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# Freeze/thaw and pH effects on freshwater dissolved organic matter fluorescence and absorbance properties from a number of UK locations

Robert G.M. Spencer<sup>a,\*</sup>, Lucy Bolton<sup>d</sup>, Andy Baker<sup>e</sup>

<sup>a</sup>Ocean Research Group, School of Marine Science and Technology, University of Newcastle-upon-Tyne, The Ridley Building, NE1 7RU, UK

<sup>d</sup>The Environment Agency, Lower Trent Area Offices, Nottingham NG2 5FA, UK

<sup>e</sup>School of Geography, Earth and Environmental Sciences, University of Birmingham, Edgbaston, Birmingham B15 8TT, UK

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## ABSTRACT

The UV–visible and fluorescence excitation–emission matrix spectrophotometric properties of dissolved organic matter (DOM) were compared for the effects of both pH and freeze/thaw on a wide range of freshwater DOM samples from the United Kingdom. It was observed that the spectrophotometric properties of our freshwater samples were sensitive to pH and that the recorded change varies with fluorescence and absorbance intensity, DOC concentration and the wavelength observed. Large and variable responses to pH were particularly severe at extremes of pH, but within the natural levels typically observed in freshwaters the response to pH was limited. For the same sample set large and variable responses were observed when subjected to freeze/thaw. From our data, knowledge of the original properties cannot be used to determine the amount of change that will occur with freezing and subsequent thawing. It is therefore recommended that in future research, to maintain the natural signal of the DOM, analysis is conducted at natural pH and without freezing to facilitate ease of comparison between studies. Our results also have implications for studies that utilise spectrophotometric techniques to investigate long-term trends in dissolved organic carbon in rivers. Spectrophotometric parameters from upland derived samples show varied responses of samples to pH and there is clear potential to complicate trends in the interpretation of long-term water colour data if pH is changing over time in a system or if samples are treated with different storage protocols with respect to acidification and freezing.

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## 1. Introduction

Aquatic dissolved organic matter (DOM) strongly absorbs energy in the UV–visible (UV–vis) wavelength range, and this has led to the use of UV–vis absorbance spectrophotometry as a method to determine composition and concentration of

DOM (Korshin et al., 1997). Typical UV–vis absorbance spectra of DOM, in both isolated and raw states, exhibit featureless trends of decreasing absorbance with increasing wavelength (Kalbitz et al., 1999). This lack of overall resolution has led to the measurement of UV–vis absorbance at single wavelengths or wavelength ratios to determine specific compositional

\*Corresponding author. Now at: Department of Land, Air and Water Resources, University of California, Davis, One Shields Avenue, Davis, CA 95616, USA, also at Department of Viticulture and Enology, University of California, Davis, One Shields Avenue, Davis, CA 95616, USA. Tel.: +1 530 754 4327; fax: +1 530 752 0382.

E-mail address: [rgspencer@ucdavis.edu](mailto:rgspencer@ucdavis.edu) (R.G.M. Spencer).

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variations in DOM (Hautala et al., 2000). For example,  $a_{465}/a_{665}$  has been used as a proxy for aromaticity (Chen et al., 2002),  $a_{254}/a_{410}$  has been used as a proxy for molecular weight (Andersen et al., 2000; Andersen and Gjessing, 2002) and specific UV absorbance  $SUVA_{254}$  ( $a_{254} \text{ m}^{-1}/\text{DOC mgL}^{-1}$ ) has been shown to increase with increased aromaticity (Weishaar et al., 2003). The relationship of UV-vis absorbance to DOC concentration in natural waters has been utilised in an attempt to develop a quick and easy analytical technique to determine DOC concentrations. In the water treatment industry, absorbance at 254 nm is measured to monitor DOC concentration (Allpike et al., 2005) and in natural waters  $\sim 340$  nm is often utilised (Tipping et al., 1988; Hernes and Benner, 2003). Water colour at longer wavelengths is often used by the water treatment industry as a simple proxy for DOM concentration, for example, 400–465 nm (Hongve and Åkesson, 1996; Hautala et al., 2000) in comparison to a standard solution of hexachloroplatinate and cobalt ions in hydrochloric acid (Pt-Co solution) as developed by Hazen (1892).

Three-dimensional fluorescence excitation–emission matrix (EEM) spectra typically cover a range of excitation and emission wavelengths from  $\sim 200$  nm (short wavelength UV) through to  $\sim 500$  nm (visible blue–green light), and may contain fluorescence centres which are attributed to both natural DOM groups such as humic and fulvic-like substances, as well as fluorescent protein-like material (Coble, 1996; Baker, 2001; Chen et al., 2003; Stedmon et al., 2003; Baker and Spencer, 2004; Spencer et al., 2007). The exact relationship between fluorescence properties and biogeochemical structure of the organic matter is unknown, but it is recognised that the fluorescence is generated by highly substituted aromatic nuclei, extensive conjugation and high-molecular-weight compounds (Senesi et al., 1989). Nevertheless, careful choice of excitation and emission wavelengths can allow the monitoring of changes in DOM composition (Coble, 1996; Kalbitz et al., 2000; McKnight et al., 2001) and DOC concentrations (Ferrari et al., 1996; Baker, 2002a).

DOM fluorescence and absorbance measurements are sensitive to changes in the environmental conditions of the sample. These conditions were reviewed by Senesi (1990) with respect to fulvic acids and fluorescence and include temperature, pH, metal ions, solvent interactions and other solutes. A typical response in DOM extracted from river water to pH was studied by Patel-Sorrentino et al. (2002) who observed an increase in fluorescence intensity with increasing pH over the range of 1 to 10–11, with a decrease at pH 12. Spectral shifts are also observed in response to changing pH. Mobed et al. (1996) observed a red shift, in fluorescence intensity maxima, with increasing pH at long wavelengths ( $EX\lambda \sim 390$  nm) and a similar red shift at shorter wavelengths ( $EX\lambda \sim 320$  nm) in soil derived humic substances. In aquatic derived DOM, shorter wavelength fluorescence peaks have been observed to blue shift with increasing pH (Mobed et al., 1996). Other authors have observed no wavelength change with pH (Tam and Sposito, 1993; Patel-Sorrentino et al., 2002).

The measurement and investigation of DOM in freshwaters by fluorescence and absorbance spectroscopy is increasing in the water sciences. In addition to the spectrophotometric measurements already described, DOM fractionation and

concentration methods such as adsorption onto solid phases (Hood et al., 2003; Kaushal and Lewis, 2003), size exclusion chromatography (Allpike et al., 2005), field flow fractionation (Boehme and Wells, 2006) and tangential flow ultrafiltration (Belzile and Guo, 2006) show potential for coupling with spectrophotometric analyses to investigate specific DOM components or size fractions. Environmental effects on DOM fluorescence and absorbance are therefore important to understand to potentially investigate DOM composition through experimental variations of environmental conditions. For example, the wide range of fluorophore responses to pH in the literature reflects the complex nature and heterogeneous composition of DOM and under carefully controlled conditions this may be used to infer DOM composition (e.g. Patel-Sorrentino et al., 2002). Similarly, changes in fluorescence and absorbance properties of DOM due to freezing could also be used to infer DOM properties; however, to the authors' knowledge this has not been previously investigated for freshwater DOM. Here, we compare the effects of both pH and freeze/thaw on a wide range of freshwater DOM samples from the United Kingdom (UK) to investigate the response of spectrophotometric measurements and thus any potential changes in DOM composition. As acidification and freezing are commonly used storage methods for spectrophotometric measurements, it is important to understand any potential impacts these protocols may have on spectrophotometric DOM measurements.

## 2. Materials and methods

### 2.1. Study sites and sampling

Samples were collected from a wide number of sites from across the UK in the course of this study (Table 1). Sample sites are dominated by rural, upland, headwater catchments, a large number of which have significant peat cover within their catchments. The Coalburn Experimental Catchment (Northumberland, UK) was used extensively for replicate analyses and to investigate seasonal variability.

Water samples were collected in 'aged' 30 mL polypropylene bottles which had been cleaned in 10% HCl and triple rinsed with distilled water or precombusted glass bottles (450 °C for 4–8 h). Water samples were filtered (Whatman GF/C ashed glass microfibre filter papers) into the bottles and the bottles were rinsed with copious amounts of filtrate before collection of the sample for analysis. All samples were stored at 4 °C in the dark until analysis within less than 24 h or were stored frozen in the dark for the freeze/thaw experiments. To investigate the potential of contamination with respect to spectrophotometric and DOC measurements from the filtration system, sample collection bottles and storage procedures both at each step and for the whole procedure, the sample was substituted with distilled water and no sources of contamination were observed.

### 2.2. EEM fluorescence spectrophotometric analysis

Fluorescence was measured using a Perkin-Elmer luminescence spectrometer LS-50B. Samples were analysed in a

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