

# Assessing contribution of DOC from sediments to a drinking-water reservoir using optical profiling

Bryan D. Downing<sup>1\*</sup>, Brian A. Bergamaschi<sup>1</sup>,  
David G. Evans<sup>2</sup> and Emmanuel Boss<sup>3</sup>

<sup>1</sup>U.S. Geological Survey, California Water Science Center,  
6000 J Street, Sacramento, CA 95819, USA

<sup>2</sup>California State University at Sacramento, Dept. of Geology,  
6000 J Street, Sacramento, CA 95819, USA

<sup>3</sup>University of Maine, School of Marine Sciences,  
Orono, ME 04469, USA

## Abstract

Downing, B.D., B.A. Bergamaschi, D.G. Evans and E. Boss. 2008. Estimating source-specific contributions of DOC into a drinking-water reservoir using optical profiling. *Lake Reserv. Manage.* 24:381–391.

Understanding the sources of dissolved organic carbon (DOC) in drinking-water reservoirs is an important management issue because DOC may form disinfection by-products, interfere with disinfection, or increase treatment costs. DOC may be derived from a host of sources—algal production of DOC in the reservoir, marginal production of DOC from mucks and vascular plants at the margins, and sediments in the reservoir. The purpose of this study was to assess if release of DOC from reservoir sediments containing ferric chloride coagulant was a significant source of DOC to the reservoir. We examined the source-specific contributions of DOC using a profiling system to measure the *in situ* distribution of optical properties of absorption and fluorescence at various locations in the reservoir. Vertical optical profiles were coupled with discrete water samples measured in the laboratory for DOC concentration and optical properties: absorption spectra and excitation emission matrix spectra (EEMs). Modeling the *in situ* optical data permitted estimation of the bulk DOC profile in the reservoir as well as separation into source-specific contributions. Analysis of the source-specific profiles and their associated optical characteristics indicated that the sedimentary source of DOC to the reservoir is significant and that this DOC is labile in the reservoir. We conclude that optical profiling is a useful technique for understanding complex biogeochemical processes in a reservoir.

Key words: absorption, dissolved organic carbon, fluorescence, multivariate analysis, sediment flux, Sweetwater Reservoir, water quality

Water stored in reservoirs for extended periods, as is the case for many drinking-water reservoirs, may be subject to physical, chemical, and microbiological processes that alter water quality over time. Long detention times can magnify the effect of *in situ* processes such as algal productivity, interaction with benthic sediments, and evaporation. Such processes can act to change the overall concentration of dissolved organic carbon (DOC) and is problematic because it can react to form disinfection by-products (DPBs) during disinfection treatments (Krasner *et al.* 1994, Barrett *et al.* 2000).

One difficult-to-quantify process is the interaction of reservoir water with benthic sedimentary processes. Benthic sediments may act as a sink for oxygen, oxidized metals, and other redox-sensitive dissolved constituents, or may act as a source for reduced metals, dissolved gasses, nutrients, and DOC (Wetzel 2001). Concentrations of DOC are often elevated near the benthic boundary layer, indicating remobilization of DOC and accumulation in the overlying water (Chen and Bada 1992, Skoog *et al.* 1996, Burdige 2002). Temporal-spatial mixing dynamics in lakes can present water quality variations, making characterization of DOC difficult using discrete grab sampling techniques. High spatial resolution measurements of DOC are thus desirable to

\* Corresponding author: bdowning@usgs.gov; phone: 916-278-3292

better quantify sources contributing to DOC concentration and character.

The goal of this study was to determine whether sediment sources significantly contributed to the DOC inventory in the Sweetwater Reservoir (Fig. 1). Sweetwater Reservoir contains natural organic carbon that has a high potential to form DBPs during the drinking-water treatment process. Previous work by Fram *et al.* (2001) provided information about sources and processes contributing organic carbon relative to DBP formation in the Sweetwater Reservoir. Sediment flux is potentially significant in this reservoir because the treatment plant has historically returned ferric chloride coagulant to the reservoir after water treatment. The coagulant effluent is returned to the deeper sections of the reservoir (Points A and B, Fig. 1). As sediments become reduced, the ferric iron is reduced to ferrous iron, subsequently releasing the previously sorbed material (including DOC), and thus contributing DOC to the overlying water (Mantoura *et al.* 1978, McKnight *et al.* 1983).

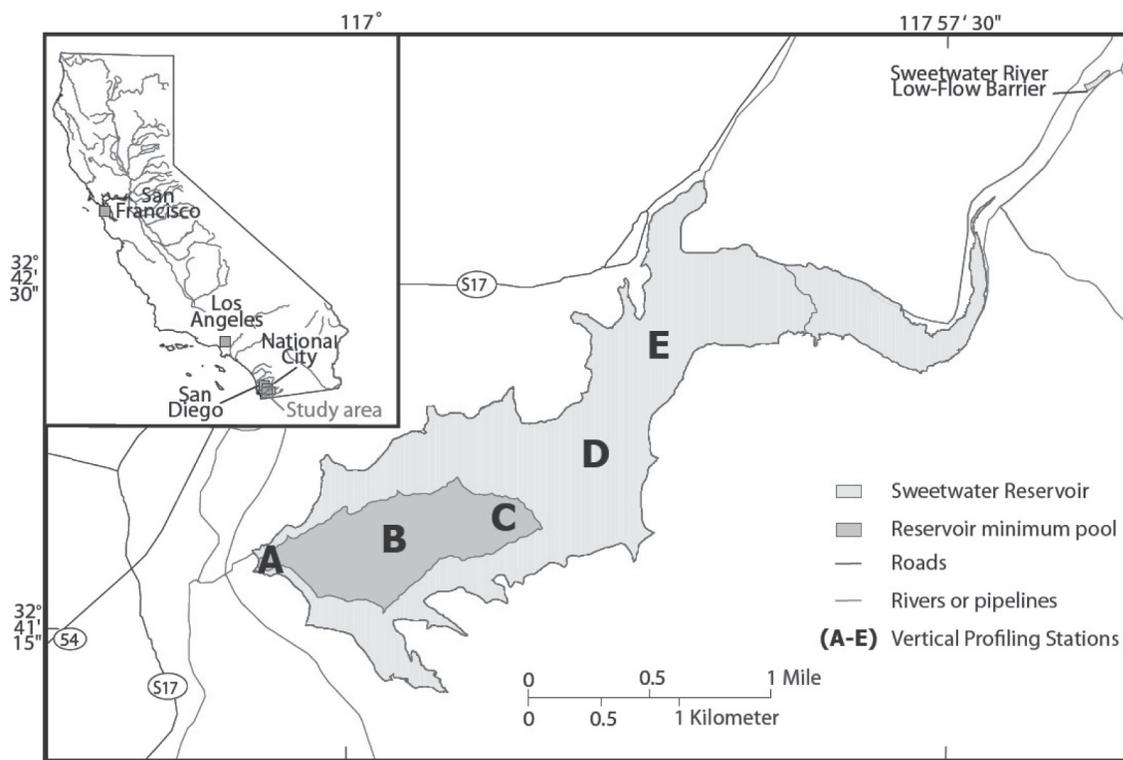
To assess the extent to which sedimentary processes released DOC to Sweetwater Reservoir, we examined the vertical distribution of DOC in the reservoir. Our approach was to use *in situ* optical instrumentation calibrated to laboratory results

from discrete samples to obtain high-resolution records of the distribution of DOC in the water column. Further, we used the spectral response for both the *in situ* and laboratory measurements to assess the distribution of DOC from the sediments and distinguish between it and DOC from different sources. We used the combination of these highly resolved profiles of DOC and corresponding physical measurements to estimate internal mixing processes, DOC concentration, and the relative contribution of various DOC sources, including the sediment source, to the reservoir.

## Methods

### Site description

Sweetwater Reservoir is located in Spring Valley, California, approximately 15 km southeast of San Diego and 10 km northeast of National City, California, along State Route 125 (Fig. 1). The reservoir was constructed in late 1888 with a drainage area of approximately 466 km<sup>2</sup> and a surface area of approximately 4.2 km<sup>2</sup>. The reservoir has a maximum storage capacity of nearly  $37 \times 10^6$  m<sup>3</sup> of water and is primarily a drinking-water reservoir, servicing approximately 200,000 residential and commercial customers in Chula Vista and National City, California. The depth of the reservoir minimum



**Figure 1.**—Sampling locations and site names in Sweetwater Reservoir, Chula Vista, CA, USA. From west to east: A = Pump Tower (PT); B = Center of Minimum Pool (CMP); C = Gum Tree (GT); D = Orchard Tree Cove (OTC); E = Inundated Vegetation area (IV).

pool is 56 m with an average depth at capacity of 9 m and maximum depth of approximately 14 m. Water is withdrawn from the reservoir pump tower via manually operated valves located at elevations of 57, 60, 63, and 68 m, usually at the lake surface, where typically water quality is highest. The reservoir is elongate in shape, bearing approximately N45E, and is approximately 3.2 km in length along the spine of the lake where sampling sites were chosen for this study. Retention time is approximately 1 year.

We chose five sampling locations in the reservoir to best model potential changes in DOC character with changing depth from the limnetic (reservoir minimum pool) to the littoral zone (Fig. 1): (1) the Pump Tower (PT) located in the west reach of the reservoir minimum pool area near the Dam; (2) the center of the minimum pool (CMP), the deepest part of the reservoir; (3) the eastern margin of the reservoir minimum pool at Gum Tree (GT); (4) Orchard Tree Cove (OTC) east of the minimum pool toward the littoral zone; and (5) in the littoral zone, an area of inundated vegetation (IV).

The four major sources of DOC to the reservoir are: (1) annual overland transfer via the Sweetwater River from the Loveland Reservoir; (2) flooded vegetation and organic rich mucks in the east end of the reservoir; (3) particulate contributions, such as phytoplankton and flocculated humic substances returned to the reservoir after disinfection treatments; and (4) sediment flux of DOC from the bottom sediments (Fram *et al.* 2001). In the water year before and during the time of this study, there were no overland water transfers from the Loveland Reservoir.

Sediment composition and atmospheric exposure vary with location in the Sweetwater Reservoir. Sand-dominated sediments along the channel of the Sweetwater River are alternately exposed to the atmosphere when water levels are low and flooded during annual water transfers from the Loveland Reservoir via the Sweetwater River. Organic-rich mucks, which dominate sediments at the east end of the reservoir where inundated vegetation is thick (Point 5), may experience an exposure-inundation cycle similar to the riverbank sands because these areas are shallow and subject to water drawdown during dry months. Iron-rich sediments at the west end of reservoir, around the intake pump to the treatment plant (Point1), occur in the deepest part of the reservoir, which remains inundated throughout the year. The reservoir is generally thermally stratified from April through October, and the hypolimnion is suboxic during this time.

### Field methods

Using the instrument package described below, we collected profiles of fluorescence, absorption, temperature, and conductivity from five locations in the Sweetwater Reservoir during 6–7 June 2002 (Fig. 1). Profiles ranged in depth from 2.0

m at the eastern end of the reservoir (Point 5), to 6.0 m just outside the reservoir minimum pool, to 14 m near the center of the minimum pool and the pump intake tower (Point 1). Weather for the week was sunny, with light wind and average low temperatures of 13.9 °C to highs of 22.2 °C (National Weather Service 2002).

High-resolution optical measurements of absorption and fluorescence were collected using instrumentation intercalibrated to laboratory measurements of DOC. Specific conductance, temperature, and depth were measured at the same time. All instrumentation was secured to a stainless-steel cage designed for *in situ* profiling. Floats were added to the deployment cage to ensure a sampling rate of approximately 50 cm/sec in free fall descent.

Fluorescence was measured *in situ* using a WET Labs model WET Star single-band excitation-emission fluorometer designed to measure CDOM (chromophoric dissolved organic matter) at an excitation of 370 nm and an emission centered at 460 nm. The fluorescence measurements act as a proxy for DOC concentration (Carder *et al.* 1989, Blough and Del Vecchio 2002). Absorption was measured *in situ* using a WETLabs model AC-9 spectral photometer (WET Labs, Philomath, OR) following protocols described by Twardowski *et al.* (1999). The AC-9 is a 9-wavelength photometer with a 10-cm path length, measuring in the visible range (400–800 nm). Temperature, conductivity, and depth were measured using a Seabird model 37CTD.

Sample water was drawn through the optical instruments using a Seabird model 5T submersible pump (Seabird Electronics, Bellevue, WA) and an Osmonics 0.2 $\mu$  25 cm membrane filter (Memtrex model # mny92egs). Instrumentation was controlled, and unprocessed data were recorded using a WET-Labs model DH-4 datalogger (WET Labs, Philomath, OR). Calibrations for all optical instruments were verified before deployment using optically pure, organic free, polished water (18 $\Omega$ ) obtained from a Hydro Picosystem Plus deionization system (Hydro, Durham, NC) as a reference.

Raw data of varying sampling frequencies from the *in situ* sensors were merged with data from the Seabird CTD to produce vertical profiles of data from all instruments for each sampling point. To accomplish compatibility with other data sources, a seven sample median filter was applied to the AC-9 absorption data. Subsequently, a 10-element running average filter was applied to the merged profile data to eliminate data fluctuations that were due to differences in the deployment rate. Only the downcast portion of the full data profiles was used for data analysis.

Discrete samples were collected at 3–5 depth intervals in each vertical profile. Samples were collected using a Wildco Kemmerer stainless-steel water sampler (Wildlife Supply Co., Buffalo, NY). Water samples were gravity filtered in the

field using 0.3- $\mu$  glass fiber filters (GFF), into carbon-free, precombusted glass vials and put on ice.

### Laboratory analysis

Concentrations of DOC were measured on filtered samples within two days of collection by high temperature catalytic oxidation using a Shimadzu TOC-5000A total organic carbon analyzer (Bird *et al.* 2003). Each DOC analysis represents the mean of three injections. Reproducibility of replicate analyses gives consistent blank values of  $<0.05$  mg/L carbon. Uncertainty in our laboratory DOC measurement is estimated to be 3% of the measured value for samples with concentrations  $>1$  mg L<sup>-1</sup> (Bird *et al.* 2003) based on the precision of the analytical technique and the uncertainty in the blank and replicate measurements.

A Cary model 300 photometer (Varian, Palo Alto, CA) with a 1-cm-pathlength cuvette was used to measure absorption of discrete water samples. Absorption was measured over ultraviolet and visible wavelengths (200–800 nm) with 1-nm resolution. Cuvettes were cleaned using an acid-base treatment and rinsed thoroughly with organic-free water before use. Degassed, organic-free water blanks were run before and after every five measurements, with acceptable blanks ( $<0.01$  m<sup>-1</sup>) subtracted from sample measurements. Samples were equilibrated to 25 °C before analysis.

Fluorescence excitation-emission spectra (EEMs) were acquired using a SPEX model Fluoromax 3 (Horiba Jobin Yvon, Ltd., Japan) using Datamax software on the filtered discrete samples. Samples were excited at wavelengths of 255–600 nm at 10-nm increments, and emissions were measured over 250–700 nm at 5-nm increments resulting in a matrix of approximately 8000 EEM pairs per sample. First and second order Raleigh scatter lines were removed by inserting zeroes outside the data area, and Raman scatter was removed by subtraction of the water blank. Cuvettes were cleaned using the same protocol in our absorption measurement method. Fluorometer performance was verified before sample analysis by measurement of the Raman emission peak ( $397 \pm 0.05$  nm) of a degassed organic-free blank water sample. Samples were equilibrated to 25 °C before analysis.

### Statistical methods

To obtain a continuous profile of DOC, a partial least squares (PLS) regression model was developed relating the laboratory DOC concentrations to *in situ* fluorescence, absorption, temperature, and conductivity measurements (The Unscrambler, version 9.2; Camo Technologies, Oslo, Norway). All of the independent variables were range-normalized to the maximum variability in the data set. The model was fully cross-validated to ensure no samples dominated the analysis.

To identify samples representative of different sources, EEMs of the discrete samples consisting of 3,775 excitation-emission pairs ( $25 \times 151$  matrix) each, were analyzed using principal component analysis (PCA; The Unscrambler, version 9.2, Camo Technologies, Oslo, Norway).

After identifying the representative samples, we decomposed the modeled DOC profiles into a linear mixture of the fractional contributions from each source identified by the PCA model. The fractional contribution from each source end-member was determined by minimizing the sum of squares of the difference between the range-normalized predicted DOC and the measured DOC.

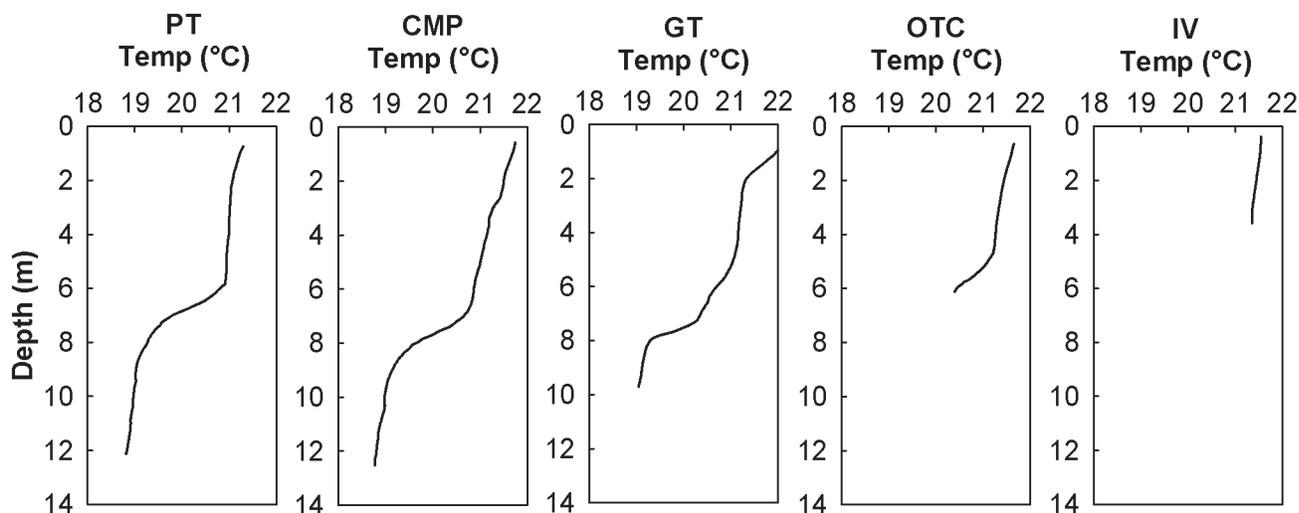
## Results and discussion

Our goal was to use vertical profiles of optical properties to assess if sedimentary sources contributed substantially to the inventory of DOC in Sweetwater Reservoir at the time of sampling, and thus, over the course of the year that the water is typically held in the reservoir. Our approach was to use the optical properties to estimate the bulk DOC concentration profiles with depth, but also to use the optical properties of the sedimentary material (and other potential sources) to develop profiles of DOC contributed by the sediments. These source-specific DOC profiles at different locations were then used to qualitatively assess the contribution of sediments to the DOC inventory. To demonstrate utility and compare how the bulk DOC flux may be different from the source specific flux, we estimated the fluxes using a simple parameterization of the physical mixing.

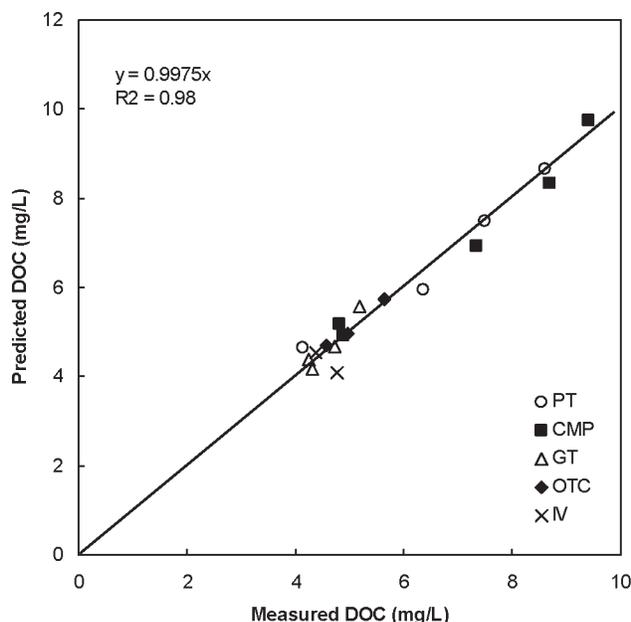
We chose to conduct the field portion of the study during a relatively quiescent period absent of major storms and long after stratification was established in the reservoir. Similar thermal stratification was evident at all stations with surface temperatures ranging from 21.5 °C in the deeper profiles at station A (PT) and B (CMP), to 21.7 °C in the shallower profiles at station C (GT) and D (OTC), and with bottom temperatures ranging from 18.8 °C in deeper profiles, to 22.5 °C at shallow sites. The metalimnion was located approximately 6 m below the surface and extended to approximately 8–9 m. The hypolimnion extends from 9 m down to the sediment boundary (Fig. 2).

### Estimating vertical distribution of DOC

The DOC values obtained from discrete samples indicated elevated bulk DOC concentrations at depth in some locations (PT and CMP, Fig. 3). These data, however, are not sufficient to permit accurate assessment of the relative contributions from different locations and sources. The vertical distribution of bulk DOC in the reservoir was estimated using a PLS regression model of properties measured *in situ* against the DOC concentration measured in grab samples from the same



**Figure 2.**—Temperature profiles for the Sweetwater Reservoir, 11 June 2002. The five locations chosen for the study are, from west to east: PT, CMP, GT, OTC, and IV. The deeper locations of PT and CMP (~12 m) in the west reach reveal stratification and have similar temperature (Temp) profiles, whereas the east end organic area of IV shows no stratification with maximum depth at ~4 m. Data averaged to lowest sampling frequency (1 Hz).



**Figure 3.**—2-D scatter plot showing predicted DOC (Y-axis) vs. measured DOC (X-axis) from the partial least squares regression model. The correlation is strong with  $R^2 = 0.98$  based on 18 grab samples (measured DOC) and the *in situ* predictors of temperature, conductivity, CDOM fluorescence, and AC-9 absorbance—PT (●), CMP (■), GT (▲), OTC (◆), and IV (X).

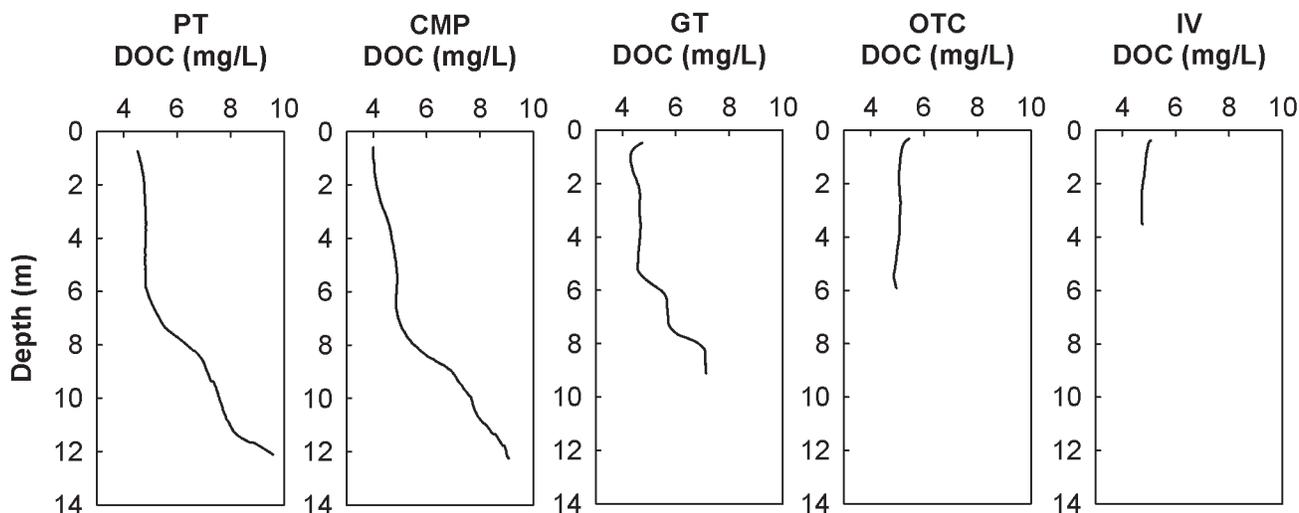
depth and location. The *in situ* variables used were fluorescence, nine wavelengths of absorption, temperature, and conductivity. For the 18 individual grab samples, ranging from those collected near the organic mucks to those collected in the epilimnion in the center of the reservoir, the relationship between the model-predicted DOC values and

the values measured in discrete samples was good (Fig. 3;  $R^2 = 0.98$ ). The PLS model was then used to predict DOC *in situ* resulting in high-resolution vertical profiles of DOC (Fig. 4).

Modeled DOC concentrations were significantly different between stations. There was little variation in concentration with depth in the eastern locations (OTC and IV), likely because of poor thermal stratification (Fig. 3). The western sampling locations (PT, CMP, GT) showed a pronounced increase in concentration with depth (Fig. 4), strongly suggestive of a sedimentary source. Because the flux of any material across the thermocline and into the epilimnion is a function of the concentration gradient, it is useful to compare the gradients that result from the DOC profiles. Modeled DOC gradients ( $dC/dz$ ) across the thermocline ranged from 0.95 mg/L-m at PT, to 1.05 mg/L-m at CMP, 0.40 mg/L-m at GT, with the lowest measurement of 0.23 mg/L-m at OTC (Table 1).

### ***Deconvolution of measured optical properties to specific DOC source***

Each parcel of water contains DOC from a variety of sources and histories. As such, the DOC profiles determined above contain contributions of DOC from several sources within the reservoir. For example, the mixed layer in the epilimnion contains the combined result of algal production, microbial degradation, and photolysis, and is thus a potential net DOC source to the reservoir (Fram *et al.* 2001). Likewise, the sediments may also be a net source of DOC to the reservoir if



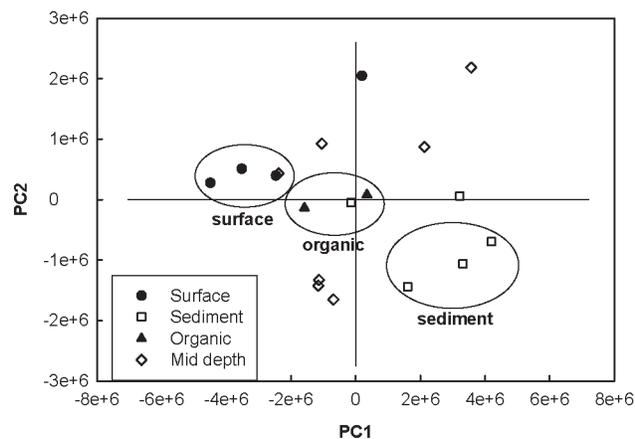
**Figure 4.**-Modeled DOC profiles of the Sweetwater Reservoir on 11 June 2002. DOC profiles were produced from the multiple linear regression model using CDOM and absorbance data collected *in situ* (WETLabs, WETStar and AC-9). Site abbreviations same as Fig. 2.

**Table 1.**-DOC gradients, eddy diffusivity ( $K_z$ ) and bulk carbon flux.

Location	$dC/dz$	$K_z$ ( $m^2/dy$ )	Flux ( $gCm^{-2}dy^{-1}$ )	Annualized Flux ( $gCm^{-2}yr^{-1}$ )
Pump Tower	0.95	2.5E-02	2.4E-02	8.8
Center of Min Pool	1.1	2.9E-02	3.0E-02	11.0
Gum Tree	0.40	1.8E-02	7.5E-03	2.7
Orchard Tree Cove	0.23	3.4E-02	8.0E-03	2.9

DOC released is greater than the amount consumed by the sediments. In this section, we assess the extent to which the sediments are a source of DOC to the reservoir by focusing specifically on the material produced by the sediments rather than the bulk DOC observed in the profiles previously presented (Fig. 4). The premise of this analysis is that the DOC from different sources has characteristic chemical properties (in this case spectrophotometric and spectrofluorometric properties), and that the differences among them are robustly distinguishable using our *in situ* and laboratory methods.

There is a rich history of using specific optical properties to understand the sources of organic material (Green and Blough 1994, Coble 1996, Blough and Del Vecchio 2002, Boss and Zaneveld 2003 and Weishaar *et al.* 2003). We first identified different sources of DOC in the reservoir from discrete samples by using laboratory fluorescence EEMs data. This step validates the premise that different sources in the reservoir are evident from the variability in fluorescence data (and underlying chemical composition) and not an artifact of experimental design or procedures. To further assess the extent to which the optical data are measuring real differences in chemical composition, we calculated two physical-chemi-

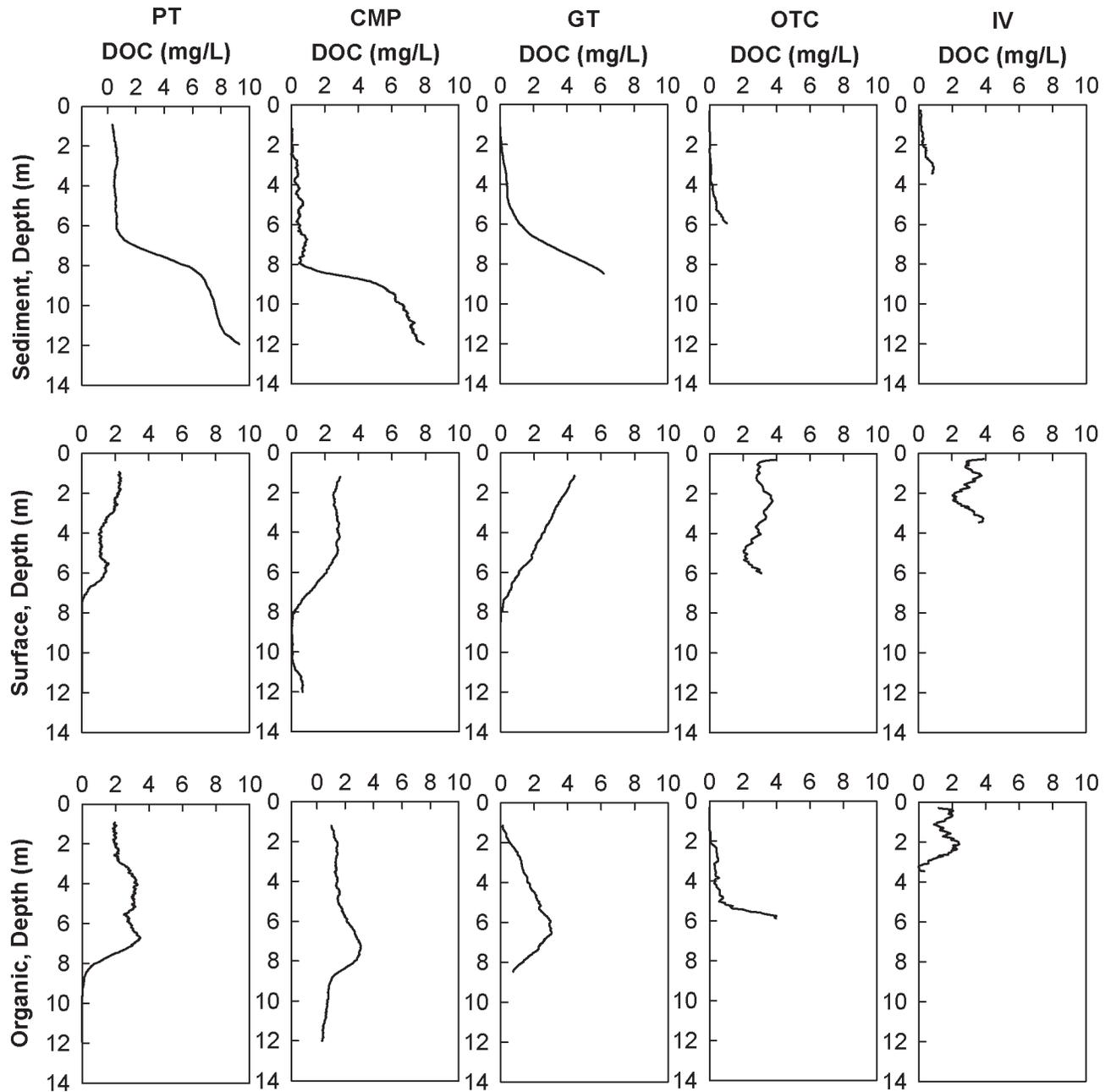


**Figure 5.**-Principal Component Analysis (PCA) scores plot. DOC source endmembers were selected from the three groupings shown in ellipses along the axis representing the greatest variability in fluorescence spectral properties among discrete samples. From left to right, they cluster by sample location into top layer (circles, ellipse 1), organic (triangles, ellipse 2), and sediment (squares, ellipse 3) endmembers.

cal parameters on the basis of chemical composition: spectral slope and quantum yield. Finally, we calculate the contribution of DOC from different sources in the reservoir.

To identify specific samples that represent the potential sources of DOC in this study, we used the fluorescence EEMs of the discrete samples. Principal Component Analysis (PCA)

of the fluorescence EEM data indicated that generally three sources were well-segregated along principal component 1 (PC1), which described 80% of the variation in the data (Fig. 5). Samples from lowest portions of the profiles of deeper sections of the reservoir clustered and had positive scores on PC1, indicating that these samples had properties related to DOC with a sediment source. Several samples from the mixed



**Figure 6.**-Results of decomposition into source-specific DOC endmembers. Plots show DOC contributed by each source endmember as a concentration (mg/L): concentrations of sediment-derived DOC strongly increase with depth at all minimum pool sampling sites (PT, CMP, GT), suggesting a significant flux to the reservoir in these locations. In contrast, modeled sediment concentrations were minimal at the OTC and IV sites, whereas surface processes (algal production and photo-alteration of material fluxing up from the hypolimnion) and organic type fluxes are seen as nearly equal fractions of DOC sources.

layer clustered and had negative values on PC1, suggesting that the properties from this group of samples represent a surface and mixed-layer source of DOC, perhaps from the combination of algal production and other surface processes, such as atmospheric deposition and photolytic alteration of organic material (Molot and Dillon 1997). Samples from the east end of the reservoir, overlying the organic mucks, cluster near the origin, suggesting that their properties represent DOC released from vegetation and organic mucks during this period as well as that present in water imported to the reservoir from upstream (Fig. 5).

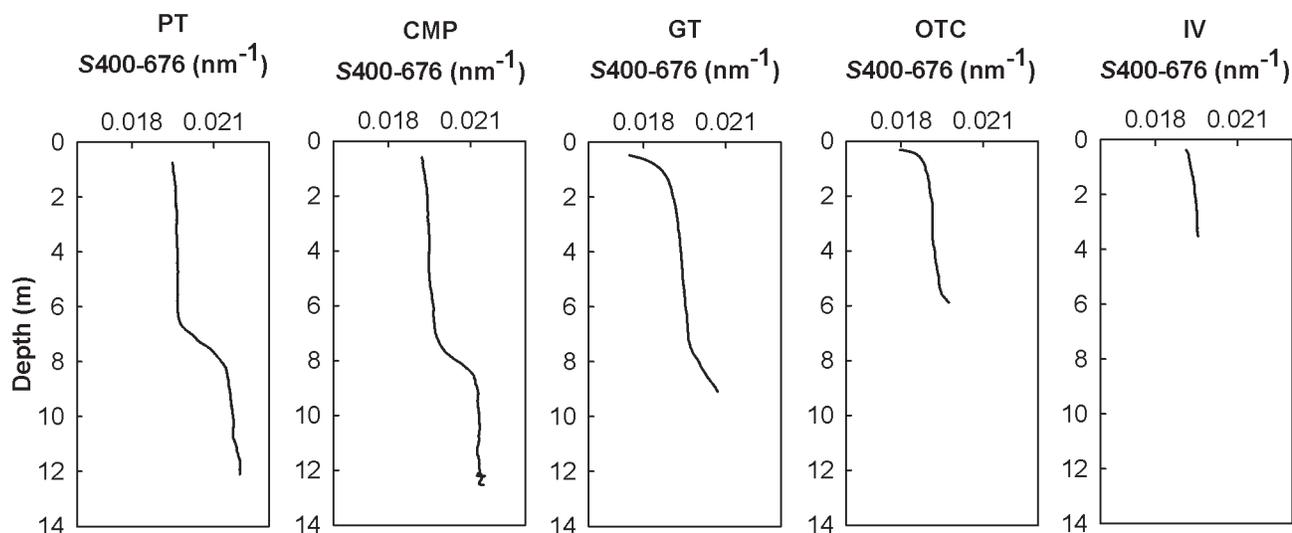
We used the samples identified by PCA as representative of the major DOC sources within the reservoir to establish the corresponding properties measured *in situ*, a smaller set of optical properties. The properties for each “source” as measured *in situ* were extracted from the profile data corresponding to the depth and time of each of the representative discrete samples. We calculated the linear combination of the three endmember contributions that best explained the observed value at every point in each profile by minimizing the sum of squares of the difference between range-normalized modeled and observed data. The result is a fractional contribution of each endmember to the net DOC observed. Thus, we can decompose the spectral properties from each point in the profile into the contribution of each of the endmembers and plot their distribution in the reservoir (Fig. 6).

### Ancillary evidence for source-specific optical properties

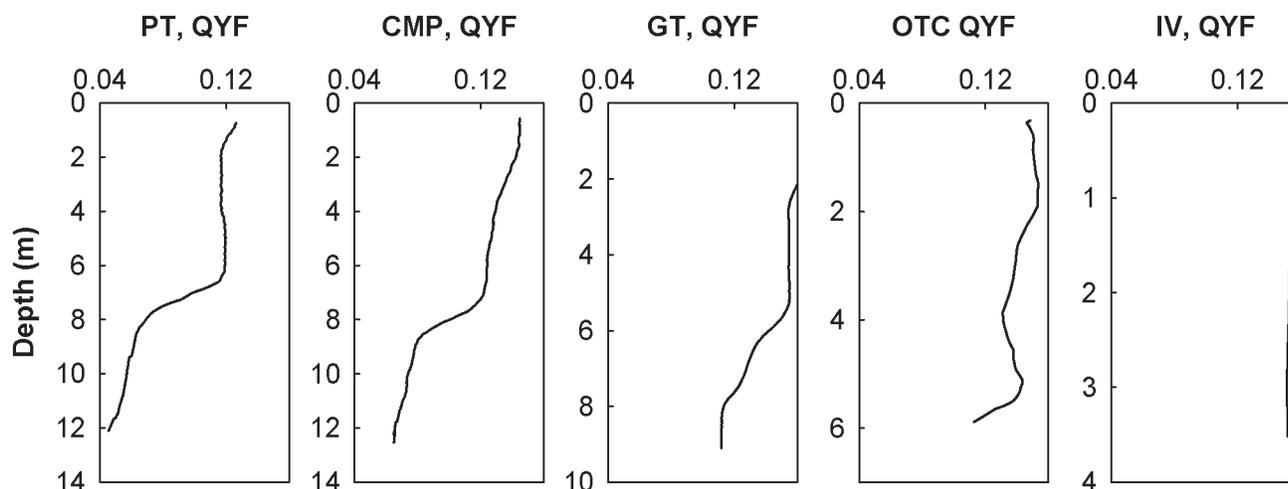
To validate the capability of the *in situ* data to discriminate chemical differences indicative of DOC source, it is useful to examine their optical properties. Two optical parameters, spectral slope ( $S$ ) and quantum yield of fluorescence ( $QYF$ ), are associated with dissolved organic matter (DOM) composition (Blough and Del Vecchio 2002). Spectral slope was computed from the *in situ* absorption spectrum by fitting a single-exponential model to the wavelength range of 412–676 nm (Twardowski *et al.* 2004). The ratio of photons emitted (fluorescence) to the photons absorbed (absorption),  $QYF$ , was calculated using the ratio of CDOM fluorescence (excitation at 370 nm) to the absorption at 370 nm.

Differences in  $S$  and  $QYF$  relate to differences in composition, where steep  $S$  coefficients ( $\sim 0.02$ ) represent lower-molecular-weight material, and smaller slope coefficients ( $\sim 0.01$ ) represent higher-molecular-weight material (Green and Blough 1994), and  $QYF$  provides an estimate of degree of aromaticity (or conjugation) in DOM independent of molecular weight (DelVecchio and Blough 2004). Both of these parameters have been used to infer DOC sources, such as terrestrial or aquatic, and characterize processes affecting DOC sources, such as photobleaching and primary production (Blough and Del Vecchio 2002, Boss and Zaneveld 2003).

Profiles of  $S$  point to distinct differences in DOC character in the epilimnion, metalimnion, and the hypolimnion (Fig. 7). In the epilimnion of the GT and OTC profiles, linear



**Figure 7.**—Results of spectral slope ( $S$ ) calculations based on the *in situ* absorbance profile data. Spectral slopes ( $S$ ) were calculated using nonlinear spectral fitting of a single exponential model that describes absorption by CDOM, ( $a_\lambda = a_{440}$ ) as a function of wavelength ( $\lambda$ ). Each profile shows trends changing with reservoir stratification, pointing to changes that relate to carbon source. For instance, linear decrease of ( $s$ ) through the metalimnion to the epilimnion may indicate simple dilution, photobleaching or changes in DOC source, such as primary production. Values of ( $S$ ) in the epilimnion reveal complete mixing in that layer. Data bin averaged to lowest sampling frequency (1 Hz). Site abbreviations same as Fig. 2.



**Figure 8.**-*QYF* based on *in situ* fluorescence and absorption data (CDOM and absorption at 440 nm). In all sampling locations (PT, CMP, GT and OTC), *QYF* values follow the general trend of the DOC concentration and reveal the same EW gradient (*QYF* increasing to the east) with the exception of the GT profile. Data averaged to lowest sampling frequency (1 Hz). Site abbreviations same as Fig. 2.

increases in  $S$  seem to be consistent with photobleaching or inputs of phytoplankton-derived material (Blough and Green 1995, Amon and Benner 1996). In the metalimnion of the profiles (except IV),  $S$  gradients are relatively consistent with the DOC concentration gradients, pointing to a mixture of surface and sediment sources. In the hypolimnion of the PT and CMP profiles,  $S$  changes little, pointing toward a constant source of DOC in those sites (Fig. 7).

The *QYF* in the PT and CMP sampling sites (Fig. 8) shows decreasing aromaticity in the surface layer relating to photolytic or microbial processes. The distribution of *QYF* with depth is characteristic of lake stratification, consistent with the spectral slope and PCA results (Fig. 8).

### Estimating DOC flux

Ultimately, collecting high-resolution data of the type presented here and resolving it into individual source-specific components may permit calculation of source-specific fluxes. The profile data qualitatively indicate that the sediments substantially contribute to the inventory of DOC in the reservoir, but they provide little information about the total amount of DOC released by the sediments. Estimating the flux across the thermocline provides a means to quantitatively estimate the contribution of the sediments to the DOC inventory as well as illustrate the potential of high-resolution measurements that provide source-specific information. To permit comparison of the bulk DOC and the sediment-specific DOC contributions, we crudely estimated the flux as the product of concentration gradient ( $dC/dz$ ) and the estimated vertical eddy diffusion coefficient ( $K_z$ ) for both the bulk and sediment-specific DOC profiles (Table 1). The concentration gradient

was derived from the DOC profile, and  $K_z$  was estimated from the density profile (Jassby and Powell 1975, Lerman 1988, Benoit and Hemond 1996).

Estimating flux in this way yielded a net upward flux of bulk DOC across the thermocline for all stations. However, there was considerable variability among stations, from  $8.0 \times 10^{-3}$  gC/m<sup>2</sup> day (OTC site) to  $3.0 \times 10^{-2}$  gC/m<sup>2</sup> day (CMP site). The deeper profiles at PT and CMP yielded the highest bulk DOC flux, ranging from  $2.4 \times 10^{-2}$  gC/m<sup>2</sup> day to  $3.0 \times 10^{-2}$  gC/m<sup>2</sup> day. The OTC location, east of the minimum pool, had the lowest carbon flux measured with  $8.0 \times 10^{-3}$  gC/m<sup>2</sup> day. These flux estimates are similar to sediment DOC fluxes reported for other lake studies. For example, Hanson (2003) found carbon fluxes from several lakes in a Wisconsin watershed ranged from 1 gC/m<sup>2</sup> yr to 150 gC/m<sup>2</sup> yr. In studies of small lakes in the Kuparuk Basin of Alaska (Kling *et al.* 2000), an average annual carbon flux of 1.3 gC/m<sup>2</sup> yr was reported.

In contrast to the bulk DOC flux, in the reservoir minimum pool, source-specific fluxes from the sediments were  $7.8 \times 10^{-2}$  gC/m<sup>2</sup> day at the PT sampling site,  $16.5 \times 10^{-2}$  gC/m<sup>2</sup> yr at the CMP site, and  $4.3 \times 10^{-2}$  gC/m<sup>2</sup> yr in the GT site, compared with  $3.7 \times 10^{-3}$  gC/m<sup>2</sup> yr at the OTC site east of the minimum pool boundary (Table 2). These values are over three times the bulk DOC flux, suggesting that sediment contributions are significant in the reservoir.

These calculations represent a snapshot in time and are only partially adequate in representing the physical dynamics in the reservoir. A better approach is described in Berg *et al.* (2003) using an eddy correlation technique, where in addition to measurements of dissolved oxygen and an acoustic

**Table 2.**—Sediment source specific carbon flux.

Location	$dC/dz$	$K_z$ ( $m^2/dy$ )	Flux ( $gCm^{-2}dy^{-1}$ )	Annualized Flux ( $gCm^{-2}yr^{-1}$ )
Pump Tower	3.1	2.5E-02	7.8E-02	28.5
Center of Min Pool	5.7	2.9E-02	16.5E-02	60.2
Gum Tree	2.4	1.8E-02	4.3E-02	15.7
Orchard Tree Cove	0.11	3.4E-02	3.7E-03	1.4

Doppler velocimeter (ADV), optical sensors measuring absorption and fluorescence could be included. Nevertheless, comparison of the bulk flux, which is affected by downwelling of surface productivity, indicates that the sediment flux is substantial and greater than would be calculated from the bulk flux alone.

## Conclusions

Optical profiling at high spatial resolution using *in situ* absorption and fluorescence sensors was useful for obtaining high quality information relating to DOC quantity, chemical composition, and source. Multivariate analysis and modeling of properties measured *in situ* and in discrete samples permitted us to robustly estimate DOC concentration as well as distinguish the likely contribution of various sources. Examination of optical properties, such as spectral slope and quantum yield of fluorescence, provided general as well as source-specific biogeochemical information about the DOC composition. Although not necessary, we found it beneficial to use PCA of the fluorescence EEMs data collected on discrete samples to identify the various endmember sources. PCA validated that the principal DOC sources to the reservoir were differentiable from the optical data and the majority of observed variability was generally explained by: (1) DOC from phytoplankton and other surface processes, (2) DOC from vegetation and organic mucks at the east end of the reservoir, and (3) DOC from ferric chloride-rich sediments.

Knowledge of the sources permitted us to model the DOC profile data successfully using a simple linear-mixing model. The model proved to be useful for segregation of the DOC in each profile into the relative contribution from each of the modeled sources. This allowed us to examine the contribution from the modeled sources at different locations in the reservoir, and we found that they were quite different. The patterns of distribution of bulk DOC, sediment-specific DOC as well as other chemical measurements and fluxes estimated from profile data all suggest that sediments in the west reach of the reservoir minimum pool contribute significant amounts of DOC to the reservoir.

As an example of the value of knowing the distribution of DOC from individual sources with depth, we estimated the bulk as well as the source-specific fluxes from the individual profiles using the concentration gradient ( $dC/dz$ ) derived directly from the profile and a simple estimate of the vertical eddy diffusion coefficient ( $K_z$ ). We found that the source-specific DOC flux was markedly different from the bulk DOC flux, suggesting that knowledge of the properties and sources of DOC in the reservoir along with the ability to decompose them in profiles is useful for understanding important biogeochemical processes.

## Acknowledgments

This work was funded by the Sweetwater Authority, San Diego, California. We thank Peter Baranov of the Sweetwater Authority, Miranda Fram, research chemist with the U.S. Geological Survey, Daniel Deocampo, professor of geology, California State University at Sacramento, anonymous reviewers for insightful reviews of earlier versions of the manuscript, and many others at the U.S. Geological Survey for their helpful discussions. The use of brand or firm names in this paper are for identification purposes only and do not constitute endorsement by the U.S. Geological Survey.

## References

- Amon, R.M.W. and R. Benner. 1996. Bacterial utilization of different size classes of dissolved organic matter. *Limnol. Oceanogr.* 41:157–168.
- Barrett, S.E., S.W. Krasner and G.L. Amy. 2000. Natural organic matter and disinfection by-products characterization and control in drinking water. American Chemical Society, Washington D.C. Distributed by Oxford University Press, 425 p.
- Berg, P., H. Roy, F. Janssen, V. Meyer, B.B. Jorgensen, M. Huettel and D. deBeer. 2003. Oxygen uptake by aquatic sediments measured with a novel noninvasive eddy correlation technique. *Mar. Ecol. Prog. Ser.* 261:75–83.
- Benoit, G. and H.F. Hemond. 1996. Vertical eddy diffusion calculated by the flux gradient method: significance of sediment-water heat exchange. *Limnol. Oceanogr.* 41:157–168.

- Bird, S.M., M.S. Fram and K.L. Crepeau. 2003. Method of analysis by the U. S. Geological Survey California District Sacramento Laboratory—determination of dissolved organic carbon in water by high temperature catalytic oxidation, method validation, and quality-control practices. U. S. Geological Survey Open-File Report. 03-366, 22 p.
- Blough, N.V. and S.A. Green. 1995. Spectroscopic characterization and remote sensing of non-living organic matter. P. 23–45. *In* R.G. Zepp and Ch. Sonntag (eds.), *The Dahlem Workshop on the role of non-living organic matter in the Earth's carbon cycle*. Berlin, 1993. Wiley, New York.
- Blough, N.V. and R. Del Vecchio. 2002. Distribution and dynamics of chromophoric dissolved organic matter (CDOM) in the coastal environment. P. 509–546. *In* D.A. Hansell and C.A. Carlson (eds.), *Biogeochemistry of Dissolved Organic Matter*. Academic Press.
- Boss, E. and J.R.V. Zaneveld. 2003. The effect of bottom substrate on inherent optical properties: evidence of biogeochemical processes. *Limnol. Oceanogr.* 48:346–354.
- Burdige, D.J. 2002. Sediment pore waters. P. 611–663. *In* D. Hansell and C. Carlson (eds.), *Biogeochemistry of marine dissolved organic matter*. Academic Press.
- Carder, K.L., R.G. Steward, G.R. Harvey and P.B. Ortner. 1989. Marine humic and fulvic acids: their effects on remote sensing of ocean chlorophyll. *Limnol. Oceanogr.* 34:68–81.
- Chen, R.F. and J.L. Bada. 1992. The fluorescence of dissolved organic matter in seawater. *Mar. Chem.* 37:191–231.
- Coble, P.G. 1996. Characterization of marine and terrestrial DOM in seawater using excitation/emission matrix spectroscopy. *Mar. Chem.* 51:325–346.
- Del Vecchio, R. and N.V. Blough. 2004. On the origin of optical properties of humic substances. *Environ. Sci. Technol.* 38:3885–3891.
- Fram, M.S., B.A. Bergamaschi and R. Fujii. 2001. Improving water quality in Sweetwater Reservoir, San Diego County, California—sources and mitigation strategies for trihalomethane (THM)-forming carbon, U.S. Geological Survey Fact Sheet FS 0112-01.
- Green, S.A. and N.V. Blough. 1994. Optical absorption and fluorescence properties of chromophoric dissolved organic matter in natural waters. *Limnol. Oceanogr.* 39:1903–1916.
- Hanson, P.C., D.L. Bade and S.R. Carpenter. 2003. Lake metabolism: Relationships with dissolved organic carbon and phosphorus. *Limnol. Oceanogr.* 48:1112–1119.
- Jassby, A. and T. Powell. 1975. Vertical patterns of eddy diffusion during stratification in Castle Lake, California. *Limnol. Oceanogr.* 20:530–543.
- Kling, G.W., G.W. Kipphut, M.M. Miller and W.J. O'Brien. 2000. Integration of lakes and streams in a landscape perspective: the importance of material processing on spatial patterns and temporal coherence. *Freshw. Biol.* 43:477–497.
- Krasner, S.W., M.J. Scrimanti and E.G. Means. 1994. Quality degradation: implications for DBP formation. *J. Am. Water Works Assoc.* 86:34–37.
- Lerman, A. 1988. *Geochemical processes—Water and Sediment Environments*. Wiley-Interscience, New York. Reprint edition, Robert E. Krieger Publishing Company. Malabar, FL. 481 pp.
- Mantoura, R.F.C., A. Dixon and J.P. Riley. 1978. The complexation of metals with humic materials in natural waters. *Estuar. Coast. Mar. Sci.* 6:387–408.
- McKnight, D.M., G.L. Feder, E.M. Thurman, R.L. Wershaw and J.C. Westall. 1983. Complexation of copper by aquatic humic substances from different environments. *Sci. Total Environ.* 28:65–76.
- Molot, L.A. and P.J. Dillon. 1997. Photolytic regulation of dissolved organic carbon in northern lakes. *Glob. Biogeochem. Cycles.* 11:357–365.
- National Weather Service. 2002. <http://www.wrh.noaa.gov/sgx/obs/stp/2002>. Accessed 10 March 2006
- Skoog, A., P. Hall, S. Hulth, N. Paxeus, M. Rutgers van der Loeff and S. Westerlund. 1996. Early diagenetic production and sediment-water exchange of fluorescent dissolved organic matter in the coastal environment. *Geochim. Cosmochim. Acta* 60:3619–3629.
- Twardowski, M.S., J.M. Sullivan, P.L. Donaghay and J.R.V. Zaneveld. 1999. Microscale quantification of the absorption by dissolved and particulate material in coastal waters with an ac-9. *Atmos. Ocean. Technol.* 16:691–707.
- Twardowski, M.S., E. Boss, J.M. Sullivan and P.L. Donaghay. 2004. Modeling the spectral shape of absorption by chromophoric dissolved organic matter. *Mar. Chem.* 89:69–88.
- Weishaar, J.L., G.R. Aiken, B.A. Bergamaschi, M.S. Fram and R. Fujii. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* 37:4702–4708.
- Wetzel, R.G. 2001. *Limnology: lake and river ecosystems*. 3rd ed., Academic Press, ISBN 0127447601.