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

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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-α in comparison to chromophoric dissolved organic matter (CDOM) fluorescence and spectral slope S250–350 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.

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; Schoefield et al., 2005; Mulholland et al., 2006), trace metals (Brick and Moore, 1996; Nimick et al., 2003) and...
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; Stubbins, 2001; 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 11274550 (37°25′42″N, 121°00′12″W). The upstream drainage area is approximately 25 107 km² 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-α concentrations in the range of 75–150 µg l⁻¹ and mineral nitrogen (NH₄⁺ + NO₃⁻; 2–2.5 mg N l⁻¹) and soluble reactive phosphorous (50–150 µg P 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
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 W m⁻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 (Kratz 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 WET Labs 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; Newsom 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 Aanderaa 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:

\[ a_\lambda = a_{\lambda_{ref}} \exp[-S(\lambda - \lambda_{ref})] \]  

where \( a_\lambda \) is the absorption coefficient of CDOM at a specified wavelength, \( \lambda_{ref} \) 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.
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 m³ 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 m³ s⁻¹ increase) and Salt Slough (0.15 m³ s⁻¹ increase) and does not indicate any diurnal variability in flow. General water quality characterization for the study period is provided in Table I for reference purposes.

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

<table>
<thead>
<tr>
<th>Date</th>
<th>Discharge (m³ s⁻¹)</th>
<th>Temp (°C)</th>
<th>EC (µS cm⁻¹)</th>
<th>DO (mg l⁻¹)</th>
<th>DO (% sat)</th>
<th>pH</th>
<th>Cations</th>
<th>Anions</th>
<th>NTU</th>
<th>TSS</th>
<th>VSS</th>
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<tr>
<td>7/28/05</td>
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<td>25.8</td>
<td>1832</td>
<td>9.69</td>
<td>106.5</td>
<td>8.08</td>
<td>111.5</td>
<td>26.7</td>
<td>115.2</td>
<td>135.6</td>
<td>34.5</td>
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<tr>
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<td>25.2</td>
<td>2400</td>
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<td>109.9</td>
<td>8.06</td>
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<tr>
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<td>135.6</td>
<td>34.5</td>
</tr>
</tbody>
</table>

Figure 1. Ancillary parameters measured during the diurnal study period in the San Joaquin River at Crows Landing: (a) discharge (m³ 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).

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...
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 ($r^2 = 0.46$).

**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 trend over diurnal cycles within analytical error. Previ-

ous studies have shown conflicting results with respect to diurnal changes in DOC in streams and agricultural chan-

nels. 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. <0.2 mg l$^{-1}$) cannot be measured within the analytical precision of conventional DOC analyses and the inability to constrain this analytical uncer-

tainty 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 vari-

able 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).

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 ($r^2 = 0.45$, $p < 0.05$) 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 broadband 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 (~68–70.5 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

![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).](image-url)
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 hypsochromic 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
in the diurnal cycling of DOM. Filtering rates for zoo-
plankton 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-α 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 max-
imum 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 depend-
ence 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 
steepen 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 chem-
ical 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 
since 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-α 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, Tran-
vik and Kokalj (1998) showed production of recalcitr-
ant 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 irradi-
ation and with phytoplankton production as observed 
in this study. Such a photochemically-mediated pro-
cess 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-α 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 can-
not 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. How-
ever, this study highlights changes in DOM composi-
tion 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 asyn-
chronous trend of DOM absorbance and chlorophyll-α 
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 parame-
ters 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
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 aromacity and molecular weight, therefore demonstrating potential in delineating the complex role that DOM undertakes in aquatic ecosystems.

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