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Landscape scale controls on the vascular plant component of dissolved organic carbon across a freshwater delta

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Abstract

Lignin phenol concentrations and compositions were determined on dissolved organic carbon (DOC) extracts (XAD resins) within the Sacramento–San Joaquin River Delta (the Delta), the tidal freshwater portion of the San Francisco Bay Estuary, located in central California, USA. Fourteen stations were sampled, including the following habitats and land-use types: wetland, riverine, channelized waterway, open water, and island drains. Stations were sampled approximately seasonally from December, 1999 through May, 2001. DOC concentrations ranged from 1.3 mg L^{-1} within the Sacramento River to 39.9 mg L^{-1} at the outfall from an island drain (median 3.0 mg L^{-1}), while lignin concentrations ranged from 3.0 μg L^{-1} within the Sacramento River to 111 μg L^{-1} at the outfall from an island drain (median 11.6 μg L^{-1}). Both DOC and lignin concentrations varied significantly among habitat/land-use types and among sampling stations. Carbon-normalized lignin yields ranged from 0.07 mg (100 mg OC)$^{-1}$ at an island drain to 0.84 mg (100 mg OC)$^{-1}$ for a wetland (median 0.36 mg (100 mg OC)$^{-1}$), and also varied significantly among habitat/land-use types. A simple mass balance model indicated that the Delta acted as a source of lignin during late autumn through spring (10–83% increase) and a sink for lignin during summer and autumn (13–39% decrease). Endmember mixing models using S:V and C:V signatures of landscape scale features indicated strong temporal variation in sources of DOC export from the Delta, with riverine source signatures responsible for 50% of DOC in summer and winter, wetland signatures responsible for 40% of DOC in summer, winter, and late autumn, and island drains responsible for 40% of exported DOC in late autumn. A significant negative correlation was observed between carbon-normalized lignin yields and DOC bioavailability in two of the 14 sampling stations. This study is, to our knowledge, the first to describe organic vascular plant DOC sources at the level of localized landscape features, and is also the first to indicate a significant negative correlation between lignin and DOC bioavailability within environmental samples. Based upon observed trends: (1) Delta features exhibit significant spatial variability in organic chemical composition, and (2) localized Delta features appear to exert strong controls on terrigenous DOC as it passes through the Delta and is exported into the Pacific Ocean.
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1. INTRODUCTION

In the context of global carbon cycling, rivers are frequently modeled as integrators of all sources and processes within the watershed, both spatially and temporally. But are they really simple integrators? There is ample evidence in the literature of significant variability in dissolved organic carbon (DOC) composition and concentration among river systems (Hopkinson et al., 1998; Aitkenhead and McDowell, 2000; Lobbes et al., 2000), likely driven by the same state factors responsible for soil and ecosystem formation—climate, source, topography, parent materials, time,

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and humans (Jenny, 1941; Amundson and Jenny, 1997). Thus, it is reasonable to assume that variability also occurs within river systems, and that not all scales and landscape features within a watershed are equally important toward determining riverine carbon concentration and composition.

The Sacramento–San Joaquin River Delta (the Delta), which encompasses the tidal freshwater portion of the San Francisco Bay–Delta system, is an example of a group of ecosystems and land-use types that could exert a strong influence on riverine DOC concentration and composition. Tidal cycles within the Delta occur twice daily, causing wetlands, channels, and open water areas to be subject to tidal pumping, and facilitating the exchange of waters among these features. The concentration and composition of terrigenous DOC is directly tied to ecosystem utilization and geochemical partitioning between dissolved and particulate phases within the estuary (Hedges and Keil, 1999). Thus, Delta processing could largely determine the fate of riverine DOC as it is exported through San Francisco Bay to the Pacific Ocean.

The Delta, like many estuaries (e.g. Findlay et al., 1991; Lucas et al., 2002), encompasses a high degree of spatial variability in biotic and physical parameters. One way to constrain the effects of a patchy environment on organic carbon dynamics is to delineate discrete areas and examine to what extent they influence DOC composition and concentration. This type of investigation can be classified as describing processes at the landscape scale, that is, at a spatial dimension that incorporates groupings of ecosystems or land uses to characterize their effects on environmental processes (Turner, 1989; Turner et al., 2001). Delta habitat and land-use types, including wetlands, rivers, open waters, channelized waterways, and agricultural islands, are each subject to different types and amounts of biological production, hydrologic characteristics, and other physical processes, and thus provide a framework of landscape scale features sufficient to investigate landscape scale DOC dynamics.

Although Hedges (1981) hypothesized that discrete organic chemical signatures exist for individual waters at the landscape scale, no researcher has, to our knowledge, tested this hypothesis. Instead, organic geochemical research investigating DOC sources and compositions in riverine systems has overwhelmingly focused on either molecular scale processes (e.g. McKnight et al., 1992; Hedges et al., 2000; Hernes and Benner, 2003) or processes at riverine, oceanic, and global macroscales (e.g. Hedges et al., 1997; Lobbes et al., 2000; Hernes and Benner, 2006). These latter studies primarily constrain overall composition and large-scale sources of DOC within, or emanating from, riverine systems; they do not resolve DOC sources or dynamics that occur among landscape scale features.

The purpose of this study was to utilize XAD resin extracts of DOC to (1) investigate the geochemical signature of DOC in freshwater portions of a highly disturbed temperate delta system, in order to resolve how natural and anthropogenic land uses influence DOC composition, (2) characterize the significance of spatial variation in lignin parameters among land-use and habitat types at the landscape scale, and (3) examine the potential for using lignin compositions to resolve and trace landscape scale sources of vascular plant-derived organic matter.

2. METHODS

2.1. The Sacramento–San Joaquin Delta system

The Sacramento–San Joaquin River Delta (the Delta) is a freshwater to oligohaline estuary that drains into the northeastern portion of San Francisco Bay, CA. The two primary sourcewaters to the Delta, the Sacramento and San Joaquin rivers, drain 1.6×10^7 ha of land including the eastern slope of the California Coastal Range, the Central Valley, the western slope of the Sierra Nevada, and the southern reaches of the Cascade Range (Jassby and Cloern, 2000). The Delta supplies drinking water to over 20 million people, irrigation water for nearly 10 million hectares of farmland, and provides 26,000 ha of habitat for fish and waterfowl (Lucas et al., 2002). The Delta has been strongly influenced by humans. Channelization of Delta waterways for farmland reclamation and transportation began as early as 1859 and has resulted in a 95% reduction in wetland habitat (Fleck et al., 2004). Agricultural island soils are peat-derived and highly susceptible to oxidative degradation, resulting in cumulative island subsidence of up to 6 m below sea level (Deverel and Rojstaczer, 1996). The Delta system is thus heavily managed and regulated in an attempt to satisfy water demands of end users while sustaining remaining habitat quality.

As addressed in the present study, several Delta land-use types provide potential sources of organic carbon (Table 1). These include remnant wetland areas (wetlands), reclaimed islands dominated by agricultural practices (agricultural islands; the outfalls from these islands are termed island drains), and open water areas that were previously reclaimed for agriculture and then, more recently, flooded to create lake-like habitats (open water).

2.2. Sampling stations

Water enters the Delta system from its tributaries, then makes its way through an array of channels, wetlands, open waters, and onto and off of agricultural islands before its final exit to aqueduct pumping plants or San Francisco Bay. To capture these important features, 14 stations were selected within and adjacent to the Delta system (Table 1 and Fig. 1), including two riverine stations (RS and RJ) located upstream of tidal and Delta influence, four wetland stations (WB, WD, WM, and WS), two open water stations (OF and OM) which have also been defined as lakes (see Stepanauskas et al., 2005), three drains from below-sea-level agricultural islands (IT, IS, and IV), one centrally-located deep water channel station (CP), one variable station located at the area where salinity = 2 as Delta waters mix into San Francisco Bay (CX), and one final station located in the channel leading directly to the intake pumps at Clifton Court for the California State Water Project aqueduct (CC).

Table 1
Delta sampling station descriptions and abbreviations

Site name	Site abbrevation	Habitat or land use ('Habitat')	Description
Sacramento River at Hood	RS	River	Sacramento River upstream of the Delta; River channel above bidirectional tidal flow
San Joaquin River at Vernalis	RJ	River	San Joaquin River upstream of the Delta; River channel above bidirectional tidal flow
Old River at Clifton Court Intake	CC	Channel	Water entering from Old River to Clifton Court, near intake pumps for the State and Central Valley water projects
San Joaquin River at Prisoner's Point	CP	Channel	Deep water tidal river channel in the central Delta
Little Frank's Tract	OF	Open water	Open water created from flooded island in 1930s, submerged aquatic vegetation (SAV); peat soil
Mildred Island	OM	Open water	Open water created from a flooded island in 1983; peat soil
Demo Pond	WD	Wetland	Constructed impounded marsh created in 1997 on Twitchell island, dominated by *Typha* spp. and *Scirpus* spp.; peat soil
Mandeville Tip	WM	Wetland	Natural freshwater marsh, dominated by *Scirpus* spp.; peat soil
Brown's Island	WB	Wetland	Natural brackish marsh dominated by *Scirpus* spp.; peat soil
Shag Slough	WS	Wetland	Tidal channel draining the Yolo bypass floodplain; mineral soil
X2	CX	Channel	Within salinity gradient of estuary; upstream boundary of salinity = 2
Twitchell Island Drain	IT	Island drain	Drain from peat island (agricultural), below sea level
Staten Island Drain	IS	Island drain	Drain from peat island (agricultural), below sea level
Venice Island Drain	IV	Island drain	Drain from peat island (agricultural), below sea level

2.3. Water sample collection and processing

Water samples were collected during seasonal boat trips from December, 1999 through May, 2001. Due to variation in environmental conditions, sampling strategies varied among stations. Wetland and open water stations were sampled during maximum ebb tide in order to obtain the strongest possible biogeochemical signal. Station CP, representative of Delta 'average,' well-mixed water (Stepanauskas et al., 2005), was sampled during maximum flow tide. Island drain stations were sampled only during island drain pumping (e.g. pumping of island water back into Delta channels), while station CC was sampled only during aqueduct pumping. Riverine stations and the location where salinity = 2 were sampled at varying times. Water was collected at mid-depth at all stations, and only station CX had significant vertical stratification, as indicated by temperature, dissolved oxygen, and conductivity profiles (Stepanauskas et al., 2005).

Water samples were filtered during collection through in-line 0.2 μm filters and stored in 40 L stainless-steel carboys, with 200 L of water collected per sample. Samples were immediately transported to the laboratory for DOC extraction and other analyses.

2.4. DOC, $\delta^{13}C$, and bioavailability analyses

DOC concentration was analyzed prior to XAD resin extraction using high temperature combustion on a Shimadzu TOC-5000 analyzer. Filtered and acidified (pH ~2) water samples were sequentially passed through nonionic macroporous XAD-8 and XAD-4 resins (Fujii et al., 1998), resulting in the combined isolation of 61–84% of total DOC. XAD resins are expected to preferentially retain hydrophobic fractions such as lignin, which would result in near-quantitative retention of lignin on the resins (Malcolm and MacCarthy, 1992).

The XAD isolates were freeze-dried and stored in glass vials for stable carbon isotope ($\delta^{13}C$) and lignin analyses. Stable carbon isotope values were determined on freeze-dried XAD isolates using a Carlo-Erba 1500 elemental analyzer coupled with GVI Optima mass spectrometer. Analysis of bioavailability was performed by Stepanauskas et al. (2005), and both the methodology and data are described therein.

2.5. Cupric oxide analysis of lignin phenols

Cupric oxide (CuO) oxidation to release lignin phenols was carried out on all XAD-8 (~5 mg) and XAD-4 (~10 mg) resin extracts, following a modified version of that outlined by Hedges and Ertel (1982) and Hernes and Benner (2002). Following oxidation in 8% NaOH in the presence of excess CuO at 155 °C for 3 h, samples were acidified and extracted three times with ethyl acetate. Excess solvent was blown off under a gentle stream of ultrapure nitrogen. Samples were then stored in a freezer until analysis. Lignin phenols were trimethylsilyl derivatized using bis-trimethylsilyltrifluoromethylacetamide (BSTFA); separation of phenols was achieved using a Hewlett Packard 6890 gas chromatograph fitted with a DB5-MS capillary column (30 m, 0.25 mm inner diameter, J&W

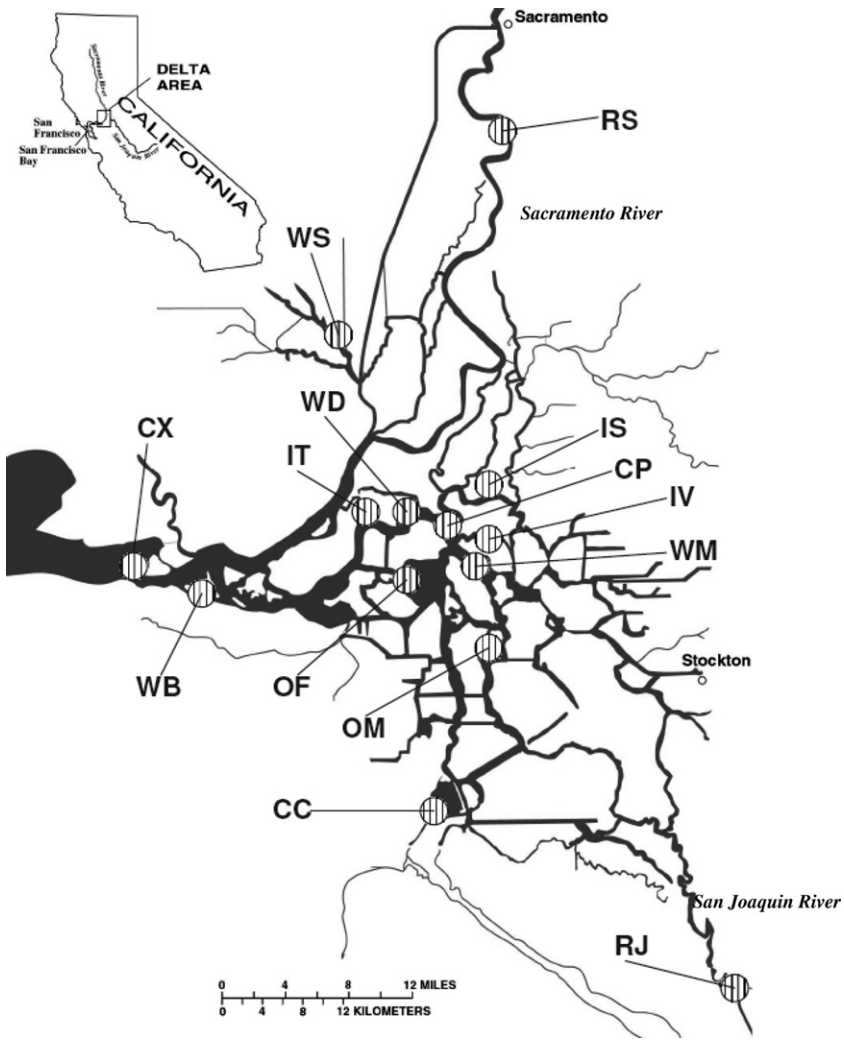

Fig. 1. Map of Sacramento–San Joaquin Delta indicating sampling stations. The first letter of each station abbreviation refers to habitat or land-use type, including channel (C), wetland (W), river (R), open water (O), and island drain (I), while the second letter delineates a specific station, as shown in Table 1.

Scientific) and equipped with a Hewlett Packard 5973 mass selective detector. Quantification was achieved using selected ion monitoring with cinnamic acid as an internal standard following the calibration scheme of Hernes and Benner (2002). All samples were blank-corrected due to the presence of trace amounts of contamination in the NaOH reagent. At least one blank was run for every 10 sample oxidations performed, and averaged 85 ng of lignin phenols as compared to >5500 ng (average is approximately 79,000 ng) in all samples. Lignin phenols for each oxidation were scaled to the total XAD8 or XAD4 recovered extracts, then the scaled XAD8 and XAD4 lignin phenols were summed for each station and sampling period to represent total lignin phenols. Only the sums of the XAD8 and XAD4 lignin phenols are presented.

2.6. Data analysis

Data were analyzed with SPLUS statistical software, version 6.1. All correlations are reported as linear Pearson Product-Moment. Due to small sample sizes, the nonparametric Kruskal–Wallis Rank test was used to test for statistical differences among populations unless noted otherwise. The Welch modified two-sample t-test was used to compare larger groupings of data and is denoted (†). All hypotheses tested were two-sided, and significant p-values are denoted as $^{*}(p < 0.05)$, $^{**}(p < 0.01)$, or $^{***}(p < 0.001)$. Degrees of freedom (df) are reported where appropriate. Large variation and sometimes skewed distributions within many portions of the data set led us to report median and median deviation (md), not mean and standard deviation. To resolve annual trends, sampling event calendar dates were converted into days numbered from the start of each calendar year, as follows: December, 1999 was converted to days 339–343 (late autumn), March, 2000 to days 55–83 (winter/early spring), July, 2000 to days 195–203 (summer), October, 2000 to days 289–294 (autumn), February, 2001 to days 35–40 (winter), and May, 2001 to days 140–145 (spring).

Data were analyzed for variation among individual sampling stations and among the five habitat and land-use types (e.g. rivers, wetlands, open waters, channelized

waterways, and island drains). For simplicity, habitat and land-use types are referred to simply as 'habitats' or 'habitat types' throughout the remainder of the article. Carbon-normalized yields of lignin phenols were calculated using XAD-extracted lignin phenols and total DOC, the latter measured directly from filtered water samples (not XAD-extracts).

3. RESULTS

3.1. DOC concentrations in the Delta

A subset of the DOC data set presented here was previously presented and discussed by Stepanauskas et al. (2005); however, the present discussion incorporates all available DOC data. Delta DOC concentrations were widely variable among habitat types within the Delta (Appendix). Overall Delta DOC concentrations ranged from 1.3 to 39.9 mg L^{-1} (median 3.0 mg L^{-1}, md 3.0). Of the landscape scale habitats, island drains exhibited the highest degree of variability, and ranged from 8.0 to 39.9 mg L^{-1} (median 16.7, md 6.5). The degree of variability from other habitat types was substantially lower, reflected by much smaller ranges in concentration and median deviations. For example, DOC at channel stations ranged from 1.3 to 4.9 mg L^{-1} (median 2.5 mg L^{-1}, md 0.72), and those at wetland stations from 2.1 to 6.0 mg L^{-1} (median 3.7 mg L^{-1}, md 0.71). At open water stations, DOC concentrations ranged from 1.6 to 4.8 mg L^{-1} (median 2.6 mg L^{-1}, md 0.7), and at riverine stations, from 1.3 to 3.7 mg L^{-1} (median 2.3 mg L^{-1}, md 0.6), nearly an order of magnitude lower than the island drains.

The concentration of DOC at island drain stations was significantly elevated as compared to other habitat types $(df = 70)^{***\dagger}$. DOC concentrations also varied significantly among habitats $(df = 4)^{***}$ and among sampling stations $(df = 13)^{***}$ (Fig. 2). Median Delta DOC concentrations varied seasonally $(df = 5)^{***}$. Median seasonal values for the entire Delta ranged from 2.2 mg L^{-1} in the summer to 4.3 mg L^{-1} during winter sampling (Fig. 2). Temporal variation in DOC concentration followed similar trends at individual sampling stations.

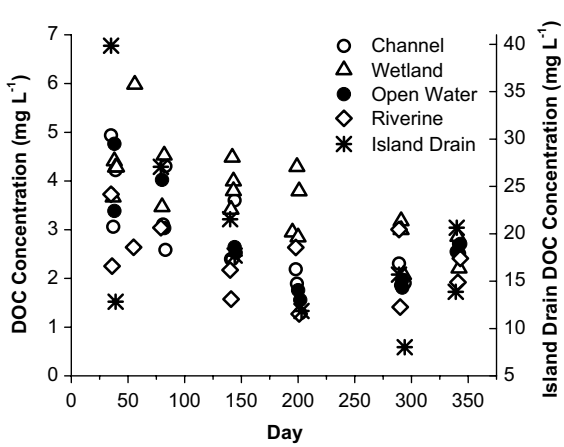

Fig. 2. DOC concentrations for all stations (mg L^{-1}). Note that the scale on the right side of the figure applies only to island drain values. Days are numbered from the first day of each calendar year.

3.2. Lignin phenol concentration and composition

3.2.1. Lignin concentrations and carbon-normalized lignin phenol yields

The summed concentrations of eight vanillyl, syringyl, and cinnamyl lignin phenols, Σ_8, for the XAD-extracted Delta water samples are shown in the Appendix. Values for the entire Delta ranged over more than an order of magnitude, from 3.0 to 111 μg L^{-1} (median 11.6 μg L^{-1}, md 11.4; Fig. 3). Island drain habitats exhibited the highest degree of variability among habitat types, and ranged from 14.9 to 111 μg L^{-1} (median 53.7 μg L^{-1}, md 28.8). Ranges in Σ_8 values for the remaining habitat types were substantially smaller. In order of decreasing median values, wetland stations ranged from 5.7 to 36.8 μg L^{-1} (median 16.9, md 7.7), open water stations ranged from 3.4 to 19.9 μg L^{-1} (median 8.2 μg L^{-1}, md 5.2), river stations ranged from 3.0 to 14.2 μg L^{-1} (median 7.3 μg L^{-1}, md 2.6), and channel stations ranged from 3.5 to 8.9 μg L^{-1} (median 5.0 μg L^{-1}, md 4.6). Lignin concentrations were also significantly different among these five habitat types $(df = 4)^{***}$ and among individual sampling stations $(df = 13)^{***}$.

Lignin phenol concentrations also varied seasonally $(df = 5)^{*}$, increasing from a minimum median value of 5.8 μg L^{-1} (md 8.1) in the summer, through 9.2 μg L^{-1} (md 8.6) in the autumn, up to 17.3 μg L^{-1} (md 11.1) in the winter, and slightly tailing off into spring (15.4 μg L^{-1}, md 12.9). No further significant trends were observed.

The carbon-normalized yields of eight lignin phenols (Λ_8,) for the XAD isolates of Delta DOC are shown in Fig. 4 and the Appendix. Across all sampling stations, Λ_8 spanned an order of magnitude, with a range of 0.07–0.85 mg $(100\ mg\ OC)^{-1}$ (median 0.36 mg $(100\ mg\ OC)^{-1}$, md 0.13). In the case of carbon-normalized yields, the variability observed among stations was relatively similar. For example, wetland Λ_8 values ranged from 0.27 to 0.85 mg OC^{-1} (median 0.44 mg OC^{-1}, md 0.13), island drain values ranged from 0.07 to 0.58 mg OC^{-1} (median 0.26 mg OC^{-1}, md 0.12), and channel values ranged from 0.13 to 0.52 mg OC^{-1} (median 0.25 mg OC^{-1}, md 0.11). Open water Λ_8 values ranged from 0.19 to 0.52 mg OC^{-1} (median 0.31, md 0.10), while river values ranged from 0.19 to 0.54 mg OC^{-1} (median 0.33, md 0.09). Carbon-normalized lignin yield values indicated significant differences among habitats $(df = 4)^{**}$ wherein channels exhibited the lowest median carbon-normalized lignin yields, followed by island drains, open water, rivers, and wetlands. Seasonal variation in Λ_8 was non-significant for habitat types and individual stations.

3.2.2. Syringyl:vanillyl and cinnamyl:vanillyl ratios

Ratios of syringyl:vanillyl (S:V) phenol yields have been used to discriminate organic matter sources from gymnosperm and angiosperm plant types, while cinnamyl:vanillyl (C:V) phenol ratios discriminate between woody and non-woody tissues (Hedges and Mann, 1979). Most Delta C:V–S:V signatures were consistent with traditionally-

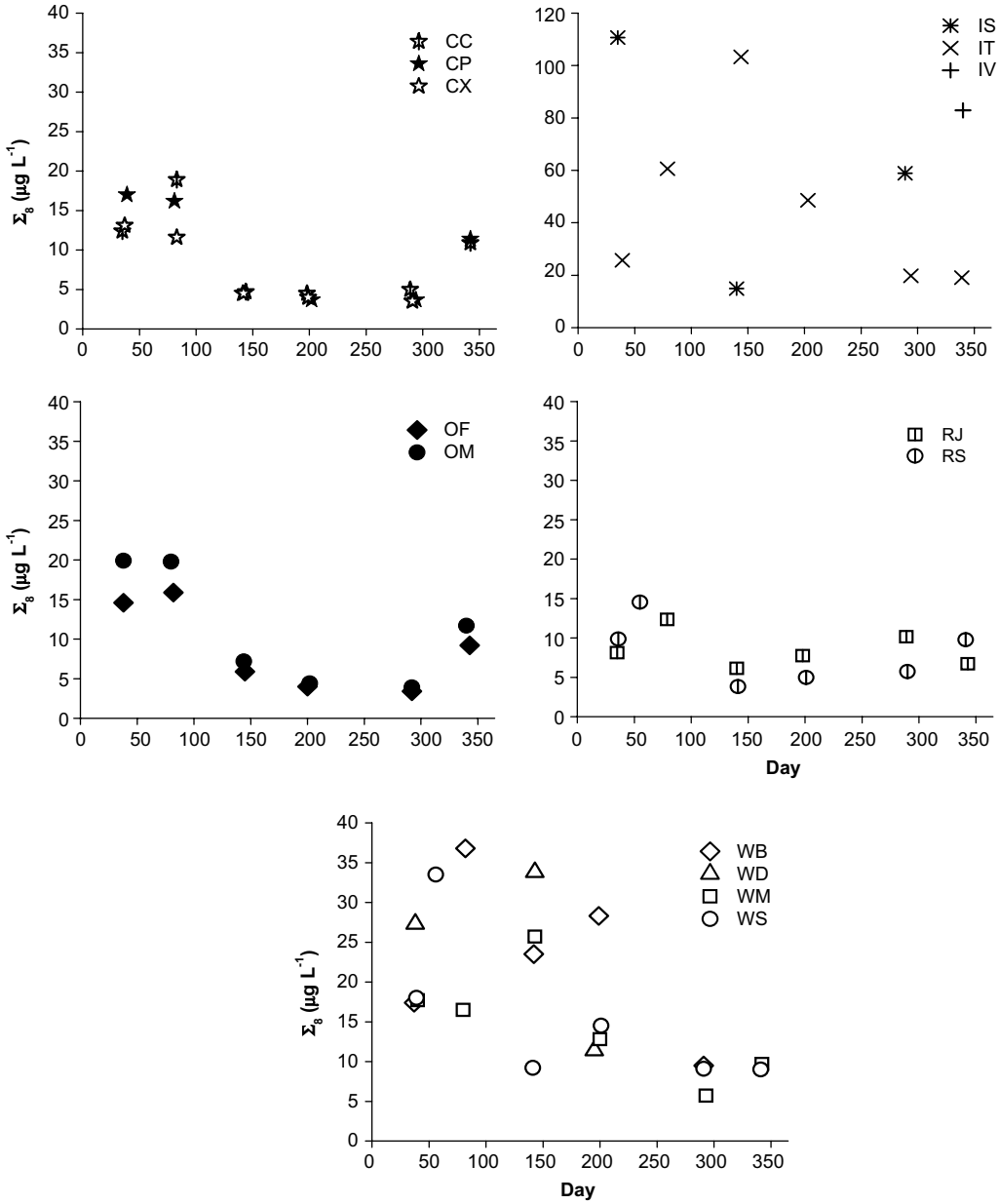

Fig. 3. Lignin concentrations (µg L^{-1}) for all sampling stations, organized by landscape scale feature. Note larger scale for Island Drain stations. Days are numbered from the first day of each calendar year. Table 1 shows station abbreviations.

defined nonwoody angiosperm vascular plant sources, although river and, in some cases, channel stations CP and CX, showed gymnosperm input (Hedges and Mann, 1979; Fig. 5; Appendix). Within the Delta, S:V and C:V varied significantly among habitats (S:V (df = 4)***, C:V (df = 4)**) and among sampling stations (S:V (df = 13)***, C:V (df = 13)*). Median S:V values for habitats were lowest for rivers (0.93, md 0.17), followed by channels (0.99, md 0.16), open water (1.07, md 0.12), and finally wetlands (1.25, md 0.15) and island drains (1.25, md 0.09). Median C:V values for habitats demonstrated a slightly different pattern, increasing from channels (0.47, md 0.11) to open water (0.52, md 0.11), rivers (0.53, md 0.16), wetlands (0.64, md 0.09), and island drains (0.78, md 0.15).

Temporally, S:V exhibited significant seasonal differences (df = 5)*, with summer S:V values lower than all other seasons (df = 70)***†. Low summer median S:V (0.90, md 0.23) increased in autumn (1.05, md 0.16) and into winter (1.20, md 0.09), falling off into spring (1.10, md 0.17). No significant temporal trends in C:V values were observed.

3.2.3. Acid:aldehyde ratios

The ratios of vanillic acid to vanillin $(Ad{:}Al)_v$ and syringic acid to syringaldehyde $(Ad{:}Al)_s$ have been shown to increase with relative degree of oxidative degradation of organic matter (e.g. Hedges et al., 1988). Acid:aldehyde ratios in the Delta are presented in the Appendix, and varied

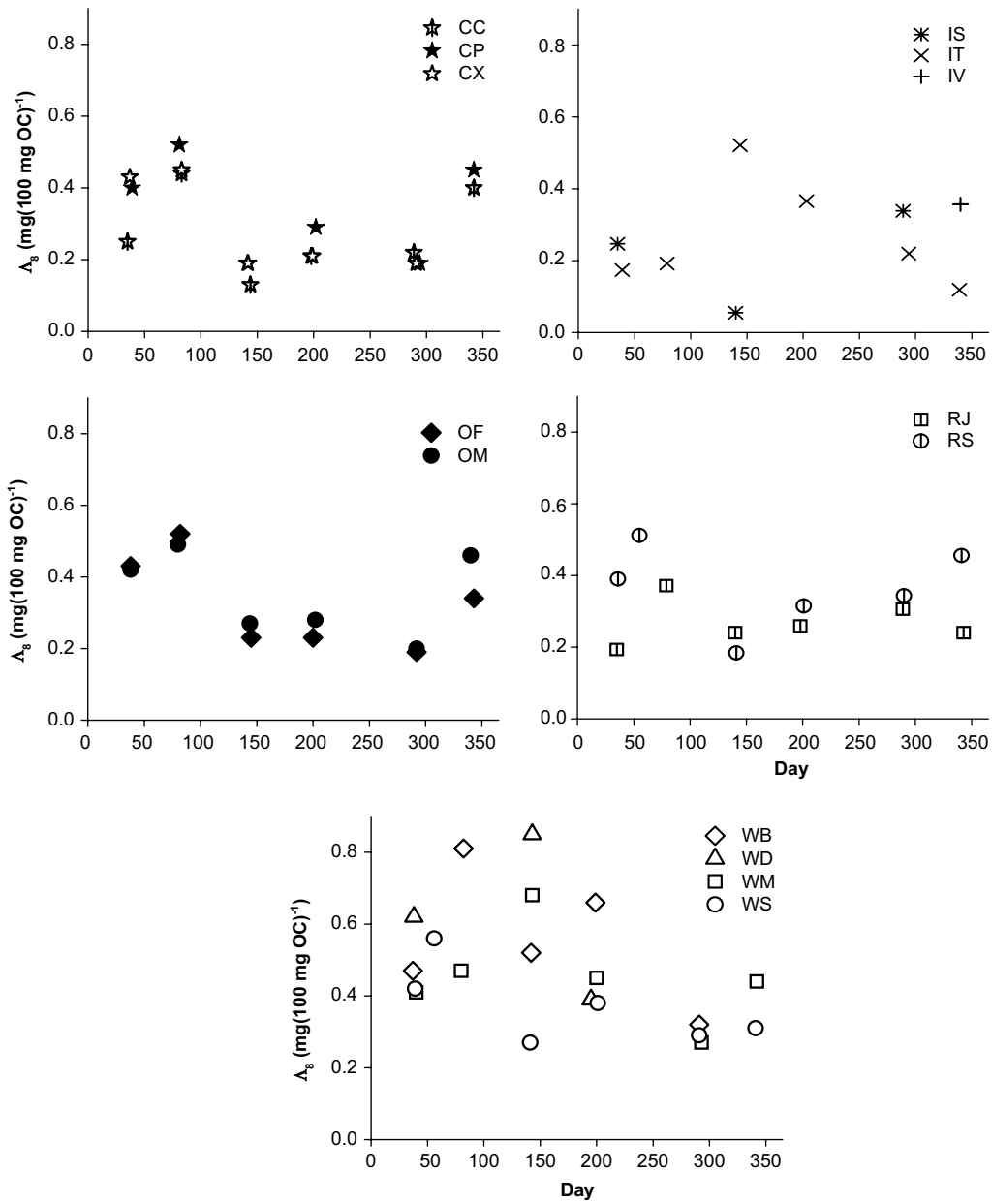

Fig. 4. Carbon-normalized lignin yields (mg (100 mg OC)$^{-1}$) for all sampling stations and organized by landscape scale feature. Days are numbered from the first day of each calendar year. Table 1 shows station abbreviations.

seasonally in the Delta (df = 5)*, with lowest median $(Ad:Al)_v$ in the late autumn (0.92, md 0.18) and highest in summer (1.32, md 0.24) and lowest $(Ad:Al)_s$ in spring (0.97, md 0.25) and autumn (0.97, md 0.22), and highest in summer (1.12, md 0.20). No further significant trends were observed.

4. DISCUSSION

4.1. DOC and lignin content of Delta waters

Lignin concentrations (Σ_8) and carbon-normalized yields (Λ_8) within the Delta were consistent with, but somewhat low in comparison to prior riverine and estuarine studies. For instance, Delta Σ_8 values (median 11.6 μg L^{-1}, md 11.4) were similar to those found in the lower Amazon (10.2 μg L^{-1}, md 7.2; Ertel et al., 1986), the upper Amazon (12.7 μg L^{-1}, md 11.2; Hedges et al., 2000), and a single value reported at the mouth of the Mississippi (12.3 μg L^{-1}; Hernes and Benner (2003)), but were somewhat lower than the median lignin concentration found in the Mississippi by Benner and Opsahl (2001; median 41.4 μg L^{-1}, md 16.6) and by Bianchi et al. (2004; median 36.6 μg L^{-1}, md 12.6). Further, Delta Λ_8 values (median 0.36 mg (100 mg OC)$^{-1}$, md 0.13) were low in comparison to the upper Amazon (1.07 mg (100 mg OC)$^{-1}$, md 0.26; Hedges et al., 2000), the lower Amazon (1.4 mg (100 mg OC)$^{-1}$, md 0.24; Ertel et al., 1986), and lower Mississippi values

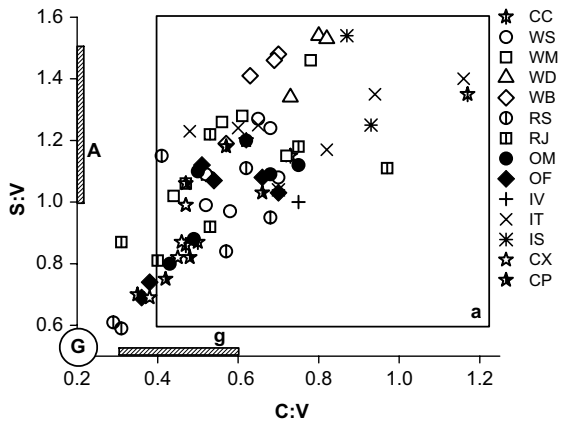

Fig. 5. Lignin cinnamyl:vanillyl (C:V) and syringyl:vanillyl (S:V) phenol ratios for all samples, listed by sampling station; boxes and lettering indicate source signatures as traditionally defined by Hedges and Mann (1979): angiosperm woody tissues (A), angiosperm nonwoody tissues (a), gymnosperm woody tissues (G), and gymnosperm nonwoody tissues (g). The first letter of each station abbreviation refers to habitat or land-use type, including channel (C), wetland (W), river (R), open water (O), and island drain (I), while the second letter delineates a specific station, as shown in Table 1.

from studies by Benner and Opsahl (2001; 1.02 mg (100 mg OC)$^{-1}$, md 0.44) and Bianchi et al. (2004; 0.75 mg (100 mg OC)$^{-1}$, md 0.24), but were equivalent to a single sample in the lower Mississippi taken by Hernes and Benner (2003) during very low flow conditions (0.38 mg (100 mg OC)$^{-1}$).

While values for Σ_8 and Λ_8 were within the range of what would be expected for riverine waters, the limited sampling regimes of previous lignin studies severely restricted the level of detail that could be described, and may have overlooked significant processes that occur at intermediate scales. For instance, DOC, Σ_8, and Λ_8 values all exhibited statistically significant variation among Delta habitats. Specifically, median DOC concentrations were at least 6-fold higher for island drains as compared to median channel, open water, and riverine DOC concentrations; median Σ_8 values were 3-fold higher for island drains as compared to wetlands, and wetlands were, in turn, 3-fold higher than median channel stations and twice median open water and riverine values; the median Λ_8 value for wetlands was nearly double those of channel and island drain values. Therefore, our data indicate that OM sources and processing within Delta habitats are quite different from each other and therefore have the capacity to produce distinct lignin and DOC signatures within waters emanating from those habitats.

On a seasonal basis, Delta DOC concentrations generally decreased from winter through autumn (Fig. 2). Trends for Delta lignin concentrations were less clear, but all habitat types, except island drains, indicated peak values in the winter and early spring (Fig. 3), which coincides with flushing due to storm events. Lignin carbon-normalized yields oscillated from peak Λ_8 values during late winter/early spring (channels, open water, rivers; Fig. 4) or spring (wetlands), followed by minima during drier sampling periods (summer through late autumn). Differences in lignin carbon-normalized yields can be attributed to changes in lignin sources and sinks, but could also reflect dilution by algal-derived carbon as hypothesized by Hernes et al. (2007). Algal primary production within the Delta (data from Jassby et al., 2002) is similar in magnitude to DOC loads input to the Delta by the Sacramento and San Joaquin Rivers, and therefore could exert considerable influence on DOC compositions and concentrations.

The headwaters of the Sacramento and San Joaquin River watersheds encompass an extensive gymnosperm forest that covers the southern Cascades and the western slope of the Sierra Nevada. Springtime releases of water from the upper watershed reservoirs to the Delta show an accordingly stronger gymnosperm source signature, as indicated by seven data points with C:V ratios of less than 0.4 (Fig. 5). This pulse of gymnosperm material was only detectable in the lignin signatures of riverine, channel stations CP and CX, and open water stations. It was not detected at the Delta export pump station (CC), which draws water across the Delta from both rivers. Thus it appears that angiosperms from a few hundred square kilometers of island agricultural fields, open waters, and wetlands were sufficient to mask the organic geochemical signature of a gymnosperm forest that covers tens of thousands of square kilometers.

4.2. Addition and loss of lignin in the Delta and evidence of photooxidation

Export of terrigenous organic matter from rivers delivers approximately 0.4×10^{15} g of carbon to the world's oceans each year (Hedges et al., 1997). However, only a small fraction of the DOC found in the ocean is terrestrially-derived (Hedges et al., 1997; Hernes and Benner, 2006), indicating substantial degradation of terrigenous organic matter in deltas, estuaries and the open ocean. Most studies of riverine carbon export are calculated using riverine endmembers located upstream of tidal influence (Meade, 1996), and therefore overlook processes affecting terrigenous DOC dynamics within the upper, tidally influenced freshwater portion of estuaries. The Sacramento–San Joaquin River Delta, which encompasses the tidally influenced freshwater portion of the San Francisco Bay estuary, provides an opportunity to examine poorly understood upper estuary influences on terrestrial DOC export and dynamics.

To address Delta processing of riverine DOC, we used a simple mass balance of the lignin content of Delta samples to (1) constrain the influence of the Delta on terrigenous DOC concentration and composition, and (2) assess whether the Delta is a net source or sink for dissolved lignin phenols. Because station CP is centrally located within the Delta (Fig. 1), and because diurnal tidal flows generate substantial mixing at this point, we used samples collected at station CP, the mainstem bidirectional river channel in the center of the Delta, to represent water of 'average' Delta organic geochemical composition (Stepanauskas et al., 2005). Riverine contributions from the Sacramento River (RS) and San Joaquin River (RJ) to the water at station

Table 2
Proportion of riverine waters at station CP and station CC, calculated as per Stepanauskas et al. (2005) using Na, Mg and Ca concentrations

Na; Mg; and Ca (mg L^{-1})					Station CP Proportions		Station CC Proportions	
Days	RS	RJ	CP	CC	RJ	RS	RJ	RS
35–40	17, 9.5, 16	110, 23, 46	26, 10, 16	48, 13, 22	0.00	1.00	0.18	0.82
55–83		33, 8.2, 17	20, 7.1, 14	32, 9.4, 19	0.23	0.77	1.00	0.00
140–145	14, 7.6, 13	33, 8.2, 18	29, 9.4, 17	40, 12, 21,	0.46	0.54	0.62	0.38
195–203	7.7, 5.3, 9.7	63, 15, 32	12, 6.1, 10	22, 7.7, 14	0.00	1.00	0.19	0.81
289–294	8.4, 5.7, 10	47, 11, 25	30, 8.9, 14	61, 13, 17	0.24	0.76	0.38	0.62
339–343	10, 7.3, 13	98, 21, 40	72, 14, 16	62, 13, 17	0.02	0.97	0.08	0.92

Marine waters were used as a third endmember (Na = 11169; Mg = 1343; Ca = 429 mg L^{-1}) to account for sea spray and dilute input from tidal influx. RS cations for days 55–83 were input as an average of days 35–40 and 140–145.

CP were calculated from cation data (Table 2), and the combined lignin load of the two rivers was compared to the load at station CP for each sampling period. A higher lignin loading in the Delta waters than river waters indicated net addition of vascular plant-derived DOC, whereas a lower loading was interpreted as net degradation of vascular plant-derived DOC.

Results from this analysis indicate that the Delta was a source of lignin from late autumn through spring, and a sink for lignin during the remainder of the year (Table 3). The Delta appears to contribute the most lignin during winter (83% increase), perhaps a result of early flushing events, and consumes lignin most effectively during low-flow periods in the autumn (39% decrease). Increased estuarine inputs of terrestrial organic matter were also indicated in the lower Tyne River during periods of high discharge accompanied by increased estuarine non-conservative mixing behavior for DOC (Spencer et al., 2007a). However, the observed seasonal contribution of lignin in the Delta is a clear break from most studies of river-estuary export, which report fairly conservative mixing of terrigenous riverine DOC into estuarine and ocean waters (e.g. Hedges et al., 1997; Mannino and Harvey, 2000; Benner and Opsahl, 2001).

The mechanism behind the observed additions and losses of Delta lignin are not clear. However, losses that occurred during low-flow periods could be attributed to (1) flocculation, which has been primarily observed within the freshwater-saltwater mixing zone well seaward of station CP where this analysis was conducted (Benner and Opsahl, 2001; Hernes and Benner, 2003); (2) bacterial remineralization, which has been found to not significantly change dissolved lignin compositional parameters (Hernes and Benner, 2003); and (3) photooxidation, which has been shown to decrease the lignin S:V ratio and increase acid:aldehyde ratios (Opsahl and Benner, 1998; Hernes and Benner, 2003). Within the Delta, our data indicate that S:V ratios were significantly lower during the summer $(df = 70)^{**\dagger}$ and autumn $(df = 70)^{***\dagger}$ sampling periods, and that $[Ad{:}Al]_v$ $(df = 70)^{*\dagger}$ and $[Ad{:}Al]_s$ $(df = 70)^{*\dagger}$ were significantly higher during the summer sampling period. These changes are consistent with photooxidation of dissolved lignin in natural waters (Opsahl and Benner, 1998; Hernes and Benner, 2003), suggesting that photooxidation was responsible for at least a portion of the observed loss in Delta lignin during the autumn and summer sampling periods. Net additions of lignin within the Delta could be attributed to increased terrestrial system exports during early season rainfall events (including first flush events). It is also possible that habitats within the Delta act as net sources of lignin to the Delta year round, but are masked by seasonal sinks such as high rates of photooxidation and bacterial remineralization in the summer. Conversely, in winter and early spring, lignin degradation rates would be substantially reduced due to decreased sunlight and colder temperatures such that lignin contributions from Delta habitats could elevate lignin concentrations in Delta channel waters.

Table 3
Mass balance indicates that the Delta is a source or sink for dissolved lignin, depending upon season

Days	Season	Lignin concentration Added or Lost (μg L^{-1})	% Change in Σ_8 from Rivers to CP
35–40	Winter	7.7	83
55–83	Early spring	2.5	18
140–145	Spring	0.4	10
195–203	Summer	−0.5	−13
289–294	Autumn	−2.4	−39
339–343	Late autumn	2.3	25

Rightmost column indicates the percent change between rivers and station CP (see Table 1). See text for a description of methodology.

Together, this variation in the amount of lignin and lignin composition highlights significant changes that occurred within the terrestrial fraction of DOC as riverine waters moved through the Delta. As Delta waters move seaward, the observed inputs and losses of terrigenous DOC of differing reactivities within the Delta have the potential to affect DOC export to the ocean. The influence of tidal freshwater areas, which may have been overlooked or under-appreciated by past studies of carbon export and estuarine dynamics, therefore appears to be critical to our understanding of terrigenous DOC export to the ocean.

The amount of lignin contributed by or lost from the Delta is also relevant to water quality management. Chemical interaction between DOC with significant double bonding (including the aromatic fraction) and chemical disinfectants likely results in the formation of federally-regulated drinking water disinfection by-products (DBPs) (Rostad et al., 2000; Fleck et al., 2004). Constraining the sources and sinks of aromatic and/or vascular plant-derived DOC both spatially and temporally will help drinking water managers to better mitigate DBP precursors. If

photooxidation of vascular plant-derived DOC is indeed a significant sink, then restoration efforts favoring open water habitats could increase photooxidation of vascular plant-derived aromatics, and, in turn, help to mitigate high levels of DBPs formed from vascular plant-derived materials.

4.3. Covariation of lignin and stable carbon isotopes

In general, vascular plants that utilize the C_3 photosynthetic pathway are more depleted in ^{13}C than those that utilize the C_4 pathway, with average values of approximately −27‰ and −13‰, respectively. Because most plants utilize the C_3 pathway, and because lignin can be used as a proxy for vascular plant-derived organic carbon, lignin yields typically correlate negatively with $\delta^{13}C$ (e.g. Ertel and Hedges, 1984; Opsahl et al., 1999; Bianchi et al., 2004), implying that vascular plant material in these systems is primarily derived from C_3 plants. This holds for dissolved, particulate, and sedimentary organic phases of marine and freshwater systems where C_3 plants dominate (Ertel and Hedges, 1984; Onstad et al., 2000; Harvey and Mannino, 2001). On the other hand, if vascular plant material is primarily derived from C_4 plants, vascular plant carbon in aqueous systems will be relatively more enriched in ^{13}C, and $\delta^{13}C$ will correlate positively with lignin yield. Select Delta habitats, and in particular Twitchell Island (station IT), contain both C_3- and C_4-derived organic matter. Therefore, evaluating the slope of the correlations between lignin and ^{13}C signatures of DOC within the Delta may provide further insight into DOC sources.

Although they were once wetland or estuarine habitats dominated by native C_3 plants, the Delta islands were drained for agricultural use during the late 1800s and early 1900s. This process exposed underlying peaty soils to air, and combined with farming practices, led to their decay and rapid land subsidence (Deverel and Rojstaczer, 1996). Deverel and Rojstaczer (1996) also found that exceedingly high DOC concentrations (48–110 mg L^{-1}) could be obtained by flooding these barren soils, suggesting that peat degradation could result in significant exports of DOC from Delta islands. Today, corn, a C_4 plant, accounts for

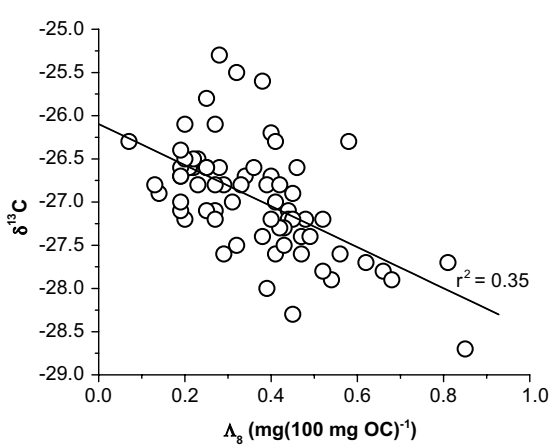

Fig. 6. Plot of $\delta^{13}C$ of XAD isolate material versus lignin phenol carbon-normalized yields (mg (100 mg OC)$^{-1}$) for all stations and sampling periods. Line shows the best-fit relationship between the two parameters, and is statistically significant ($p < 0.01$).

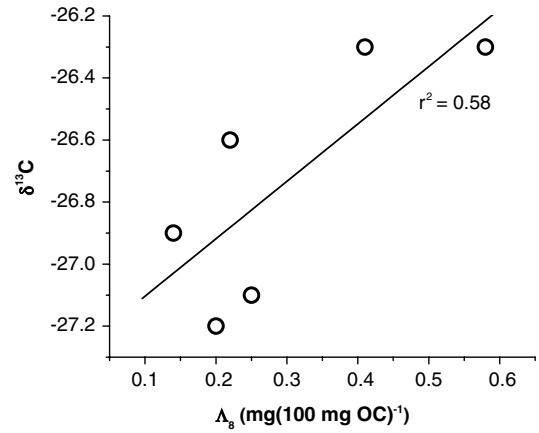

Fig. 7. Plot of $\delta^{13}C$ of XAD isolate material versus lignin phenol carbon-normalized yields (mg (100 mg OC)$^{-1}$) for station IT only. Line shows the best-fit relationship between the two parameters.

most of the agricultural production in the Delta, including Twitchell Island (station IT; Fleck et al., 2004), which is located within the central Delta. Thus, the $\delta^{13}C$ signature of DOC exported from Twitchell Island could provide important clues about the sources of lignin exported from agricultural islands.

In the Delta as a whole, Λ_8 values for Delta DOC correlate negatively with $\delta^{13}C$ ($r^2 = 0.35$; $p < 0.01$; df = 70; Fig. 6), consistent with the fact that the watershed supplying the Delta contains predominantly C_3 plants. But when only station IT is considered, the trend reverses and $\delta^{13}C$ values become less depleted as Λ_8 increases ($r^2 = 0.57$; Fig. 7). Note that stations IV and IS were not considered individually in this analysis due to small sample size ($n = 3$ and 1, respectively), and that all non-island drain stations exhibited negative correlations. This suggests that vascular plant DOC exported from Twitchell Island (station IT) is not solely derived from peat soils, but also contains a significant component of ^{13}C-enriched sources, likely including corn and potentially submerged vascular plant sources within the drainage ditches and other standing water bodies within the islands. These potential sources have been shown to have an enriched ^{13}C signature relative to peat soils (Cloern et al., 2002). It is therefore probable that fresh organic matter from farm and in situ production contributes substantially to DOC export from Delta islands, even though peaty soils represent a much larger pool of vascular plant-derived organic matter. Similar trends have been found in the arctic and UK temperate peatlands, where rivers that drain ancient peat soils also carry recently photosynthesized organic carbon (Benner et al., 2004; Ahad et al., 2006). However, even in watersheds without ancient peats, riverine DOC ages can be much younger than soil organic matter (e.g. Mayorga et al., 2005).

4.4. Lignin and bioavailability

A prior investigation of DOC dynamics in the Delta indicated low bioavailability relative to other river systems (median values ranging from 10% to 12%), and attributed

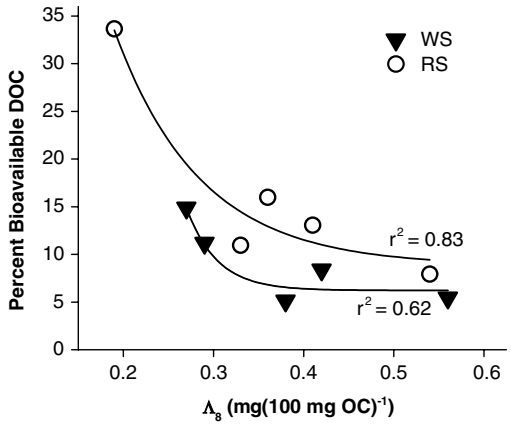

Fig. 8. Plot of % bioavailable carbon versus lignin phenol carbon-normalized yields (mg (100 mg OC)$^{-1}$) for stations RS and WS (as defined in Table 1). The correlation line shown is a first-order exponential decay model.

this to high levels of vascular plant-derived material (Stepanauskas et al., 2005). It follows then that carbon-normalized lignin yields—a proxy for the proportion of DOC that is derived from vascular plant—could exhibit an inverse correlation to DOC bioavailability within the Delta. Correlation analysis of bioavailability data (Fig. 8) provides evidence for such a relationship: at stations RS and OM, Λ_8 explains 83% (df = 4)* and 62% (df = 4)* of the variation in bioavailability, respectively (Fig. 8). The trend is also strong for WS and OF, where Λ_8 explains 62% and 52% of the variation in bioavailability, respectively. The non-linear relationship appears to indicate a threshold response to the amount of vascular plant-derived DOC in these samples. Correlations generally decrease in intensity as water moves from the Sacramento River (station RS) toward station CC (14.4%) and CX (23.4%), suggesting that bioavailability may become less influenced by vascular plant-derived DOC as river water moves through the Delta. This finding is, to our knowledge, the first to indicate a relationship between dissolved lignin and DOC bioavailability in environmental samples. One mechanism that could explain this relationship is the addition of algal-derived DOC, which would simultaneously increase the concentration of fresh, bioavailable carbon while decreasing Λ_8 with the addition of non-vascular plant carbon.

4.5. Landscape scale sources of DOC to Delta waters

4.5.1. Endmember mixing model

A three-parameter mixing model was generated to estimate the extent to which individual landscape scale sources contribute to the composition of DOC at the export pumping station (station CC) based on S:V and C:V lignin signatures unique to each landscape. Essentially all water received at the pumping station passes through the Delta (cdec.water.ca.gov; Stepanauskas et al., 2005) and is subsequently exported into the California Aqueduct. While 98% of the water delivered to the Delta (and subsequently to station CC) comes from the Sacramento and San Joaquin Rivers (cdec.water.ca.gov), significant differences in S:V and C:V ratios at station CC as compared to riverine values indicate that DOC at station CC is not derived solely from rivers. The focus of the model was to estimate contributions of DOC at station CC from sources within the Delta, and thus it includes all landscape scale features that were found to contribute DOC and lignin to waters in the Delta. For example, water exiting from wetlands and island drains was found to be higher in DOC (df = 60)* and lignin (df = 60)* concentrations than average Delta waters (represented by station CP; see Stepanauskas et al., 2005), indicating that these features typically act as DOC and lignin sources. Open water stations were not found to be sources of DOC (Stepanauskas et al., 2005) or lignin, and were therefore not included in the analysis.

For each sampling period, the model was implemented by linearly mixing average carbon-normalized yields of total vanillyl (V), syringyl (S), and cinnamyl (C) phenols for Wetland, Island, and River sources. Calculated C:V and S:V values from these mixtures were compared to C:V and S:V values from station CC, and the model iteratively solved for the fractions of Wetland, Island, and River endmembers required to minimize the sum of the square of the residuals (SSR) between the modeled and observed C:V and S:V values (Excel Solver, Microsoft, 2003). Conditions for the model include source fractions $\geqslant 0.00$, and the sum of the fractions must equal 1.00. The composition of the River endmember was taken to be the average of the composition of the Sacramento and San Joaquin Rivers, weighted according to the proportion of water from each river received at Station CC, based on the major ion concentrations (Table 2). The composition of the Wetland and Island endmembers was taken to be the average concentration of all samples representing respective sources.

For three of the sampling periods (days 35–40, days 195–203, and days 339–343), the relative position of the endmembers and station CC as well as the near-zero value of the SSR indicate that the simple mixing model adequately represents a likely mixing scenario (Fig. 9). For the remaining sampling periods (days 55–83, days 140–145, and days 289–294), the three endmembers did not adequately represent the composition of potential sources as evidenced by a non-zero SSR and the fact that the C:V and S:V composition of station CC is not spanned by the three end-members. Therefore the model would need to allow negative end-member fractions in order to resolve the composition at station CC. The sampling periods for which the model residual was low is used below to explore the extent to which landscape-scale features within the Delta may contribute to observed DOC compositions at station CC (Fig. 10).

4.5.2. Implications

Hedges (1981) reasoned that high diversity in potential organic matter sources and diagenetic processes within a basin should impart distinct chemical signatures that integrate the contribution of these processes to the composition of the DOC. This view is consistent with data from a limited number of DOC samples from various tributaries to the Amazon mainstem (Hedges et al., 2000). Hernes and Benner (2002) further posited that lignin has potential as a tracer for individual oceanic water masses, especially

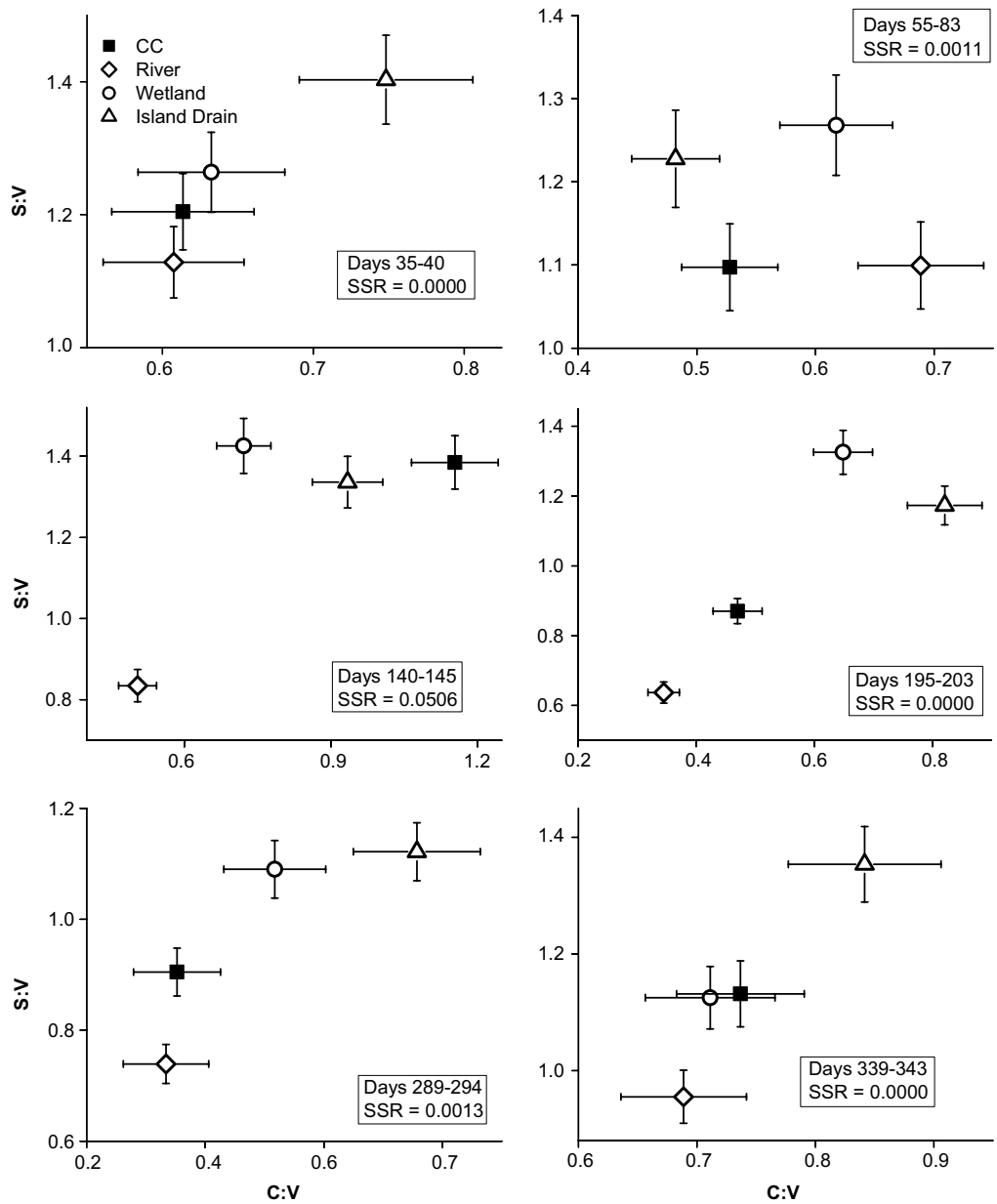

Fig. 9. Graphical presentation of River, Wetland, and Island endmember compositions (C:V and S:V) used to model DOC at station CC (see text for model implementation). Error bars depict analytical precision for CuO oxidation method as determined by Goni and Montgomery (2000). "SSR" refers to the sum of the squares of the residuals as described in the text for the model.

those not undergoing photooxidation. Generally, distinct DOC compositional signatures could, in theory, have been used in these previous studies to calculate source apportionment via endmember mixing models. However, in part because of past limits on sample throughput for molecular-level characterization of biochemicals like lignin, studies have never been undertaken with the spatial and temporal resolution appropriate to test this idea.

In this study, DOC originating from various sources exhibited distinct signatures of S:V and C:V (Fig. 5), and coverage was sufficient to construct the simple three parameter mixing model of DOC sources in the Delta outlined above (Figs. 9 and 10). Numerical models incorporating optical and molecular carbohydrate data in addition to all lignin data have also been constructed to address DOC sources to station CC (Bergamaschi et al., 2007) and essentially confirm the results that we were able to achieve with this much simpler model. Relative DOC contributions as indicated by lignin from each habitat varied on a seasonal basis (Fig. 10). Whereas DOC derived from island drains represented only 10% of DOC at station CC during winter and summer seasons, in late autumn island drains accounted for 40% of the DOC. Conversely, rivers were responsible for 50% of the DOC export during winter and summer, but only 20% in late autumn, likely a reflection of reduced flows at that time. Wetlands were a consistent

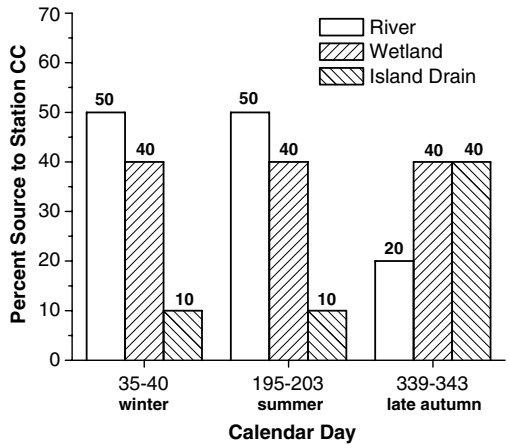

Fig. 10. Results from the simple three parameter model indicating estimated landscape scale sources of DOC exported from the Delta at station CC. Values are rounded to the nearest 10%. Days are numbered from the first day of each year.

source of exported DOC at 40% for all three time periods. These results suggest that wetland and island drain tailwaters provide an important, seasonal addition of DOC exported from the Sacramento–San Joaquin Delta system. Specifically, wetland sources may provide up to ~40% of the DOC exported from the Delta at station CC throughout the year, while wetlands plus island drain tailwaters may be the dominant source of DOC exported during late autumn low flow conditions.

This modeling exercise clearly demonstrates the potential for using molecular-level data to constrain source inputs, the importance of wetland and island DOC sources, and the significant influence of localized landscape features within the Delta on exported DOC. However, in order to optimize future studies incorporating this approach, there are various uncertainties that will need to be addressed. The model's inability to converge during three time periods indicates the presence of either additional significant sources that we did not sample, or diagenetic alteration of S:V and C:V values on the timescale of water transport through the Delta. For instance, it is known that S:V is sensitive to photooxidation (Opsahl and Benner, 1998; Hernes and Benner, 2003), and that S:V and C:V ratios can be altered by sorptive partitioning to mineral surfaces (Hernes et al., 2007). In general, the high turbidity precludes significant light penetration needed for photooxidation; however, as indicated previously, there is some evidence for photooxidation during summer and autumn months. A prior incubation study indicates that microbial degradation of lignin in aqueous environments has no discernible effects on S:V and C:V ratios (Hernes and Benner, 2003).

Nevertheless, the ability to constrain landscape scale sources of DOC at a point in a riverine system represents a major step forward in organic matter source characterization. This type of intermediate scale mass balance could facilitate further study in several disciplines, including (1) the importance of organic matter derived from specific ecosystems, landscapes, or river reaches to carbon processing and export to the oceans; (2) the effects of land-use change on organic matter sources and dynamics; (3) constraining chemical, nutrient, and energy interactions among ecosystems; and (4) intermediate scale DOC cycling within the framework of the river continuum concept (Vannote et al., 1980). When possible and beneficial, inclusion of non-lignin tracer parameters, for example fatty acids, amino acids, or cation signatures, has the potential to further refine results and differentiate among numerous sources.

4.6. Landscape-scale spatial heterogeneity affects Delta organic chemical signatures

Ertel et al. (1986) portrayed rivers as basinwide integrators of organic geochemical processes, and that viewpoint has served as an implicit basis for many riverine organic geochemical investigations, especially those that utilize lignin as a tracer. The present study strongly indicates that localized features within the river system can have a disproportionate influence on riverine DOC compositions, and thus river DOC compositions do not necessarily reflect basinwide integration. Lignin concentration, DOC concentration, carbon-normalized lignin yields, S:V and C:V ratios, and $\delta^{13}C$ values (df = 4)*** all indicate statistically significant differences among Delta habitats. Source signatures from these features appear to alter the composition of DOC as it passes across the Delta, as evidenced by landscape scale source analyses (e.g. Fig. 10) and the apparent lack of gymnosperm lignin at the export station CC during spring samplings despite strong evidence for gymnosperm lignin in the riverine inputs. Localized differences in the relationships between parameters, such as the observed positive correlation between Λ_8 and $\delta^{13}C$ at station IT, and negative correlations between Λ_8 and bioavailability at several, but not all stations, further underscores the importance of landscape scale spatial heterogeneities.

If Delta features are not unique in their ability to influence DOC composition, it follows that DOC signatures may in many cases more closely represent the geochemistry of features local to a given sampling site, rather than an overall, integrated signature. Characterizing landscape scale heterogeneities in DOC signature may therefore be critical to our continued understanding of terrigenous DOC sources and export to the oceans. Our data is consistent with a growing body of literature indicating that the riverine pool of organic matter is much fresher and more dynamic than previously thought (e.g. Kendall et al., 2001; Hernes et al., 2007; Spencer et al., 2007b). If, in fact, a significant portion of riverine DOC export originates from recently photosynthesized sources near the mouth of the river, then this could explain in part the highly reactive nature of terrigenous DOC in marine environments (Hedges et al., 1997) and offer important clues as to the role of terrigenous DOC in supporting coastal foodwebs.

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APPENDIX A

This Appendix presents original data generated during this investigation

Station	Habitat type	Date	Day	DOC (mg L^{-1})	V (μg L^{-1})	S (μg L^{-1})	C (μg L^{-1})	Λ_8 (mg (100 mg OC)$^{-1}$)	Σ_8 (μg L^{-1})	C:V	S:V	$[Ad:Al]_v$	$[Ad:Al]_s$	$\delta\ ^{13}C$
IT	Island drain	12/05/99	339	13.9	5.4	7.5	6.2	0.14	19.1	1.16	1.40	2.13	1.46	−26.9
OM	Open water	12/06/99	340	2.6	4.1	4.6	3.1	0.46	11.7	0.75	1.12	0.91	0.99	−26.6
IV	Island drain	12/06/99	340	20.6	26.8	36.0	20.1	0.40	82.9	0.75	1.34	1.15	0.99	−26.2
RS	River	12/07/99	341	1.9	3.5	3.3	2.4	0.48	9.2	0.68	0.95	0.83	0.98	−27.2
WS	Wetland	12/07/99	341	2.9	3.2	3.5	2.3	0.31	9.0	0.70	1.08	1.02	1.01	−27.0
CP	Channel	12/08/99	342	2.5	4.2	4.3	2.8	0.45	11.4	0.66	1.03	0.89	1.02	−26.9
WM	Wetland	12/08/99	342	2.2	3.4	3.9	2.4	0.44	9.7	0.72	1.15	0.92	0.97	−27.1
CC	Channel	12/08/99	342	2.7	3.8	4.3	2.8	0.40	10.9	0.73	1.15	0.92	1.02	−26.7
OF	Open water	12/09/99	343	2.7	3.4	3.5	2.4	0.34	9.2	0.70	1.03	0.91	1.05	−26.7
RJ	River	12/09/99	343	2.4	2.0	2.4	1.5	0.25	6.0	0.75	1.18	1.00	0.90	−25.8
RS	River	02/24/00	55	2.6	5.5	6.3	2.3	0.54	14.2	0.41	1.15	0.83	0.66	−27.9
WS	Wetland	02/25/00	56	6.0	11.5	14.3	7.8	0.56	33.5	0.68	1.24	0.81	0.95	−27.6
IT	Island drain	03/19/00	79	27.1	22.4	27.5	10.8	0.22	60.6	0.48	1.23	1.41	1.05	−26.6
RJ	River	03/19/00	79	3.0	5.5	4.8	1.7	0.39	11.9	0.31	0.87	1.10	0.97	−26.8
WM	Wetland	03/20/00	80	3.5	6.7	6.8	3.0	0.47	16.5	0.44	1.02	1.17	0.97	−27.4
OM	Open water	03/20/00	80	4.0	7.6	8.4	3.8	0.49	19.8	0.50	1.10	1.05	0.97	−27.4
CP	Channel	03/21/00	81	3.1	6.4	6.8	3.0	0.52	16.2	0.47	1.06	1.02	0.94	−27.2
OF	Open water	03/22/00	82	3.0	6.0	6.8	3.1	0.52	15.9	0.51	1.12	1.03	0.95	−27.2
WB	Wetland	03/22/00	82	4.5	11.6	17.1	8.1	0.81	36.8	0.70	1.48	1.06	0.87	−27.7
CC	Channel	03/23/00	83	4.3	7.2	7.9	3.8	0.44	18.9	0.52	1.09	1.04	0.98	−27.2
CX	Channel	03/23/00	83	2.6	4.7	4.7	2.2	0.45	11.6	0.47	0.99	0.93	0.90	−27.2
WD	Wetland	07/13/00	195	2.9	3.4	5.3	2.7	0.39	11.4	0.80	1.54	0.96	0.69	−28.0
CC	Channel	07/16/00	198	2.2	1.9	1.7	0.9	0.21	4.5	0.50	0.87	1.23	1.02	−26.6
RJ	River	07/16/00	198	2.6	2.9	2.7	1.5	0.27	7.1	0.53	0.92	0.97	0.95	−26.1
CX	Channel	07/17/00	199	1.9	1.8	1.4	0.8	0.21	4.0	0.45	0.82	1.00	0.88	−26.6
WB	Wetland	07/17/00	199	4.3	9.0	13.2	6.2	0.66	28.3	0.69	1.46	1.10	0.90	−27.8
OF	Open water	07/18/00	200	1.8	2.0	1.4	0.7	0.23	4.0	0.36	0.69	1.79	1.47	−26.5
WM	Wetland	07/18/00	200	2.8	4.4	5.7	2.7	0.45	12.8	0.61	1.28	1.70	1.25	−28.3
RS	River	07/19/00	201	1.3	2.2	1.3	0.7	0.33	4.2	0.31	0.59	1.73	1.61	−26.8
WS	Wetland	07/19/00	201	3.8	5.8	5.7	3.0	0.38	14.5	0.52	0.99	1.38	1.17	−27.4
CP	Channel	07/20/00	202	1.3	1.8	1.3	0.6	0.29	3.7	0.35	0.70	1.46	1.27	−26.8
OM	Open water	07/20/00	202	1.6	1.9	1.6	0.9	0.28	4.4	0.49	0.88	1.37	1.08	−26.6
IT	Island drain	07/21/00	203	11.9	16.2	19.0	13.3	0.41	48.6	0.82	1.17	1.27	1.17	−26.3
IS	Island drain	10/15/00	289	15.7	21.5	22.4	15.0	0.38	58.9	0.70	1.04	0.98	1.15	−25.6
RJ	River	10/15/00	289	3.0	3.1	3.5	3.0	0.32	9.6	0.97	1.11	2.86	2.48	−25.5

(*continued on next page*)

Appendix A (*continued*)

Station	Habitat type	Date	Day	DOC (mg L^{-1})	V (μg L^{-1})	S (μg L^{-1})	C (μg L^{-1})	Λ_8 (mg (100 mg OC)$^{-1}$)	Σ_8 (μg L^{-1})	C:V	S:V	$[Ad:Al]_v$	$[Ad:Al]_s$	$\delta^{13}C$
CC	Channel	10/15/00	289	2.3	2.1	1.9	1.0	0.22	5.0	0.47	0.86	1.07	0.92	−26.5
RS	River	10/16/00	290	1.4	2.6	1.6	0.8	0.36	5.0	0.29	0.61	0.97	1.04	−26.6
WS	Wetland	10/17/00	291	3.2	3.6	3.5	2.1	0.29	9.1	0.58	0.97	0.95	0.90	−27.6
CX	Channel	10/17/00	291	1.9	1.7	1.2	0.6	0.19	3.5	0.38	0.69	0.94	0.92	−26.7
WB	Wetland	10/17/00	291	3.0	3.4	4.1	2.0	0.32	9.5	0.57	1.19	1.07	0.92	−27.5
OF	Open water	10/18/00	292	1.8	1.6	1.2	0.6	0.19	3.4	0.38	0.74	1.13	1.02	−26.6
OM	Open water	10/18/00	292	2.0	1.8	1.4	0.8	0.20	3.9	0.43	0.80	1.31	1.12	−26.5
WM	Wetland	10/19/00	293	2.1	2.2	2.4	1.1	0.27	5.7	0.47	1.06	1.01	0.81	−27.1
IT	Island drain	10/20/00	294	8.0	6.8	8.5	4.4	0.25	19.8	0.65	1.25	1.19	0.88	−27.1
CP	Channel	10/20/00	294	1.9	1.7	1.3	0.7	0.19	3.7	0.42	0.75	1.40	1.23	−26.4
RJ	River	02/04/01	35	3.7	2.7	3.3	1.4	0.20	7.5	0.53	1.22	1.14	1.01	−26.1
IS	Island drain	02/04/01	35	39.9	32.4	49.9	28.4	0.28	110.7	0.87	1.54	1.63	1.17	−25.3
CC	Channel	02/04/01	35	4.9	4.4	5.3	2.7	0.25	12.4	0.62	1.20	1.21	1.06	−26.6
RS	River	02/05/01	36	2.3	3.4	3.8	2.1	0.41	9.3	0.62	1.11	1.17	1.23	−27.6
WB	Wetland	02/06/01	37	3.7	6.3	7.5	3.6	0.47	17.4	0.57	1.19	1.55	1.32	−27.6
CX	Channel	02/06/01	37	3.1	5.3	5.3	2.5	0.43	13.1	0.47	0.99	0.99	1.00	−27.5
OM	Open water	02/07/01	38	4.8	7.1	8.5	4.4	0.42	19.9	0.62	1.20	1.06	0.91	−26.8
OF	Open water	02/07/01	38	3.4	5.6	6.0	3.0	0.43	14.6	0.54	1.07	1.01	0.98	−27.3
WD	Wetland	02/07/01	38	4.4	8.9	11.9	6.5	0.62	27.3	0.73	1.34	1.34	1.03	−27.7
IT	Island drain	02/08/01	39	12.8	9.0	11.2	5.4	0.20	25.7	0.60	1.24	1.70	1.13	−27.2
WS	Wetland	02/08/01	39	4.3	6.2	7.8	4.0	0.42	18.0	0.65	1.27	1.04	1.04	−27.3
CP	Channel	02/08/01	39	4.2	6.2	7.3	3.5	0.40	17.0	0.57	1.18	1.66	1.43	−27.2
WM	Wetland	02/09/01	40	4.3	6.3	7.9	3.5	0.41	17.7	0.56	1.26	1.07	0.90	−27.0
RJ	River	05/20/01	140	2.2	2.5	2.0	1.0	0.25	5.4	0.40	0.81	1.24	1.10	−26.6
IS	Island drain	05/20/01	140	21.5	4.7	5.9	4.3	0.07	14.9	0.93	1.25	1.86	1.33	−26.3
WS	Wetland	05/21/01	141	3.4	3.5	3.8	1.8	0.27	9.2	0.52	1.09	1.14	0.99	−27.2
RS	River	05/21/01	141	1.6	1.3	1.1	0.7	0.19	3.0	0.57	0.84	3.21	3.02	−27.1
CP	Channel	05/21/01	141	2.4	2.0	1.6	0.9	0.19	4.5	0.48	0.82	1.13	0.98	−26.7
WB	Wetland	05/22/01	142	4.5	7.7	10.9	4.9	0.52	23.5	0.63	1.41	1.07	0.89	−27.8
CX	Channel	05/22/01	142	2.4	1.9	1.7	0.9	0.19	4.5	0.46	0.87	1.09	0.98	−27.0
WD	Wetland	05/23/01	143	4.0	10.1	15.5	8.2	0.85	33.8	0.82	1.53	0.89	0.74	−28.7
WM	Wetland	05/23/01	143	3.8	7.9	11.6	6.2	0.68	25.7	0.78	1.46	1.02	0.88	−27.9
IT	Island drain	05/24/01	144	17.7	31.5	42.4	29.5	0.58	103.3	0.94	1.35	1.06	0.97	−26.3
CC	Channel	05/24/01	144	3.6	1.3	1.8	1.5	0.13	4.7	1.17	1.35	1.03	0.76	−26.8
OM	Open water	05/24/01	144	2.6	2.6	2.8	1.8	0.27	7.2	0.68	1.09	1.15	0.97	−26.8
OF	Open water	05/25/01	145	2.5	2.2	2.3	1.4	0.23	5.9	0.66	1.08	1.12	0.94	−26.8

Abbreviations and terms are defined within the text.

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