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Sources, bioavailability, and photoreactivity of dissolved organic carbon in the Sacramento–San Joaquin River Delta

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Abstract. We analyzed bioavailability, photoreactivity, fluorescence, and isotopic composition of dissolved organic carbon (DOC) collected at 13 stations in the Sacramento–San Joaquin River Delta during various seasons to estimate the persistence of DOC from diverse shallow water habitat sources. Prospective large-scale wetland restorations in the Delta may change the amount of DOC available to the food web as well as change the quality of Delta water exported for municipal use.Our study indicates that DOC contributed by Delta sources is relatively refractory and likely mostly the dissolved remnants of vascular plant material from degrading soils and tidal marshes rather than phytoplankton production. Therefore, the prospective conversion of agricultural land into submerged, phytoplankton-dominated habitats may reduce the undesired export of DOC from the Delta to municipal users.A median of 10% of Delta DOC was rapidly utilizable by bacterioplankton. A moderate dose of simulated solar radiation (286 W m^{-2} for 4 h) decreased the DOC bioavailability by an average of 40%, with a larger relative decrease in samples with higher initial DOC bioavailability. Potentially, a DOC-based microbial food web could support $\leq 0.6 \times 10^9$ g C of protist production in the Delta annually, compared to $\approx 17 \times 10^9$ g C phytoplankton primary production. Thus, DOC utilization via the microbial food web is unlikely to play an important role in the nutrition of Delta zooplankton and fish, and the possible decrease in DOC concentration due to wetland restoration is unlikely to have a direct effect on Delta fish productivity.

Introduction

Microbial and photochemical processing of dissolved organic carbon (DOC) has significant impacts on aquatic food webs (Pomeroy 1974; Azam et al. 1983); water column optical properties (Moran et al. 2000); consumption of oxygen (Amon and Benner 1996; Reitner et al. 1997); and production of inorganic carbon (Lindell et al. 2000). Likewise, altered concentration and chemical composition of DOC may affect the commercial value of water, e.g. by changing its suitability for municipal use (Bergamaschi et al. 1999). Most of the existing DOC bioavailability and photoreactivity studies have been conducted in homogenous, undisturbed ecosystems, and they are usually focused

on the DOC-bacterioplankton trophic link (Sondergaard and Middelboe 1995; Moran and Covert 2002). However, ecosystems where knowledge of DOC cycling may have significant management implications are often complex, with diverse and poorly understood DOC sources and sinks, complicated hydrology, and conflicting economic and environmental interests.

The Sacramento–San Joaquin River Delta, located at the eastern end of the Northern San Francisco Bay, California, is complex, intensely managed system of natural and human-made channels and lakes, diked agricultural fields, and relicts of tidal marshlands (Figure 1). The watershed of the Delta (16×10^6 ha) comprises 40% of the area of the State of California (Jassby and Cloern 2000). The Sacramento and San Joaquin Rivers contribute 84 and 13%, respectively, of the freshwater influx to the Delta (total ca. 35×10^9 m^3 year^{-1}; Paulsen 1997). An equivalent of about a third of these freshwater inputs are removed from the southern end of the Delta by the California State Water Project (3×10^9 m^3 year^{-1}) and the Delta-Mendota Canal (9×10^9 m^3 year^{-1}), providing drinking water for over 22 million people and irrigation water to over 10 million hectares of farmland.

The cycling of Delta DOC may have conflicting impacts on municipal water quality and on the biological productivity of the Delta ecosystem. On the one hand, high DOC concentration in the Delta has been a concern in drinking water treatment. During water disinfection (chlorination or ozonation), toxic halogenated organic compounds are formed at a rate related to the

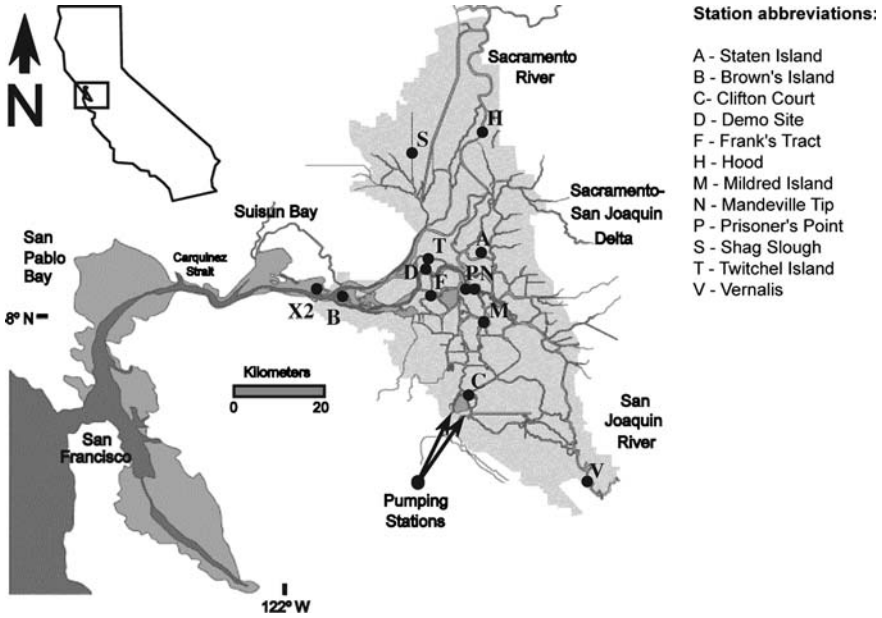

Figure 1. Map of the Sacramento–San Joaquin River Delta, California, showing the location of sampling stations.

concentration and chemical composition of DOC (Bergamaschi et al. 1999). Concentrations of these disinfection byproducts in treated Delta water often exceed limits set by the US Environmental Protection Agency. On the other hand, DOC may play an important role as a source of carbon to the Delta ecosystem. The Delta serves as a habitat for 130 species of fish, including endangered salmonids. Delta fish populations have been declining since the 1970s, and decreased food availability has been suggested as the main cause (Jassby et al. 2002). Because phytoplankton photosynthesis comprises only a minor fraction of carbon inputs to the Delta (Jassby et al. 1993; Jassby and Cloern 2000), bacterial assimilation of allochthonous DOC and subsequent carbon transfer to the upper trophic levels via the microbial food web (Pomeroy 1974; Azam et al. 1983) may be providing an additional food source to fish.

The Sacramento and San Joaquin Rivers are major sources of DOC to the Delta, although it is likely that both quantity and composition of DOC is altered during the riverine water passage through the Delta (Jassby et al. 1993; Jassby and Cloern 2000). Diverse shallow water habitats, including lakes, marshlands, and diked agricultural fields, are likely to contribute and/or remove various DOC compounds to/from the passing water. Due to the diverse hydrology, geology, and vegetation of these habitats, they may have contrasting impact on the quantity and quality of DOC released to the Delta. Therefore, it is plausible that the prospective conversion of about 40,000 ha (about 10% of the total Delta area) of agricultural land to wetlands (Fleck et al. 2004), will affect the concentration and composition of DOC. In turn, this land use change is likely to affect both the microbial food web and the drinking water quality.

In this study we tested the following hypotheses: (1) diverse types of shallow water habitats have differing effects on the concentration and bioavailability of DOC in the Delta; (2) the prospective conversion of Delta agricultural land into wetlands will increase DOC export from the Delta; (3) microbial food web, based on the DOC utilization by heterotrophic bacterioplankton, is an important food source to the Delta fish populations; and (4) solar radiation enhances the bioavailability of Delta DOC.

Materials and method

Sampling strategy

Water samples were collected from a total of thirteen stations in the Delta on seasonal basis (Table 1 and Figures 1 and 2). Five stations were sampled from the main Delta watercourses, in order to monitor changes in DOC concentration, bioavailability, and chemical composition during water passage through the Delta. These stations include the Sacramento and San Joaquin Rivers upstream the Delta (Hood and Vernalis), deep-water channels in the central Delta (Prisoner's Point and Clifton Court), and the 2% salinity front in the oligohaline reach of the San Francisco Bay (X2). Clifton Court station is located near

Table 1. Sampling stations: names, abbreviations, description, location, and sampling time.

Name and abbreviation	Habitat type	Coordinates	Sampling time
Staten Island, A	Drain from an agricultural, below-sea-level island	38°07′33″ N, 121°31′30″ W	Varying
Brown's Island, B	Natural brackish marsh dominated by *Scirpus*	38°02′20″ N, 121°52′01″ W	Max ebb
Clifton Court, C	Main inlet to the California State Water Project	37°49.85′ N, 121°33.35′ W	During water intake
Demo Site, D	Marsh reconstructed in 1997, dominated by *Typha* and *Scirpus*	38°06′29″ N, 121°38′52″ W	Varying
Frank's Tract, F	Lake created from a flooded island in 1930s	38°02′46″ N, 121°38′50″ W	Max ebb
Hood, H	Sacramento River upstream of the Delta	38°22′07″ N, 121°31′12″ W	Max ebb
Mildred Island, M	Lake created from a flooded island in 1983	37°59′43″ N, 121°30′52″ W	Max ebb
Mandeville Tip, N	Natural freshwater marsh dominated by *Scirpus*	38°03′34″ N, 121°32′20″ W	Max ebb
Prisoner's Point, P	Deep-water channel in the central Delta	38°03′35″ N, 121°33′26″ W	Max flood
Shag Slough, S	Channel of the Yolo Bypass floodplain	38°18′22″ N, 121°41′32″ W	Max ebb
Twitchel Island, T	Drain from an agricultural, below-sea-level island	38°05′48″ N, 121°39′01″ W	Varying
Vernalis, V	San Joaquin River upstream of the Delta	37°40′32″ N, 121°15′49″ W	Varying
X2	2% salinity front in North San Francisco Bay	Varying	Varying

the California State Water Project and the Delta-Mendota Canal pump stations and represents water diverted to the municipal and agricultural users.

The remaining eight stations were sampled to characterize DOC originating from various types of shallow water habitats in the Delta: a natural freshwater marsh (Mandeville Tip); a reconstructed freshwater marsh (Demo Site); a natural brackish water marsh (Brown's Island); the Yolo Bypass freshwater floodplain (Shag Slough); freshwater lakes, originating from flooded agricultural fields due to levee breaches (Frank's Tract and Mildred Island); and drains of below-sea-level islands (Staten Island and Twitchel Island; Table 1 and Figure 1). Samples collected in the deep water in the central Delta (Prisoner's Point) served as a reference for pairwise water chemistry comparisons to the samples collected in shallow water habitats in the central Delta (Staten Island, Twitchel Island, Demo Site, Frank's Tract, Mildred Island, and Mandeville Tip). The Sacramento River above the Delta (station Hood) served as a reference to the floodplain station Shag Slough. The 2% salinity front in San Francisco Bay (station X2) served as a reference to the brackish marsh station Brown's Island.

In order to better identify material originating from the various shallow water habitats, tidal wetlands (Brown's Island, Frank's Tract, Mildred Island, Mandeville Tip, and Shag Slough) were sampled during maximum ebb tide, while the corresponding reference stations (Hood and Prisoner's Point) were sampled at maximum flood tide. The non-tidal stations (Vernalis, Staten Island, Twitchel Island, and Demo Site) and the fluctuating salinity front (station X2) were sampled at various times in the tidal cycle. Clifton Court was sampled during water intake from the Delta to the Clifton Court forebay (first section of the California State Water Project), which occurred 1–2 h before the maximum flood tide.

Five sampling campaigns were performed to cover the annual range of hydrological and climatic conditions and the plant productivity cycle in the Delta: March 19–24, July 16–21, and October 15–20 of 2000; and February 4–9 and May 20–25 of 2001 (Figure 2). March 00 samples were taken at the end of a large winter flood with temperatures starting to rise after the winter minimum. February 01 samples were taken between several small winter flood episodes with water temperature at its annual minimum. July 00, October 00, and May 01 samples represented early to late summer conditions with low river water flow and temperatures at their annual maximum (July 00 and May 01) or beginning to decline (October 00).

Water was collected at mid-depth at each station. However, only station X2 had significant vertical stratification, indicated by temperature, dissolved oxygen, and conductivity profiles.

Solar irradiations and DOC bioavailability assays

Immediately after collection, water was filtered through pre-combusted A/E glass fiber filters (nominal pore size 1.2 μm; Pall) and stored refrigerated.

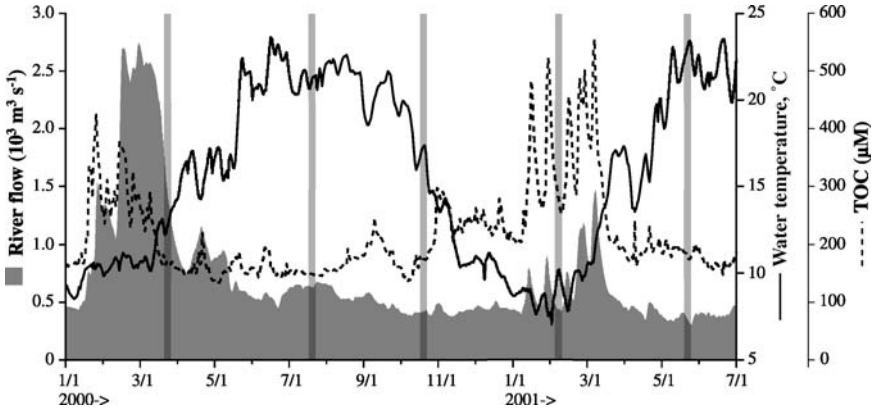

Figure 2. Combined flows of the Sacramento and San Joaquin Rivers (at Hood and Vernalis), water temperature at Hood, and total organic carbon (TOC) at Hood during the study period. Data acquired from California Department of Water Resources, http://cdec.water.ca.gov. Gray vertical bars indicate sampling campaigns.

Irradiations and bioassays were started within a week of the date of sampling. DOC concentration measurements before and after the storage demonstrated no significant changes ($p > 0.05$, paired t-tests, $n = 62$), indicating that refrigeration was an adequate means of storage for this period of time. Irradiations were conducted in an Atlas Sunset CPS solar simulator under a 1 kW Xe lamp, producing PAR and UV spectra similar to solar radiation (Miller et al. 2002). Water was dispensed into 160-ml quartz flasks, which were positioned beneath the lamp in a temperature-controlled water bath kept at 4 °C. Samples were exposed for 4 h at a lamp intensity of 286 W m^{-2} in the range of 280–700 nm, of which 33 W m^{-2} were in the range of 280–400 nm. This is equivalent to the solar radiation intensity at the Delta water surface in mid-afternoon in July. Control samples, treated in an identical way and dispensed in glass flasks, were wrapped in aluminum foil and placed in the solar simulator during the irradiations.

Concentration of potentially bioavailable DOC in control and irradiated water was determined as oxygen consumption by the natural microbial assemblage during a 14 day bioassay as in Covert and Moran (2001). A mixture of inorganic nutrients (final concentration 5 μM NH_4Cl, 5 μM $NaNO_3$, and 1 μM NaH_2PO_4) was added to ensure carbon limitation, and the water was dispensed to six replicate 30-ml BOD bottles. Three of the six replicate bottles were immediately fixed with Winkler reagents to determine initial dissolved oxygen concentrations. All bottles were incubated in dark at 15 °C for 14 days. At the end of the incubation, the remaining three bottles were fixed with Winkler reagents and initial and final oxygen concentrations were measured using an automated titrator (Mettler Toledo, Columbus, OH; Pomeroy et al. 1994). The bioavailability of DOC in control and irradiated samples was

estimated by dividing the consumption of oxygen (μM O_2) by the initial concentration of DOC (μM C), assuming that on average, two atoms of oxygen are needed to oxidize one atom of carbon. The obtained DOC bioavailability values should be viewed as the upper limit for the 2-week period, which is similar to the median water residence time in the Delta (Jassby and Cloern 2000). Nutrient limitation and other factors may limit DOC degradation *in situ*, although the Delta is replete in N and P most of the time (Jassby and Cloern 2000).

Water chemistry

Concentration of DOC was measured with a Shimadzu TOC-5000 analyzer (Moran et al. 2000). The ratio of fluorescence at 450 and 500 nm under excitation at 370 nm, which is directly related to the fraction of DOC of planktonic vs. terrestrial origin (McKnight et al. 2001), was determined using SPEX FluoroMax-3 spectrofluorometer with 5 nm excitation and emission slit widths, controlled with DATAMAX and GRAMS/32 software. Cation (Na, Ca, and Mg) concentrations, used as inert tracers in hydrological modeling, were analyzed by inductively coupled plasma mass spectrometry (American Public Health Association 1998). Water flow, temperature, and total organic carbon concentration data for the Sacramento and San Joaquin Rivers (stations Hood and Vernalis; Figure 2) was obtained from the State of California Department of Water Resources (http://cdec.water.ca.gov).

To discriminate DOC originating from C3 and C4 plants, ^{13}C isotope fraction in DOC (δ^{13}DOC) was determined. The 200–300 ml aliquots of filtered (as above) water were acidified to pH 2 with HCl to remove dissolved inorganic carbon from the samples. Then the samples were concentrated to approximately 25 ml by rotary evaporation at 45 °C and at a vacuum of 70 kPa less than atmospheric pressure. The concentrates were freeze-dried, and the carbon isotopic composition was analyzed on a Carlo-Erba 1500 elemental analyzer attached to a Micromass Optima mass spectrometer.

Hydrological modeling and statistical analyses

The fractions of water arriving at station Clifton Court from the Sacramento and San Joaquin rivers were estimated using least squares methods for overdetermined systems with the Matlab 3 software package (MathWorks) according to Paulsen (1997):

$$\begin{bmatrix} \mathbf{C_a}_{,\mathrm{Hood}} & \mathbf{C_a}_{,\mathrm{Vernalis}} & \mathbf{C_a}_{,\mathrm{Ocean}} \\ \mathbf{C_b}_{,\mathrm{Hood}} & \mathbf{C_b}_{,\mathrm{Vernalis}} & \mathbf{C_b}_{,\mathrm{Ocean}} \\ \mathbf{1} & \mathbf{1} & \mathbf{1} \end{bmatrix} \times \begin{bmatrix} \mathbf{f}_{\mathrm{Sacramento\_R}} \\ \mathbf{f}_{\mathrm{San\_Joaquin\_R}} \\ \mathbf{f}_{\mathrm{Ocean}} \end{bmatrix} = \begin{bmatrix} \mathbf{C_a}_{,\mathrm{Clifton\_Court}} \\ \mathbf{C_b}_{,\mathrm{Clifton\_Court}} \\ \end{bmatrix}, \quad (1)$$

where **C** represents the concentration of a trace element **a** or **b**, and **f** represents the fraction of water arriving at Clifton Court from the two major rivers and from the ocean. Tracer pairs Mg–Ca and Na–Ca were used, according to the recommendations provided for the Delta by Paulsen (1997). Concentrations of Mg, Ca, and Na were measured during all sampling campaigns except March 00. Ocean water was included in the model as the third source (in mg l^{-1}: 10770 Na, 1290 Mg, and 412 Ca; Wetzel 1983). Although the influx of ocean water to Clifton Court is reportedly negligible, even minor intrusions and sea spray may have a significant effect on the concentration of the tracers and on the outcome of the model.

Using results from the mass balance mixing model (above), we estimated the relative contributions of the Sacramento and San Joaquin Rivers and the Delta to the pool of DOC at Clifton Court. First, the estimate was performed assuming that riverine DOC was inert during the passage through the Delta:

$$\mathbf{DOCcontribution}_{\mathrm{Sacramento\_R}} = (\mathbf{DOC}_{\mathrm{Hood}} \times \mathbf{f}_{\mathrm{Sacramento\_R}} \times 1.1) / \mathbf{DOC}_{\mathrm{Clifton\_Court}} \quad (2)$$

$$\mathbf{DOCcontribution}_{\mathrm{San\_Joaquin}} = (\mathbf{DOC}_{\mathrm{Vernalis}} \times \mathbf{f}_{\mathrm{San\_Joaquin\_R}} \times 1.1) / \mathbf{DOC}_{\mathrm{Clifton\_Court}} \quad (3)$$

$$\mathbf{DOCcontribution}_{\mathrm{Delta}} = 1 - \mathbf{DOCcontribution}_{\mathrm{Sacramento\_R}} - \mathbf{DOCcontribution}_{\mathrm{San\_Joaquin\_R}} \quad (4)$$

where **DOCcontribution** is the fraction of DOC at Clifton Court arriving from the various sources, **DOC** is the concentration of DOC at corresponding stations, and **f** is the fraction of water arriving at Clifton Court from the two rivers. The coefficient 1.1 was introduced to account for the evapotranspiration in the Delta, reported to constitute about 10% of river inflow (Jassby and Cloern 2000).

The calculation was repeated assuming that all potentially bioavailable riverine DOC was consumed within the Delta before reaching Clifton Court. For this, $\mathbf{DOC}_{\mathrm{Hood}}$ and $\mathbf{DOC}_{\mathrm{Vernalis}}$ in Eqs. (2) and (3) were replaced by $\mathbf{DOC'}_{\mathrm{Hood}}$ and $\mathbf{DOC'}_{\mathrm{Vernalis}}$, which represent the concentration of biologically refractory DOC:

$$\mathbf{DOC}'_{\mathrm{Hood}} = \mathbf{DOC}_{\mathrm{Hood}} \times (1 - \mathbf{DOCB}_{\mathrm{Hood}}), \quad (5)$$

$$\mathbf{DOC}'_{\mathrm{Vernalis}} = \mathbf{DOC}_{\mathrm{Vernalis}} \times (1 - \mathbf{DOCB}_{\mathrm{Vernalis}}), \quad (6)$$

where **DOCB** is DOC bioavailability at respective stations.

Correlation analyses, regression analyses, *t*-tests, and ANOVAs were performed using Statview 5 (SAS Institute) software.

Results and discussion

DOC export from the Delta

Deep-water channels in the central Delta (stations Clifton Court and Prisoner's Point) had consistently higher DOC concentration than the Sacramento and San Joaquin Rivers upstream of the Delta (stations Hood and Vernalis), indicating that the Delta serves as a net source of DOC to the passing water (Figure 3a). Most of the water exported from the Delta for municipal and agricultural use is diverted near the Clifton Court station (Figures 1 and 3a). From a water management point of view, it is important to differentiate various sources of DOC arriving at this station. Because DOC concentration differed significantly between the Sacramento and San Joaquin Rivers, an estimate of external (from upper catchment) vs. internal (from the Delta) contribution of DOC to Clifton Court was only possible after determining the fractions of water arriving at station Clifton Court from the two rivers. We estimated that 63–81% of the water at Clifton Court originated from the Sacramento River, and the remaining from the San Joaquin River (Table 2). In all cases, the estimated contribution of the ocean water was below 1%. For the sampling campaigns of July 00, October 00, and February 01, the two pairs of tracers (Mg–Ca and Na–Ca) produced very similar results, with a coefficient of variation below 4%. The model did not produce satisfactory results for the May 01 sampling campaign; **f** values above 100% and below 0%, as well as large differences between the estimates based on the two tracer pairs were obtained, probably due to a significant fluctuation in the water flow at time scales shorter than the water residence time in the Delta.Using results from the mass balance mixing model, we estimated that internal Delta sources contributed between 3 and 50% (average = 29%) of DOC arriving at Clifton Court, depending on the season and on assumptions about the microbial utilization of DOC (Table 2). The estimated local DOC inputs were much lower in October 00 (3–17%) than in July 00 (25–33%) and February 01 (45–50%).

DOC sources in the Delta

The average DOC concentration was higher, DOC bioavailability was lower, and fluorescence ratio was lower in most semi-isolated, shallow water habitats (except lakes, stations Frank's Tract and Mildred Island), compared to the respective reference, deep-water stations (Figure 3). In fact, the average DOC bioavailability and the fluorescence ratio at the upstream stations Hood and Vernalis were higher than at any other sampling station in the Delta. This

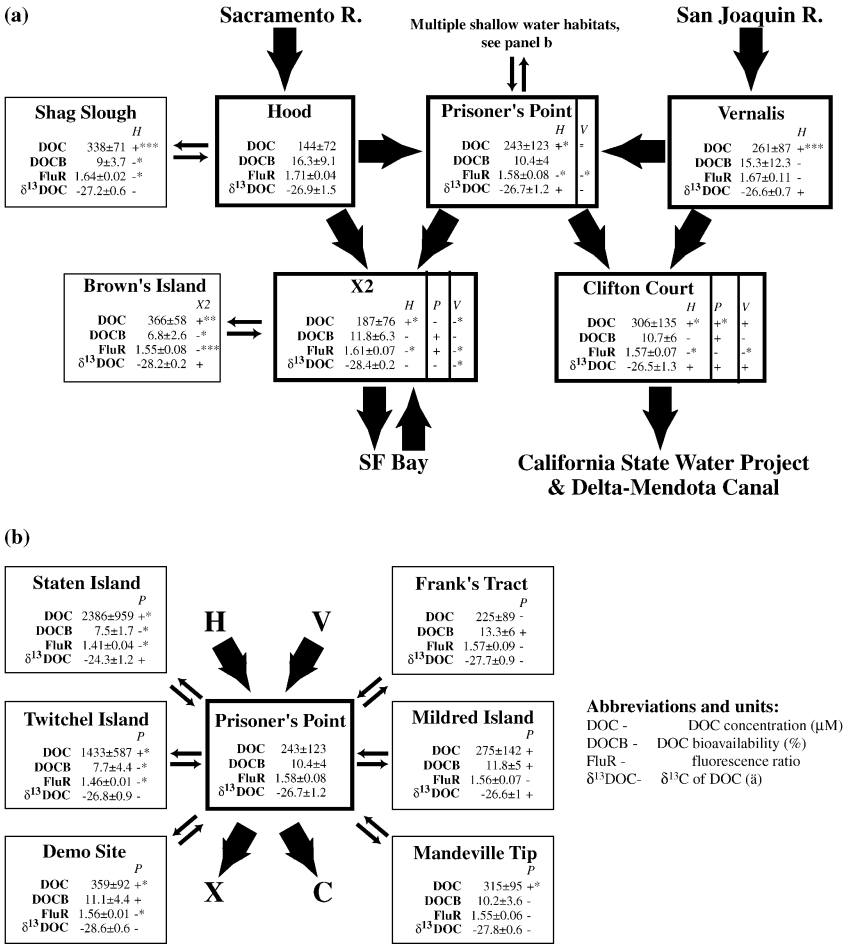

Figure 3. DOC concentration (DOC), bioavailability (DOCB), fluorescence ratio (FluR), and isotopic signature (δ^{13}DOC) at various sampling stations in the Delta. Thick frames and arrows indicate deep-water stations and main water flow directions. Thin frames and arrows indicate shallow water habitat stations and water exchange between them and the reference, deep-water stations. Numbers indicate means ± standard deviations for all sampling campaigns. Signs "+" and "−" indicate if a given mean value was above (+) or below (−) the reference station, which is indicated above the numbers (H = Hood, V = Vernalis, and P = Prisoner's Point). Stars indicate the level of significance in the difference between the means, obtained from a one-way ANOVA and Fisher's PLSD *post hoc* test on log-transformed data; $p < 0.05$, 0.005, and 0.001 is indicated by *, **, and ***, respectively.

implies that bulk of the Delta-derived DOC is of low nutritional value, or that bioavailable DOC is rapidly consumed in the Delta. The low fluorescence ratio indicates primarily terrestrial (soil and vascular plant) sources for the residual material, as opposed to phytoplankton production (McKnight et al. 2001). The predominantly terrestrial origin of Delta-derived DOC corroborates with the

Table 2. Estimated contributions of DOC to the Clifton Court station from Sacramento and San Joaquin Rivers upstream the Delta and from local Delta sources.

Station[a]	Na; Ca; and Mg (mg l^{-1})			f[b] (%)		DOC (μM)			DOCB[c] (% DOC)			DOC contribution[d] (%)		
	H	V	C	H	V	H	V	C	H	V	C	H	V	Delta
July 00	7.7; 9.7; 5.3	63; 32; 15	22; 14; 7.7	81 ± 0	19 ± 0	109	234	178	11	10	5	50 (44)	25 (22)	25 (33)
October 00	8.4; 10; 5.7	47; 25; 11	61; 17; 13	63 ± 1	36 ± 1	136	265	186	16	13	21	46 (39)	51 (45)	3 (17)
February 01	17; 16; 9.5	110; 46; 23	48; 22; 13	81 ± 0	19 ± 1	284	412	539	13	11	12	43 (37)	15 (13)	43 (50)
May 01	14; 13; 7.6	33; 18; 8.2	40; 21; 12	−50 ± 18	150 ± 18	81	143	260	34	39	10	ND	ND	ND

[a]Station abbreviations: H = Hood, V = Vernalis, C = Clifton Court.
[b]f is the fraction of water arriving at Clifton Court from Hood and Vernalis, estimated using Eq. (1). Mean ± SD for the estimates based on two tracer pairs: Mg & Ca and Na & Ca.
[c]DOCB is DOC bioavailability in non-irradiated samples.
[d]Contribution to the Clifton Court DOC pool from Hood and Vernalis as well as from local Delta sources. The first value is calculated assuming no riverine DOC is consumed during water passage through the Delta. The value in parenthesis is calculated assuming all of the bioavailable DOC present at the Hood and Vernalis stations was consumed before reaching Clifton Court. ND = not determined because of a model failure to estimate f values.

fact that phytoplankton production in the Delta is typically low, owing to light limitation (Jassby et al. 2002).

There were no significant differences in the DOC isotopic signature (δ^{13}DOC) in main Delta waterways (Hood, Vernalis, Prisoner's Point, and Clifton Court). The δ^{13}DOC averaged -26.9 to -26.5 at these stations, which falls in the lower range of the C3 plant material signature in the Delta (-32 to -12) and differs significantly from C4 plants (-17 to -12; Cloern et al. 2002). Corn (*Zea mays* L.), a C4 plant, is a predominant agricultural crop in the Delta. The DOC in one of the island drains, Staten Island, tended to be enriched in ^{13}C (average δ^{13}DOC $= -24.3$, compared to -26.7 at the reference station at Prisoner's Point), consistent with fresh leachates from C4 agricultural crops (Figure 3b).

The generally observed combination of low DOC bioavailability and fluorescence ratio suggests that vascular plant material from degrading soils and from tidal marshes are major sources of DOC at most Delta wetland sites rather than *in situ* phytoplankton production. The drainage of Delta wetlands and their conversion to agricultural land, which started in 1859, has oxygenated peat deposits and induced their rapid degradation (Fleck et al. 2004). Currently, Delta soils subside 1–3 cm yr^{-1}, and some have subsided 6 m below sea level, mostly due to microbial degradation of oxygenated peat deposits (Fleck et al. 2004). Peat soil carbon is released to surface waters by agricultural practices in other disturbed wetland ecosystems, e.g. the Everglades in South Florida (Wang et al. 2002). Tidal marsh vegetation and associated soils, dominated by *Scirpus* sp., may also contribute refractory DOC with low fluorescence ratio and deplete in ^{13}C, see the comparison between Brown's Island vs. X2 in Figures 3a and 4f.

Water passage through various types of shallow water habitats in the Delta had contrasting seasonal effects on DOC concentration and bioavailability. The DOC concentration was substantially higher and DOC bioavailability was consistently lower in the two island drains (Twitchel and Staten Islands) and the Yolo Bypass (Shag Slough station) compared to their reference stations year-round (Figure 4a–c).

Marshes (Demo Site, Mandeville Tip and Browns Island) had DOC concentrations above that in respective reference stations throughout the year (Figure 4d–f). However, the ratio of DOC bioavailability at these stations vs. respective reference stations varied seasonally. Marsh DOC had elevated bioavailability (ratio above 1) in March 00 (Brown's Island and Mandeville Tip), July 00 (Demo Site and Mandeville Tip), and in May 01 (Demo Site and Mandeville Tip). In contrast, DOC bioavailability was lower in all three marshes compared to their reference stations in October 00 and February 01.

Finally, the two lakes, Frank's Tract and Mildred Island, had DOC concentrations similar to their reference station (Prisoner's Point) year-round. In contrast, DOC bioavailability at these two lakes exceeded DOC bioavailability at Prisoner's Point during March 00 (Mildred Island), July 00 (both

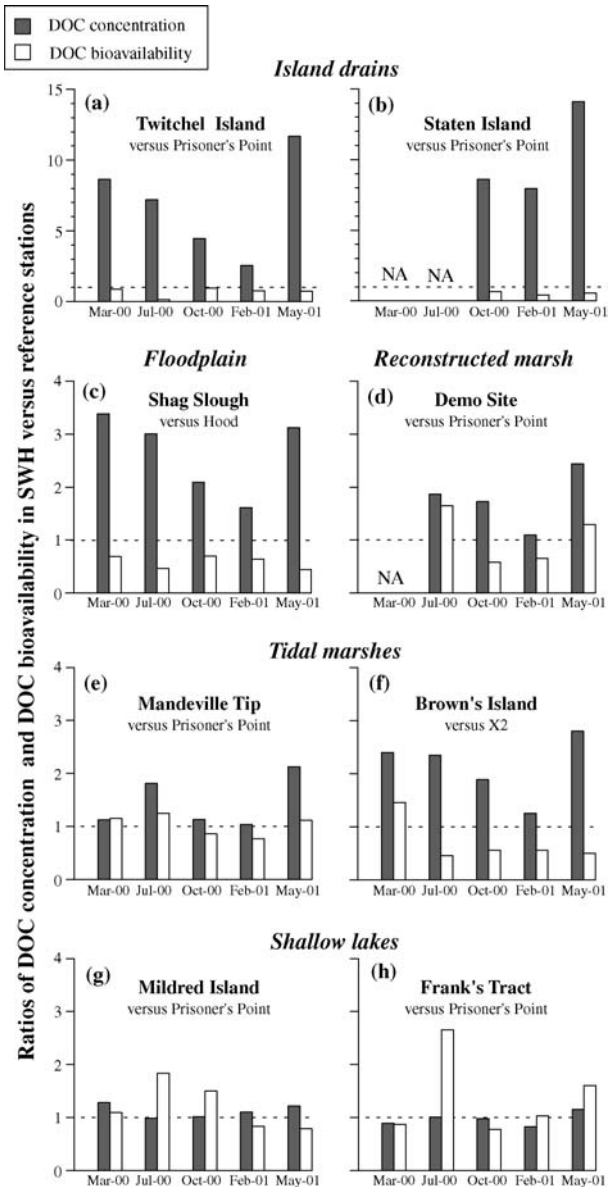

Figure 4. Ratios of DOC concentration and bioavailability in shallow water habitat stations vs. respective reference stations during the five sampling campaigns.

lakes), October 00 (Mildred Island), and May 01 (Frank's Tract), while lake DOC bioavailability was slightly below Prisoner's Point's during the rest of the year.

In summary, our results indicate that island drains and the Yolo Bypass provide the Delta with predominantly terrestrial, refractory DOC throughout the year, most likely due to the long water residence time in contact with organic-rich soils. Water passage through marshes provides relatively bioavailable material during spring–summer and relatively refractory material during the rest of the year. Water passage though shallow lakes (flooded islands) replaces refractory DOC with more bioavailable DOC during spring–summer, possibly through a combination of microbial DOC degradation and the production of new, labile material by phytoplankton and vascular aquatic vegetation. Water passage through lakes appears to have little effect on DOC concentration or bioavailability during the rest of the year.

DOC role in the Delta food web

The median Delta DOC bioavailability before the simulated solar irradiations was 10% (range 0.8–38.9%) and compared well with the 12% median DOC bioavailability determined for the same system by Sobczak et al. (2002). Thus, Delta DOC appears of lower nutritional value than the global averages for rivers (19%) and lakes (14%) determined using similar bioassays (Sondergaard and Middelboe 1995). The observed low DOC bioavailability in the Delta may be caused by several factors, including: (1) the predominance of terrestrial vs. algal DOC sources (see discussion above) and (2) the nutrient-replete conditions in the Delta (Jassby and Cloern 2000), which may allow bacterioplankton to rapidly utilize the labile component of DOC. Solar radiation may further lower the nutritional value of DOC during water passage through the Delta (see discussion below).

It is estimated that about 66×10^9 g DOC is annually loaded to the Delta by tributaries, while additional 22×10^9 g DOC is imported from agricultural drainage and Delta wetlands (Jassby and Cloern 2000). Assuming that at most 16% of tributary DOC and 9% of locally produced DOC is consumed by bacterioplankton during water residence in the Delta (Figrue 3), and that bacterial growth efficiency is 25% (del Giorgio and Cole 1998), this DOC can support no more than 3.1×10^9 g C bacterial production annually. Most metazooplankton are unable to feed on bacterial-sized particles, and an intermediate, protist food chain is necessary for the carbon transfer to metazooplankton. Assuming 20% energy transfer efficiency from bacterioplankton to protists (Ducklow et al. 1986), DOC loaded to the Delta from agricultural drainage, wetlands, and the upper catchment can support no more than 0.6×10^9 g C of protist production annually. For a comparison, the estimated annual phytoplankton production in the Delta is 17×10^9 g C (Jassby and Cloern 2000).

We may underestimate the potential role of locally produced DOC in the Delta food web if a significant fraction of this DOC is utilized by bacterioplankton very rapidly, before reaching sampling stations. However, Sobczak

et al. (2002) show that *in situ* rates of bacterioplankton secondary production (9–23 μg C l^{-1} d^{-1}) are lower than the rates of phytoplankton primary production (10–295 μg C l^{-1} d^{-1}) in similar habitat types in the Delta. Low rates of bacterioplankton secondary production (11–40 μg C l^{-1} d^{-1}) are also reported by Hollibaugh and Wong (1996) and Murrell et al. (1999) from the main channel of the Sacramento River. Other studies have also indicated that Delta bacterioplankton do not contribute significantly to the nutrition of *Daphnia* (Muller-Solger et al. 2002), and clams (Canuel et al. 1995). Thus, it appears that carbon and energy supplies provided to the Delta invertebrates and fish by phytoplankton primary production greatly exceed those provided by the pelagic microbial food web utilizing DOC originating from the upper catchment and from Delta wetlands and island drains.

DOC photoreactivity

A moderate dose of simulated solar radiation, equivalent to a half-day of natural exposure at the water surface, decreased the amount of DOC available to heterotrophs by a median of 40% (Figure 5). The difference between the

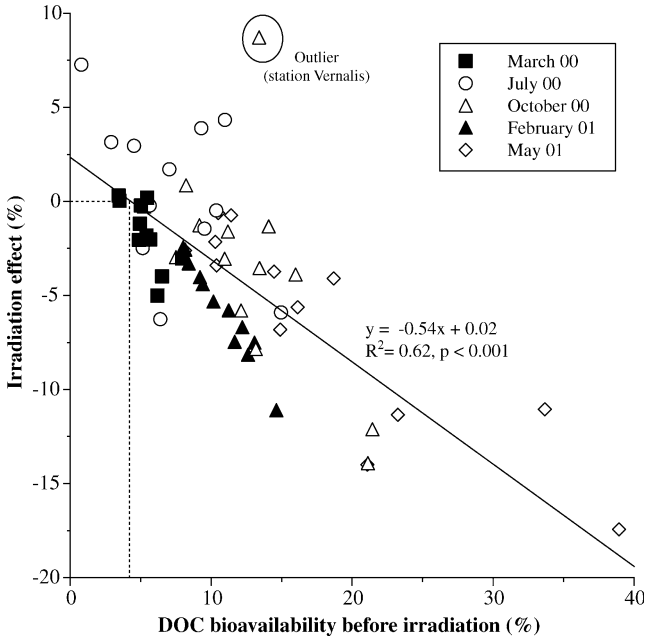

Figure 5. Correlation between DOC bioavailability in non-irradiated samples (*X*-axis) and the effect of simulated solar irradiation on DOC bioavailability (*Y*-axis). The irradiation effect was calculated by subtracting DOC bioavailability before irradiation from DOC bioavailability after irradiation.

DOC bioavailability before and after the irradiation was statistically significant ($p < 0.001$, two-tailed paired t-test, $n = 62$). The decrease in bioavailable DOC could not be explained by photooxidation of DOC to inorganic carbon, because no change in DOC concentration was detected after the irradiation ($p > 0.05$, two-tailed paired t-test, $n = 62$). The irradiation may have suppressed bacterial growth by direct inhibition (Herndl et al. 1993; Kaiser and Herndl 1997) or by the formation of inhibitory substances, such as hydroxyl radicals (Mopper and Zhou 1990). However, both effects are reportedly short-lived, ranging from minutes to hours, and are unlikely to affect the 14-day bioassays of this study. Therefore, the most likely explanation for the observed solar radiation effect is photochemical transformation of labile DOC into more refractory organic compounds.

Most of the work on the photochemical transformation of dissolved organic matter in natural waters has focused on processes converting refractory, high-molecular-weight DOC into small, biologically labile molecules (e.g. Kieber et al. 1989; Lindell et al. 1995; Miller et al. 2002). However, reduction of DOC bioavailability as a result of solar irradiation has also been observed in a variety of water bodies, including the surface ocean (Benner and Biddanda 1998; Obernosterer et al. 1999; Orellana and Verdugo 2003), eutrophic lakes (Tranvik and Bertilsson 2001), and a blackwater river (Amon and Benner 1996).

In this study, solar radiation had a more negative effect on DOC bioavailability in Delta samples with higher initial DOC bioavailability (Figure 5) and higher fluorescence ratio ($p < 0.05$, $R^2 = 0.28$, correlation analysis). Similar to our results, Obernosterer et al. (1999) observed a positive correlation between the initial DOC bioavailability and the decrease in bioavailability after a UV exposure. Accordingly, Tranvik and Bertilsson (2001) demonstrated a negative correlation between chlorophyll concentration (a proxy for phytoplankton productivity) and UV enhancement of bacterial growth in a series of Swedish lakes. Thus, it appears that solar radiation usually reduces the bioavailability of labile, phytoplankton-derived DOC. This hypothesis has been supported by manipulative experiments where various labile substrates, such as algal extract (Tranvik and Kokalj 1998), algal exudates (Pausz and Herndl 1999), protein (Keil and Kirchman 1994; Obernosterer et al. 1999), and tryptophan (Reitner et al. 2002) were rendered less bioavailable after exposure to UV radiation. In contrast, terrestrial DOC (Wetzel et al. 1995), high-molecular-weight DOC (Tranvik and Bertilsson 2001), and extracts of humic acids (Reitner et al. 1997), representative material generally considered refractory to microbial degradation, is usually rendered more bioavailable upon an exposure to solar radiation (Miller et al. 2002; Moran et al. 2000). Our study shows that solar radiation can have a net negative effect on DOC bioavailability even in water bodies dominated by refractory DOC.

The simulated solar radiation reduced DOC bioavailability in winter samples (Mar 00 and Feb 01) more than in summer samples (Jul 00, Oct 00, May 01) with the same initial DOC bioavailability ($p < 0.001$, ANCOVA;

Figure 5). Most likely, this seasonal variation was caused by a longer exposure of DOC to solar radiation prior to sampling during summer because of the slower river flow, lower average water depth, greater transparency, higher sun angles, and longer days during summer compared to winter. Accordingly, solar radiation had a more pronounced effect on DOC bioavailability in a Swedish lake in winter relative to summer (Lindell et al. 2000), and in a riparian stream shielded by vegetation relative to an exposed stream (Findlay et al. 2001). However, in contrast to our results, the latter two studies report increased rather than decreased DOC bioavailability as a result of solar irradiation.

Conclusions

This study supports the observation that the Sacramento–San Joaquin River Delta serves as a net source of DOC to the passing water, with the greatest local contribution in winter. Island drains, the Yolo Bypass floodplain, and various types of marshes contribute DOC to the water passing the Delta, while there is no evidence of net DOC input from fields converted into shallow lakes. Thus, the conversion of agricultural land into shallow lakes will likely have little effect on the export of DOC from the Delta. However, additional, mass-balance-based studies are needed to quantify DOC contributions from the various Delta habitats and to predict the effects of wetland restoration on DOC exports from the Delta.

Delta DOC has low bioavailability to microbial heterotrophs, which is further depressed by exposure to solar radiation. As a consequence, DOC utilization via the pelagic microbial food web does not seem to play an important role in the nutrition of Delta zooplankton and fish. Therefore, the possible decrease in DOC concentration due to land use changes is unlikely to have a direct effect on Delta fish productivity.

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