HYDROLOGICAL PROCESSES
Hydrol. Process. **21**, 3181–3189 (2007)
Published online 25 September 2007 in Wiley InterScience
(www.interscience.wiley.com) DOI: 10.1002/hyp.6887

Diurnal variability in riverine dissolved organic matter composition determined by *in situ* optical measurement in the San Joaquin River (California, USA)

Robert G. M. Spencer,[1,2]*,† Brian A. Pellerin,[3,†] Brian A. Bergamaschi,[3] Bryan D. Downing,[3] Tamara E. C. Kraus,[3] David R. Smart,[2] Randy A. Dahlgren[1] and Peter J. Hernes[1]

[1] *Department of Land, Air and Water Resources, Veihmeyer Hall, Aqueous Organic Geochemistry Group, University of California, Davis, One Shields Ave, California 95616, USA*
[2] *Department of Viticulture and Enology, University of California, Davis, One Shields Ave, California 95616, USA.*
[3] *United States Geological Survey, 6000 J Street, Placer Hall, Sacramento, California 95819, USA*

Abstract:

Dissolved organic matter (DOM) concentration and composition in riverine and stream systems are known to vary with hydrological and productivity cycles over the annual and interannual time scales. Rivers are commonly perceived as homogeneous with respect to DOM concentration and composition, particularly under steady flow conditions over short time periods. However, few studies have evaluated the impact of short term variability (<1 day) on DOM dynamics. This study examined whether diurnal processes measurably altered DOM concentration and composition in the hypereutrophic San Joaquin River (California) during a relatively quiescent period. We evaluated the efficacy of using optical *in situ* measurements to reveal changes in DOM which may not be evident from bulk dissolved organic carbon (DOC) measurement alone. The *in situ* optical measurements described in this study clearly showed for the first time diurnal variations in DOM measurements, which have previously been related to both composition and concentration, even though diurnal changes were not well reflected in bulk DOC concentrations. An apparent asynchronous trend of DOM absorbance and chlorophyll-*a* in comparison to chromophoric dissolved organic matter (CDOM) fluorescence and spectral slope $S_{290-350}$ suggests that no one specific CDOM spectrophotometric measurement explains absolutely DOM diurnal variation in this system; the measurement of multiple optical parameters is therefore recommended. The observed diurnal changes in DOM composition, measured by *in situ* optical instrumentation likely reflect both photochemical and biologically-mediated processes. The results of this study highlight that short-term variability in DOM composition may complicate trends for studies aiming to distinguish different DOM sources in riverine systems and emphasizes the importance of sampling specific study sites to be compared at the same time of day. The utilization of *in situ* optical technology allows short-term variability in DOM dynamics to be monitored and serves to increase our understanding of its processing and fundamental role in the aquatic environment. Copyright © 2007 John Wiley & Sons, Ltd.

KEY WORDS dissolved organic matter; absorbance; fluorescence; diurnal; water quality; San Joaquin River

Received 12 March 2007; Accepted 26 July 2007

INTRODUCTION

In aquatic environments, dissolved organic matter (DOM) is ubiquitous and plays a central role in ecosystem biogeochemistry. Riverine DOM is important as it mediates light in the water column, plays a central role in carbon dynamics and nutrient budgets and participates in the complexation of trace metals and the mobilization of pollutants (e.g. Findlay and Sinsabaugh, 2003). Riverine DOM is also a key water quality constituent, impacting the cost and efficacy of drinking water treatment as well as disinfection by-product (DBP) formation. A better understanding of the variation in the concentration and composition of DOM in riverine systems and the underlying mechanisms affecting its dynamics is therefore directly relevant to a wide range of studies. It is widely recognized that dissolved organic carbon (DOC) concentrations in rivers vary annually and interannually (e.g. Worrall *et al*., 2003; Worrall and Burt, 2004; Worrall *et al*., 2004; Hood *et al*., 2005), usually responding to hydrological and productivity cycles. However, few studies have evaluated changes in DOC concentrations in rivers over shorter time scales, such as the diurnal cycle (Manny and Wetzel, 1973; Kaplan and Bott, 1982).

Rivers are commonly perceived as homogeneous with respect to DOM concentration and composition over short time scales and particularly under steady flow conditions. Other biogeochemical parameters have been shown to vary on short time scales in streams and rivers. For example, recent research has shown that concentrations of dissolved oxygen (Mulholland *et al*., 2005; Parker *et al*., 2005), inorganic nitrogen (Harrison *et al*., 2005; Scholefield *et al*., 2005; Mulholland *et al*., 2006), trace metals (Brick and Moore, 1996; Nimick *et al*., 2003) and

* Correspondence to: Robert G. M. Spencer, Department of Land, Air and Water Resources, Veihmeyer Hall, Aqueous Organic Geochemistry Group, University of California, Davis, One Shields Ave, California 95616, USA. E-mail: rgspencer@ucdavis.edu
† Joint 1st authors.

chlorophyll and nutrients vary considerably over diurnal cycles in streams and rivers due to a combination of biological, physical and chemical processes. The paucity of information with respect to any change in DOC concentrations over the diurnal cycle in rivers and streams is potentially due to the fact that variation may be small in relation to the background concentrations in many systems and so within the analytical uncertainty of the DOC measurement. Furthermore, sampling at high enough frequencies to assess diurnal patterns has historically been challenging. Finally, given the complexity of DOM interactions, changes in DOC and therefore DOM concentrations are only part of the story.

Changes in DOM composition either due to autochthonous production or alteration of allochthonous material may for example change its nutritive value, ability to bind contaminants or interact with sediments and propensity to form DBPs, among numerous other important biogeochemical processes. In addition to understanding how any diurnal and short time scale processes may impact DOM concentration, it is therefore also important to understand to what extent these processes may impact on DOM composition.

The measurement of the absorbance and fluorescence optical properties of natural waters has been extensively employed to characterize the concentration, source and composition of DOM (Coble, 1996; McKnight *et al*., 2001; Baker, 2002; Her *et al*., 2003; Stedmon *et al*., 2003; Spencer *et al*., 2007a). Chromophoric dissolved organic matter (CDOM) absorbance measurements have been shown to be related to DOC concentrations in a number of studies (Ferrari *et al*., 1996; Hernes and Benner, 2003; Spencer *et al*., 2007b). The spectral slope measurement defines the spectral dependence of the CDOM absorption coefficient and as a result provides information in relation to the nature of the CDOM (Blough and Del Vecchio, 2002). Spectral slope varies with CDOM source and processing (i.e. biological and chemical modification) and has been related to a number of molecular properties (Blough and Del Vecchio, 2002). For example, spectral slope has been shown to become steeper with decreasing molecular weight and decreasing aromaticity (Blough and Green, 1995; Stubbins, 2001), thus shallower spectral slope values indicate material that is richer in high molecular weight DOM and has a higher aromatic content. CDOM fluorescence measurements have also been related to DOC concentrations (Ferrari *et al*., 1996; Baker *et al*., in press; Cumberland and Baker, 2007) and, for example, hypsochromic shifts in fluorophores attributed to humic and fulvic-like material are indicative of a breakdown in aromaticity (Coble, 1996; Blough and Del Vecchio, 2002).

Spectroscopic techniques thus provide a potential means to investigate the impact of diurnal and short time scale processes on DOM concentration and composition. The ability to deploy *in situ* optical absorbance and fluorescence technology also allows for high frequency, real-time monitoring of aquatic systems. For this study, an *in situ* analytical system capable of measuring a broad suite of optical parameters was constructed using a combination of repurposed commercial instrumentation and recently developed *in situ* instrumentation. This provided the ability to measure variations in optical properties *in situ* at frequent intervals for four days, which were then compared to discrete samples, collected and analysed every two hours over two days of the study. There were two principal aims of this study. Firstly, to assess if diurnal processes measurably altered the DOM concentration and composition in the San Joaquin River (California) during a relatively quiescent summer period. Secondly, to evaluate if *in situ* optical measurements revealed changes in DOM concentration and composition that are not evident from bulk DOC measurement alone and therefore to assess the value of *in situ* optical measurements in the future research of DOM dynamics in riverine systems.

MATERIALS AND METHODS

Study site

The *in situ* optical instrumentation package deployment and diurnal sampling occurred in the San Joaquin River near Crows Landing in the Central Valley of California, downstream of the USGS discharge gauging station 11 274 550 (37°25′42″N, 121°00′12″W). The upstream drainage area is approximately 25 107 km^2 and is dominantly row crop agriculture, orchard and wetlands (Kratzer *et al*., 2004) and the area has a semi-arid to arid climate. The San Joaquin River within the study area is a low gradient river with a mean gradient of 0·0156% and a dominant bed material of sand. During the summer months, the lower portion of the river is disconnected from its headwaters in the Sierra Nevada mountain range due to water diversion for agricultural and urban use. In summer, river flows are re-established about 40 km upstream from our study site due to agricultural return flows from Bear Creek basin. During the study period (July 28–August 1, 2006), about 50% of the flow at the Crows Landing study site originated from the Merced River, a mixture of reservoir waters from the Sierra Nevada and agricultural runoff. The remaining flow originated from agricultural drainage from Salt Slough (15%), San Luis Drain (4%), Bear Creek (2%), Orestimba Creek (2%), Mud Slough above the San Luis Drain (1·5%), Los Banos Creek (1%), and ~25% from unknown sources such as small agricultural drains and groundwater discharge (http://cdec.water.ca.gov; http://waterdata.usgs.gov/nwis/sw).

The San Joaquin River is a hypereutrophic river with peak summer chlorophyll-*a* concentrations in the range of 75–150 μg l^{-1} and mineral nitrogen ($NH_4^+ + NO_3^-$; 2–2·5 mgN l^{-1}) and soluble reactive phosphorous (50–150 μgP l^{-1}) concentrations generally exceeding values believed to limit algal production (Kratzer *et al*., 2004). The phytoplankton growth rate in the lower San Joaquin River is believed to be limited by light

DOI: 10.1002/hyp

and flow regime rather than by nutrients (Leland *et al.*, 2001). The phytoplankton community is dominated by 'r-selected' centric diatoms (Thalassiosirales) (Leland *et al.*, 2001). Pronounced diurnal fluctuations in phytoplankton biomass, as measured by chlorophyll-*a* concentration, consistently occur during the growing season. The diurnal pattern in chlorophyll-*a* at a given sampling location results primarily from daytime algae growth and nighttime advection (or washout) of algae. The ramifications of diurnal patterns in phytoplankton growth–advection dynamics extends to other water quality parameters associated with algal growth (e.g. nitrate, phosphate and silica). However, these previous studies of diurnal patterns in water quality on the San Joaquin River did not evaluate DOM concentration and composition.

This study was conducted during a rain-free period. Mean daily flux of solar radiation ranged from 276–292 W m^{-2} with 14 hours of solar radiation daily, as recorded by the California Irrigation Management Information System (CIMIS) station near Patterson, approximately 14 km north of the sampling site (37°26′24″N, 121°08′20″W) (http://www.cimis.water.ca.gov/cimis/welcome.jsp). Peak solar radiation occurred daily at noon and ranged from 810–845 Wm^{-2} with average daily air temperatures ranging from 25·1–27·3 °C.

In situ optical measurements

The *in situ* optical instrumentation package was deployed in the thalweg (main channel) on the channel bottom at a depth of ~4 m for a continuous 4 day period (noon July 28–noon August 1, 2005) with sample times of 1 minute every 30 minutes. Deployment of the *in situ* optical instrumentation package for greater than 4 days resulted in issues with filter clogging at this study site. Water was pumped from mid-channel at a depth of ~2 m and filtered through in-line 10 and 0·2 μm membrane filters (Osmonics Memtrex, 25·4 cm) with acid-rinsed Tygon tubing.

Previous studies have shown that dissolved constituents and algal biomass are well-mixed throughout the water column at this sampling location (Kratzer *et al.*, 2004). Chromophoric dissolved organic matter (CDOM) *in situ* spectral absorption was measured in the visible range (412–715 nm) using a WET Labs AC-9 photometer with a 10 cm pathlength as described by Twardowski *et al*. (1999). CDOM was also measured in the UV range (290–350 nm) using a Satlantic *in situ* UV spectrophotometer with a 1 cm pathlength (ISUS, Satlantic Inc., Halifax, Nova Scotia, Canada). A WET Labs single-band excitation–emission *in situ* fluorometer was also installed in the filtered path to measure fluorescence of DOM with an excitation at 370 nm and over a broad emission band centred at 460 nm, a peak that has been attributed to terrestrial humic-like and fulvic-like material (Baker, 2001; McKnight *et al*., 2001; Newson *et al*., 2001; Baker, 2002). Fluorescence intensity of DOM in this region was converted from instrument output (vDC) and is expressed in units equivalent to parts per billion of quinine sulphate (QSE) (WET Labs, 2003).

Unfiltered water was also passed through a WET Labs single-band fluorometer to measure fluorescence indicative of chlorophyll-*a* (excitation 460 nm, emission 695 nm). Fluorescence intensity was converted from instrument output (vDC) and expressed as chlorophyll-*a* (μg l^{-1}) (WET Labs, 2003). A Seabird CTD (SeaBird, Bellevue, WA) was used in conjunction with the optical instrumentation to measure temperature, depth and electrical conductivity. Dissolved oxygen concentrations were measured with an Aanderraa model 4175 oxygen optode (Aanderaa Instruments, Bergen, Norway). All of the *in situ* optical instrumentation was controlled, data logged and time-stamped using a WET Labs datalogger/controller model DH-4. Following data merging and binning, standard temperature corrections were applied to the AC-9 data as described by Pegau *et al*. (1997). Deionized organic-free water blanks measured in the laboratory and field were subtracted from the fluorometer and absorbance spectrophotometer samples.

Spectral slope S was calculated using a nonlinear fit of an exponential function to the absorption spectrum in the range of 290–350 nm from the ISUS instrument using the equation:

$$a_g(\lambda) = a_g(\lambda_{ref}) \exp[-S(\lambda - \lambda_{ref})] \quad (1)$$

where $a_g(\lambda)$ is the absorption coefficient of CDOM at a specified wavelength, λ_{ref} is a reference wavelength and S is the slope fitting parameter. Spectral slope serves as an indicator of changes in CDOM composition (Blough and Del Vecchio, 2002; Boss and Zaneveld, 2003). A steep spectral slope (e.g. closer to 0·02) indicates low molecular weight material or decreasing aromaticity while a shallower spectral slope (e.g. closer to 0·01) indicates humic-like or higher molecular weight material with a higher aromatic content (Blough and Del Vecchio, 2002). *In situ* spectral slope values were calibrated against discrete samples run on a laboratory based Cary model 300 spectrophotometer (Varian, Inc, Palo Alto, CA) to correct for any observed offset. All calculations and data analysis in this study were carried out using MatLab 7·1 (The MathWorks, Inc., Natick, MA).

Sample collection and analyses

Discrete samples were collected every two hours beginning at noon for two days (July 28–30, 2005) from the same depth and location as the intake to the *in situ* optical package. Samples were filtered through 10 μm and 0·2 μm in-line membrane filters (Osmonics Memtrex, 25·4 cm) in the field and stored in 250 ml amber glass bottles on ice in the dark for subsequent DOC analysis and laboratory optical measurements. Samples were typically analysed on return to the laboratory within 24 hours of collection.

DOC concentrations were measured on acidified samples (pH ~ 2) with a Shimadzu TOC-5000A carbon analyser measuring non-purgeable organic carbon. The mean of three to five injections of 100 μl is reported

DOI: 10.1002/hyp

for every sample and precision, described as a coefficient of variance (CV), was <2% for the replicate injections. The absorption spectra of discrete samples were measured in the laboratory between 200–800 nm at constant temperature (25 °C) in a 10 mm quartz cell using a Cary 300 spectrophotometer. All sample spectra were referenced to a blank spectrum of deionized water and were corrected for an occasional small offset, arising from possible long-term baseline drift (Blough *et al*., 1993), by subtracting the average absorbance between 700 and 800 nm. All absorbance data in this manuscript are expressed as the absorption coefficient, in units of m^{-1} (Green and Blough, 1994). A number of discrete samples were also measured for fluorescence in the laboratory on a SPEX FluoroMax-3 spectrofluorometer (150 watt Xenon lamp) in a 10 mm quartz cell at constant temperature (25 °C). Samples were analysed at a single-band excitation–emission to compare to the *in situ* fluorometer (excitation 370 nm; emission 460 nm). On comparison between discrete laboratory absorbance (a_{350}) and fluorescence (excitation 370 nm; emission 460 nm) measurements and *in situ* measurements, a strong relationship was observed for both measurements ($r^2 > 0{\cdot}95$; $p < 0{\cdot}05$; $n = 12$). In addition to detailed DOC and DOM spectrophotometric characterization, standard water quality analyses were conducted on the discrete samples to provide reference data following the methods outlined by Kratzer *et al*. (2004).

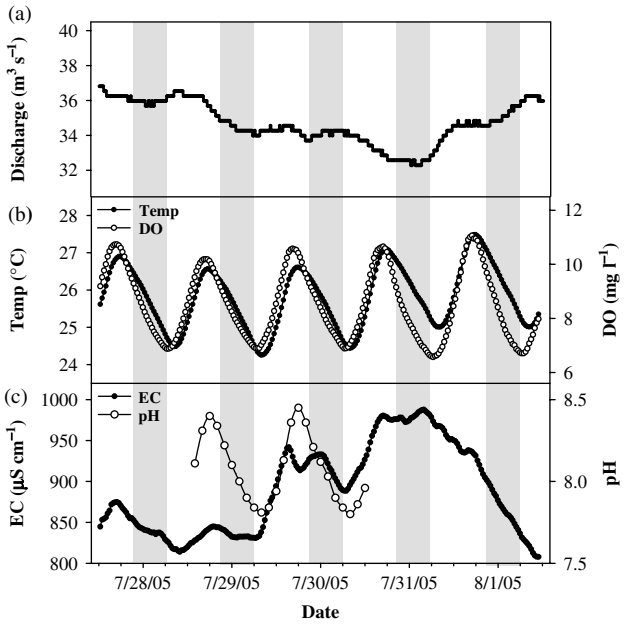

Figure 1. Ancillary parameters measured during the diurnal study period in the San Joaquin River at Crows Landing: (a) discharge ($m^3 s^{-1}$); (b) temperature (°C) and dissolved oxygen (mg l^{-1}); (c) electrical conductivity (µS cm^{-1}) and pH (grey shaded blocks represent night-time)

RESULTS AND DISCUSSION

Ancillary data

During the course of the study, riverine discharge was observed to fluctuate over a small range (~32·2–36·3 $m^3 s^{-1}$) as shown in Figure 1a. Riverine discharge showed a general decline from 27–31 July 2005 followed by a small increase on 31 July 2005. The increased flow originated primarily from the Merced River (1·3 $m^3 s^{-1}$ increase) and Salt Slough (0·15 $m^3 s^{-1}$ increase) and does not indicate any diurnal variability in flow. General water quality characterization for the study period is shown in Table I for reference purposes.

Over the study period, temperature, dissolved oxygen (DO) and pH all showed clear diurnal patterns (Figures 1b and 1c) that were independent of variability in river flow. Daily maxima in the late afternoon were observed for temperature, DO and pH, with corresponding minima for each variable recorded in the early morning. Such a pattern in DO and pH is consistent with changes observed due to aquatic photosynthesis and respiration as described previously (Mulholland *et al*., 2005; Parker *et al*., 2005).

It is important to note that pH has been shown to impact on the optical properties of riverine CDOM, particularly at extremes (e.g. Patel–Sorrentino *et al*., 2002). However, pH has been observed to have little impact on spectrophotometric measurements within natural levels typically observed in freshwaters (Reynolds, 2003; Spencer *et al*., 2007c). San Joaquin River water was manipulated across the pH range through a series of

Table I. General water quality characterization parameters measured during the diurnal study period in the San Joaquin River at Crows Landing, California

	Temp (°C)	EC (µS cm^{-1})	DO (mg l^{-1})	DO (% sat)	pH	Cations			Anions		NTU	TSS mg l^{-1}	VSS mg l^{-1}
						Na^+ (mg l^{-1})	Mg^{2+} (mg l^{-1})	Ca^{2+} (mg l^{-1})	Cl^- (mg l^{-1})	SO_4^{2-} (mg l^{-1})			
Mean	25·82	893·3	8·69	106·5	8·08	111·5	26·7	62·3	115·2	135·6	34·5	59·5	8·8
Std. Dev.	0·77	40·0	0·78	10·8	0·21	6·6	1·2	2·0	7·4	8·2	3·7	8·7	1·0
Median	25·95	901·1	8·70	107·3	8·07	114·9	27·0	62·3	118·8	138·0	34·1	59·7	8·8
Minimum	24·24	829·0	6·52	90·0	7·80	100·6	24·7	59·0	102·8	122·7	28·0	44·4	7·2
Maximum	27·72	986·1	10·91	123·5	8·45	121·8	28·5	65·9	124·1	151·2	40·7	77·2	10·8

Note: Temp: temperature, °C; EC: electrical conductivity, µS cm^{-1}; DO: dissolved oxygen, mg l^{-1} and % saturation; pH; cations: Na^+, Mg^{2+}, Ca^{2+} mg l^{-1}); anions: Cl^-, SO_4^{2-}, mg l^{-1}; turbidity: nephelometric turbidity units; TSS: total suspended solids, mg l^{-1}; VSS: volatile suspended solids, mg l^{-1}.

DOI: 10.1002/hyp

laboratory experiments and no significant difference in CDOM spectrophotometric measurements was observed within the range of pH values (Table I) measured in the course of this study. Electrical conductivity (Figure 1c) showed an increase as river flow declined. The subsequent decrease was associated with increasing discharge from the Merced River on 31 July 2005. Overall electrical conductivity did not show a clear diurnal signal and was weakly negatively correlated with discharge ($r^2 = 0{\cdot}46$).

Dissolved organic matter

DOC concentrations in the San Joaquin River near Crows Landing varied from 3·1–3·4 mg l^{-1} over the two day sampling period (Figure 2) and exhibited no apparent trend over diurnal cycles within analytical error. Previous studies have shown conflicting results with respect to diurnal changes in DOC in streams and agricultural channels. For example, Harrison *et al*. (2005) found higher DOC concentrations during night-time hours along with declining chlorophyll-*a* concentrations in a 24 hour study of an agricultural channel while Kaplan and Bott (1982) reported late afternoon DOC maxima in a Piedmont stream. In contrast, Manny and Wetzel (1973) reported little diurnal variation in DOC concentrations in a small Michigan headwater stream. One common issue of concern is that any relatively small diurnal changes in DOC concentration (e.g. $<0{\cdot}2$ mg l^{-1}) cannot be measured within the analytical precision of conventional DOC analysers and the inability to constrain this analytical uncertainty may not, therefore, allow for observation of small diurnal trends.

Furthermore, bulk DOC analyses alone were not shown to reveal the dynamic behaviour of different DOM components (Benner and Opsahl, 2001), and small changes in DOM composition can have a large influence on the biogeochemical reactions it will undertake and thus on its role in aquatic ecosystems. There is often little if any relationship between bulk DOM concentration and its lability as the proportion of labile DOM is highly variable and unrelated to DOC concentration. Small changes in DOM composition can therefore result in large impacts on DOM bioavailability if they affect the size of the rapidly turning-over labile pool, with only minor impacts on DOC concentrations (del Giorgio and Davis, 2003; Findlay, 2003).

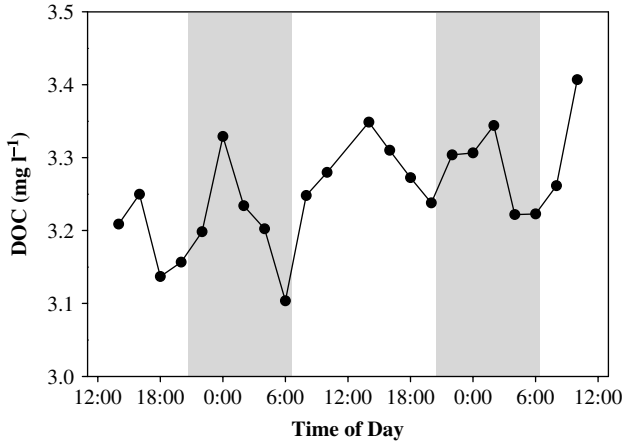

Figure 2. Dissolved organic carbon (DOC) concentrations (mg l^{-1}) during discrete diurnal sample collection (July 28–30, 2005), San Joaquin River, California (grey shaded blocks represent night-time)

The optical properties of DOM offer a potential alternative for examination of DOM variation over short time scales. For example, the absorption coefficient of CDOM at ~350 nm (a_{350} m^{-1}) was shown in a number of studies to be strongly correlated with bulk DOC concentrations (Hernes and Benner, 2003; Spencer *et al*., 2007b). In this study, a_{350} measured *in situ* showed a clear diurnal pattern (Figure 3a). The highest a_{350} values in the diurnal cycle (~5·4–5·8 m^{-1}) were observed in the early evening and the lowest values around dawn (~4·2–4·6 m^{-1}).

The same diurnal pattern in CDOM was recorded across the absorbance spectral range and was consistent for other commonly-reported wavelengths in CDOM investigations, e.g. a_{254} and a_{440} (Kirk, 1994; Weishaar *et al*., 2003). The a_{350} values observed in this study are toward the lower end of the range of 5–15 m^{-1} reported for a number of large rivers (Blough and Del Vecchio, 2002) and low compared to organic-rich waters with a_{350} values up to around 80 m^{-1} (Moran *et al*., 2000; Spencer *et al*., 2007b). The diurnal pattern in CDOM absorbance showed a range greater than or equivalent to that observed in the annual variation at this site in the San Joaquin River under steady flow conditions (i.e. excluding large storm events). Chlorophyll-*a* fluorescence (Figure 3a) shows the same diurnal pattern as CDOM absorbance with early evening maxima (~29–34 μg l^{-1}) and dawn minima (~16–21 μg l^{-1}). The synchronous patterns of chlorophyll-*a* and CDOM absorbance implies a coupling between the production of light-absorbing CDOM with diurnal phytoplankton growth. The linear regression analysis between CDOM absorbance and chlorophyll-*a* ($r^2 = 0{\cdot}45$, $p < 0{\cdot}05$) over the diurnal cycles in this study, although significant, does not show a strong correlation. Hence, it seems likely that changes in the absorption coefficient over the diurnal cycle are not solely related to phytoplankton growth trends but also due to other processes.

In situ DOM fluorescence measured at an excitation of 370 nm and over a broad emission band centred at 460 nm also exhibited a diurnal trend (Figure 3b). Interestingly, the diurnal trend in DOM fluorescence was asynchronous with the diurnal trend present in the absorbance data (Figure 3a). For DOM fluorescence, the highest values were observed in the morning shortly after sunrise (~68·5–70·5 QSE) and typically declined during the day to the lowest values (~62·8–65·2 QSE) around sunset. Field and laboratory studies have suggested that algal exudates are not a source of fluorescent DOM in the excitation–emission region measured in this study (Rochelle–Newall *et al*., 1999; Rochelle–Newall and Fisher, 2002; Nguyen *et al*., 2005). However, the utilization of algal-derived DOM by bacteria and subsequent release of bacterially-produced metabolites could

DOI: 10.1002/hyp

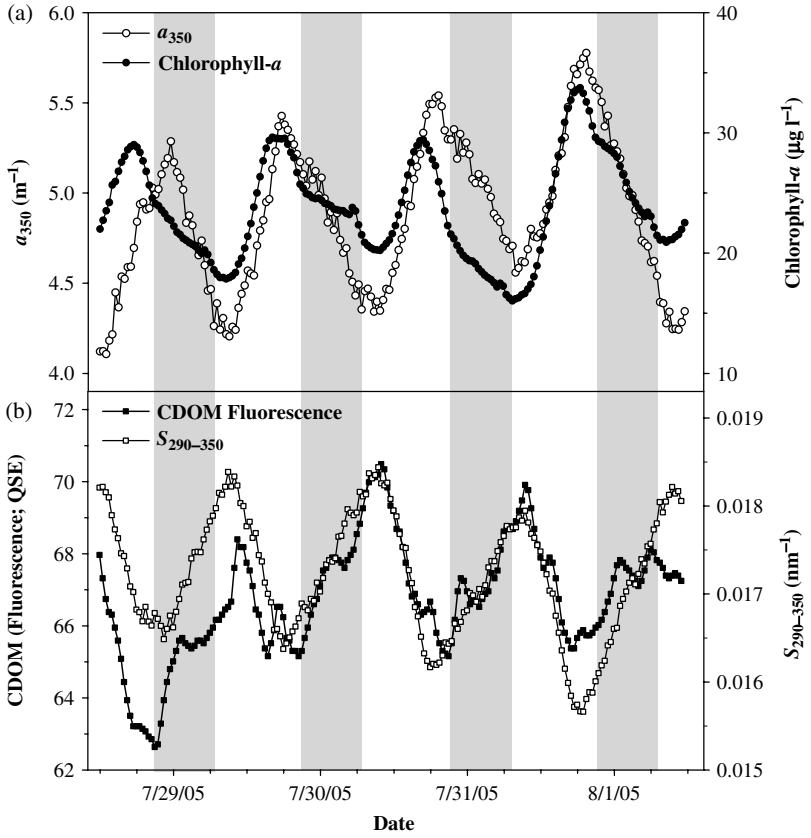

Figure 3. (a) *In situ* CDOM absorption measured at 350 nm (m^{-1}) and chlorophyll-*a* fluorescence (excitation 460 nm, emission 695 nm; µg l^{-1}). (b) *In situ* CDOM fluorescence (excitation 370 nm, emission 460 nm; QSE) and spectral slope $S_{290-350}$ (grey shaded blocks represent night-time)

represent a source of fluorescent DOM in aquatic systems in the region of fluorescence measured in this study (Rochelle–Newall and Fisher, 2002; Elliott *et al*., 2006). Bacterial transformations of algal-derived DOM cannot explain the trends observed in this study with increasing DOM fluorescence at night, as naturally chlorophyll-*a* levels are highest during the day (Figure 3a).

One potential explanation for the observed decrease during the day in the region of DOM fluorescence measured in this study is that the excitation and emission maxima of the fluorophore is changing due to variations in source or processing of the DOM (Moran *et al*., 2000). The daytime decrease in DOM fluorescence (Figure 3b), despite increasing CDOM absorbance, potentially implies photobleaching of fluorophores. If CDOM photobleaching was occurring in the day this does not necessarily imply the removal of photochemical impacts at night to explain the observed daily trends. Our measurements were undertaken at a fixed location; downstream transport of water continues at night and thus water at the study site is replaced with upstream water similar to the previous day under steady flow conditions.

Such a model was observed to explain over 98% of the diurnal variability in chlorophyll-*a* at the Crows Landing site and is also supported by observed increasing chlorophyll-*a* concentrations downstream (i.e. further away from the 'seed' water source). The impact of photobleaching on DOM fluorescence in the region measured in this study typically results in a hyposchromic shift in the fluorophore and a decrease in intensity accompanied by a breakdown in aromaticity and decrease in molecular weight (Coble, 1996; Moran *et al*., 2000). Conversely, bathochromic shifts in the region of DOM fluorescence examined in this study have been observed due to degradation and an increase in age (Senesi *et al*., 1991; Moran *et al*., 2000; Parlanti *et al*., 2000) and the increased relative abundance of certain functional groups to aromatic compounds (Senesi, 1990). Either a hypsochromic or bathochromic shift in the measured fluorophore at excitation 370 nm and emission 460 nm would likely result in a decrease in intensity as observed during the day in this study due to a decrease in fluorescence intensity as the peak of maximum intensity shifted to shorter or longer wavelengths.

Although showing a clear diurnal trend, DOM fluorescence also shows a secondary peak imposed on the daily cycle that occurs around dusk (Figure 3b). It is hypothesized that this secondary peak could be due to zooplankton grazing as they rapidly increase in density around dusk in the San Joaquin River. As a_{350} continues to decline at the time of the secondary fluorescence peak, this results in the secondary peak being more fluorescent per unit absorbance which has been linked to decreasing molecular weight (Mopper *et al*., 1996) and would be consistent with zooplankton grazing. Previous studies have shown zooplankton to release fluorescent DOM at various excitation–emission maxima dependent on diet (Urban–Rich *et al*., 2004) and they likely play a role

DOI: 10.1002/hyp

in the diurnal cycling of DOM. Filtering rates for zooplankton suggest that they can account for at most a 4% filtering of the water column in a 12 hour dark period in the San Joaquin River. They therefore do not appear to be the main driver behind the diurnal cycles observed in chlorophyll-*a* and CDOM.

Consistent with the observed diurnal trend in DOM fluorescence, the spectral slope parameter $S_{290-350}$ also exhibited similar behaviour with respect to the daily maximum and minimum values. However, $S_{290-350}$ does not show a secondary maximum as observed with DOM fluorescence. $S_{290-350}$ had the highest values in the morning shortly after sunrise ($\sim$0·0179–0·0184 nm^{-1}) and declined during the day to the lowest observed values ($\sim$0·0157–0·0165 nm^{-1}) around early evening (Figure 3b). Spectral slope defines the spectral dependence of the CDOM absorption coefficient and as a result provides information relating to the nature of CDOM (Blough and Del Vecchio, 2002). Spectral slope has been shown to vary with the source of CDOM and also to change in response to biological and chemical alteration of the source material (Blough and Del Vecchio, 2002). In addition, spectral slope has been related to a number of molecular properties and has been shown to become steeper with decreasing molecular weight and decreasing aromaticity (Blough and Green, 1995; Stubbins, 2001).

Studies of DOM spectral slope in systems that have strong terrestrial character and high aromaticity were shown to typically result in an increase in spectral slope upon irradiation and an increase in bioavailability of the DOM (Moran and Zepp, 1997; Mopper and Kieber, 2002). Conversely, a number of recent studies have shown that upon irradiation of fresh algal, derived DOM bioavailability decreased (Tranvik and Bertilsson, 2001; Obernosterer and Benner, 2004). Spectral slope has typically been shown to increase upon irradiation due to photobleaching; however, since the diurnal $S_{290-350}$ pattern in this study becomes shallower during the day, photobleaching as a potential driver of the diurnal changes in spectral slope (Figure 3b) seems unlikely.

The magnitude of the change in spectral slope observed in this study is relatively large for freshwaters and is comparable to the differences observed between allochthonous- and autochthonous-dominated systems or the magnitude of change seen due to biological and chemical degradation (Moran *et al*., 2000; Blough and Del Vecchio, 2002; Obernosterer and Benner, 2004; Spencer *et al*., 2007a). Blough and Del Vecchio (2002) describe a spectral slope range of 0·013–0·018 nm^{-1} as typical for freshwaters or coastal waters influenced by riverine input so the results presented here are toward the higher end of the range and are higher than those of organic-rich rivers such as the Satilla (southeast US) which ranges from 0·0137–0·0156 nm^{-1} (Moran *et al*., 2000).

The observed diurnal pattern in $S_{290-350}$, with a decrease throughout the day and an increase at night, is potentially due to a combination of photochemical processing and the *in situ* production highlighted by chlorophyll-*a* trends (Figure 3a). The observed decrease in $S_{290-350}$ upon irradiation in this system could be explained by a photochemical formation pathway of humic substances from algal-derived fatty acids as hypothesized by Harvey *et al*. (1983). Furthermore, Tranvik and Kokalj (1998) showed production of recalcitrant DOM from autochthonous DOM by interaction with humic substances in addition to irradiation, and this appears to be a strong possibility in the San Joaquin River.

The method outlined by Tranvik and Kokalj (1998) involved the binding of autochthonous DOC to humic substances, which would be expected to result in a decrease in spectral slope during the day under irradiation and with phytoplankton production as observed in this study. Such a photochemically-mediated process would likely result in increasing absorbance and a bathochromic shift in the region of DOM fluorescence reported. Other processes that could potentially explain the apparently asynchronous trends of DOM absorbance and chlorophyll-*a* in comparison to DOM fluorescence and $S_{290-350}$ include microbial degradation of irradiated DOM which has been shown to decrease spectral slope (Moran *et al*., 2000), the mixing of water from other sources or sedimentary release of DOM, but these cannot be identified from our study. Photodissolution of particulate organic matter into the dissolved phase from suspended sediments has been described and this could play a role in riverine organic matter cycling over the diurnal cycle (Mayer *et al*., 2006). Photodissolution was found to be almost equally as active between low and highly turbid suspensions as it has a low requirement for irradiation (Mayer *et al*., 2006) and thus could even be occurring in light limited rivers such as the San Joaquin.

CONCLUSIONS

The *in situ* optical measurements described in this study clearly show, for the first time, diurnal variations in DOM concentration and composition-related measurements in a riverine system, even though diurnal changes are not well-reflected in bulk DOC concentrations. DOM in riverine systems such as the San Joaquin is often viewed as homogeneous in character over short time scales. However, this study highlights changes in DOM composition over a diurnal cycle that could ultimately impact riverine biogeochemistry. The observed diurnal changes in DOM composition likely reflect both photochemical and biologically-mediated processes. The apparent asynchronous trend of DOM absorbance and chlorophyll-*a* in comparison to DOM fluorescence and $S_{290-350}$ suggest that no single CDOM spectrophotometric measurement captures the dynamics of DOM diurnal variation in this system and the measurement of multiple optical parameters is recommended.

With respect to DOM in streams and rivers, clearly the time of sample collection during the day could have an impact on its optical characteristics. A number of recent studies have used fluorescence and absorbance

DOI: 10.1002/hyp

measurements to distinguish different DOM sources in riverine and estuarine systems (e.g. Baker, 2002; Spencer *et al*., 2007a), but these source assignments could be confounded by short-term variability. It is therefore recommended that sampling be conducted at the same time of day for each location and mean daily flux of solar radiation data, if available, be checked against the data for any trends. The potential of optical analyses for DOM characterization are clear from this study as they allow *in situ* high resolution measurements to be undertaken and show changes in DOM composition within a short time scale. As variation in DOM composition and concentration has been related to the production of carcinogenic DBPs during chlorination of drinking water (e.g. trihalomethanes) (Bergamaschi *et al*., 1999; Nikolaou *et al*., 2004a, b), optical monitoring tools such as described here may even aid in the timing of drinking water extractions. Finally, the ability to monitor such short-term variability in DOM dynamics serves to increase our understanding of its processing in the aquatic environment by monitoring measurements related to aromaticity and molecular weight, therefore demonstrating potential in delineating the complex role that DOM undertakes in aquatic ecosystems.

ACKNOWLEDGEMENTS

We thank Turlock Pistol Club for site access and Klaus Kaiser, Anthony Aufdenkampe, Carol Kendall, Dan Doctor, Steve Silva, two anonymous USGS internal reviewers for constructive discussion and three external anonymous reviewers for comments leading to the improvement of this manuscript. We also thank Mark Rollogg, Sal Henson and Emily Volkmar for field and laboratory assistance. The use of brand names in this manuscript is for identification purposes only and does not imply endorsement by the US Geological Survey.

REFERENCES

Baker A. 2001. Fluorescence excitation-emission matrix characterization of some sewage-impacted rivers. *Environmental Science and Technology* **35**(5): 948–953.

Baker A. 2002. Spectrophotometric discrimination of river dissolved organic matter. *Hydrological Processes* **16**(16): 3202–3213.

Baker A, Bolton L, Newson M, Spencer RGM. Spectrophotometric properties of surface water dissolved organic matter in an afforested upland peat catchment. *Hydrological Processes*. DOI: 10.1002/hyp.6827.

Benner R, Opsahl S. 2001. Molecular indicators of the sources and transformations of dissolved organic matter in the Mississippi river plume. *Organic Geochemistry* **32**(4): 597–611.

Bergamaschi BA, Fram MS, Kendall C, Silva SR, Aiken GR, Fuji R. 1999. Carbon isotopic constraints on the contribution of plant material to the natural precursors of trihalomethanes. *Organic Geochemistry* **30**(8A): 835–842.

Blough NV, Green SA. 1995. Spectroscopic characterization and remote sensing of NLOM. In *The Role of Non-Living Organic Matter in the Earth's Carbon Cycle*. Zepp RG, Sonntag C (eds). John Wiley and Sons: NYC; pp. 23–45.

Blough NV, Del Vecchio R. 2002. Chromophoric DOM in the coastal environment. In *Biogeochemistry of Marine Dissolved Organic Matter*. Hansell DA, Carlson CA (eds). Academic Press: San Diego; 509–546.

Blough NV, Zafiriou OC, Bonilla J. 1993. Optical absorption spectra of water from the Orinoco River outflow: Terrestrial input of colored organic matter to the Caribbean. *Journal of Geophysical Research* **98**(C2): 2271–2278.

Boss E, Zaneveld JRV. 2003. The effect of bottom substrate on inherent optical properties: Evidence of biogeochemical processes. *Limnology and Oceanography* **48**(1): 346–354.

Brick CM, Moore JN. 1996. Diel variation of trace metals in the upper Clark Fork River, Montana. *Environmental Science and Technology* **30**(6): 1953–1960.

Coble PG. 1996. Characterization of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy. *Marine Chemistry* **51**(4): 325–346.

Cumberland SA, Baker A. 2007. The freshwater dissolved organic matter fluorescence-total organic carbon relationship. *Hydrological Processes* **21**(16): 2093–2099.

del Giorgio PA, Davis J. 2003. Patterns in Dissolved Organic Matter Lability and Consumption across Aquatic Ecosystems. In *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter*. Findlay SEG, Sinsabaugh, RL (eds). Academic Press: Oxford; pp. 400–424.

Elliott S, Lead JR, Baker A. 2006. Characterisation of the fluorescence from freshwater, planktonic bacteria. *Water Research* **40**(10): 2075–2083.

Ferrari GM, Dowell MD, Grossi S, Targa C. 1996. Relationship between the optical properties of chromophoric dissolved organic matter and total concentration of dissolved organic carbon in the southern Baltic Sea region. *Marine Chemistry* **55**: 299–316.

Findlay S. 2003. Bacterial Response to Variation in Dissolved Organic Matter. In *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter*. Findlay SEG, Sinsabaugh, RL (eds). Academic Press: Oxford; pp. 363–379.

Findlay SEG, Sinsabaugh RL. 2003. Preface. In *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter*. Findlay SEG, Sinsabaugh, RL (eds). Academic Press: Oxford; xvii–xx.

Green SA, Blough NV. 1994. Optical absorption and fluorescence properties of chromophoric dissolved organic matter in natural waters. *Limnology and Oceanography* **39**(8): 1903–1916.

Harrison JA, Matson PA, Fendorf SE. 2005. Effects of a diel oxygen cycle on nitrogen transformations and greenhouse gas emissions in a eutrophied subtropical stream. *Aquatic Sciences* **67**(3): 308–315.

Harvey GR, Boran DA, Chesal LA, Tokar JM. 1983. The structure of marine fulvic and humic acids. *Marine Chemistry* **12**(2–3): 119–132.

Her N, Amy G, McKnight DM, Sohn J, Yoon YM. 2003. Characterization of DOM as a function of MW by fluorescence EEM and HPLC-SEC using UVA, DOC, and fluorescence detection. *Water Research* **37**(17): 4295–4303.

Hernes PJ, Benner R. 2003. Photochemical and microbial degradation of dissolved lignin phenols: Implications for the fate of terrigenous dissolved organic matter in marine environments. *Journal of Geophysical Research—Oceans* **108**(C9): Art. 3291.

Hood E, Williams MW, McKnight DM. 2005. Sources of dissolved organic matter (DOM) in a Rocky Mountain stream using chemical fractionation and stable isotopes. *Biogeochemistry* **74**(2): 231–255.

Kaplan LA, Bott TL. 1982. Diel fluctuations of DOC generated by algae in a piedmont stream. *Limnology and Oceanography* **27**(6): 1091–1100.

Kirk JTO. 1994. *Light and Photosynthesis in Aquatic Ecosytems* (2nd Ed.) Cambridge University Press: Cambridge, UK; pp. 509.

Kratzer CR, Dileanis PD, Zamora C, Silva SR, Kendall C, Bergamaschi BA, Dahlgren RA. 2004. Sources and transport of nutrients, organic carbon, and chlorophyll-*a* in the San Joaquin River upstream of Vernalis, California, during summer and fall, 2000 and 2001. US Geological Survey Water Resources Investigations Report 03–4127.

Leland HV, Brown LR, Mueller DK. 2001. Distribution of algae in the San Joaquin River, California, in relation to nutrient supply, salinity and other environmental factors. *Freshwater Biology* **46**(9): 1139–1167.

Manny BA, Wetzel RG. 1973. Diurnal changes in dissolved organic carbon and inorganic carbon and nitrogen in a hardwater stream. *Freshwater Biology* **3**: 31–43.

Mayer LM, Schick LL, Skorko K, Boss E. 2006. Photodissolution of particulate organic matter from sediments. *Limnology and Oceanography* **51**(2): 1064–1071.

McKnight DM, Boyer EW, Westerhoff PK, Doran PT, Kulbe T, Andersen DT. 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic matter and aromaticity. *Limnology and Oceanography* **46**(1): 38–48.

Mopper K, Kieber DJ. 2002. Photochemistry and the cycling of carbon, sulfur, nitrogen and phosphorous. In *Biogeochemistry of Marine Dissolved Organic Matter*. Hansell DA, Carlson CA (eds). Academic Press: San Diego; 456–507.

Mopper K, Feng ZM, Bentjen SB, Chen RF. 1996. Effects of cross-flow filtration on the absorption and fluorescence properties of seawater. *Marine Chemistry* **55**(1–2): 53–74.

Moran MA, Zepp RG. 1997. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. *Limnology and Oceanography* **42**(6): 1307–1316.

Moran MA, Sheldon WM, Zepp RG. 2000. Carbon loss and optical property changes during long-term photochemical and biological degradation of estuarine dissolved organic matter. *Limnology and Oceanography* **45**(6): 1254–1264.

Mulholland PJ, Houser JN, Maloney KO. 2005. Stream diurnal dissolved oxygen profiles as indicators of in-stream metabolism and disturbance effects: Fort Benning as a case study. *Ecological Indicators* **5**(3): 243–252.

Mulholland PJ, Thomas SA, Valett HM, Webster JR, Beaulieu J. 2006. Effects of light on NO_3^- uptake in small forested streams: diurnal and day-to-day variations. *Journal of the North American Benthological Society* **25**(3): 583–595.

Newson M, Baker A, Mounsey S. 2001. The potential role of freshwater luminescence measurements in exploring runoff pathways in upland catchments. *Hydrological Processes* **15**(6): 989–1002.

Nguyen ML, Westerhoff PE, Baker L, Hu Q, Esparza-Soto M, Sommerfeld M. 2005. Characteristics and reactivity of algae-produced dissolved organic carbon. *Journal of Environmental Engineering* **131**(11): 1574–1582.

Nikolaou AD, Golfinopoulos SK, Lekkas TD, Kostopoulou MN. 2004a. DBP levels in chlorinated drinking water: Effect of humic substances. *Environmental Monitoring and Assessment* **93**(1–3): 301–319.

Nikolaou AD, Golfinopoulos SK, Arhonditsis GB, Kolovoyannis V, Lekkas TD. 2004b. Modeling the formation of chlorination by-products in river waters with different quality. *Chemosphere* **55**(3): 409–420.

Nimick DA, Gammons CH, Cleasby TE, Madison JP, Skaar D, Brick CM. 2003. Diel cycles in dissolved metal concentrations in streams: Occurrence and possible causes. *Water Resources Research* **39**(9): Art. No. 1247.

Obernosterer I, Benner R. 2004. Competition between biological and photochemical processes in the mineralization of dissolved organic carbon. *Limnology and Oceanography* **49**(1): 117–124.

Parker SR, Poulson SR, Gammons CH, Degrandpre MD. 2005. Biogeochemical controls on diel cycling of stable isotopes of dissolved O_2 and dissolved inorganic carbon in the Big Hole River, Montana. *Environmental Science and Technology* **39**(18): 7134–7140.

Parlanti E, Worz K, Geoffrey L, Lamotte M. 2000. Dissolved organic matter fluorescence spectroscopy as a tool to estimate biological activity in a coastal zone submitted to anthropogenic inputs. *Organic Geochemistry* **31**(12): 1765–1781.

Patel-Sorrentino N, Mounier S, Benaim JY. 2002. Excitation-emission fluorescence matrix to study pH influence on organic matter fluorescence in the Amazon Basin rivers. *Water Research* **36**(10): 2571–2581.

Pegau WS, Gray D, Zaneveld JRV. 1997. Absorption and attenuation of visible and near-infrared light in water: dependence on temperature and salinity. *Applied Optics* **36**(24): 6035–6046.

Reynolds DM. 2003. Rapid and direct determination of tryptophan in water using synchronous fluorescence spectroscopy. *Water Research* **37**(13): 3055–3060.

Rochelle-Newall EJ, Fisher TR. 2002. Production of chromophoric dissolved organic matter fluorescence in marine and estuarine environments: an investigation into the role of phytoplankton. *Marine Chemistry* **77**(1): 7–21.

Rochelle-Newall EJ, Fisher TR, Fan C, Glibert PM. 1999. Dynamics of chromophoric dissolved organic matter and dissolved organic carbon in experimental mesocosms. *International Journal of Remote Sensing* **20**(3): 627–641.

Scholefield D, Le Goff T, Braven J, Ebdon L, Long T, Butler M. 2005. Concerted diurnal patterns in riverine nutrient concentrations and physical conditions. *Science of the Total Environment* **344**(1–3): 201–210.

Senesi N. 1990. Molecular and quantitative aspects of the chemistry of fulvic acid and it's interactions with metal ions and organic chemicals. Part II The fluorescence spectroscopy approach. *Analytica Chimica Acta* **232**(1): 77–106.

Senesi N, Miano TM, Provenzano MR, Brunetti G. 1991. Characterization, differentiation and classification of humic substances by fluorescence spectroscopy. *Soil Science* **152**(4): 259–271.

Spencer RGM, Baker A, Ahad JME, Cowie GL, Ganeshram R, Upstill-Goddard RC, Uher G. 2007a. Discriminatory classification of natural and anthropogenic waters in two U.K. estuaries. *Science of the Total Environment* **373**(1): 305–323.

Spencer RGM, Ahad JME, Baker A, Cowie GL, Ganeshram G, Upstill-Goddard RC, Uher G. 2007b. The estuarine mixing behaviour of peatland derived dissolved organic carbon and its relationship to chromophoric dissolved organic matter in two North Sea estuaries (U.K.). *Estuarine, Coastal and Shelf Science* **74**(1–2): 131–144.

Spencer RGM, Bolton L, Baker A. 2007c. Freeze/thaw and pH effects on freshwater dissolved organic matter fluorescence and absorbance properties from a number of U.K. locations. *Water Research* **41**(13): 2941–2950.

Stedmon CA, Markager S, Bro R. 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Marine Chemistry* **82**(3–4): 239–254.

Stubbins AP. 2001. Aspects of aquatic CO photoproduction from CDOM. Marine Sciences and Coastal Management. Ph.D. thesis. University of Newcastle-upon-Tyne, U.K. pp. 201.

Tranvik LJ, Kokalj S. 1998. Decreased biodegradability of algal DOC due to interactive effects of UV radiation and humic matter. *Aquatic Microbial Ecology* **14**(3): 301–307.

Tranvik LJ, Bertilsson S. 2001. Contrasting effects of solar UV radiation on dissolved organic sources for bacterial growth. *Ecology Letters* **4**(5): 458–463.

Twardowski MS, Sullivan JM, Donaghay PL, Zaneveld JRV. 1999. Microscale quantification of the absorption by dissolved and particulate material in coastal waters with an AC-9. *Journal of Atmospheric and Oceanic Technology* **16**(6): 691–707.

Urban-Rich J, McCarty JT, Shailer M. 2004. Effects of food concentration and diet on chromophoric dissolved organic matter accumulation and fluorescent composition during grazing experiments with the copepod *Calanus finmarchicus*. *ICES Journal of Marine Science* **61**(4): 542–551.

Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fuji R, Mopper K. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental Science and Technology* **37**(20): 4702–4708.

WET Labs. 2003. WET Star User's Guide. http://www.wetlabs.com/products/pub/wetstar/wetstarm.pdf. pp. 1–31.

Worrall F, Burt T. 2004. Time series analysis of long-term river dissolved organic carbon records. *Hydrological Processes* **18**(5): 893–911.

Worrall F, Burt T, Shedden R. 2003. Long term records of riverine dissolved organic matter. *Biogeochemistry* **64**(2): 165–178.

Worrall F, Harriman R, Evans CD, Watts CD, Adamson J, Neal C, Tipping E, Burt T, Grieve I, Monteith D, Naden PS, Nisbet T, Reynolds B, Stevens P. 2004. Trends in dissolved organic carbon in UK rivers and lakes. *Biogeochemistry* **70**(3): 369–402.