Understanding the diurnal cycle in fluvial dissolved organic carbon – the interplay of in-stream residence time, day length and organic matter turnover

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Abstract

There is increasing interest in characterising the diurnal fluctuation of stream solute concentrations because observed data series derived from spot samples may be highly subjective if such diurnal fluctuations are large. This can therefore lead to large uncertainties, bias or systematic errors in calculation of fluvial solute fluxes, depending upon the particular sampling regime. A simplistic approach would be to assume diurnal fluctuations are constant throughout the water year, but this study proposes diurnal cycles in stream water quality can only be interpreted in the context of stream residence time and changing day length. Three years of hourly dissolved organic carbon (DOC) concentration and flow data from the River Dee catchment (1674 km^2) were analysed, and statistical analysis of the entire record shows there is no consistent diurnal cycle in the record. From the 3-year record (1095 days) there were only 96 diurnal cycles could be analysed. Cycles were quantified in terms of their: relative and absolute amplitude; duration; time to maximum concentration; asymmetry; percentile flow and in-stream residence time.

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The median diurnal cycle showed an amplitude that was 9.2% of the starting concentration; it was not significantly asymmetric; and occurred at the 19th percentile flow. The median DOC removal rate was 0.07 mg C/l/hr with an inter-quartile range of 0.052 – 0.100 mg C/l/hr. Results were interpreted as controlled by two, separate, zero-order kinetic rate laws, one for the day and one for the night. There was no single diurnal cycle present across the record, rather a number of different cycles controlled by the combination of in-stream residence time and exposure to contrasting light conditions. Over the 3-year period the average in-stream loss of DOC was 32%. The diurnal cycles evident in high resolution DOC data are interpretable, but require contextual information for their influence on in-stream processes to be understood or for them to be utilised.

Keywords: residence times; DOC; solute dynamics, greenhouse gases.

1. Introduction

Diurnal (or diel) cycles in stream flow have long been observed (Troxell, 1936; Dunford and Fletcher, 1947; Meyboom, 1965), caused by the daily cycle of evaporation losses from shallow riparian aquifers. Wondzell et al. (2010) make the point that for diurnal variations to be observed at the basin outlet, two requirements must be met: first, there must be a process to generate the fluctuations and transfer them to the stream channel; second, the cumulated effects of the diurnal process must arrive at the basin outlet as a coherent signal. Given such constraints, it seems clear that the effects are most likely to be observed in small catchments at low flow. For any nutrients which are biologically-active within the fluvial network, it can be expected that they too will experience a diurnal cycle, under certain conditions (e.g. low flow) if not every day. Such cycles may be driven by the two-phase process described above by Wondzell et al. (2010) but could also be generated in-stream rather than catchment-wide, which implies that the residence time of channel water must be long relative to the nutrient dynamics.

Many in-stream biological processes require light and so will be inactive during hours of darkness. It is generally true that the hours of darkness are cooler than daylight hours and so both photic and temperature conditions in the stream water show a diurnal cycle (Poole and Bermann, 2001), so rates of biological processes will tend to vary on a diurnal cycle with higher rates during daylight than in darkness. Examples of diurnal cycles at a single river location have been shown for: dissolved CO_2 (Neal et al., 2002); dissolved organic matter (Kaplan and Bott, 1982); nitrate (Heffernan and Cohen, 2010); Fe concentration and speciation (McKnight et al., 1988). Nimick et al. (2011) in their review of diurnal cycling in biogeochemistry concluded that diurnal cycling had not been incorporated into models and loading studies, i.e. the fact of the occurrence of diurnal cycles has not been applied or used. However, the diurnal cycle observed from spot samples of water chemistry at a single location will not reflect the true diurnal cycle unless the measurements are examined relative to the streamflow. The magnitude of the diurnal cycle will depend on the amount of time a parcel of water has been exposed to daylight and darkness and that in turn is controlled by how long that particular parcel of sampled water has been in the river. The stream flow will reflect the time each parcel of sampled water has experienced light and dark conditions during its passage through the fluvial system. Without a consideration of the in-stream residence time, i.e. the amount of time a parcel of water has been in light or dark conditions, and then it would be impossible to assess what diurnal cycles had actually been experienced. For example, if a study were concerned with the diurnal cycle of a solute and in-stream residence time was 12 hours, then a sample taken close to dawn would have experienced almost complete dark conditions whereas a sample taken at dusk would have experienced almost nothing but light conditions including the peak light conditions which would be expected to be at or near noon and peak air temperature conditions soon after. By contrast, a sample taken at noon would have experienced almost equal proportions of light and dark. Therefore, if nitrate is removed only under daylight conditions, the minimum in the nitrate diurnal cycle would not be at mid-day but rather towards sunset. Note that the situation could be further complicated if there were diurnal fluctuations in discharge caused by the diurnal cycle in evapotranspiration (e.g. Grivbovski et al., 2010).

Because, for most latitudes, day length varies across an annual cycle, the diurnal cycle will also vary, which will mean, for example, longer daylight periods in June than in December in the northern hemisphere. Therefore, even for the same river flow conditions, a diurnal cycle for a given solute could itself exhibit a seasonal cycle simply by virtue of intra-annual changes in day length. In addition, the in-stream residence time varies with flow and so, even between consecutive days, a parcel of water sampled at the same time will have experienced different proportions of day and night because even baseflow changes between consecutive days. Even sampling strategies that systematically vary the time of day at which the sampling is taken (e.g. Halliday et al., 2013) will only partially mitigate the issue as samples will have been taken at different flow conditions and so the water sampled will have experienced differing amounts of daytime and night-time conditions. Therefore, without adjusting for variations in day length and in-stream residence time, diurnal cycles measured in rivers will be difficult if not impossible to interpret meaningfully.

A number of studies of diurnal cycles of dissolved organic carbon (DOC) have been conducted. While some note an absence of diurnal cycles in streams (e.g. Beck et al., 2009), others have found them (e.g. Manny and Wetzel, 1973). Nimick et al. (2011) suggest that the diurnal cycle in DOC is dominated by maxima during daylight and minima at night caused by utilisation at night and production during the day. However, such an interpretation makes the assumption that in-stream production can dominate over utilisation even in daylight when experimental evidence is that most streams are net consumers of DOC (Moody et al., 2013). Furthermore, studies of the kinetics of DOC over diurnal cycles have shown that net increases in DOC concentration can occur but they occur at night due to aphotic turnover of particulate organic carbon (POC) producing DOC at a rate faster than the DOC can itself turnover (Worrall and Moody, 2014). An alternative explanation would be that the in-stream residence could be, for example, 18 hours such that a sample measured at midnight on an equinox would have experienced more daylight than a sample taken at midday on the same day thus leaving a diurnal cycle with a minimum at midnight and a maximum at midday.

If the day length and in-stream residence time can be estimated, then the diurnal cycle becomes a measure of the comparative removal rates in light and dark. Worrall et al. (2013a) have proposed a simple method for correcting fluvial flux methods for diurnal variation within which is a simple kinetic equation to remove the component of interest. The simple kinetic model was based on separate zero-order removal rates in both light and dark - zero-order removal was proposed by Worrall et al. (2006). Although more complex rate laws for DOC removal have been proposed (Worrall and Moody, 2014) they rely on a level of parameterisation that requires direct experimentation.

The turnover and loss of DOC as greenhouse gases from rivers is now understood to be an important component of terrestrial greenhouse fluxes. Cole et al. (2007) 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. Battin et al. (2009) suggested a lower removal rate of 21%, and Raymond et al. (2013) estimated a value of CO_2 lost from global rivers of 1.8 Pg C/yr and 0.32 Pg C/yr from lakes and reservoirs. A more detailed analysis of diurnal cycles could provide a means of measuring *in situ* removal rates of DOC and other determinands. Therefore, the aim of this study is to consider the diurnal cycle of DOC as observed in high-frequency river monitoring and assess the diurnal cycle in terms of changing in-stream residence times, changing day length across the year and the turnover rates of DOC. Given the detail available to this study it is then also possible to test the applicability of having information on only a limited number of diurnal cycles.

2. Approach & Methodology

The approach of this study was to consider sub-daily monitoring of the DOC concentrations and river flow over a 3-year period at fixed location on the River Dee at Chester, UK. The detailed time series of concentration and flow enabled the detailed analysis of observed diurnal cycles. These were characterised by: amplitude (both in absolute and relative terms); the maximum concentration in the cycle; the minimum concentration in the cycle; duration (asymmetry in sequences of diurnal cycles may mean that they are not necessarily always 24 hours long); and asymmetry. Given the context of the DOC monitoring, it is also possible to consider not only the river flow but perhaps more importantly the in-stream residence time over the cycle and then also the time any sample would have spent in the river in daylight or during the night.

2.1. Study site

Data were collected for the River Dee just upstream of the city of Chester where data could be paired with flow records (Figure 1). The River Dee to the Chester monitoring site has a catchment area of 1674 km^2, with annual average rainfall (1961 – 1990) of 1143 mm. Ten percent of the catchment is classified as mountain, heath and bog which can be considered as the major source of the DOC considered in this study (National River Flow Archive – http://www.ceh.ac.uk/data/nrfa/). Monthly climatic summaries (average monthly temperature and total monthly sunshine hours) for the study period were available for Shawbury (Figure 1 - UK Meteorological Office – http://www.metoffice.gov.uk). The concentration data were collected hourly between 1st January 2009 and 31st December 2011 and the flow data every 15 minutes over the same period. Over the 3-year period the median river discharge was 15.5 m^3/s with 95% exceedance flow of 5.8 m^3/s and 5% exceedance flow of 101.4 m^3/s. The DOC concentration data were collected using an UV absorbance probe (ABB AV400) calibrated for DOC concentration using potassium hydrogen phthalate on a regular basis. For the DOC concentration over the 3-year period the median concentration was 11.2 mg C/l with a 95th percentile of 21.3 mg C/l and a 5th percentile of 4.6 mg C/l. The calibration between UV absorbance and DOC concentration is not necessarily stationary and would be a source of uncertainty, the further discussion of which is beyond the scope of this study (Watts et al., 2001).

2.2. Preliminary analysis

The 3 years of data were visually inspected for diurnal cycles. It was difficult to define precise and objective criteria for identifying diurnal cycles but periods of between 18 and 36 hours were selected where there was a systematic deviation and return to the starting value were further examined. Each identified diurnal cycle was taken as starting at a minimum point and the following were recorded: Julian day; calendar month; hour of the minimum; flow at the minimum; the flow expressed as the percentile of all flows of the period of study; DOC concentration at the minimum; DOC concentration at the maximum; amplitude; the amplitude expressed as percentage of the minimum DOC concentration at the start of the cycle; time at the maximum; and cycle period. By taking the times of each minimum, maximum and cycle length, it was possible to assess symmetry of the cycles. The in-stream residence time at the minimum and maximum of each cycle, the hours of day and night experienced at the time of minimum and maximum in each cycle, and the kinetic turnover parameters were calculated as described below.

2.3. In-stream residence time

In-stream residence time (t_r) can be defined as:

$$t_r = \int_{x_e}^{x_m} \frac{x}{v} dx \qquad \text{(i)}$$

where: v = the mean cross-sectional velocity at point x; x = the downstream distance along the river channel; x_m = the downstream monitoring point; and x_e = the point along the river length where the water enters the river. In Worrall et al. (2014) point x_e was taken as the expected distance of the river discharge, i.e. the point at which the “average” discharge could be expected to enter the river, however, this study will instead consider the point at which DOC would have expected to enter the river.

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

$$v = \left(\frac{1}{n}\right)\left(\frac{a_{cross}}{p}\right)^{\frac{2}{3}} s^{\frac{1}{2}} \qquad \text{(ii)}$$

where: a_{cross} = cross-sectional area of the river at point x; p = the wetted perimeter; s = the water surface slope; and n = the Manning coefficient. If Equation (ii) is expressed in terms of x, i.e. the down-channel distance along the river, then Equation (i) can be used to estimate velocity as a function of down-channel distance.

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

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

where S_x = the bed slope at point x; S_0 = the bed slope at source; φ = a constant. At the scale of the entire river length and at steady state, it can be assumed that bed slope is a good approximation of the water surface slope in Equation (ii) (Wilson, 1994). Equation (iii) can be readily calibrated for any catchment; here this was done by reference to altitudes of gauging stations on the River Dee.

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

$$\frac{a_{cross}}{p} = \frac{dw}{(2d+w)} \qquad \text{(iv)}$$

where d = river channel depth and w = river channel 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 width change with river length. The assumption of a rectangular section is the simplest possible formulation but could be readily replaced if more complex formulations of the river cross-section were required. A possible alternative formulation for Equation (iv) is to consider a v-shaped, or triangular cross-section:

$$\frac{a_{cross}}{p} = \frac{dw}{\sqrt{w^2+4d^2}} \qquad \text{(v)}$$

Other formulations of the channel-section, e.g. trapezoidal, would mean that additional parameters would be required to calculate cross-sectional area, e.g. the angle of the river bank. Since the angle of channel banks could not readily be known for any individual catchment, this cannot be a general approach.

The further advantage of using the formulation in equation (iv) is that river width does not vary with river depth. To calibrate equation (iv) with respect to width, we used data collected by Dangerfield (1997) to create an empirical equation for river width variation with catchment area. Dangerfield (1997) lists the bankfull width of 124 UK rivers; these data were augmented with data from the River Tees (Worrall et al., 2014) to give the following equations:

$w = 0.061C + 9.0$ r^2 = 0.73, n= 129 (vi)

$l = 1.75C^{0.54}$ r^2 = 0.77, n= 129 (vii)

where C = catchment area (km^2); and w_0 = river channel width at source (m).

River channel depth, the other component of equation (iv), will vary with flow and we propose the following form of equation:

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

where: ${}^{f}d_x$= depth at exceedence flow f (eg. 10% exceedence) at river length x (m); ${}^{f}d_m$ = depth of the river at the monitoring point m for exceedence flow f; and β, γ, δ = constants where β approximates to ${}^{f}d_m - {}^{f}d_0$. Equation (viii) can be calibrated against of observations of river depths at a given point for a given exceedance flow; furthermore, a Weibull function has a physical interpretation whereas a simple power law approach does not. For example, a Weibull function can represent a range of shapes of response, including sigmoidal, and the parameters in the equation can have physical meaning and be directly read from the data, e.g. the minimum and maximum values observed are explicitly included in the equation.

Note this is a reasonable approach as long as the critical Froude number is not exceeded and so no consideration of kinematic wave velocity is required. Given the assumptions of a rectangular cross-section, the critical Froude number at the point of interest (F_x) can be defined as:

$$F_x = \frac{v_x}{\sqrt{g d_x}} > 1 \qquad \text{(ix)}$$

where all terms are as above and g is the acceleration due to gravity (ms^{-2}). Given the calculations of velocity profile above, then this assumption can readily be tested. This approach also assumes that the river is not impacted in any substantial way by impoundment, for the River Dee FARL = 0,96 (FARL - Flood and Attenuation by Reservoirs and Lakes, NERC, 1975).

2.4. Extent of daylight

Given that the in-stream residence time can be calculated, it is important to know the proportion of that time which is daylight and how much is during darkness. The day length at any given latitude can be calculated from:

$$h = 12\left(1 - \tan(l)\, tan(0.409 cos(0.0172N)\right) \qquad \text{(x)}$$

where: l = latitude (radians); N = day of the year with 21st December = 1. The time of sunrise (Julian hour) was then taken to be:

$$S = 12 - \frac{h}{2} \quad \text{(xi)}$$

The number of hours of daylight that the sample has experienced (D) is then dependent upon the time of sampling (t_s):

If $t_s > S$, then

$$D = \frac{h}{2} + t_s - 12 \quad \text{(xii)}$$

If $t_s < S$, then:

$$D = 24 - h + t_s - S \quad \text{(xiii)}$$

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The total number of hours of darkness (H) experienced by a sample can be judged if the residence time of the river from point of the water containing the solute joining the river to the point of sampling (t_r) is known. If $D > t_r$ and t_s-S <= 0, then:

$$H = t_r \quad \text{(xiv)}$$

Else

$$H = D \quad \text{(xv)}$$

The above equations could be applied relative to the monitoring point by calibration with the data readily available for gauging stations on the River Dee (Figure 1) as reported within the

National River Flow Archive (www.nrfa.ac.uk) and the Flood Studies Report (NERC, 1975). The data required were: mainstream river length to the gauge; altitude of the gauging station; flow duration curve (values for Q_{10}, Q_{50}, Q_{95} and Q_{bf} are routinely reported for river flow gauging stations in the UK); and the bankfull width and depth.

Based upon the distribution of land use and habitats of the catchment as defined by the land cover map of the UK (www.ceh.ac.uk/landcovermap2007), it was assumed that DOC had entered the river by the point at 54 km river length (56 km from the monitoring point) at a catchment area of 261 km^2 – this is also downstream of the major impoundments in the catchment.

2.5. Removal rates

Given the calculation of the in-stream residence time and the amounts of time any sample of water had spent in darkness and light, it is possible to go further and consider the removal rates. Worrall et al. (2013a) used a zero-order kinetic law to calculate the amount removed as:

$$T = [DOC]_0 - [DOC]_{min} = k_H H_{min} + k_D D_{min} \qquad \text{(xvi)}$$

where T = total amount removed; k_x = zero-order removal rates (mg C/l/hr) where x = H or D for removal rate in dark or daylight conditions; and $[DOC]_x$ = DOC concentration (mg C/l) with x = 0 for the initial concentration of DOC entering the stream and min for the concentration at the minimum in the diurnal cycle. Zero-order removal rates for DOC in UK rivers have been observed (Worrall et al., 2006), but it might be reasonable to consider that k_D would be a function of light and temperature conditions as well as dependent upon DOC concentration, i.e. not zero-order. Worrall and Moody (2014) used the approach of

Bukaveckas and Robbins-Forbes (2000) to show that for the River Tees, northern England (catchment area = 818 km^2) that full depth light penetration would occur in all but 7% of the highest flows. Moody et al. (2013) measured the activation energy of DOC turnover in a UK river and found it was only 2.6 Kj/g, i.e. negligible variation in k_D with temperature. However, Moody et al. (2013) did show empirical rate laws for DOC turnover that were not zero-order and that apparent quantum yield of DOC photodegradtion was between 9.6 and -1.7 mmol C/mol photons, i.e. both photodegradation and photoproduction were possible. As suggested in the introduction, without specific empirical evidence it would be difficult to invoke more complex rate laws for this study.

An equivalent to Equation (xvi) can be written for the conditions at the maximum concentration of the diurnal cycle instead of the minimum of the diurnal cycle. Although it would be unreasonable to assume that the initial concentration of DOC at the source of the river ($[DOC]_0$) was constant across the annual cycle or across an hydrological event, it is reasonable to assume that the $[DOC]_0$ is constant over a diurnal cycle especially if it is also assumed that in-stream residence time were constant over that same diurnal cycle, i.e. that there was no hydrological event on that same day such as a runoff event whose duration is entirely within one diurnal cycle. Then utilising Equation (xvi) in terms of both min and max concentrations in the diurnal cycles, it is possible to say:

$$\frac{A}{2(H_{min}-H_{max})} = k_H + k_D \qquad \text{(xvii)}$$

Where: A = amplitude of the diurnal (mg C/l). Given that A, H_{max} and H_{min} can be measured or calculated for each diurnal cycle, it was possible to assess $k_H + k_D$. The calculated $k_H + k_D$ for each observed diurnal cycle was compared to the characteristic of those diurnal cycles using multiple regression.

The flux of DOC that passed the monitoring point was calculated in Worrall et al. (2013b); these flux calculations were compared to the removal rates ($k_H + k_D$) meaning that it was possible to calculate annual removal rates of DOC.

2.6. Statistical analysis

If a consistent and coherent diurnal cycle exists for DOC concentration at the study site, it should be a significant factor in the variation of the DOC concentration. The entire hourly record from the 3 years of the study was subjected to an analysis of variance (ANOVA) where year, month and time day were included as factors. The year factor has 3 levels (2009 – 2011); the month factor will have 12 levels, one for each calendar month, and the time of day factor will have 24 levels. Given the large quantity of data, it was possible to consider all two-way interactions between the three factors. River flow at the time of measurement was included as a covariate. The normality of the DOC concentration and river flow data was tested prior to analysis using the Anderson-Darling test (Anderson and Darling, 1952) and the data were log-transformed as required with no further transformations proving necessary. The difference between levels of any significant factors was subjected to *post hoc* testing using the Tukey test. The proportion of variation in the response variable that is explained by a given factor or covariate was determined using the generalised omega squared statistic (ω^2- Olejnik and Algina, 2003). The level of each factor was assessed using least squares means (also known as estimated marginal means). However, it should be noted that, given the hypothesis of this paper, no significant diurnal cycle would be expected as the hypothesis of this study is that diurnal cycles will be dependent on flow and season leading to a wide variation in diurnal cycles.

A further ANOVA was conducted in which the diurnal cycles recorded in June during the three years of available data were compared to data for all other months. June is the month which at UK latitudes has the largest proportion of daylight hours even if not the highest monthly air temperatures in the UK. Therefore, we would expect June to have the most developed diurnal cycles and those with the largest amplitude. Furthermore, June in the northern hemisphere was the popular month for all previous studies conducted into diurnal cycles and so if the hypothesis of this study is that diurnal cycles can only be understood in the context of their in-stream residence time then diurnal cycles in June would be expected to be distinct from those at other times of the year.

Measures of the diurnal cycles (amplitude, k_D, k_H) were compared to the drivers (calendar month, flow, in-stream residence time; time in daylight and time in night) using multiple linear regression. The calendar month was transformed to a continuous variable as $cos\left(\frac{m\pi}{6}\right)$ and $sin\left(\frac{m\pi}{6}\right)$ where m is the month number (January = 1 to December = 12). Variables were tested for normality and transformed as necessary prior to regression and only variables found to be significant at the 95% probability of being greater than zero were included.

3. Results

3.1. Testing for a single diurnal cycle

For the DOC concentration over the 3-year period, the median concentration was 11.2 mg C/l with a 95th percentile of 21.3 mg C/l and a 5th percentile of 4.6 mg C/l. The ANOVA found that all the factors were significant at $P< 0.05$ but only the interaction between year and month factors was found to be significant (Table 1). The most important factor was the difference between months (explaining 28.2% of the variance in the original dataset); the least important but still predicted to be significant factor was the difference between hours of the day which explained only 0.04% of the original variance – it should be remembered that there are 26,280 data in the original dataset. Despite the ANOVA finding a significant difference due to hour of the day, the *post hoc* testing found no differences between hours of the day that were significant at better than $P < 0.1$, i.e. the importance of the hour factor is so small that different tests disagree. Furthermore, the least squares means plot shows that the pattern of the hour factor is not diurnal but semi-diurnal, i.e. has a frequency of 12 hours and not 24, the shape of this diurnal cycle peaks at 12 noon and again at midnight (Figure 2). This semi-diurnal cycle has an amplitude of 0.4 mg C/l or 3.6% variation from the median. If this is a significant cycle, it could represent a management process within the dataset, e.g. reservoir release; or peaks in sewage treatment, but it might unlikely that management processes in the upstream portion of the catchment would give such a regular pattern with maxima at at noon and midnight. Alternatively the cycle could represent an interference pattern between several diurnal cycles operating across the study period. There is no significant diurnal cycle discernible across the whole record and, given the discussion above, this would be due to shifting diurnal cycles with shifting flow and season.

3.2. Analysis of observed diurnal cycles

From the 3 years of monitoring, it was possible to consider 96 diurnal cycles. The median properties of the diurnal cycles are shown in Table 2 and examples in Figure 3. It was noticeable that diurnal cycles were only discernible on the lowest flows with all the examined diurnal cycles being observed at flows less than the long-term median river flow at the study site. Of the 96 diurnal cycles. 29 were in Spring (March-May); 42 in summer (June – August); and 25 in autumn (September –November) – there were diurnal cycles observed in Winter (December – February). Similarly, the median minimum and maximum concentrations in the observed diurnal cycles were both below the median DOC concentration for the entire 3-year record (3-year median DOC concentration = 11.2 mg C/l). The median amplitude was 9.2% or 0.95 mg C/l (Table 2). Due to changing flow conditions within a diurnal cycle, the duration of the observed diurnal cycles was not always exactly 24 hours. The median time of maximum concentration was 0800 hours which would be just after dawn and, given the median in-stream residence time of the diurnal cycles examined was 12.9 hours, then river water at 8 am would have experienced maximum darkness and, therefore, minimum opportunity for photo-mediated processes to have effect. The asymmetry was 48%, i.e. the maximum concentration was achieved slightly before the mid-point although 50% was within the inter-quartile range suggesting that there is little difference from symmetric cycles. Given the lack of asymmetry this characteristic was not analysed further. The variation due to the diurnal cycle is small compared to the variation due to flow events (Figure 3a and b).

Over the three years there were 23 diurnal cycles measured in June. The ANOVA comparing those June diurnal cycles with diurnal cycles from all other months shows significant (probability being zero, $P < 0.05$) differences between maximum and minimum concentration in the diurnal cycles; and the amplitude of the diurnal cycles. Unsurprisingly there were no significant differences between duration, time to maximum and asymmetry, i.e. no significant variation between those measures of the diurnal that showed very little variation anyway. When the relative amplitude was considered there was no significant difference between June and other months.

The rate of removal can be considered as the amplitude of the diurnal cycle over half the wavelength, in which case the removal rates had a median of 0.070 mg C/l/hr with an inter-quartile range of 0.052 – 0.100 mg C/l/hr. If it was assumed that removal only occurred in daylight hours, then the removal rate has an inter-quartile range of 0.04 to 0.15 mg C/l/hr. Moody et al. (2013) found removal rates over a 10-day period varying from 1.25 mg C/l/hr to -0.15 mg C/l/day, i.e. increases or no change in DOC concentrations were observed in those experiments.

Comparing the observed characteristics of the 96 diurnal cycles to characteristics of their occurrence shows that the best-fit equation for $k_H + k_D$ was:

$$ln(k_1 + k_2) = 0.7\, cos\left(\frac{m\pi}{6}\right) - 1.9 - 0.05D_{max} \qquad \text{n = 92, } r^2 = 0.17 \text{ (xviii)}$$

(0.2) (0.2) (0.01)

where all terms are as defined above and the terms in the brackets below the equation are the standard errors in the coefficients. The sample was smaller than 96 as not all metrics were available for all diurnal cycles. The fit of Equation (xviii) was significant even if it explained only 17% of the original variance in the dataset. The rate of loss is at a maximum in December and a minimum in June. Such an annual cycle could be considered to be a mimic of, or represent, day length changes through the year; however, the relationship is the reverse of that expected and Equation (xviii) does also contain a term in D_{max}, i.e. an allowance for day length. Therefore, we would suggest that the monthly variation in Equation (xviii) actually represents a change in the degradability of the source material, i.e. DOC entering the stream in December is more readily turned over than that in June. The average monthly temperature for the 3-year study period did reach its maximum in June (7.6 ^{o}C) and minimum in December (2.2 ^{o}C) but sunshine hours were maximum in May (76 hours) and minimum in September (31 hours).

For the absolute value of the amplitude (A) the best-fit equation was:

$$lnA = 0.03D + 0.04H - 0.39sin\left(\frac{m\pi}{6}\right) - 0.79 \qquad \text{n = 92, } r^2 = 0.3 \text{ (xix)}$$

(0.02) (0.007) (0.1) (0.3)

Only variables significant from zero at the 95% probability were included in equation (xix) and the values in the bracket represent the standard errors in the coefficients. The partial regression analysis shows that the least important variable was time in light explaining only 4.4% of the variance in the original dataset but, as would be expected, the amplitude increases with increasing hours of daylight experienced by the sample. The most important variable is the hours spent in darkness which explains 26.2% of the original variance. The month variable explained 15.1%. The month variable suggests that the lowest amplitudes were in March and the amplitudes peaked in September but this does not match the seasonal cycle observed in Equation (xviii).

4. Discussion

How does the diurnal cycle measured here compare to previous results? This study was able to find and consider 96 diurnal cycles, far more than in previous studies. For example, Gammons et al. (2011), Parker et al. (2010), Spencer et al. (2007) and Scott et al. (2002) considered only two diurnal cycles, Bourg and Berlin (1996) considered only hourly samples for 26 hours, Johnson and Tank (2009) only considered two events but across six streams (12 cycles in total): all of these studies considered summer conditions only. With such small sample sizes seasonal and flow factors could not be considered and it was impossible to define a statistically significant diurnal cycle. For example, Volkmar et al. (2011) suggested that the diurnal cycle in algae created a diurnal cycle in nutrients but their data showed no significant correlation between algal pigments and nutrients (including N, P and C) even over the 16 diurnal cycles considered. This is not to say there are not diurnal cycles discernible at single locations and these include algae, chlorophyll-a, temperature (e.g. Pokrovsky and Shirokova, 2013), dissolved oxygen and dissolved CO_2 (Hannes et al., 2014) and, of course, this study restricts itself to consideration of rivers and not lakes or other standing waters (e.g. Forget et al., 2009). One alternative explanation is that many studies that have considered DOC have involved systems with low DOC concentrations relative to the river considered here. For example, the streams considered by Parker et al. (2010) had peak DOC concentrations of 2 mg C/l compared to median value of 11.2 mg C/l for the river in this study, i.e. the DOC in the catchment in this study was dominated by a strong source of DOC in its headwaters (i.e. peat soils) and any internal contribution will be small in comparison.

The rate laws proposed in this study have been shown to be a reasonable description of the data but even zero-order kinetic rates would be controlled by temperature as described in the Arrhenius Equation with rates increasing with increased temperature. However, this was explicitly not observed in Equation (xviii); indeed, if the data for $\ln(k_D+k_H)$ were fitted to the Arrhenius equation using the observed absolute monthly temperature, this gives a negative activation energy. Although negative activation energies are known in chemistry, it would suggest that the dominant effect in the case of DOC flux through the River Dee is change in source composition over the year compared to changes in air temperature.

The median in-stream residence time for the River Dee over the 3 years was 25.5 hours, and this varied from 112 hours for 95% exceedance flow and 7.4 hours at bankfull flow. 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. Moody et al. (2013), coupling models of total loss of DOC with estimates of in-stream residence times, showed that annual loss rates of DOC across a 818 km^2 catchment (River Tees, England) would be between 48 and 69%, estimated at an equivalent removal rate of DOC for this catchment of between 7.7 and 21.4 tonnes C/km^2/yr, over a median in-stream residence time of 35 hours. 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 catchment losses. A net loss of DOC up to 78% was found, equivalent to between 9.0 and 12.7 tonnes C/km^2 of UK land area/yr.

When Equation (xviii) was applied to the three years of record from the study site, the equivalent flux lost can be compared to the flux at the study site. The DOC flux from the site was between 10.3 and 17.1 ktonnes C/yr (6.1 to 10.3 tonnes C/km^2/yr); a flux of DOC from the terrestrial source of between 15. 1 and 25.3 ktonnes C/yr (9.0 to 15.1 tonnes C/km^2/yr).The equivalent flux lost was 4.8 and 8.1 ktonnes C/yr (2.9 to 4.9 tonnes C/km^2/yr), giving a removal rate of 32% relative to the terrestrial source. It should be pointed that although this finding is based upon 96 diurnal cycles this is only 6.6% of the sampled period. When only data from June was considered the median removal rate was 0.055 mg C/l/hr but other months 0.081 mg C/l/hr, meaning that if only June data were considered then a removal rate of 22% relative to the terrestrial source would be predicted, i.e. an underprediction relative to all the available data. At the UK scale, the median in-stream residence time has been estimated to be 26.7 hours which suggests that removal rates observed for the River Dee might be reasonable estimate for the UK. Worrall et al. (2013b) corrected previous estimates of the UK DOC flux for sampling bias and estimated that the flux at the tidal limit in the 2000s was on average 2420 ktonnes C/yr (9.2 tonnes C/km^2/yr) which, given the removal rate measured here, means 3305 ktonnes C/yr (13.5 tonnes C/km^2/yr) lost from the terrestrial biosphere as DOC and 1057 ktonnes C/yr (4.3 tonnes C/km^2/yr) lost from the streams to the atmosphere. At the global scale, Cole et al. (2007) proposed an in-stream removal rate for total fluvial carbon of 42%, and Battin et al., (2009) suggested a lower removal rate of 21%.

5. Conclusions

This study could find no single consistent diurnal cycle in DOC over three years of hourly concentration data. However, 96 cycles were identified, all under low-flow conditions; the dominant feature was concentration peaking early in the morning as a result photic removal processes of DOC decreasing to zero during the night. The median amplitude of the diurnal cycles was 9.2%. It was possible to consider the diurnal cycles as controlled by two, zero-order kinetic removal process, i.e. separate day and night removal processes. The application of the best-fit model to the annual flux data for the study river suggested that over a year the in-stream removal processes could remove 32% of the incoming DOC over a median in-stream residence time of 25.5 hours. If only summer data for diurnal cycles were considered, as in previous studies, then the amplitude of diurnal cycles and removal rates would have been underestimated.

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Table 1. The results of the ANOVA of all DOC and riverflow results over the three year study period.

Factor/Interaction	Percentage of variance (ω^2 - %)
Log(river flow)	15.7
Year	11.7
Month	28.2
Hour	0.04
Year*Month	14.3
Error	30.4

Table 2. Properties of the studied diurnal cycles.

Property	Median	Inter-quartile range
Min. concentration (mg C/l)	9.7	6.8 – 13.0
Max. concentration (mg C/l)	10.2	7.8 – 14.4
Amplitude (mg C/l)	0.95	0.59 – 1.26
Amplitude (%)	9.2	7.0 – 14.2
Duration (hrs)	25	23 - 28
Time of max. concentrations	8	4 - 16
Asymmetry (%)	48	40 - 55
Percentile flow (%)	19	7 - 39
In-stream residence time (hrs)	12.9	8.3 – 23.2

Figure 1. Location of the study site and River Dee catchment. Chester is the location of the high frequency monitoring and Shawbury is the location of the climatic data.

Figure 2. The main effects plot of the diurnal cycle from all observed data across 3 years of the study.

Figure 3. Examples of the diurnal cycles observed at the study site: a) 24th September 2009 starting at 4am; and b) 3rd April 2010 starting at 8am..