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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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SUMMARY

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.

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.

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

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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 h, 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 h 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 and 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 h 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 (Fig. 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 (Fig. 1 – UK Meteorological Office – http://www.metoffice.gov.uk). The concentration data were collected hourly between 1st January 2009 and 31st