

Quantifying fluxes and characterizing compositional changes of dissolved organic matter in aquatic systems in situ using combined acoustic and optical measurements

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Abstract

Studying the dynamics and geochemical behavior of dissolved and particulate organic material is difficult because concentration and composition may rapidly change in response to aperiodic as well as periodic physical and biological forcing. Here we describe a method useful for quantifying fluxes and analyzing dissolved organic matter (DOM) dynamics. The method uses coupled optical and acoustic measurements that provide robust quantitative estimates of concentrations and constituent characteristics needed to investigate processes and calculate fluxes of DOM in tidal and other lotic environments. Data were collected several times per hour for 2 weeks or more, with the frequency and duration limited only by power consumption and data storage capacity. We assessed the capabilities and limitations of the method using data from a winter deployment in a natural tidal wetland of the San Francisco Bay estuary. We used statistical correlation of in situ optical data with traditional laboratory analyses of discrete water samples to calibrate optical properties suited as proxies for DOM concentrations and characterizations. Coupled with measurements of flow velocity, we calculated long-term residual horizontal fluxes of DOC into and out from a tidal wetland. Subsampling the dataset provides an estimate for the maximum sampling interval beyond which the error in flux estimate is significantly increased.

Introduction

It is well established that dissolved organic matter (DOM) plays a major role in biogeochemical processes: it supplies energy to heterotrophic organisms, binds metals and pesticides, affects light penetration, and influences particle aggregation and interaction of biota with synthetic organic compounds and trace metals (e.g., Mantoura et al. 1978, Aiken et al. 1985). The full ecological significance of DOM has not been

fully elucidated, however, in part because of the difficulties involved in quantifying changes in concentration, source, composition, and bioavailability at timescales appropriate to physical forcings such as tides and storms. This study examines the efficacy of using a combination of in situ optical and acoustic measurements to quantify fluxes and examine changes in chemical properties of DOM in a tidal wetland system, but the results could be of use for studies in many lotic environments.

Optical properties measured in natural waters are used as proxies to concentration of biogeochemical parameters such as nitrate, sulfide, dissolved organic carbon (DOC), particulate organic material, chlorophyll, and others (e.g., Johnson et al. 2006, Boss et al. 2007, Claustre et al. 2008). Recently developed, commercially available instrumentation provide the ability to measure optical properties in situ, potentially permitting nearly continuous assessment of the concentration of some important biogeochemical parameters. For example, the deployment of an in situ spectrophotometer with 0.2- μm prefilters provides the opportunity to measure the absorption properties of DOM and its spectral behavior (Twardowski et al. 1999).

Therefore, in situ deployment of optical instrumentation may permit the collection of biogeochemical data on temporal and

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spatial scales needed to resolve episodic, rapid, and short-timescale environmental forcing (time scales of tens of minutes)—an undertaking that is impractical with conventional discrete sampling and laboratory analysis (Dickey 2001). For example, Johnson et al. (2006) demonstrated the utility of high-frequency in situ absorption measurements for determination of nitrate concentrations and their dynamics in an estuary. We describe below the relationship between optical parameter values and laboratory measurements of DOC concentration, and use this relationship to obtain a multiweek high-resolution record of DOC concentration from in situ optical data. In principle, a similar technique could be used for other biogeochemical parameters having an optical proxy. We do not propose that in situ optical parameter measurements replace conventional discrete sampling, but rather that it be used to interpolate between or extrapolate beyond the discrete samples.

Importantly, for DOM, simultaneous measurement of spectral absorption and DOM fluorescence provides an opportunity to characterize DOM in terms of its absorption spectral slope and the ratio of fluorescence to absorption parameters related to the chemical composition of DOM (Carder et al. 1989, Blough and Green 1995, Yacobi et al. 2003).

Previous studies have used optical measurements and discharge measurements to compute sediment fluxes in riverine and tidal environments (Suk et al. 1999, Ganju et al. 2005, Goni et al. 2005, Ganju and Schoellhamer 2006). For example, Ganju et al. (2005) used an acoustic Doppler velocity meter (ADV) to obtain water flux and, by using optical backscatter as a proxy for suspended sediment concentration (SSC), estimated the suspended sediment flux over spring–neap cycles from a tidal wetland in the Sacramento–San Joaquin River Delta. Boss and Zaneveld (2003) coupled in situ measurements of velocity and colored dissolved organic matter (CDOM) absorption to highlight the role of tides in fluxing CDOM away from the Bahamas banks. Johnson et al. (2006) and Chapin et al. (2004) computed nitrate fluxes in a slough by coupling a hydrological model with in situ measurements of nitrate estimated from absorption measurements in UV light. The current study represents the first we are aware of that describes use of combined optical and acoustic measurements to quantify fluxes of DOM and document changes of DOM composition.

A major aim of the study was to develop a robust protocol for using optical and hydrologic measurements to quantify concentrations and fluxes of DOC in tidal wetland systems. Determination of DOC flux in tidal environments is particularly difficult because of variability in concentration due to tidal, meteorological, and climatic forcing. To assess the capabilities and limitations of the approach, we collected data during multiweek deployments from a wetland channel adjacent to the San Francisco Estuary. Discrete samples were collected systematically through the deployment for measurement of DOC and optical parameters in the laboratory. The data were

used to establish the relationships between measured values of optical properties and DOC concentration. Comparison between in situ and laboratory optical properties validated that the in situ optical measurements were not significantly affected by biofouling.

Materials and procedures

Study location—Browns Island is a natural tidal wetland in the San Francisco Bay estuary. The 2.8-km² wetland is located near the confluence of the Sacramento River, San Joaquin River, and Suisun Bay, approximately 77 km from the estuary mouth. Island vegetation is dominated by tules/hardstem bulrushes (*Scirpus californicus* and *S. acutus*), cattails (*Typha angustifolia*), saltgrass (*Distichlis spicata*), and other sedges growing on deep peat soils.

Browns Island contains a well-defined main channel with numerous side channels (Figure 1). Tides in this area are mixed semidiurnal, with a maximum spring tidal range of 1.8 m and a minimum neap tide range of 0.20 m. At high water, the main channel is approximately 17 m wide, with a maximum depth of 4.5 m. This channel opens to the west, in the direction of tidal inflow, and terminates at a lagoon in the eastern wetland interior. The main-channel sampling site was upstream of major side channels approximately 300 m from the channel mouth (Figure 1). Instrumentation was moored on the channel bottom at the center of the main drainage channel.

Sampling procedure—Acoustic and optical instrument packages were deployed in the Browns Island main channel approximately 15 m apart for a 4-week period in the winter, January–February 2006, and left unattended except for weekly service visits to download data, clean optical sensors, and replace filter cartridges. Sampling periods were longer than 2 weeks to resolve the spring–neap frequency of the tides.

During the sampling period, discrete samples were collected hourly for a 26-h period during the time of greatest tidal range to capture the maximum variability in DOC concentration and character (Ganju et al. 2005). Laboratory measurements of light absorption and DOC were then cross-calibrated with the accompanying in situ optical measurements.

Moored optical system—The optical instrument package consisted of a stainless-steel cage containing submersible sampling pumps, membrane filters, and optical and hydrographic sensors (Figure 2). Measurements were collected over multiple weeks at 30-min intervals by pumping water through a 9-wavelength visible spectrophotometer (WET Labs ac-9 spectrophotometer; WET Labs, Philomath, OR, USA) and a CDOM fluorometer (WET Labs WETStar; excitation wavelength 370 nm, emission wavelength nominal bandpass 460 nm). Water was pumped simultaneously through a filtered flowpath for measurement of optical properties related to dissolved constituents and an unfiltered flowpath for characterization of particulates. Conductivity, salinity, and pressure were measured with a Sea-Bird model SB37-SI CTD (Sea-Bird Electronics, Bellevue, WA, USA). Pumps and instruments were controlled

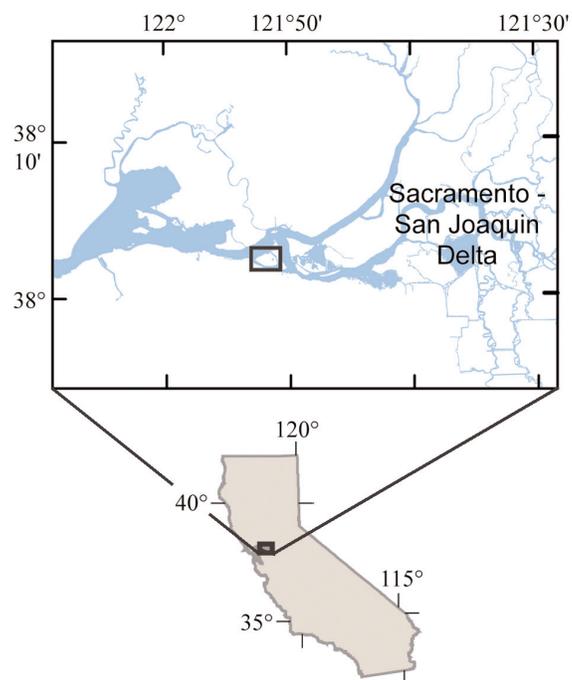
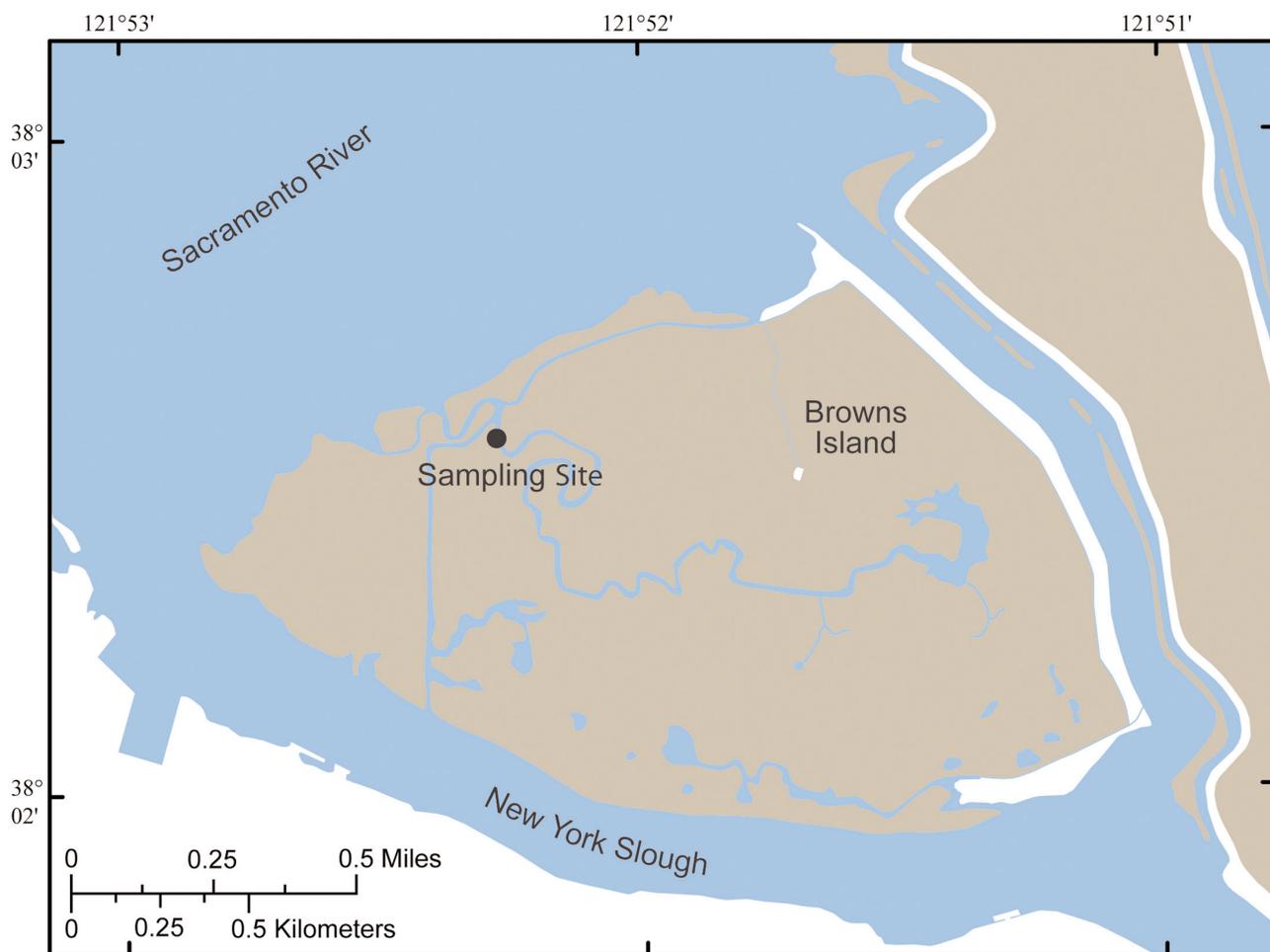


Fig. 1. Browns Island study area, Sacramento–San Joaquin River Delta, CA, USA.

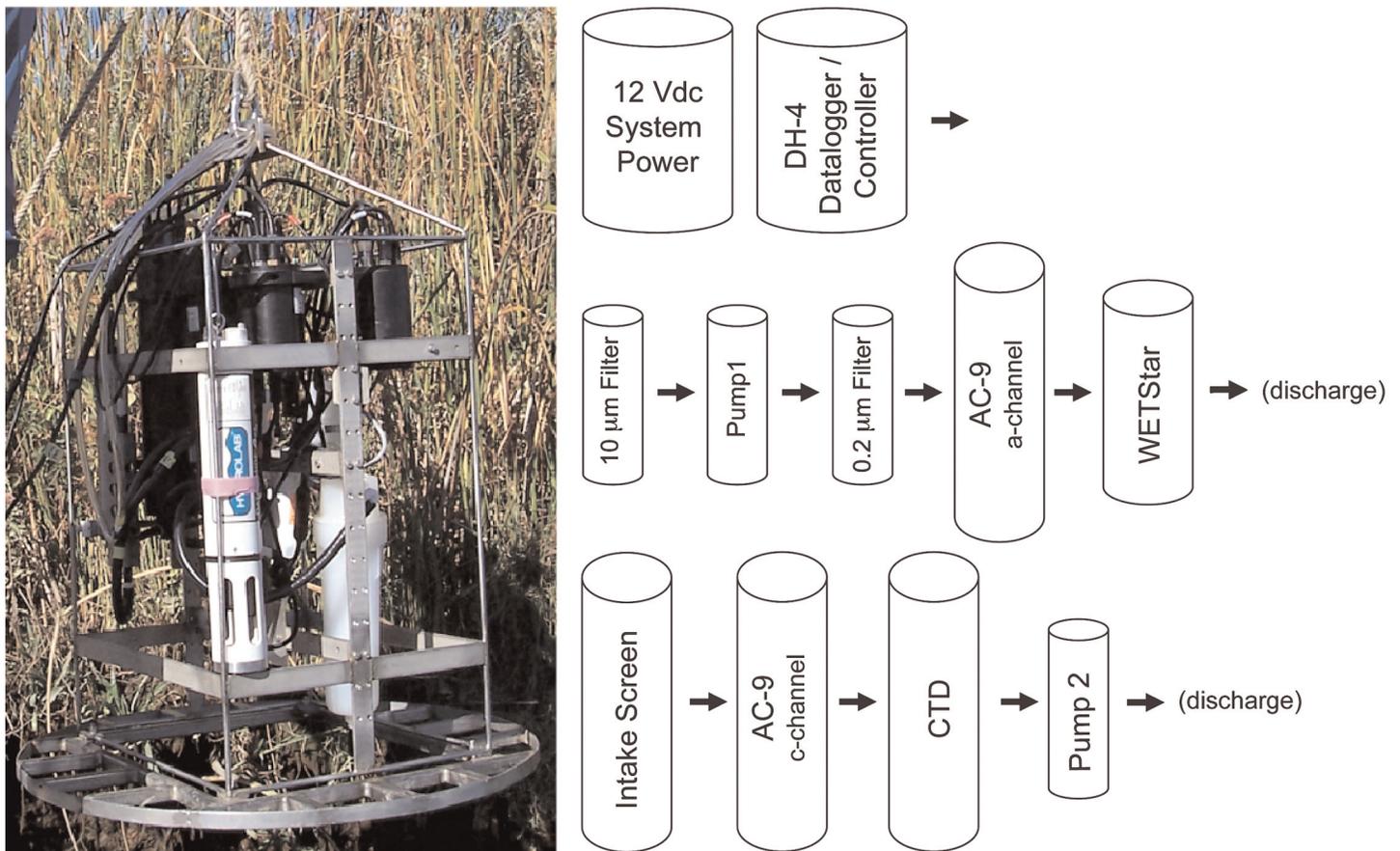


Fig. 2. The optical instrument package is a parallel flow-through system with one filtered and one unfiltered channel, allowing simultaneous characterization of dissolved and particulate fractions within the water column. The system, which is capable of week-long deployments, autonomously measures absorption in the ultraviolet and visible spectra; absorption, backscatter, and attenuation in the visible spectrum; and CDOM, temperature, and water depth.

and most data logged using an in situ data and power handler (DH-4; WET Labs). CTD data were collected using their onboard dataloggers.

Filtration and pumping system—For measurements of dissolved components, water was drawn through a prefilter (Osmonics model Memtrex, 25 cm length, 10 µm pore size; Osmonics, Inc., Minnetonka, MN, USA) and drawn through a finer filter (Osmonics model Memtrex, 25 cm length, 0.2 µm pore size; Osmonics, Inc.) using a SHURflo model 1100 pump (SHURflo, Cypress, CA, USA) modified by the addition of a submersible power relay. These waters were then drawn through the absorption flow cell of the ac-9 and the WETStar fluorometer. In the nonfiltered flowpath, a single Sea-Bird 5T pump with a Teflon screen (1 mm mesh size, to exclude very large detritus) was used to draw samples through the Sea-Bird SB37-SI CTD and the attenuation flow cell of the ac-9.

The flow-through instruments were connected using Tygon plasticizer-free tubing (Saint-Gobain Performance Plastics, www.tygon.com) prerinse with dilute HCl and organic-free water. The clear tubing was wrapped with black electrical tape to minimize the effects of external light biasing the sensitive

ac-9 photometer. The tape-wrapped tubing was also soaked overnight in organic-free water to leach possible contaminants from the tape.

In the field, tubing and filters were replaced every week, after the data download and instrumentation servicing/cleaning, to minimize the effects of biological fouling.

CDOM absorption—Absorption by CDOM was measured at 9 visible wavelengths by the WET Labs ac-9 spectrophotometer: 412, 440, 488, 510, 532, 555, 650, 676, and 715 nm. The protocol of Twardowski et al. (1999) for ac-9 data collection and processing was modified to accommodate the relatively high DOC and particulate loads of the Browns Island waters. A larger (5-m²) 0.2-µm membrane filter and a 10-µm prefilter were used as well as 10-cm pathlength ac-9. The large filtration cartridge permitted longer deployments than would have been possible with smaller filters. The shorter flow cell was needed because of the high DOC concentration. The ac-9 flow cells and detectors (absorption flow cell and attenuation flow cell) were cleaned using a combination of lens papers, 0.5% solution of Liquinox, and organic-free water, plus a final rinse of organic-free water. Pure water offsets were checked in the

lab before and after each field deployment and monitored in the field by logging air reading before and after weekly service.

CDOM fluorescence—The fluorescent fraction of the DOM pool (FDOM) was measured in situ using a WET Labs WETStar single-band excitation-emission in situ fluorometer (370 nm excitation, 10 nm full width half max, FWHM; 460 nm emission, 120 nm FWHM). The fluorometer was installed in the filtered path after the ac-9. The fluorometer flowpath was cleaned using lens papers, 0.5% solution of Liquinox, and organic-free water, plus a final rinse of organic-free water as described in the users guide provided by WET Labs. Blank water offsets were collected before every field deployment and subtracted from the field measurements. Raw data collected from the WETStar fluorometer were converted from volts DC (VDC) to quinine sulfate units (QSU) using the factory-supplied QSU scale factor ($\mu\text{g L}^{-1}$).

CDOM composition—Two optical parameters associated with DOM composition, spectral slope (S) and relative fluorescence efficiency (RFE) (Blough and Green 1995, Klinkhammer et al. 2000, Blough and Del Vecchio 2002) were calculated. S has been shown to increase with decreasing bulk molecular weight (Carder et al. 1989; Yacobi et al. 2003) or with decreasing aromatic content. These two parameters have also been used to identify DOC originating from different sources (terrestrial versus marine) and to characterize processes affecting the DOC pool (e.g., photooxidation, primary production) (Vodacek and Blough 1997, Twardowski and Donaghay 2001).

S was calculated using a nonlinear spectral fit of an exponential function with a baseline offset correction (Chen et al. 2007) to the absorption spectrum in the range of 440–676 nm using the *fninsearch* function in MatLab:

$$a_s(\lambda) = a_s(\lambda_{\text{ref}}) \exp[-S(\lambda - \lambda_{\text{ref}})] + K \quad (1)$$

where $a_s(\lambda)$ is the absorption coefficient of CDOM at a specified wavelength, λ_{ref} is a reference wavelength, S is the slope fitting parameter, and K is the offset correction, also calculated by *fninsearch* in MatLab. We opted to fit the absorption spectra using the exponential fit (e.g., Blough and Del Vecchio 2002; Babin et al. 2003, Twardowski et al. 2004) and a spectrally fitted offset, K , as an alternative to offset correction methods (e.g., Bricaud et al. 1981), using subtraction of absorption in the red (see discussion below).

RFE ($\mu\text{g L}^{-1}$ quinine sulfate m^{-1}) was calculated as the ratio of the CDOM fluorescence (excited at 370 nm) to the CDOM absorption at 370 nm (a_{370} ; m^{-1}) extrapolated from the ac-9 spectra via the spectral slope.

Attenuation of visible light—The unfiltered attenuation flow cell of the ac-9 provided measurements of total attenuation, that is, the sum of absorption and scattering by both dissolved and particulate material.

Power, control, and data logging—Most in situ optical instrumentation and data were controlled, logged, and time-stamped using a WET Labs model DH-4 data handler. The DH-4 was programmed to take field measurements every 30 min,

with each data-collection interval consisting of a 1-min pumping preflush and instrument-warming period followed by a 1-min sampling period. The DH-4 is designed to provide power to pumps and sensors with a 1.25-A maximum output. The SHURflo model pump in the filtered flowpath draws approximately 4.0 A at 12 Vdc and required an external solid-state relay device to power the pump without damaging the DH-4. Power (12 Vdc) was supplied using a land-moored battery package. Total equipment power consumption was 6.5 amperes, resulting in 10.4 amp-hours needed each day; thus it required two 100-amp-hour batteries in parallel to operate continuously over a 7-day period. To ensure reliable power supply over a 1-week service interval, we used four 100-amp-hour batteries instrumented in parallel.

Hydrologic measurements—The CTD measuring temperature salinity and pressure was deployed on the channel bottom as described by Ganju et al. (2005). Water velocity measurements were made using a Sontek Argonaut XR upward-looking ADV (Sontek/YSL, San Diego, CA, USA) deployed on the main channel bed. The ADV was programmed to collect the depth-averaged velocity and water depth above the unit for 6 min during the beginning of every 15-min period as well as the water depth. Surveys using a downward-looking acoustic Doppler profiler provided the cross-sectional width ($W(z, t)$) of the channel as a function of depth (z , at each tidal phase) as well as the along channel velocity and were used to compute the along channel averaged velocity $u(t)$.

Discrete water sampling—Discrete water samples were taken hourly over a 24-h period, over a maximum tidal range to provide data for the in situ optical measurements as well as biogeochemical analysis. The intent was to collect data on concentration and composition over the dynamic range encountered in situ during an entire tidal cycle. Discrete samples were also collected during a shorter period 2 weeks earlier to assess possible changes in the biogeochemistry/optics relationships over 2 weeks.

Because concentrations and velocities may vary across and with depth in the tidal channel, water samples were collected using an isokinetic D-77 bottle sampler with a quarter-inch nozzle (Edwards and Glysson 1999). Equal discharge increment (EDI) sampling based on five equally spaced centroids was used to represent the average conditions in the main channel. The sampler was lowered to just above the sediment-water interface and then raised to the surface at a rate such that an equal volume of water was collected at each centroid location, providing a vertically integrated sample at five points across the channel. All samples were gravity-filtered in the field as quickly as practical through precombusted 47-mm diameter, 0.3- μm pore-size glass fiber filters (GFF) (Advantec MFS model GF-7547mm; Advantec MFS, Dublin, CA, USA) into carbon-free, precombusted glass vials and immediately packed on ice. The resulting concentration theoretically equals the cross sectionally (horizontally and vertically) averaged velocity-weighted concentration ($C(t)$).

Laboratory measurements—

DOC—DOM measurements are expressed here as DOC concentration, measured on filtered samples using a Shimadzu TOC-5000A total organic carbon analyzer (Shimadzu, Columbia, MD, USA) according to the method of Bird et al. (2003). Each DOC analysis represents the mean of three or more injections. The instrument gave consistent blank values of <0.05 mg L⁻¹ carbon. Uncertainty in our laboratory DOC measurement is estimated to be 3% of the measured value for samples with concentrations >1 mg L⁻¹ (Bird et al. 2003), based on the precision of the analytical technique and the uncertainty in the blank and replicate measurements.

*Data processing and calculations—*Raw data from all in situ sensors were merged together to the common time of the CTD, which had the lowest sampling frequency (1.16 Hz). Data were then binned by averaging the final 20 s of each 1-min sampling interval. The 40 s of data at the outset of each sampling interval were used as a quality control measure to ensure that in situ pumping rates were sufficient to clear the flowpath during the instrument warmup period.

After data merging and binning, standard temperature corrections were applied to the ac-9 data (Pegau et al. 1997). Deionized, organic-free water blanks (Hydro Picosystem Plus; Hydro, Durham, NC, USA) were measured by both lab and field instruments and subtracted from the respective fluorometer and spectrophotometer values. Weekly service gaps in the in situ data record (typically about 2 h in duration) were interpolated using linear interpolation in MatLab.

*Flux calculations—*The water flux through the channel was taken to be the integral of the velocity, $u(t)$, in the cross section:

$$Q(t) = \int u \, dA \quad (2)$$

where u is the along-channel averaged velocity and A the cross-sectional area. The EDI sampling procedure described above provided the cross-sectionally averaged concentration:

$$C(t) = \frac{\int uc \, dA}{\int u \, dA} \quad (3)$$

in which c is the concentration of a constituent (here DOC). The numerator of Equation 3 is the constituent flux (DOC flux) through the cross-section with units of mass per unit time. The denominator of Equation 3 is the water discharge $Q(t)$ (Equation 2). Thus, flux was given by the product of $C(t)$ and $Q(t)$. $C(t)$ was calculated from the optical surrogate time series calibrated to the EDI samples, and $Q(t)$ was available from the calibrated ADVm time series.

Assessment

*Discrete measurements: variation in DOC concentration—*DOC concentrations in the tidal channel varied tidally. For example, 25 discrete samples collected during the winter deployment ranged from 2.5 to 3.9 mg L⁻¹ (Figure 3). The higher DOC concentrations were observed during the low flows of

ebb tide, whereas lower concentrations (2.5 mg L⁻¹) occurred during higher flows of flood tides.

*Optical properties—*Optical properties varied tidally with FDOM, ranging from 65 QSU ppb during flood to 110 QSU ppb during ebb (Figure 3). Absorption coefficients measured at 440 nm ($a_{\lambda 440}$) exhibited similar periodicity, and the variability was consistent with that of FDOM (Figure 3). Intercalibration of in situ CDOM absorption and laboratory absorption ranged from $R^2 = 0.97$ to 0.99.

*Relation between DOC and field optical measurements—*Several of the optical measurements were strongly related to the DOC concentration for the deployment period. Although deviations in each measurement were observed, the general agreement between the field optical measurements and lab-measured DOC concentration is highly significant (Figure 4).

*Multivariate correlation and DOC prediction—*The generally good relationship between DOC concentration and optical proxies, FDOM, $a_{\lambda 440}$, and $a_{\lambda 650}$ (Figure 4) shows the utility of even single optical measurements as predictors of DOC. Using multiple optical property values to predict DOC concentrations, however, resulted in a significantly better-correlated predictive tool.

We used a partial least squares regression (PLS1; The Unscrambler 9.2; Camo Technologies, Woodbridge, NJ, USA) to relate values of 17 optical properties to measured DOC concentrations (Figure 5). We obtained the best results using measured values for CDOM fluorescence (ex370nm/em460 nm), CDOM absorption from the ac-9 at 8 wavelengths ($a_{\lambda 412} - a_{\lambda 656}$ nm), and total attenuation from the ac-9 at 8 wavelengths (c412 – c656 nm). The model was fully cross-validated, and no pretreatments to the variables such as weighting or normalization were used. Model predictions were within 0.2 mg L⁻¹ of the measured value for three discrete DOC measurements obtained on January 19, 2006, and not part of the model calibration set.

*DOC time series—*The PLS regression model was used to convert high-frequency time series of optical data to modeled in situ DOC concentrations (Figure 6A). The time series of DOC concentration is very nonsymmetric with respect to tide. DOC values were highest at the lowest water depths and decreased with increasing depth (Figure 6A). This pattern suggests that DOC concentration and source are dominated by wetland sediment porewater rather than circulating water forced by tide. In other words, as water depth in the channel decreases, sediment porewater drains into the channel, elevating DOC values. DOC concentrations are therefore maximal when water levels are lowest.

*Discharge—*The water discharge time series shows flood and ebb tides to be somewhat symmetrical, dominated by flood tide discharge of approximately 3.5% by volume. In contrast, the peak instantaneous ebb flows were 20% greater than flood flows (Figure 6B). Spring tides occurred on January 15, 2006, and January 31, 2006, and the neap tide occurred on January 23, 2006. The full spring–neap range and the accompanying

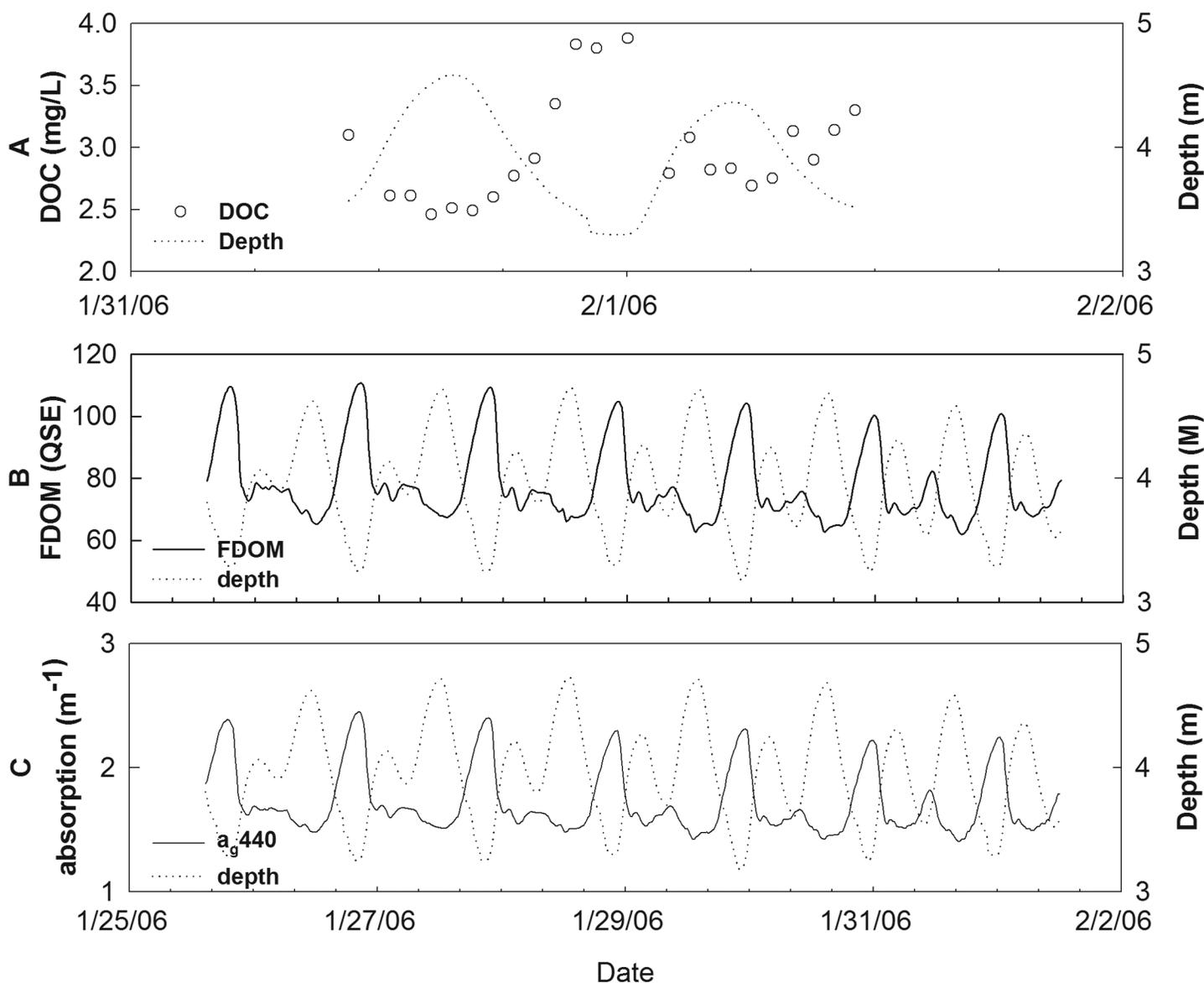


Fig. 3. (A) Water depth and DOC ($mg\ L^{-1}$) concentrations measured over the 24-h period of discrete sampling. DOC concentrations (open circles) were higher during ebb tide and lower during flood tide. (B and C) Continuous measurements display tidal variation in CDOM properties of FDOM (WETStar) and a_{g440} (ac-9) from 1 week of deployment. As in the 24-h DOC sampling (A), each optical property is generally inversely related to water depth in the main channel.

complete matching DOC concentration time series are needed to calculate the DOC flux over this period.

DOC flux—Instantaneous DOC flux is dominated by the tidal discharge which is, in general, more semidiurnally dominated and symmetrical than the DOC concentration (Figure 6C). The 14.7 days (spring–neap) integrated flux varied over time, in response to physical forcings (Figure 6D). Although there was a net off-island transport of DOC over this time period, the flux varied in both sign and magnitude, depending on the specific period of integration in the time series. This demonstrates that discrete sampling over one or a few tidal cycles cannot capture the true variability in flux. Net

DOC flux must be calculated at least over a full spring–neap period (14.7 days), and even then the choice of start time matters. It is important to select starting and ending times with similar water depths, to minimize bias.

Uncertainties in DOC flux—The uncertainty in DOC flux was calculated similarly to that presented in Ganju et al. (2005) for sediment flux and was found to be less than 25% (based on a 3% uncertainty in modeled DOC values) and assuming the uncertainties in water velocity and modeled DOC to be uncorrelated. This is compared to a calculated uncertainty in the sediment flux of sediments of 27%, as presented previously (Ganju et al. 2005).

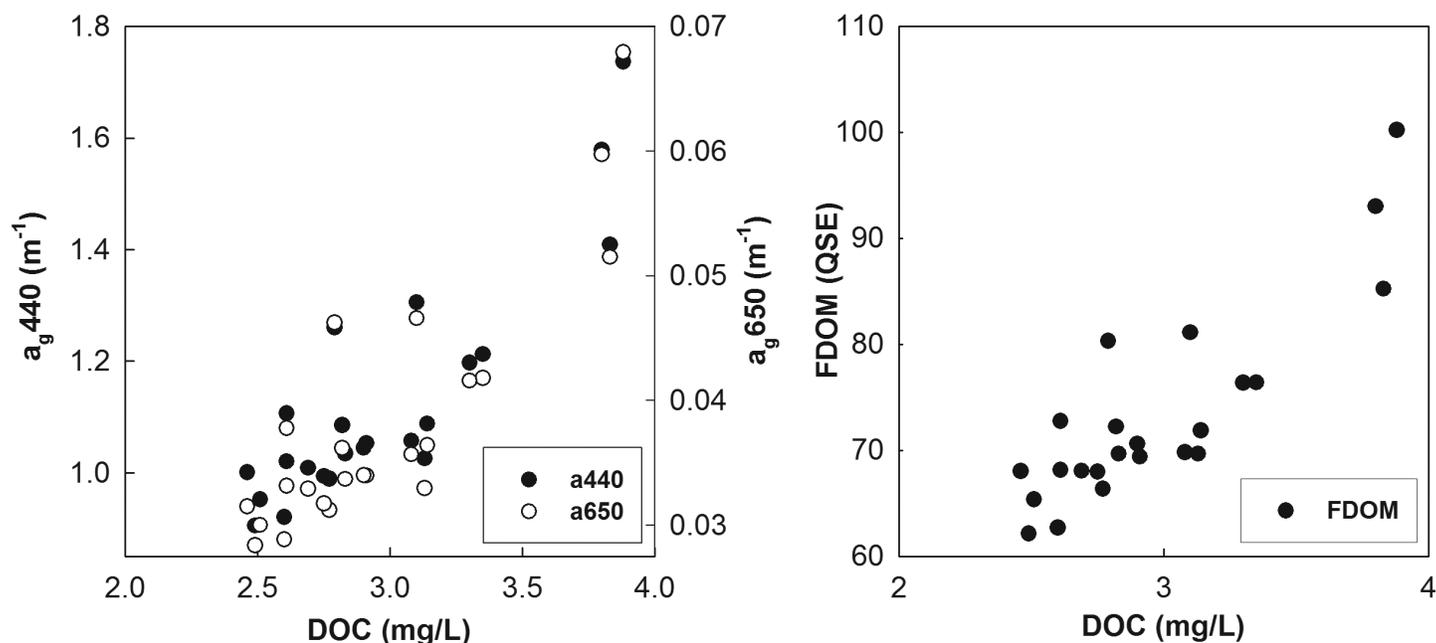


Fig. 4. DOC concentrations measured from discrete samples and optical properties measured in situ. In the left panel, a_{g440} and a_{g650} from the ac-9 correlate well with DOC ($R^2 = 0.76, 0.75$). In the right panel, correlation of FDOM (WETStar CDOM fluorometer) to DOC is shown, with $R^2 = 0.74$.

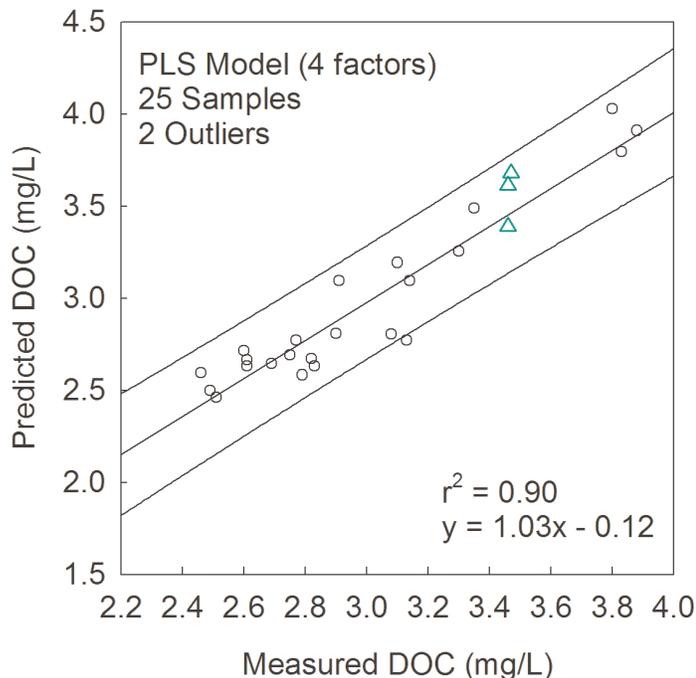


Fig. 5. Measured DOC versus predicted DOC from the partial least squares regression model. Triangles show measured DOC values for samples collected before (January 19, 2006) the 24-h sampling period (January 31 to February 1). The individually collected samples were not used to construct the regression model and were used to validate the modeled DOC. The 1:1 regression line is shown, along with 95% prediction intervals on each side of the regression line.

Effect of sampling interval—To evaluate the extent to which the choice of beginning and end time affected the calculation of net DOC flux, we recalculated the flux for all the full spring–neap periods ($\Delta t \sim 14.7$ days) within a representative time series (~ 21 days; 22 cycles total). We found the calculated net DOC flux off the wetland over the 22 optimal cycles to vary from 0.9×10^6 g C to 2.9×10^6 g C, with a mean of 1.8×10^6 g C, indicating that the specific time period chosen affected the calculated flux, and that the value of flux provided above could be biased by as much as a factor of 3 if we were to measure the spring–neap flux over a single 14.7-day interval. Time series greater than the spring–neap interval are thus recommended.

To assess the effect of sampling interval on DOC flux, we subsampled the modeled DOC time series at successively larger intervals and then interpolated back the data to the 15-min water flux data (to avoid confounding physical sampling with the optics). We found a cubic-spline interpolation (as implemented in MatLab) to consistently outperform linear interpolation, and we show only results using that interpolation method. Averaged over the 22 possible spring–neap cycles, we found no significant deterioration in the flux estimate for sampling intervals of 90 min or less (Figure 7). For sampling intervals of 3 h or more, biases larger than 20% were common.

Dynamics of DOM optical character—DOM quality parameters also varied over tidal and spring–neap time scales. Time series of the spectral slope, S , exhibited lower values during ebb tides (commonly associated with high-molecular-weight DOM) and higher values during flood tides. This is consistent with changes in DOM composition (associated with lower-molecular-weight DOM; e.g., Carder et al. 1989, Yacobi et al.

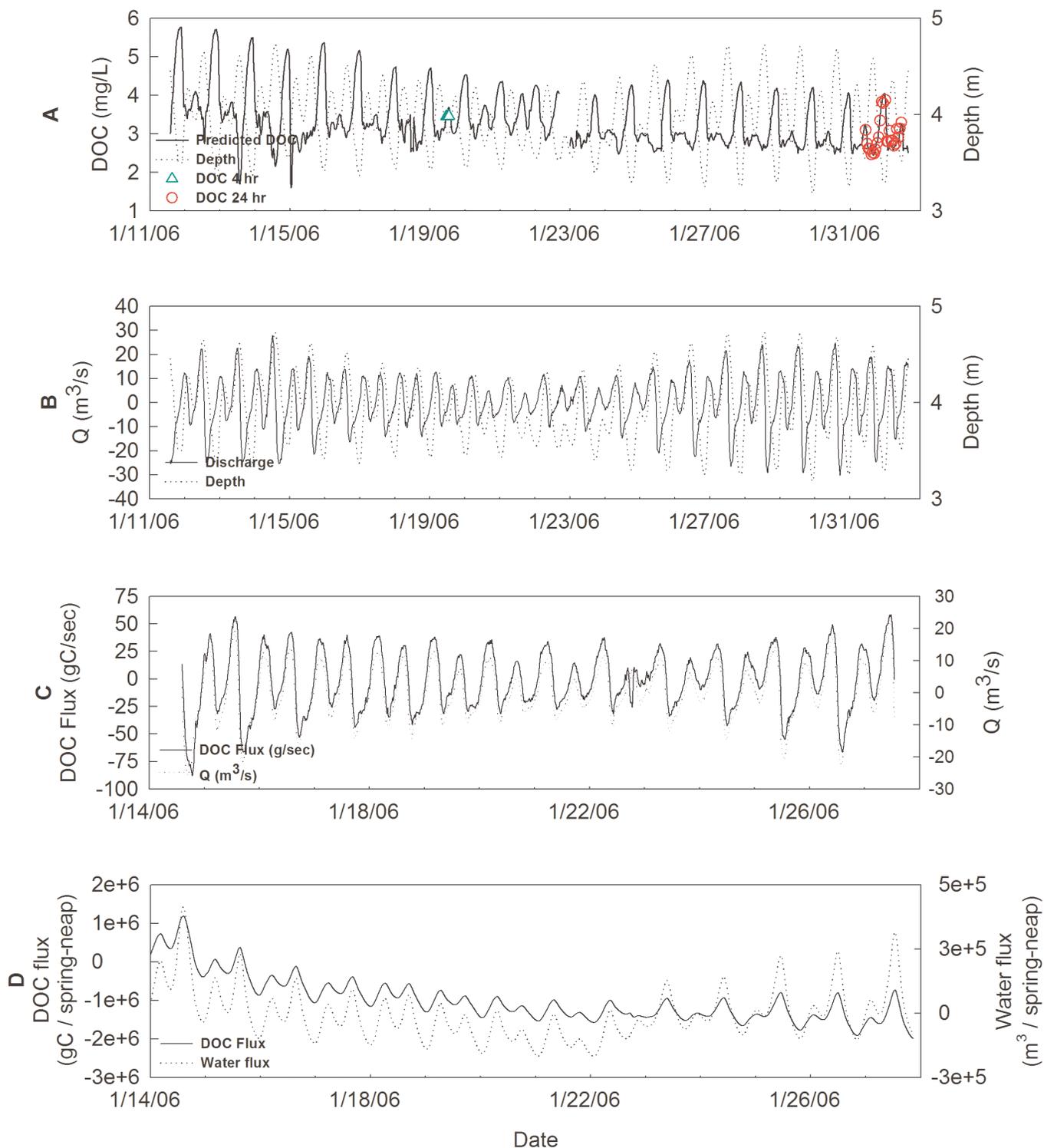


Fig. 6. (A) Modeled DOC time series and measured DOC (28 discrete samples). The PLS predictive model results for 25 discrete sample values are shown as red circles. The discrete sample values shown as green triangles validate model performance. (B) Instantaneous discharge (Q) and water depth in the Browns Island main channel during the entire deployment. Negative discharge values indicate ebb tides or off-island direction, whereas positive indicate flood tides or on-island direction. (C) Instantaneous discharge (Q) and modeled DOC flux. The sign of the discharge relates to the tidal cycle, where flood (positive) signifies on-island direction and ebb (negative) signifies off-island direction. (D) The cumulative spring–neap DOC flux and water flux (integrated over 14.7 days starting from January 14, 2006). Note that in the beginning of the time series, as the tide is transitioning from spring to neap, there is a transition from on-island (positive) DOC flux to off-island (negative) flux.

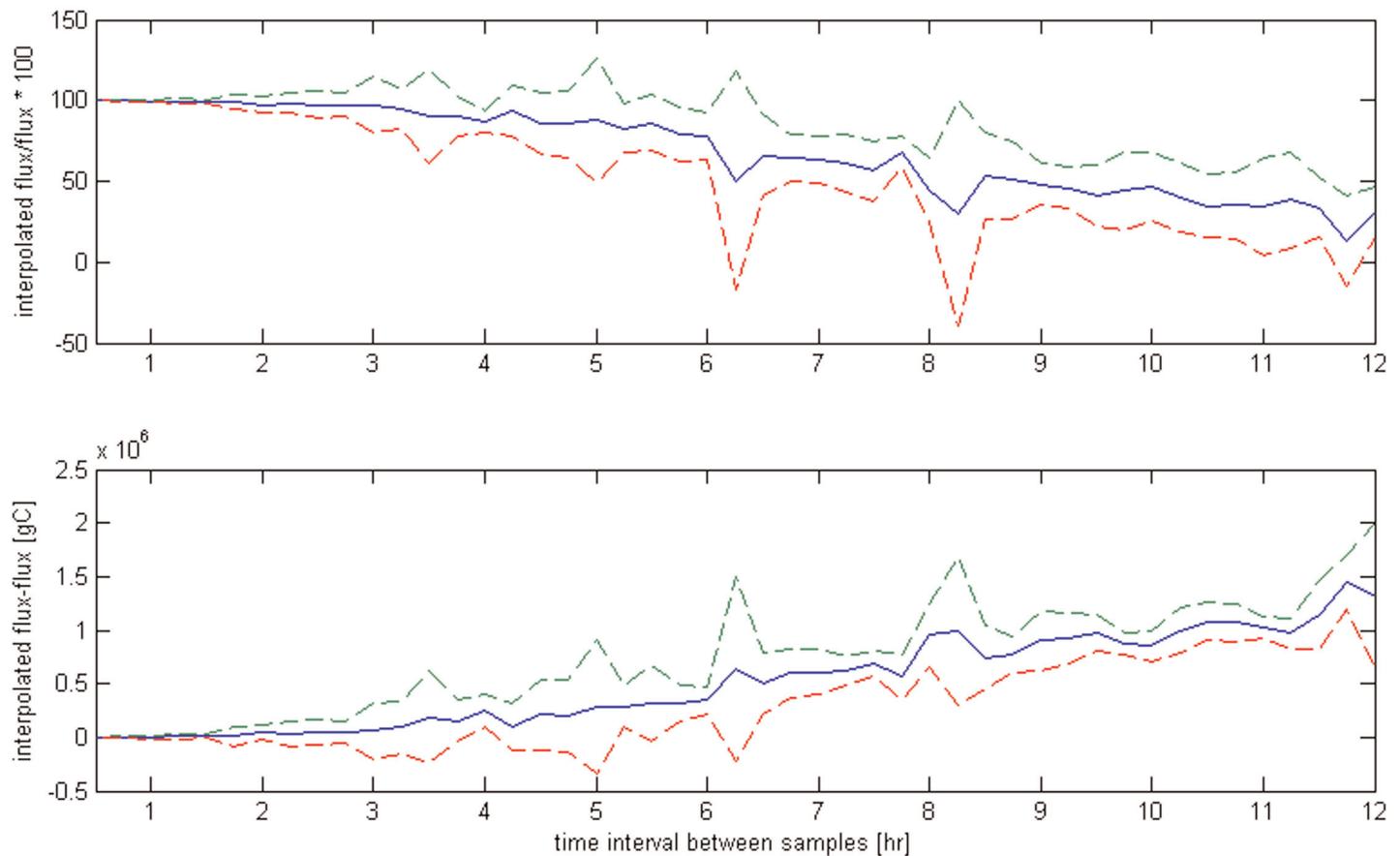


Fig. 7. (A) Ratio of interpolated spring-neap DOC flux at indicated interval to DOC flux calculated using a 0.5-h sampling interval. (B) Difference between interpolated spring-neap DOC flux at indicated interval and DOC flux calculated using a 0.5-h sampling interval. Solid blue lines denote the mean over 22 spring-neap tide realizations; dashed lines denote one standard deviation around the mean.

2003) associated with tidal forcing and sources—riverine inputs via the Sacramento and San Joaquin Rivers during flood tides and mixtures of wetland and riverine waters during ebb tides (Figure 8). Lower S values are associated with higher DOC concentrations measured during ebb tides and higher S with lower DOC concentrations over flood tides.

Relative fluorescence efficiency—The time series of RFE (Figure 8), like that of the CDOM spectral slope, shows evidence of tidally forced changes in DOM composition and is consistent with the observed S time series (Figure 8). Linear regression of FDOM (370 nm) with absorption (a_{370}) was well correlated ($R^2 = 0.98$), with a regression slope of 16, similar to reported values for RFE of CDOM in estuaries (Klinkhammer et al. 2000, Chen et al. 2007). The time series of RFE (Figure 8) displays lower RFE values consistent with wetland porewater entering the channel during ebb tides.

Discussion

An optical instrumentation package was designed and deployed to obtain continuous, high-quality DOM estimates over time scales ranging from minutes to weeks. In a shallow,

sediment-loaded slough, the package performed remarkably well and provided high-quality measurements of dissolved optical properties. Several of the optical measurements were found to provide an excellent proxy for DOC, which improved with the use of a multivariate predictive model. Concurrent discharge measurements allowed us to calculate quantitative estimates of DOC flux. In situ multispectral measurements of filtered absorption and fluorescence allowed us to examine the time-dependent compositional evolution in DOM as source contributions varied (e.g., wetland porewaters versus riverine sources).

We used a spectral model (Equation 1) to obtain the spectral slope and baseline offsets. We compared this method with another method of correcting absorption offsets and effects on spectral slope (S)—subtracting absorption in the red (e.g., a_{715}) from the a_{412} – a_{715} nm (e.g., Babin et al. 2003). Although both techniques yielded similar, but not identical, results in both the offset value (essentially a_{715}) and S , we preferred Equation 1 because it does not assume $a_g(715) = 0$ for these high CDOM-laden waters. Further work needs to be completed to substantiate that this correction is superior.

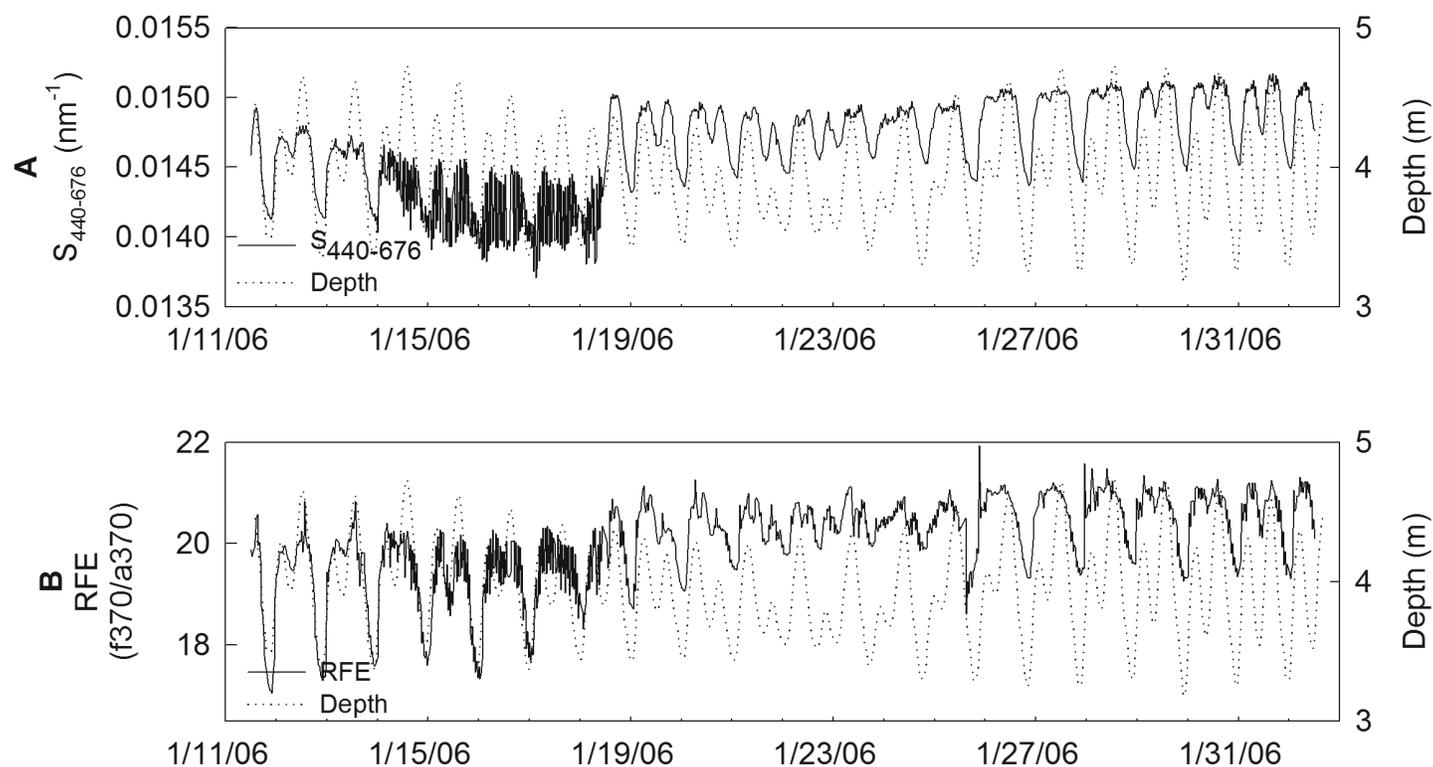


Fig. 8. (A) Time series of CDOM spectral slope (S) and water depth in the main channel over the deployment period. (B) Time series of RFE and water depth. Variations in the slope of RFE are consistent with changes in spectral slope at tidal scales. Changes in signal character at times of instrument servicing (~ 4 h on 1/18/06 and 1/25/06) reveal the sensitivity of its value to biofouling.

However, for the purpose of obtaining DOC concentration using the PLS analysis, both methods as well as no baseline correction provided fits of similar quality (most likely due to the inclusion of the attenuation data in the PLS analysis that substantially increased the quality of the fit).

Assessment of the method indicates that DOM can be reliably measured in situ by optical means over timescales ranging from minutes to months. Measurements at these timescales allow investigation of many biogeochemical processes, including those related to carbon and nitrogen cycling (e.g., primary production, biodegradation and photodegradation, and interaction with trace metals and pesticides)—processes that are important to aquatic and marine food webs and to drinking water quality.

Methods using high-frequency sampling can also capture the occurrence and consequences of episodic but important events that might be missed with less frequent discrete sampling. For example, even weekly field sampling may miss brief forcing events such as precipitation or changes in prevailing winds that may result in significant resuspension of sediments containing DOM.

The method presented here was designed to provide a high-frequency view of not only DOC concentrations, but also optical surrogates for DOM character. The in situ optical measurements enabled differentiation of incoming and out-

going DOC and thus contributed to an improved understanding of the underlying processes regulating DOC concentration and character.

This study demonstrated that redundancy is an important element in designing optical-hydrologic packages to characterize biogeochemical quantities, character, and fluxes (for example, CDOM fluorescence and CDOM absorption). It is important to include in the package design a number of measurements looking at the same parameter from different points of view. Selecting an appropriate sampling interval—appropriate to the targeted biogeochemical processes and to the environment of deployment—is another important element. By sampling at high frequency (every 30 min in this case) and then subsampling the resulting high-frequency time-series at a range of intervals, we determined that we could have—in the case of the Browns Island channel—sampled every 90 min and achieved similar results (Figure 7). Sampling at intervals >90 min would have resulted in a significant degradation of results.

One challenge for the future will be extending deployment duration. The use of multiple filters that can automatically be changed as filtration capabilities degrade is a possible solution. Automated cleaning and field calibration (e.g., periodic automatic injection of cleaning fluid and then deionized water) would also extend deployment capabilities.

Lengthier deployments will likely require collection of additional calibration and validation samples to ensure that the link between optics and biochemistry is robust.

Comments and recommendations

The sampling method described here is intended to supplement discrete sampling analysis, and thus great care should be taken to adapt the instrument package to the environment and to establish the relationships between the measured optical properties (proxies) and DOC or any other biogeochemical parameters of interest. We found that multiple overlapping measurements were useful for establishing robust models useful for extrapolation and interpolation of time series data.

Filtration system design—Because several of the core optical parameters are related to dissolved constituents (e.g., CDOM spectral slope, FDOM), particular care must be devoted to finding a filtration system appropriate to the deployment environment. In the case of the Browns Island channel—a tidal channel with elevated particulate concentrations—we achieved long deployment periods only through addition of large surface area filters and weekly service intervals. This would be impractical for many studies.

Sampling interval—At Browns Island, we found that the sampling interval of the optical properties could be as great as 90 min without significant loss of DOC flux data quality (compared to 30-min intervals). This threshold, however, would be expected to vary by environment and probably seasonally as well. Any new deployment should therefore initially include high-frequency sampling, plus calculations (Figure 7) to determine whether less frequent sampling could be conducted without significant degradation of data quality. Less frequent sampling can extend battery and filter life and can therefore facilitate less frequent service visits and perhaps longer deployments if biofouling is not observed. The interval at which field samples must be collected for model calibration will also be a function of environment and season.

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