



## Improved automation of dissolved organic carbon sampling for organic-rich surface waters

Richard P. Grayson\*, Joseph Holden

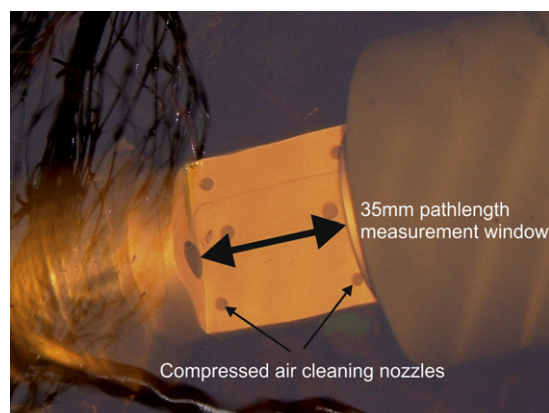
*water@leeds, School of Geography, University of Leeds, Leeds LS2 9JT, UK*



### HIGHLIGHTS

- We test an in-situ probe to measure high DOC concentrations in peatland streams.
- Linear regression modelling enabled DOC measurement far beyond stated upper limits.
- Models combining absorbance for several wavelengths achieved greatest accuracy.
- Our approach enables improved in situ long-term fluvial DOC flux measurements.

### GRAPHICAL ABSTRACT



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### ABSTRACT

In-situ UV–Vis spectrophotometers offer the potential for improved estimates of dissolved organic carbon (DOC) fluxes for organic-rich systems such as peatlands because they are able to sample and log DOC proxies automatically through time at low cost. In turn, this could enable improved total carbon budget estimates for peatlands. The ability of such instruments to accurately measure DOC depends on a number of factors, not least of which is how absorbance measurements relate to DOC and the environmental conditions. Here we test the ability of a S::can Spectro::lyser™ for measuring DOC in peatland streams with routinely high DOC concentrations. Through analysis of the spectral response data collected by the instrument we have been able to accurately measure DOC up to  $66 \text{ mg L}^{-1}$ , which is more than double the original upper calibration limit for this particular instrument. A linear regression modelling approach resulted in an accuracy >95%. The greatest accuracy was achieved when absorbance values for several different wavelengths were used at the same time in the model. However, an accuracy >90% was achieved using absorbance values for a single wavelength to predict DOC concentration. Our calculations indicated that, for organic-rich systems, in-situ measurement with a scanning spectrophotometer can improve fluvial DOC flux estimates by 6 to 8% compared with traditional sampling methods. Thus, our techniques pave the way for improved long-term carbon budget calculations from organic-rich systems such as peatlands.

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\* Corresponding author.

E-mail address: [r.grayson@leeds.ac.uk](mailto:r.grayson@leeds.ac.uk) (R.P. Grayson).

## 1. Introduction

Aquatic carbon fluxes from organic-rich systems such as peatlands are thought to be very important. For peatlands, estimates suggest that carbon released into river waters is equivalent to between a third to over half of the annual net ecosystem exchange (Dinsmore et al., 2010; Nilsson et al., 2008; Roulet et al., 2007). Traditionally, DOC flux measurements, particularly in peatlands, are based on occasional (e.g. weekly) grab sampling of river water (Strack et al., 2015; Tipping et al., 2010). However, this can be highly problematic. For example, in ombrotrophic peatland systems, river flow regimes can be very flashy (Holden and Burt, 2003; Price, 1992) and the greatest fluxes of dissolved organic carbon (DOC) may occur during short intervals at high flow (Holden et al., 2012b). Therefore, sampling DOC at monthly or weekly intervals in rivers draining ombrotrophic peatlands is likely to be inadequate for deriving annual flux estimates because crucial phases of flow will probably be under-represented by the samples. For this reason some researchers also supplement their weekly (or less frequent) sampling regime with storm event sampling for a handful of events throughout the year (Clark et al., 2007; Worrall et al., 2012). While this additional storm sampling may provide improved estimates of DOC flux there will still be large uncertainties because the relationship between discharge and DOC concentration is non-linear and may vary strongly depending on antecedent conditions. There is therefore an urgent need for a system to provide high resolution DOC sampling over time for organic-rich aquatic systems.

Samples collected from rivers and lakes which require DOC analysis in the laboratory are often directly measured using thermal catalytic oxidation (Billett et al., 2012; Clark et al., 2007). The method is well established and thought to have good accuracy and precision but can be expensive due to the relatively high cost of TOC analysers and consumables. A widely accepted alternative, for cases where it is neither possible nor practical to directly measure DOC using thermal oxidation, involves the use of UV–Vis absorbance as a proxy measure of DOC. Humic substances strongly absorb light over the UV–Vis spectrum and a spectrophotometer approach offers both lower instrument and consumable costs. Most such proxy analysis has been conducted in the laboratory, on samples previously collected in the field. As such this technique merely reduces cost and does not deal with the need for a high resolution sampling frequency of river waters in organic-rich systems. However, the advent of logging UV–Vis spectrophotometers which can be left in situ in the field offers a potential opportunity to significantly improve the quantification of aquatic DOC fluxes and our understanding of how types of aquatic DOC change through time (Grayson and Holden, 2012). Nevertheless, these devices have not been fully tested under field situations for use as a DOC proxy.

Logging UV–Vis spectrophotometers were developed to provide 'on-line' water quality measurements within water and sewage treatment works. Their apparent ability to 'measure' DOC relies on the fact that humic acids strongly absorb light over the UV–Vis range (Chen et al., 2002). Thus these spectrophotometers require effective calibrations using laboratory-based DOC measurements and this may be constrained by local conditions and spatial variability in the relationship between absorbance and DOC. Absorbance measurements at numerous wavelengths have been proposed as the most effective proxy for DOC including 254 (Spencer et al., 2007), 272 (Spencer et al., 2007), 285 (Kalbitz et al., 1999), 340 (Baker et al., 2008; Spencer et al., 2007; Tipping et al., 1988; Tipping et al., 1999), 360 (Kalbitz et al., 1999), 365 (Baker et al., 2008; Spencer et al., 2007), 400 (Clay et al., 2009; Worrall et al., 2003; Worrall and Burt, 2007), 410 (Baker et al., 2008; Spencer et al., 2007), 465 (Hautala et al., 2000; Wallage and Holden, 2010) and 470 nm (Kalbitz et al., 1999). The use of a single wavelength for a calibration to DOC has been questioned (Wallage and Holden, 2010). Indeed, the exact make up and composition of DOC can vary between sites, typically being made up of a combination of humic and fulvic acids (Thurman, 1985). Indices such as E4/E6 (absorbance at

465 nm divided by absorbance at 665 nm) and specific UV absorbance (SUVA; ratio of UV absorbance at 254 nm to DOC concentration), have been used to characterise the composition of DOC. The very fact that scientists use SUVA as a variable, shows that it is expected that the relationship between DOC concentration and absorbance at 254 nm is not stable. As a result Tipping et al. (2009) developed a 'universal' two-wavelength model that uses absorbance at 254 and 340 nm as a proxy for DOM. This model was further developed by Carter et al. (2012) who suggested that the relationship between absorbance at 254 nm and DOC concentration might not be reliable in samples with high DOC concentrations ( $>50 \text{ mg L}^{-1}$ ) and hence proposed using 270 and 350 nm. The use of multiple wavelengths may allow measurement errors associated with a single wavelength to be minimised. This is particularly important for in-situ measurements where sampling conditions are outside of the user's control. For example, in peatland systems, particulate organic carbon (POC) may make up a significant proportion of suspended sediment concentrations (SSC) and it remains unclear how effective optical instruments are in quantifying POC due to differences in the properties of POC compared with mineral dominated SSC which affects how particles scatter and absorb light (Evans and Warburton, 2007).

If the above absorbance proxy issues can be overcome, then the development of submersible in-situ UV–Vis spectrophotometers offers the potential for hitherto unobtainable high-resolution aquatic DOC concentration change measurements and flux calculations. Grayson and Holden (2012) previously explored the use of an in-situ UV–Vis spectrophotometer to measure absorbance across the UV–Vis spectrum within a UK peatland stream. However, their study was focussed on the response of absorbance to flow conditions and did not include a DOC calibration. As yet, the use of in-situ UV–Vis spectrophotometers to measure DOC in aquatic systems remains relatively low, particularly in peatland systems (Grayson and Holden, 2012; Koehler et al., 2009) where DOC concentrations can routinely exceed  $20 \text{ mg L}^{-1}$  (Clark et al., 2007). The pathlength of submersible, in situ, UV–Vis samplers determines the concentration range over which they can measure, as with lab based UV–Vis methods narrow pathlengths are required where concentrations, and hence absorption, are high.

The overall aim of our study was, for the first time to produce high resolution aquatic DOC flux measurements in organic-rich environmental waters with routinely high DOC concentrations. In order to convert high resolution absorbance data to DOC concentrations we use data across the UV–Vis spectrum to determine the most appropriate calibrations. We also establish whether these calibrations can be used to extend instrument use well beyond the narrow manufacturer quoted instrumental measurement range. In doing so we demonstrate that wider pathlength devices, which are designed to measure lower concentrations but are less susceptible to biofouling, can in fact be used over a much greater measurement range which is suitable for capturing natural variability in streamwater DOC concentrations.

## 2. Materials and methods

### 2.1. Sites

Two blanket peatland catchments were used to conduct field trials in the study. Cottage Hill Sike (CHS) is located in the Moor House World Biosphere Reserve in upper Teesdale ( $54^{\circ}41'41.0''\text{N}$ ,  $2^{\circ}22'57.7''\text{W}$ ), northern England (Fig. 1). This site has been extensively used for carbon flux measurements (Billett et al., 2012; Clark et al., 2005; Holden et al., 2012b), with weekly regular sampling under strict protocols as part of the UK's Environmental Change Network programme (Sykes and Lane, 1996). Of the 7.4 ha catchment (Smart et al., 2013) blanket bog covers approximately 98% (Adamson et al., 1998; Miller et al., 2001), with peat depth varying across the site, being typically 3 to 4 m thick and extending up to 8 m in places (Holden et al., 2012a). The stream is gauged with a rated flume and water level sensor.

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