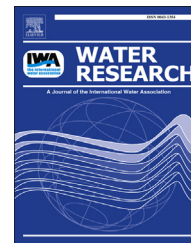


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# Characterisation of dissolved organic matter fluorescence properties by PARAFAC analysis and thermal quenching

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## ABSTRACT

The fluorescence intensity of dissolved organic matter (DOM) in aqueous samples is known to be highly influenced by temperature. Although several studies have demonstrated the effect of thermal quenching on the fluorescence of DOM, no research has been undertaken to assess the effects of temperature by combining fluorescence excitation – emission matrices (EEM) and parallel factor analysis (PARAFAC) modelling. This study further extends previous research on thermal quenching by evaluating the impact of temperature on the fluorescence of DOM from a wide range of environmental samples, in the range 20 °C – 0 °C. Fluorescence intensity increased linearly with respect to temperature decrease at all temperatures down to 0 °C. Results showed that temperature affected the PARAFAC components associated with humic-like and tryptophan-like components of DOM differently, depending on the water type. The terrestrial humic-like components, C1 and C2 presented the highest thermal quenching in rural water samples and the lowest in urban water samples, while C3, the tryptophan-like component, and C4, a reprocessed humic-like component, showed opposite results. These results were attributed to the availability and abundance of the components or to the degree of exposure to the heat source. The variable thermal quenching of the humic-like components also indicated that although the PARAFAC model generated the same components across sites, the DOM composition of each component differed between them. This study has shown that thermal quenching can provide additional information on the characteristics and composition of DOM and highlighted the importance of correcting fluorescence data collected in situ.

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## 1. Introduction

In recent years, fluorescence spectroscopy has been increasingly applied to the analysis of aqueous dissolved organic matter (DOM). The effectiveness of this technique in water quality analysis has been proven by studies on numerous types of water systems (Drozdowska, 2007; Kelton et al., 2007; Murphy et al., 2008; Gher vase et al., 2012; Kothawala et al., 2012; Carstea et al., 2014). Fluorescence has been correlated with standard parameters such as biological oxygen demand (Reynolds and Ahmad, 1997; Hudson et al., 2008; Hur and Kong, 2008), total organic carbon (Vodacek et al., 1995), nitrogen and chemical oxygen demand (Hur and Cho, 2012; Bridgeman et al., 2013). Due to its potential, researchers have applied fluorescence spectroscopy in studies such as the monitoring of riverine DOM and diesel pollution (Spencer et al., 2007; Carstea et al., 2010), analysis of recycled waters (Henderson et al., 2009), evaluation of drinking water treatment processes (Bieroza et al., 2009; Shutova et al., 2014), monitoring of viral abundance in wastewater (Pollard, 2012), quantification of pesticides (Ferretto et al., 2014) or testing of potable waters microbial quality (Cumberland et al., 2012). The intensive use of fluorescence spectroscopy in water quality analyses arises from its advantages, which include high sensitivity, small quantities of sample needed, very little or no sample preparation and short measuring time (Coble, 1996; Birdwell and Valsaraj, 2010). However, the fluorescence signal can be affected by so-called “matrix effects” which include inner filter effects and fluorescence quenching (Lakowicz, 2006; Henderson et al., 2009; Korak et al., 2014). With regard to fluorescence quenching, it has been shown that fluorescence spectroscopy is highly sensitive to temperature variations. An increase in temperature increases the probability of the excited electrons returning to ground state through radiationless decay. Baker (2005) studied temperature quenching on several types of water samples and observed a decrease in fluorescence intensity ranging from 16% to 48%, depending on the samples and DOM component analysed. Elliott et al. (2006) observed a decrease in fluorescence of more than 40% for fluorophores produced by bacterial cultures isolated from river samples and Seredyńska-Sobecka et al. (2007) studied thermal quenching on colloids obtaining similar results. However, in each case the researchers did not study the impact of temperature on DOM fluorescence below 10 °C, due to condensation which could form on the cuvette walls. Patsayeva et al. (2004) and, more recently, Watras et al. (2011) have analysed thermal quenching to almost 5 °C and developed a correction method for fluorescence spectra but both research teams concentrated only on marine water samples. Consequently, no research has been made, so far, to study fluorescence thermal quenching below 5 °C on water samples from a wide range of different sources.

This study seeks to characterise the fluorescence properties of DOM, from water samples with different sources, using thermal quenching and the combination of excitation – emission matrices (EEM) and parallel factor analysis (PARAFAC). Several studies have shown that PARAFAC is a powerful tool in separating and analysing DOM components (Ohno et al., 2008; Yamashita and Jaffé, 2008; Guéguen et al., 2011; Meng

et al., 2013; Murphy et al., 2014; Sanchez et al., 2014; Yang et al., 2014). Specifically, the aims of this study were: (1) to investigate the response of DOM, from different sources (urban and rural areas), at low temperatures for a better understanding of DOM characteristics; (2) to evaluate the impact of temperature on the most labile fractions of DOM; (3) to assess the potential of applying the Watras et al. (2011) correction tools at temperatures below 5 °C; (4) to investigate the use of EEM-PARAFAC tool combined with thermal quenching to improve our understanding of DOM character. To date, EEM-PARAFAC has not been applied to the investigation of thermal quenching of DOM components from water samples and could provide a better understanding of DOM properties.

## 2. Materials and methods

### 2.1. Sample preparation and analysis

Samples were collected from two areas: Birmingham and Buxton, located in the Midlands area, UK (Fig. 1). The sampling sites, with different characteristics, were selected to reflect a gradient from rural to urban areas. In Birmingham, 5 types of water were sampled, hereafter named: brook (Sutton Park), lake (Sutton Park), pond (Edgbaston pond), surface runoff from storm sewers (University of Birmingham campus) and canal (Worcester and Birmingham Canal). Brook and lake samples were collected from Sutton Park, which is a National Nature Reserve and presents a relatively rural, pristine character (<http://www.birmingham.gov.uk/suttonpark>). Canal, storm sewer and pond samples were collected from an urban zone; however, the pond was located in a small park with lower anthropogenic activity compared to canal and storm sewer. From Buxton, a river water sample was collected. Buxton town is located along the Wye River, within The Peak District National Park, having low anthropogenic impact, according to the Environment Agency (<http://www.peakdistrict.gov.uk/microsites/sopr/landscape/river-quality>).

Water was sampled in polypropylene bottles, cleaned with 10% HCl and thoroughly rinsed with deionised water prior to use. All measurements were performed within 24 h from collection. The samples were measured for conductivity, pH, dissolved organic carbon (DOC) and absorbance, from 200 nm to 700 nm. Conductivity and pH were measured using a Myron meter, absorbance measurements were made with a WPA lightwave UV-VIS diode-array S2000 spectrophotometer and DOC with a Shimadzu TOC-Vcpn analyzer.

Fluorescence EEMs were recorded using a Varian Cary Eclipse spectrofluorometer, with the following parameters: excitation wavelength domain 200–400 nm, emission wavelength domain 280–500 nm, steps of 5 nm and 2 nm for excitation and emission, respectively, and slits of 5 nm. The instrument stability was checked by recording the Raman values (at excitation wavelength 348 nm and emission wavelength 395 nm) before each set of measurements. The average Raman value was 24.38 a.u. with a standard deviation of 0.58. The fluorescence intensity of all spectra were normalized to a maximum value of 1000 a.u. and corrected to the average Raman value. Every set of measurements was made in triplicate in order to check the instrument reproducibility ( $\pm 5\%$ ).

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