of DOC loss in light conditions over time in the experiment (1 = January, 12= December) in comparison to the average air temperature during each month's experiment. Error bar is given as the standard error.

Figure 7. The estimated export of DOC at the peat source (Cottage Hill Sike) in comparison to the estimated areal loss of DOC and therefore the expected DOC export at the tidal limit.

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*Table 1. Areas and locations of all field sites. Catchment areas and percentage peat covers are taken from literature.*

Site	Site code	National grid reference	Catchment area (km <sup>2</sup> )	Mountain/ heath/ bog cover (%)
Cottage Hill Sike	CHS	NY 744 327	0.2	100
Trout Beck	TB	NY 759 336	11.4	90.8
Middleton-in-Teesdale	MIT	NY 950 250	242.1	47.6
Broken Scar	DBS	NZ 259 138	818.4	33.9

*Table 2. Details of River Tees gauging stations as required for calibration of in-stream residence time.*

Gauging station	Catchment area (km <sup>2</sup> )	Mainstream river length (km)	Altitude (m asl)	1085Slope( m/km)
Broken Scar	818	79	37	6.9
Barnard Castle	509	51	133	9.8
Middleton	242	32	211	12.9
Dent Bank	217	29	227	17.8
Harwood Beck	25.1	9.7	374	26.5
Trout Beck (Moor House)	11.4	5.1	533	35.8

Gauging station	Bankfull discharge (Q <sub>bf</sub> – m <sup>3</sup> /s)	Bankfull width (w <sub>bf</sub> - m)	Bankfull depth (d <sub>bf</sub> – m)
Broken Scar	384	12	2.44
Barnard Castle	257	10.4	2.04
Middleton	115	9.4	2.19
Dent Bank	93	9.3	2.36
Harwood Beck	19	8.8	1
Trout Beck (Moor House)	4	6.1	0.53

Table 3. Mean and coefficient of variation (CV - %) for Cottage Hill Sike (CHS) and Broken Scar (DBS) for the range of times considered in the study. \* Average values taken from all sampling reported for CHS from Environmental Change Network monitoring.

Determinand	Cottage Hill Sike (CHS)				Broken Scar (DBS)			
	Day 0		Day 10		Day 0		Day 10	
	Mean	CV(%)	Mean	CV (%)	Mean	CV(%)	Mean	CV (%)
POC (mg C/l)	95	103	21	45	28	45	10	52
Conductivity (µS/cm)	35	38	57	36	317	90	528	151
pH	4.5	13	6.3	5	7.0	6	7.3	7
DOC (mg C/l)	112	67	24	77	30	55	9	83
Abs400	0.14	37	0.16	35	0.06	47	0.08	26
E4/E6	6.1	31	5.7	34	4.8	69	5.6	88
Bromide (mg/l)	0.0	62	0.02	210	0.22	92	0.37	89
Chloride (mg/l)	5.9	71	9.3	136	51.8	130	24.4	163
Fluoride (mg/l)	0.2	42	0.5	119	0.3	39	0.6	56
Nitrate (mg/l)	0.3	70	0.6	58	13.2	156	7.6	188
Phosphate (mg/l)	0.9	45	1.3	127	2.6	167	1.8	173
Sulphate (mg/l)	4.4	123	10.4	80	39.7	93	25.7	85
Iron (mg/l)*	0.62	70						
Aluminium (mg/l)*	0.09	71						

Table 4. Results of ANOVA for relative DOC concentrations for all experiments across both daylight and dark treatments. (na = not applicable; and ns = not significant).

Factor (or covariate)	without covariates		With covariates	
	P	$\omega^2$	P	$\omega^2$
day <sub>0</sub>	na		0.00	9.6
Specific Absorbance	na		0.00	24.0
Site	0.04	0.4	0.04	2.4
Treatment	0.00	8.9	0.00	6.1
Day	0.00	12.6	0.00	11.4
Month	0.00	6.4	0.00	1.9
Treatment*Day	0.00	3.7	0.00	2.0
Treatment*Month	0.00	3.5	0.00	9.5
Day*month	0.00	2.3	ns	-
Error		37.3		33.0



Table 5. Results of ANOVA for relative DOC concentrations for all experiments across both daylight and dark treatments. (na = not applicable; and ns = not significant).

Factor (or covariate)	without covariates		With covariates	
	P	$\omega^2$	P	$\omega^2$
day <sub>0</sub>	na		0.00	9.6
Specific Absorbance	na		0.00	24.0
Site	0.04	0.4	0.04	2.4
Treatment	0.00	8.9	0.00	6.1
Day	0.00	12.6	0.00	11.4
Month	0.00	6.4	0.00	1.9
Treatment*Day	0.00	3.7	0.00	2.0
Treatment*Month	0.00	3.5	0.00	9.5
Day*month	0.00	2.3	ns	-
Error		37.3		33.0

Table 6. The results of ANOVA of the degradation rate of DOC in the light.

Factor	without covariates		with covariates	
	P	$\omega^2$	P	$\omega^2$
1/Temp	na		0.00	1
Ln(day <sub>0</sub> )	na		0.00	6.9
Site	0.00	3.3	ns	
Day	0.00	47.3	0.00	48.3
Month	0.00	9.5	ns	
Error		39.9		43.9

Table 7. ANOVA of the degradation rate of DOC in the dark.

Factor	without covariates		with covariates	
	P	$\omega^2$	P	$\omega^2$
1/Temp	na		0.04	1.0
Ln(Day0)	na		0.00	6.5
Site	0.00	4.8	ns	
Day	0.00	23.8	0.00	29.3
Month	0.00	28.3	0.00	14.3
Error		43.2		48.9

Table 8. ANOVA of the photo-induced degradation rate of DOC.

Factor	without covariates		with covariates	
	P	$\omega^2$	P	$\omega^2$
$\Sigma$ PAR	na		0	1.8
ln(day <sub>0</sub> )	na		0	1
Site	0.05	1.8	ns	
Day	0.00	40.5	0	30.1
Month	0.00	13.5	0	3.3
Error		44.2		63.0

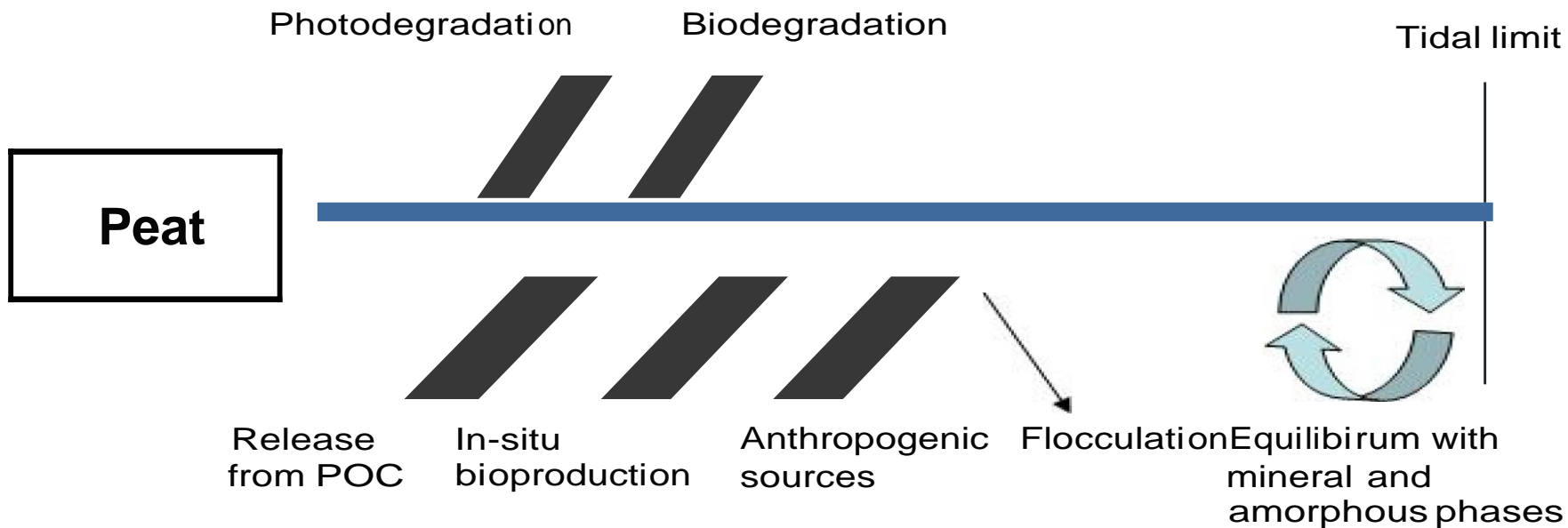


Figure 1.

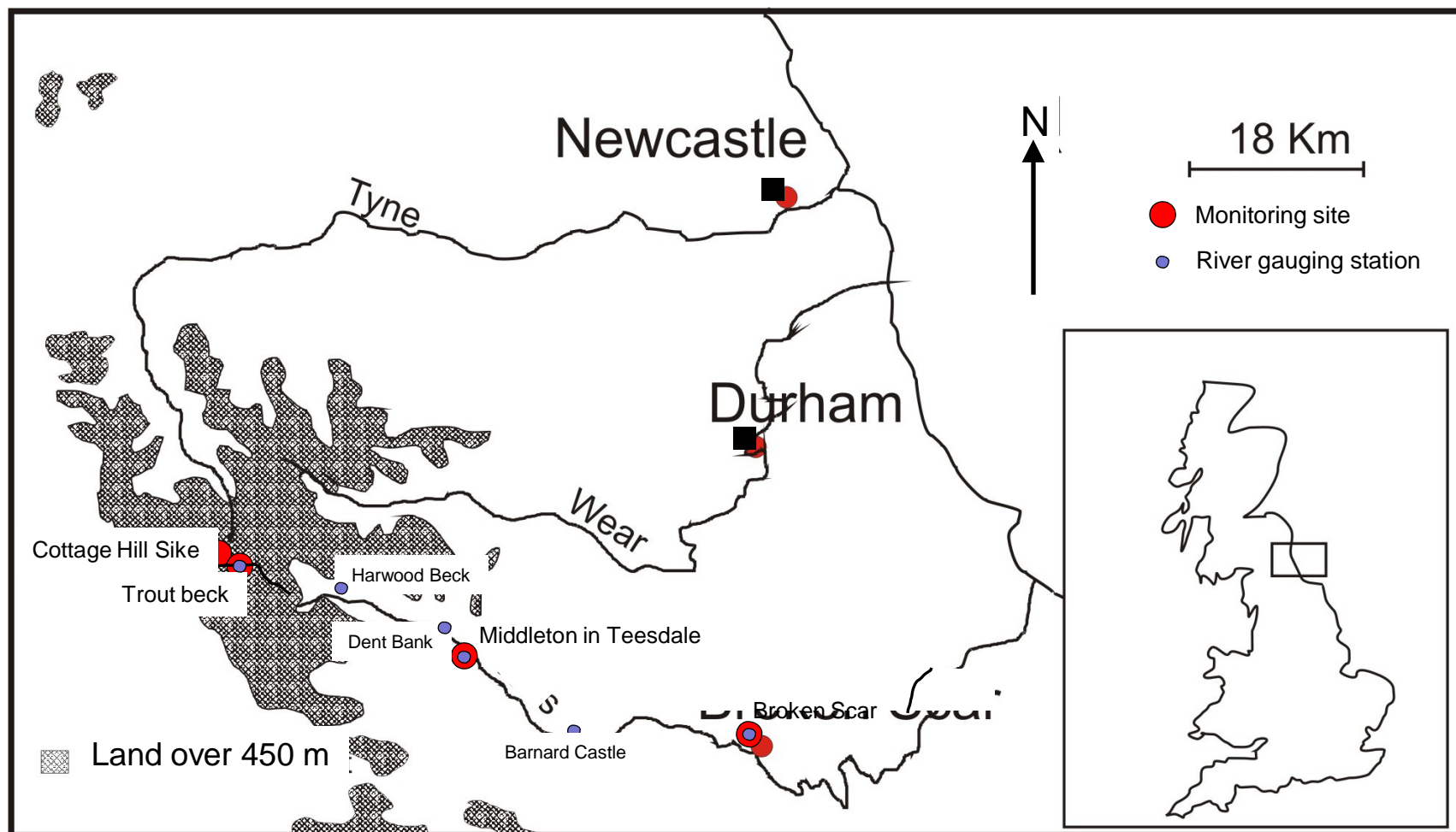


Figure 2

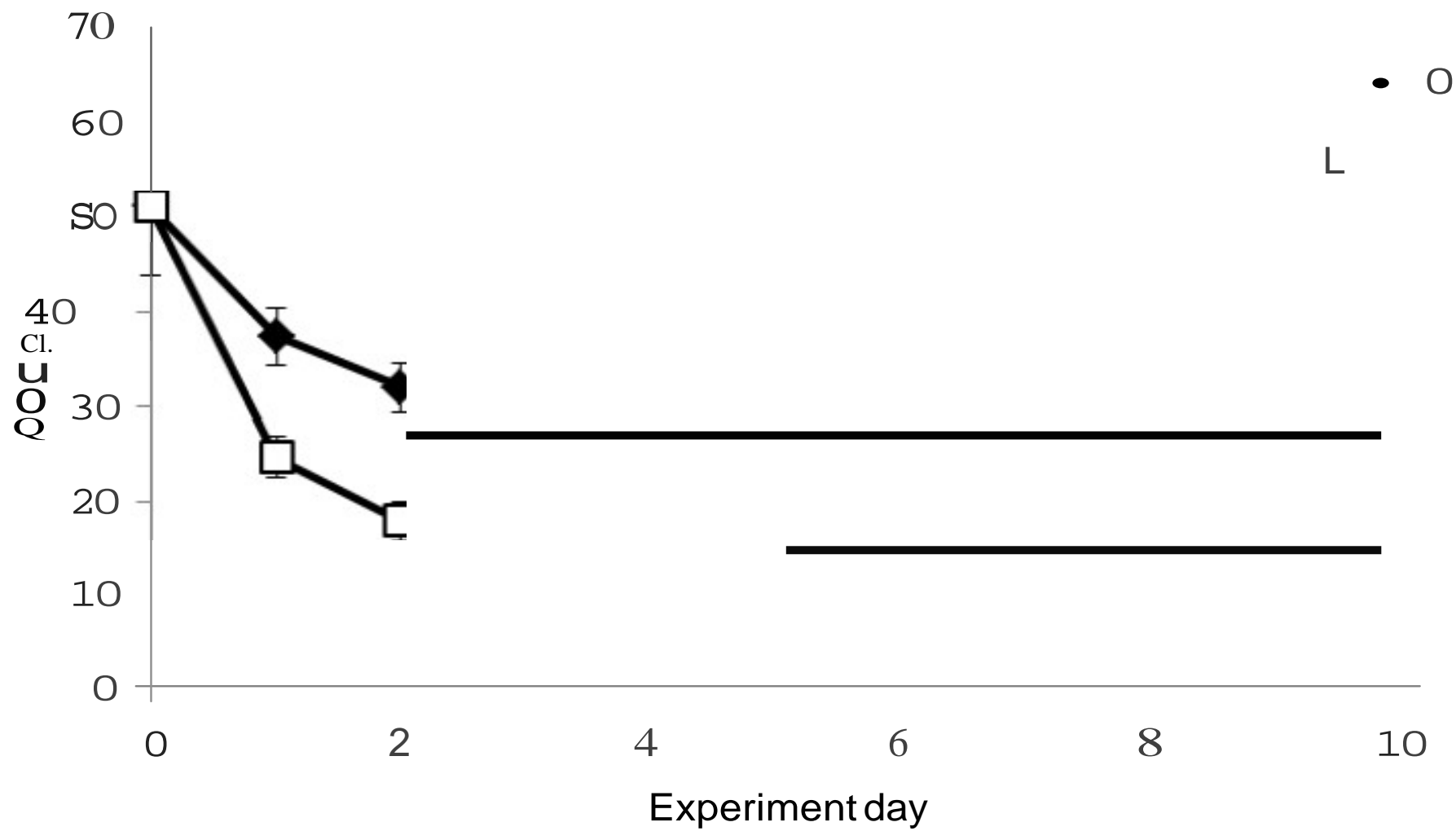


Figure 3

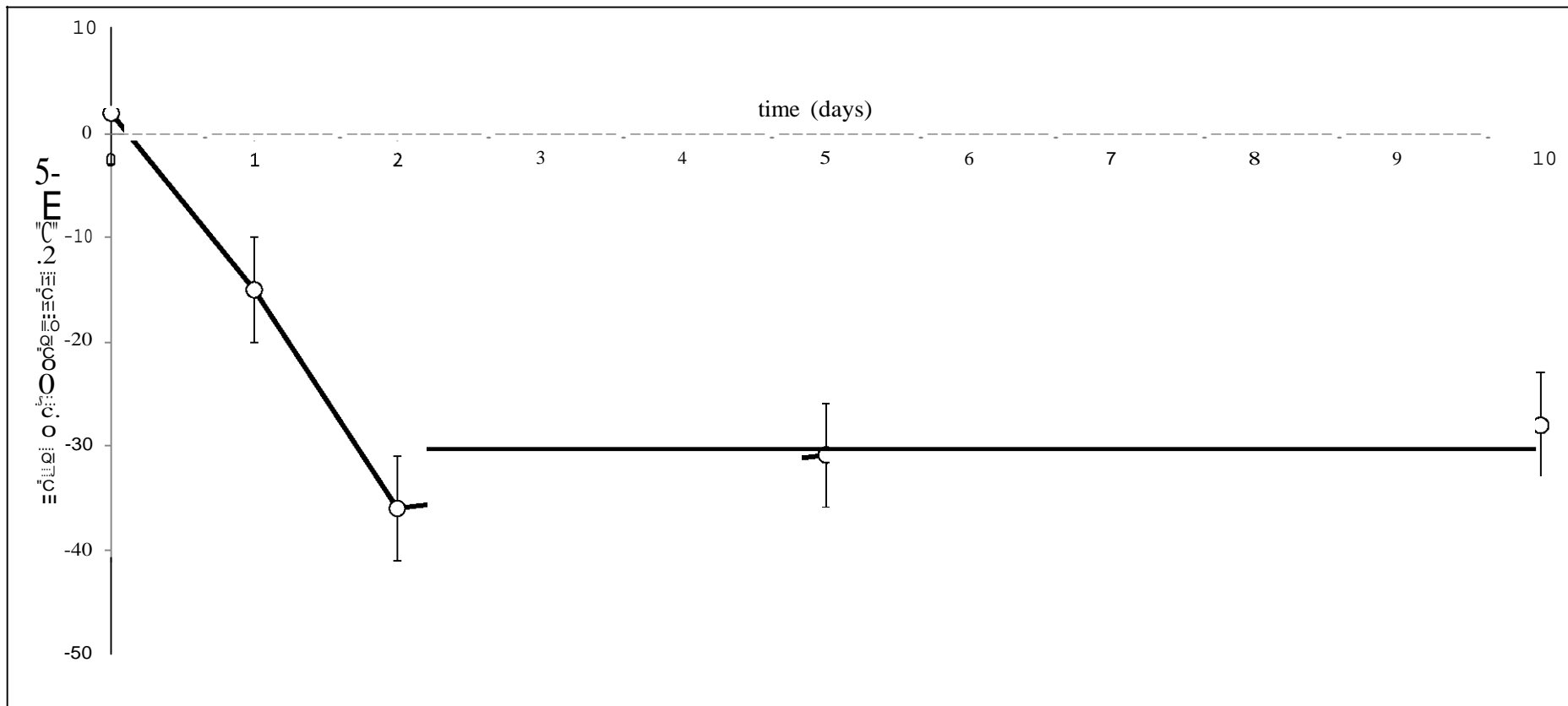


Figure 4



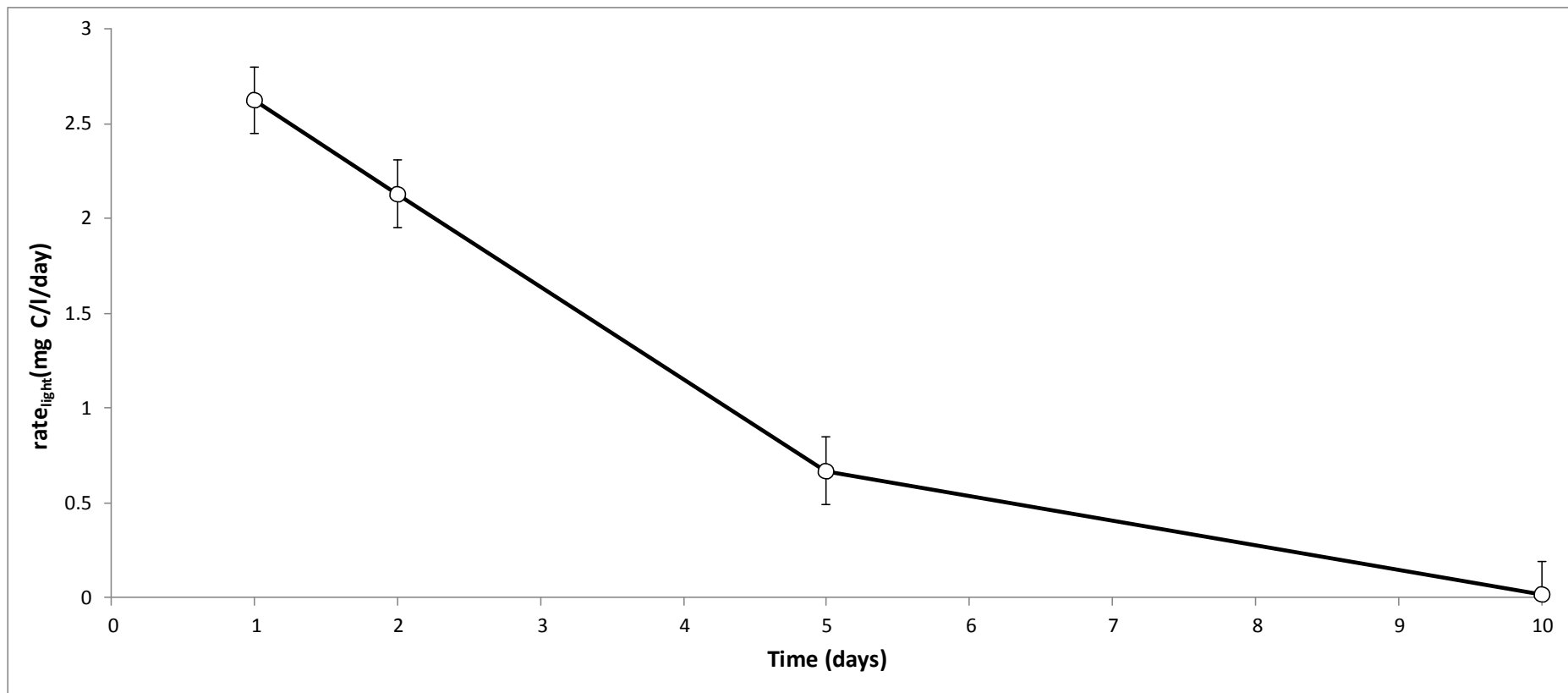


Figure 5

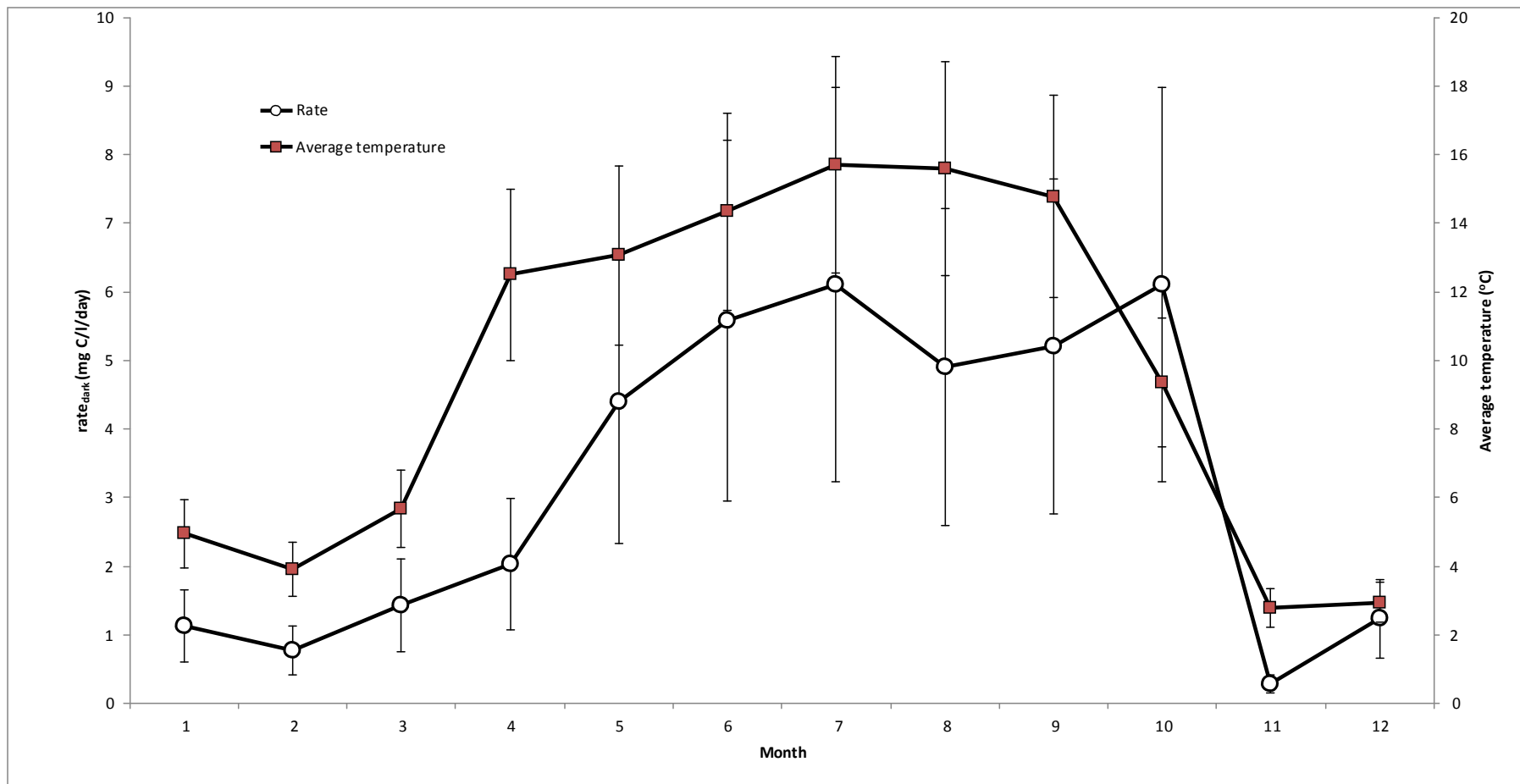


Figure 6

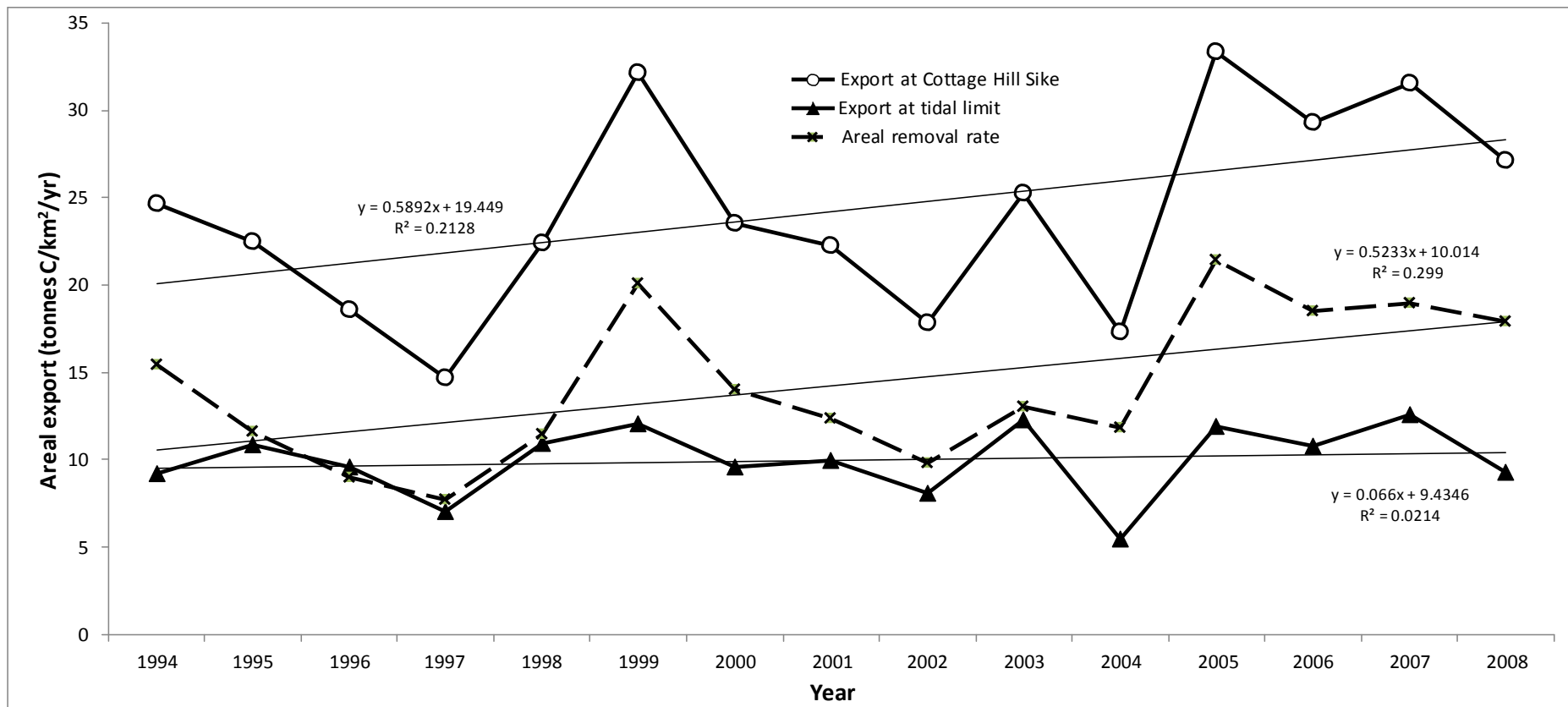


Figure 7