



## The role of hydrologic regimes on dissolved organic carbon composition in an agricultural watershed

Peter J. Hernes<sup>a,\*</sup>, Robert G.M. Spencer<sup>a</sup>, Rachael Y. Dyda<sup>a</sup>, Brian A. Pellerin<sup>b</sup>, Philip A.M. Bachand<sup>c</sup>, Brian A. Bergamaschi<sup>b</sup>

<sup>a</sup> Department of Land, Air and Water Resources, University of California, One Shields Avenue, Davis, CA 95616, USA

<sup>b</sup> United States Geological Survey, Placer Hall MIS 6129, 6000 J Street, Sacramento, CA 95819, USA

<sup>c</sup> Bachand & Associates, Davis, CA 95616, USA

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### Abstract

Willow Slough, a seasonally irrigated agricultural watershed in the Sacramento River valley, California, was sampled weekly in 2006 in order to investigate seasonal concentrations and compositions of dissolved organic carbon (DOC). Average DOC concentrations nearly doubled from winter baseflow (2.75 mg L<sup>-1</sup>) to summer irrigation (5.14 mg L<sup>-1</sup>), while a concomitant increase in carbon-normalized vanillyl phenols (0.11 mg 100 mg OC<sup>-1</sup> increasing to 0.31 mg 100 mg OC<sup>-1</sup>, on average) indicates that this additional carbon is likely vascular plant-derived. A strong linear relationship between lignin concentration and total suspended sediments ( $r^2 = 0.79$ ) demonstrates that agricultural management practices that mobilize sediments will likely have a direct and significant impact on DOC composition. The original source of vascular plant-derived DOC to Willow Slough appears to be the same throughout the year as evidenced by similar syringyl to vanillyl and cinnamyl to vanillyl ratios. However, differing diagenetic pathways during winter baseflow as compared to the rest of the year are evident in acid to aldehyde ratios of both vanillyl and syringyl phenols. The chromophoric dissolved organic matter (CDOM) absorption coefficient at 350 nm showed a strong correlation with lignin concentration ( $r^2 = 0.83$ ). Other CDOM measurements related to aromaticity and molecular weight also showed correlations with carbon-normalized yields (e.g. specific UV absorbance at 254 nm ( $r^2 = 0.57$ ) and spectral slope ( $r^2 = 0.54$ )). Our overall findings suggest that irrigated agricultural watersheds like Willow Slough can potentially have a significant impact on mainstem DOC concentration and composition when scaled to the entire watershed of the main tributary.

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### 1. INTRODUCTION

Carbon cycling research is increasingly driven by issues of temporal/spatial scales and anthropogenic perturbations. A natural confluence in riverine systems for these two drivers are smaller agricultural watersheds, in which dissolved organic carbon (DOC) and particulate organic carbon (POC) export influenced by agricultural practices can be related to field and smaller scales as well as scaled up to the entire river drainage basin. Whereas global car-

bon cycling studies have frequently modeled entire watersheds for large rivers based on integrated constituents at the mouth, research at the sub-watershed scale indicates that local features can exert considerable influence on concentrations (Spencer et al., in press) and compositions of DOC and POC (Eckard et al., 2007; Stepanauskas et al., 2005). Thus to fully understand anthropogenic influences on riverine carbon cycling such as agricultural practices, it is imperative to study those anthropogenic changes at scales appropriate to their influence.

As an example of matching process to scale, several recent studies in the literature have examined long-term data sets to demonstrate that DOC concentrations and export from northern peatlands have been increasing,

\* Corresponding author. Fax: +1 530 752 5262.

E-mail address: pjhernes@ucdavis.edu (P.J. Hernes).

possibly due to long-term climate change and global warming (e.g. Freeman et al., 2004). Riverine DOC concentrations and loads can vary by over an order of magnitude during a single storm (Dalzell et al., 2005; Hinton et al., 1997), between seasons due to precipitation changes or spring melts (Coynel et al., 2005; Raymond et al., 2007; Spencer et al., in press), and between wet and dry years (Burns et al., 2008; Waterloo et al., 2006), thus long-term data sets are needed to capture changes due to long-term perturbations. However, agricultural impacts on riverine DOC are readily observed at short time and spatial scales. DOC concentrations from agricultural areas in a Denmark watershed showed a much stronger relationship to precipitation than that from natural areas over the course of 13 months, indicating fundamental shifts in hydrologic flowpaths and release of DOC from soils (Stedmon et al., 2006). Tile drain waters from individual manured fields that eventually flow into the San Joaquin River in California contain DOC concentrations that are 2- to 3-fold higher than concentrations in the San Joaquin River (Chomycia et al., 2008). Similar drains from agricultural peat islands in the Sacramento River/San Joaquin River Delta (the Delta) in California release DOC into the Delta that can be nearly an order of magnitude greater concentration than Delta waters (Eckard et al., 2007; Kraus et al., 2008; Stepanauskas et al., 2005). In spite of the significant DOC changes observed at the small watershed scale due to agriculture, these changes are not readily apparent at the mouth of the main tributary due to dilution and other factors, thus emphasizing the importance of small sub-watersheds for process-based studies.

In addition to changes in bulk DOC due to anthropogenic perturbations, fundamental questions exist as to the effects of associated compositional changes. Ultimately, the importance of DOC in natural systems is tied to its (bio)reactivity. If agricultural practices mobilize soil organic matter (SOM) that is more or less bioavailable than natural landscapes, then this can have significant ramifications for downstream foodwebs. Although DOC reactivity can be measured directly by a number of techniques, ultimately monitoring compositional changes provides more information about the processes at work. In river systems, for instance, measurements of molecular-level lignin, a polyphenol unique to vascular plants, have proven extremely informative, highlighting compositional changes due to photooxidation (Hernes and Benner, 2003; Opsahl and Benner, 1998), changes in vascular plant content between baseflow and flooding events (Dalzell et al., 2005), source differences between tributaries (Spencer et al., in press), and for discerning individual landscape contributions to bulk DOC (Eckard et al., 2007; Kraus et al., 2008). Mobilization of vascular plant-derived SOM is an important process for determining DOC concentration and compositions, thus lignin biomarkers have the potential to be very useful toward understanding the effects of agricultural practices on stream DOC.

Optical measurements of chromophoric dissolved organic matter (CDOM) have also proven their utility in riverine systems for examining DOC. CDOM absorption

coefficients have been previously related to DOC concentrations in freshwater systems (Baker et al., 2008; Baker and Spencer, 2004). Absorbance-derived measurements have also been related to dissolved organic matter (DOM) composition by examination of the spectral slope parameter ( $S$ ) and specific UV absorbance determined at 254 nm ( $SUVA_{254}$ ). Spectral slope has been shown to vary with the source of CDOM and also its subsequent degradation (Battin, 1998; Blough and Del Vecchio, 2002; Spencer et al., 2007a). A breakdown in molecular weight or decrease in aromaticity of DOM has been shown to result in the spectral slope becoming steeper and conversely DOM of higher molecular weight and greater aromaticity has been shown to have a shallower spectral slope (Blough and Del Vecchio, 2002; Blough and Green, 1995).  $SUVA_{254}$  has been related to the percent aromaticity of DOM with lower values indicative of a lower percent aromaticity and higher values to increasingly aromatic samples (Weishaar et al., 2003).

This study combined bulk, molecular, and optical characterization of DOC in a small agricultural watershed over the course of 2006. Specific goals were to (1) investigate the dominant processes that contribute to the concentration and composition of DOC at the mouth of the watershed, and ultimately, total DOC export, and (2) investigate the use of optical measurements as proxies for molecular measurements.

## 2. METHODS

### 2.1. The Willow Slough watershed

Willow Slough is an agricultural watershed in the Sacramento River valley in California (Fig. 1), with an area of 425 km<sup>2</sup> and a range of land uses representative of the California central valley. Approximately 40% of the watershed contains natural vegetation, predominantly the upper, western portion of the watershed that drains the Coast Range. The remaining 60%, consisting of foothills and alluvial plain, contains mixed agriculture, including rice, orchards, vineyards, row crops, and pasture. Soils vary from generally coarse-textured and well drained soils in the upper watershed, foothills and alluvial plain to increasingly fine textured and more poorly drained soils toward the watershed outlet. Some soils in the lowest elevation of the watershed are saline, indicating high water table conditions. Average annual precipitation in the study area varies from 460 mm in the lower eastern end of the watershed to 860 mm in the Coast Range (Jones and Stokes Associates, Inc., 1996) and occurs primarily from November to April. In summer months, irrigation supplies up to 1070 additional mm's of water in the agricultural portions (Borcalli and Associates, 2000). Irrigation of field crops occurs primarily by furrow irrigation with return waters flowing either onto adjacent fields or back into the channels/canals. Orchards primarily receive spray irrigation with limited runoff. Rice fields are continuously flooded from before or shortly after planting in April to the end of May until about 2 weeks before harvest, typically in mid-September to mid-October.

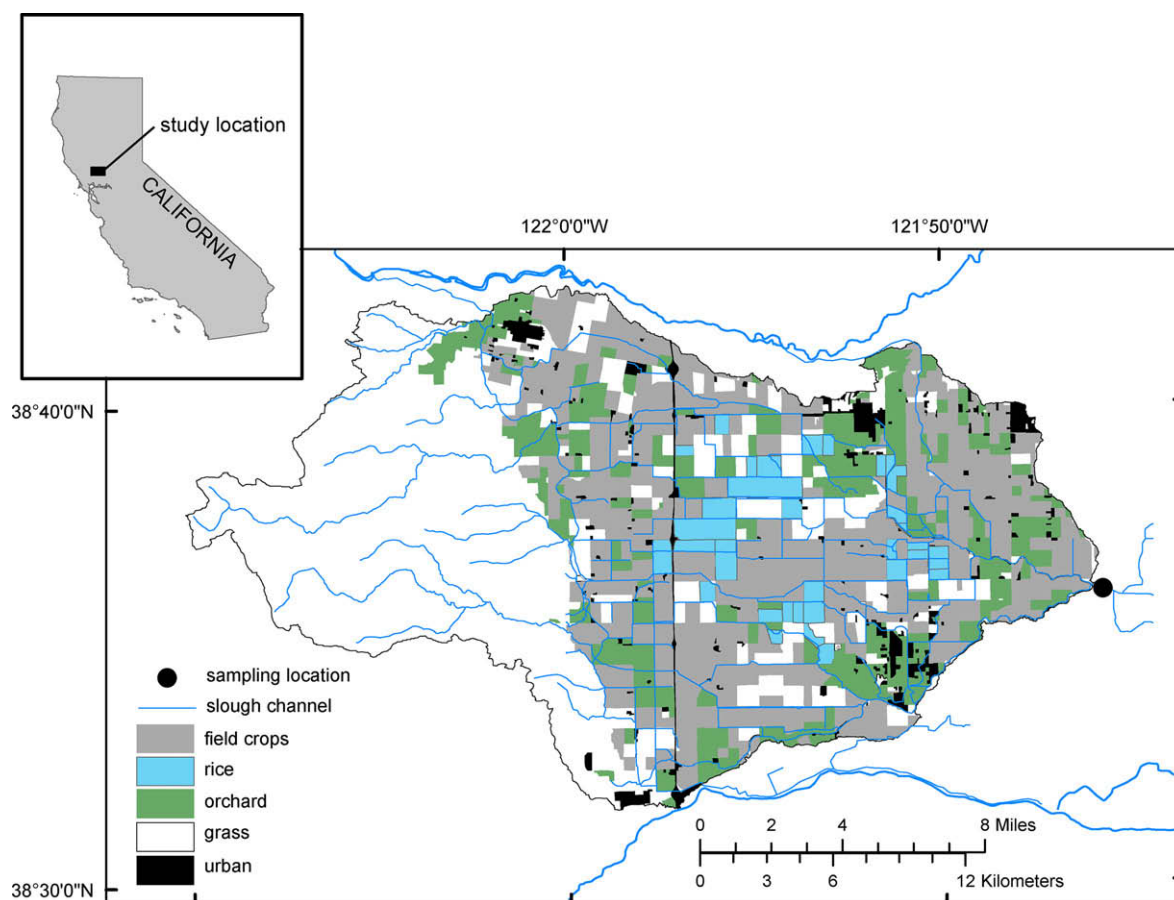


Fig. 1. Map of the Willow Slough watershed.

## 2.2. Water sample collection and processing

Water samples were collected weekly during baseflow from the mouth of the Willow Slough watershed, as well as more intensively during several high flow rainfall-runoff events. The sampling location differed during several weeks of the study due to agricultural management issues (e.g. damming and water diversion), but sites were within one mile of the primary long-term watershed mouth sampling location. Discrete samples from storm events were collected at either 2 or 3 h time intervals, manually or by autosampler. Samples were returned to the laboratory and immediately filtered (pre-combusted 0.3  $\mu\text{m}$  glass-fiber filters, Advantec MFS, Inc.), with DOC samples acidified (pH  $\sim$  2) and refrigerated until analysis, and lignin samples frozen until analysis. Prior to cupric oxide (CuO) oxidation for lignin measurements, 200–250 mL of water was thawed, acidified to pH 2 to minimize precipitation, then rotary evaporated to  $\sim$ 3 mL. The concentrate was then transferred to monel reaction vessels (Prime Focus, Inc.) and dried under vacuum centrifugation in preparation for lignin analysis.

## 2.3. DOC and UV–vis analyses

DOC concentrations were measured on acidified samples (pH  $\sim$  2) with a Shimadzu TOC-5000A high temperature

catalytic oxidation analyzer measuring non-purgeable organic carbon. The mean of 3–5 injections of 100  $\mu\text{l}$  is reported for every sample and precision, described as the coefficient of variance (C.V.), was  $<$ 2% for the replicate injections. Reported values were corrected for the instrument blank, which was measured at the time of analysis (Benner and Strom, 1993). The absorbance values of discrete samples were measured in the laboratory on a Cary 300 spectrophotometer between 200 and 750 nm at constant temperature (25  $^{\circ}\text{C}$ ) in a 10 mm quartz cell. All sample spectra were referenced to a blank spectrum of deionized water and were corrected for an occasional small offset by subtracting the average absorbance between 700 and 750 nm. This small offset can be derived from possible long-term baseline drift or potentially from glass-fiber particles acquired during filtration (Blough et al., 1993). All absorbance data in this manuscript are expressed as absorption coefficients,  $a(\lambda)$ , in units of  $\text{m}^{-1}$ , and were calculated from

$$a(\lambda) = 2.303A(\lambda)/l \quad (1)$$

where  $A(\lambda)$  is the absorbance and  $l$  is the cell pathlength in meters (Green and Blough, 1994). The spectral slope parameter ( $S$ ) was calculated using a non-linear fit of an exponential function to the absorption spectrum:

$$a_g(\lambda) = a_g(\lambda_{\text{ref}})e^{-s(\lambda-\lambda_{\text{ref}})} \quad (2)$$

where  $a_g(\lambda)$  is the absorption coefficient of CDOM at a specified wavelength,  $\lambda_{\text{ref}}$  is a reference wavelength and  $S$  is the slope fitting parameter.  $S$  was calculated over the wavelength range 290–350 nm as previous studies have shown this region to be sensitive to changes in DOM source and processing (Spencer et al., 2007a,b), and, as it is in the short wavelength range, is subject to fewer errors due to higher absorption coefficients at shorter wavelengths.  $\text{SUVA}_{254}$  values were determined by dividing the UV absorbance measured at  $\lambda = 254$  nm by the DOC concentration and are reported in the units of  $\text{L mg C}^{-1} \text{m}^{-1}$  (Weishaar et al., 2003).

#### 2.4. Lignin analyses

Lignin analyses were carried out by CuO oxidation 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 frozen 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 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 five-point calibration scheme of Hernes and Benner (2002). Sensitivity analyses of the calibration curves indicated that optimal quantification is achieved with a vanillin to internal standard ratio of 4:1. 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. Blank concentrations of lignin phenols were low (40–55 ng) for the eight lignin phenols measured in this study (three vanillyl phenols: vanillin, acetovanillone, vanillic acid; three syringyl phenols: syringaldehyde, acetosyringone, syringic acid; and two cinnamyl phenols: *p*-coumaric acid, ferulic acid). Total blanks for these eight

Table 1

Willow Slough discharge ( $\text{m}^3 \text{s}^{-1}$ ), DOC ( $\text{mg L}^{-1}$ ), carbon-normalized lignin phenol yields ( $\text{mg 100 mg OC}^{-1}$ ), absorption coefficient at 350 nm ( $\text{m}^{-1}$ ), and specific UV absorbance at 354 nm ( $\text{L mg C}^{-1} \text{m}^{-1}$ ) for all samples

Date	Disch.	DOC	VAL	VON	VAD	SAL	SON	SAD	CAD	FAD	$a_{350}$	$\text{SUVA}_{254}$
1/10/2006	1.443	3.25	0.058	0.033	0.126	0.060	0.064	0.087	0.026	0.035	6.11	3.42
1/24/2006	1.026	2.93	0.037	0.023	0.049	0.050	0.033	0.048	0.013	0.046	3.66	2.80
1/31/2006	0.813	2.18	0.026	0.015	0.045	0.034	0.020	0.039	0.026	0.032	3.28	2.75
3/9/2006*	5.045	3.59	0.158	0.108	0.222	0.201	0.205	0.275	0.119	0.250	7.74	3.68
SMD*	—	0.04	0.039	0.032	0.028	0.060	0.051	0.033	0.015	0.053	0.16	0.07
3/16/2006	1.770	3.37	0.127	0.091	0.181	0.148	0.144	0.219	0.085	0.161	5.90	3.23
3/23/2006	0.913	2.20	0.057	0.028	0.082	0.045	0.038	0.101	0.038	0.084	3.01	2.71
3/28/2006	5.628	5.70	0.135	0.124	0.198	0.116	0.171	0.172	0.098	0.173	14.41	3.85
3/30/2006	4.990	6.30	0.207	0.148	0.222	0.183	0.197	0.203	0.088	0.165	14.40	3.68
4/6/2006	5.619	5.53	0.209	0.143	0.266	0.197	0.219	0.229	0.109	0.195	14.99	4.10
4/13/2006	25.743	6.65	0.214	0.176	0.217	0.216	0.143	0.218	0.129	0.291	26.25	5.03
4/20/2006	2.718	2.32	0.060	0.039	0.078	0.063	0.054	0.091	0.065	0.091	2.79	2.62
4/27/2006	1.243	2.13	0.055	0.067	0.089	0.082	0.083	0.129	0.049	0.059	2.58	2.51
5/4/2006	0.864	2.07	0.089	0.092	0.111	0.129	0.097	0.134	0.059	0.060	2.95	2.90
5/10/2006	1.646	3.12	0.096	0.078	0.143	0.075	0.090	0.110	0.075	0.133	5.36	2.97
5/18/2006	3.346	4.11	0.136	0.128	0.186	0.099	0.169	0.136	0.103	0.167	7.84	3.06
5/23/2006	3.857	5.26	0.159	0.148	0.190	0.130	0.183	0.186	0.110	0.252	11.50	3.19
6/1/2006	3.253	5.05	0.110	0.083	0.232	0.101	0.162	0.204	0.118	0.234	8.15	2.79
6/15/2006	2.250	5.15	0.101	0.090	0.142	0.079	0.111	0.112	0.062	0.112	8.09	2.64
6/28/2006*	1.572	6.05	0.089	0.061	0.131	0.082	0.102	0.130	0.078	0.149	9.60	2.70
SMD*	—	0.00	0.006	0.007	0.021	0.012	0.018	0.022	0.015	0.024	—	—
7/5/2006	1.287	6.33	0.097	0.080	0.112	0.089	0.102	0.105	0.060	0.077	11.83	3.14
7/11/2006	2.197	7.01	0.070	0.063	0.104	0.059	0.087	0.106	0.060	0.119	11.62	2.77
7/26/2006*	2.264	7.12	0.089	0.065	0.103	0.077	0.085	0.096	0.057	0.091	12.01	2.79
SMD*	—	0.09	0.004	0.001	0.009	0.006	0.009	0.018	0.009	0.017	<0.01	0.09
8/9/2006	2.199	6.40	0.095	0.079	0.101	0.086	0.101	0.092	0.060	0.084	11.09	2.92
9/5/2006	2.766	5.68	0.087	0.062	0.119	0.079	0.105	0.109	0.068	0.123	8.94	2.64
10/11/2006	3.359	3.56	0.077	0.057	0.080	0.078	0.090	0.085	0.051	0.102	5.77	2.69
10/18/2006	2.233	5.19	0.128	0.098	0.145	0.130	0.143	0.165	0.105	0.225	9.00	2.83
11/14/2006	0.998	2.98	0.027	0.017	0.064	0.033	0.041	0.053	0.148	0.022	3.74	2.47
11/28/2006	0.695	2.42	0.026	0.014	0.031	0.027	0.047	0.021	0.028	0.030	3.24	2.49
12/5/2006	0.623	2.76	0.027	0.015	0.037	0.037	0.037	0.038	0.078	0.022	3.19	2.27

Abbreviations: VAL, vanillin; VON, acetovanillone; VAD, vanillic acid; SAL, syringaldehyde; SON, acetosyringone; SAD, syringic acid; CAD, *p*-coumaric acid; FAD, ferulic acid.

\* Sample analyzed in duplicate or triplicate, SMD refers to sample mean deviation.

compounds never exceeded 5% of the Willow Slough yields (average 1.3%).

### 3. RESULTS AND DISCUSSION

#### 3.1. Temporal trends in DOC concentration and CDOM

Over the course of 2006, Willow Slough can be classified according to three hydrologic regimes: winter baseflow (W) in which Willow Slough is dominated by groundwater input (January 1 through February 21, and November 1 through December 31), winter and spring storms (S) in which input is dominated by either overland flow or shallow lateral transport through soils (February 22 through April 27 plus one late storm that affected the May 23 sample), and summer irrigation (I) in which water from adjacent Cache Creek and groundwater pumping is released onto fields and subsequently runs off into Willow Slough (April 28

through October 31, less the May 23 sample). Groundwater contributions to irrigation vary considerably depending on availability of surface water, but in general contribute about half of irrigation waters (Borcalli and Associates, 2000).

Concentrations of DOC at the mouth of Willow Slough varied significantly according to the hydrologic regime, with values during winter baseflow from 2.0 to 3.0 mg L<sup>-1</sup>, then more than doubling to 5.0–7.2 mg L<sup>-1</sup> during storms and summer irrigation (Table 1 and Fig. 2a). In natural systems, DOC concentrations typically vary with the hydrograph, with highest concentrations associated with high discharge (Q) flushing events and lowest concentrations during lowest baseflow Q (Lewis and Grant, 1979; McGlynn and McDonnell, 2003). In this agricultural watershed, such a relationship is observed during the winter and spring when the only significant water input to Willow Slough (typical Q of 0.15–0.85 m<sup>3</sup> s<sup>-1</sup>) is groundwater baseflow

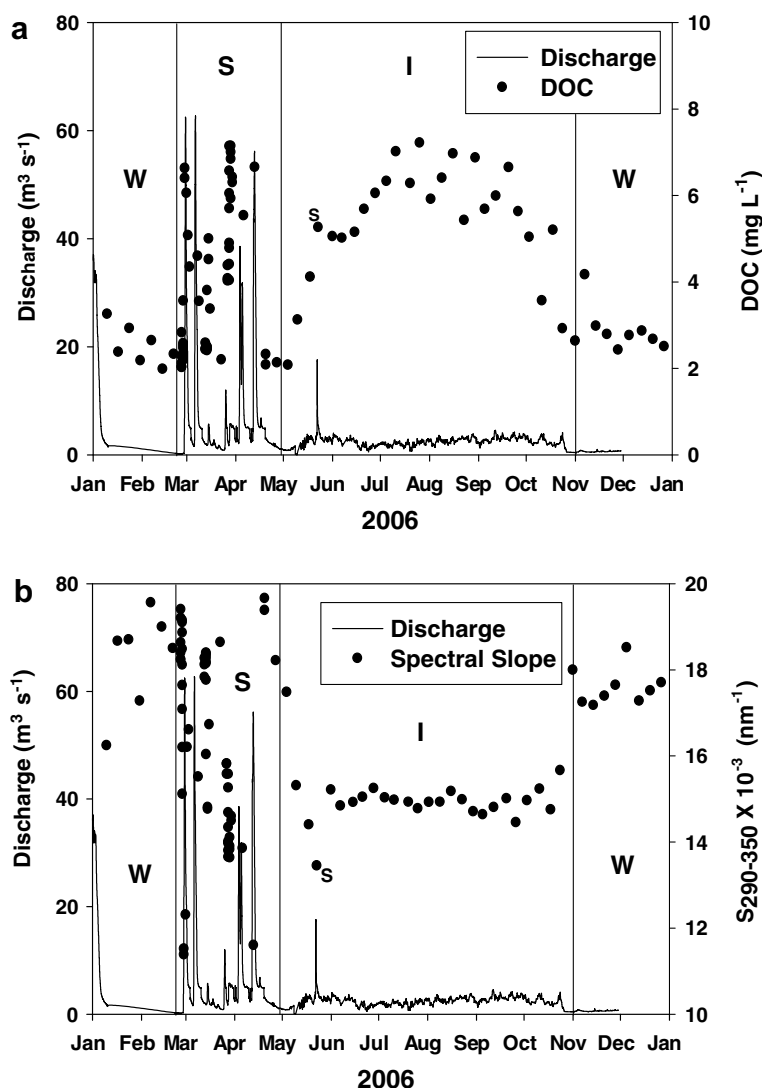


Fig. 2. Relationship between discharge and (a) DOC, and (b) spectral slope during 2006. Portions of the year dominated by winter baseflow are denoted by “W”, storm-influenced by “S”, and summer irrigation by “I”.

or precipitation (in which  $Q$  can be  $>60 \text{ m}^3 \text{ s}^{-1}$ ). However, the relationship does not hold true during summer irrigation in which  $Q$  is moderately elevated over winter baseflow (typical irrigation  $Q$  is  $1.7\text{--}3.4 \text{ m}^3 \text{ s}^{-1}$ ) but DOC concentrations match or exceed those measured during storm  $Q$ 's that are 10- to 20-fold higher. The rationale for the relationship between  $Q$  and DOC concentration in natural systems relates to hydrologic flowpaths, in which high  $Q$  values lead to a saturated vadose zone and water passing through the upper, organic-rich horizons of the soil column, while low  $Q$  values occur when the vadose zone is unsaturated and water flows through the deeper, organic-poor soil horizons (Lewis and Grant, 1979; McGlynn and McDonnell, 2003). At very low flows ( $<1 \text{ m}^3 \text{ s}^{-1}$ ) in three small agricultural watersheds in Illinois, Royer and David (2005) observed increases in DOC as *in situ* primary production became significant, particularly in the summer when there was a high incidence of available light. Although winter baseflow in Willow Slough was similarly low ( $0.15 \text{ m}^3 \text{ s}^{-1}$ ), we did not observe a similar increase in DOC concentration, likely due to significantly lower light availability. During summer irrigation in Willow Slough, return waters from fields are traveling over and through the upper-most horizons of the soil—in essence mimicking storm conditions. Nevertheless, in field runoff samples measured as part of our overall study, DOC concentrations in the runoff is often similar to DOC concentration of the irrigation water (data not shown), indicating that flowpaths/discharge alone may not be sufficient to explain DOC concentrations in agricultural systems that rely on irrigation.

DOC measurements in this small watershed can be put into context of the greater Sacramento River watershed. In a year-long study of the Sacramento River/San Joaquin River Delta (hereafter referred to as the Delta), concentrations of DOC in the Sacramento River across the hydrograph ranged from 1.4 to  $2.6 \text{ mg L}^{-1}$  (Eckard et al., 2007; Stepanauskas et al., 2005), indicating that agricultural watersheds similar to Willow Slough could be a significant

source of additional carbon to the Sacramento River and hence the Delta. The higher DOC concentrations measured in this study during storms and summer irrigation were more typical of concentrations emanating from Delta wetlands ( $2.1\text{--}6.0 \text{ mg L}^{-1}$ ) although still significantly lower than drain waters from agricultural islands within the Delta ( $8.0\text{--}39.9 \text{ mg L}^{-1}$ ) (Eckard et al., 2007; Stepanauskas et al., 2005). The latter, however, consist of organic-rich peaty soils, which could readily explain the higher values.

Optical measurements of DOC can provide insight as to composition and sources (Baker and Spencer, 2004; Spencer et al., 2007a). In aquatic systems, the spectral slope of UV–vis absorbance spectra can be related to molecular weight or aromaticity. A steeper spectral slope signifies lower molecular weight material or decreasing aromaticity, while a shallower spectral slope signifies higher molecular weight material with an increasing aromatic content (Blough and Del Vecchio, 2002; Blough and Green, 1995).  $S_{290-350}$  in this study ranged from  $11.38$  to  $19.66 \times 10^{-3} \text{ nm}^{-1}$ , with mean values during winter baseflow of  $17.90 \times 10^{-3} \text{ nm}^{-1}$  ( $16.24\text{--}19.56 \times 10^{-3} \text{ nm}^{-1}$ ), during irrigation of  $14.95 \times 10^{-3} \text{ nm}^{-1}$  ( $14.40\text{--}15.66 \times 10^{-3} \text{ nm}^{-1}$ ), and storm-influenced means were  $16.36 \times 10^{-3} \text{ nm}^{-1}$  but also encompassed the extreme values on either end of the spectrum ( $11.38\text{--}19.66 \times 10^{-3} \text{ nm}^{-1}$ ; Fig. 2b). Thus, it can be inferred from  $S_{290-350}$  that DOC composition during winter baseflow consists of relatively lower molecular weight material with lower aromaticity than during summer irrigation, while DOC composition during storm regimes can be highly variable due to flushing events.

Another commonly measured optical parameter is the carbon-specific UV absorbance at 254 nm,  $SUVA_{254}$ , which is commonly interpreted as an index of aromaticity (Weishaar et al., 2003). Over the course of 2006 in Willow Slough,  $SUVA_{254}$  varied from 2.27 to  $5.03 \text{ L mg C}^{-1} \text{ m}^{-1}$ , with the highest values during storms (range  $2.51\text{--}5.03 \text{ L mg C}^{-1} \text{ m}^{-1}$ ; average  $3.46 \text{ L mg C}^{-1} \text{ m}^{-1}$ ) while winter (range  $2.27\text{--}3.42 \text{ L mg C}^{-1} \text{ m}^{-1}$ ; average  $2.70 \text{ L mg C}^{-1}$

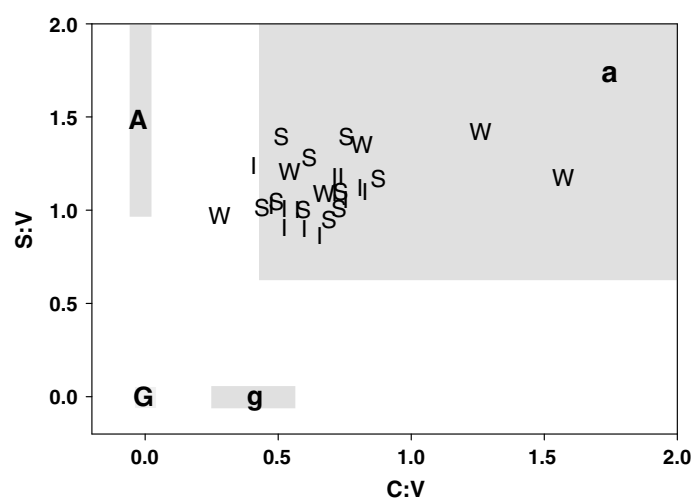


Fig. 3. Plot of S:V vs. C:V for all samples. Winter baseflow samples are denoted by “W”, storm-influenced samples by “S”, and summer irrigation by “I”. Shaded regions indicate traditionally defined endmembers (Hedges and Mann, 1979) as defined by angiosperm woods (A), gymnosperm woods (G), angiosperm nonwoody tissues (a), and gymnosperm nonwoody tissues (g).

$\text{m}^{-1}$ ) and irrigation values (range 2.64–3.14  $\text{L mg C}^{-1} \text{m}^{-1}$ ; average 2.83  $\text{L mg C}^{-1} \text{m}^{-1}$ ) were similar (Table 1). Thus, interpretation of  $\text{SUVA}_{254}$  values would suggest that aromaticity is similar between winter and irrigation flow regimes, which is in contrast to  $S_{290-350}$  interpretations and indicates that the  $\text{SUVA}_{254}$  and  $S_{290-350}$  could be controlled by different processes (Minor et al., 2006). However, together  $\text{SUVA}_{254}$  and  $S_{290-350}$  demonstrate that although DOC concentrations between storm and irrigation hydrologic regimes might be similar, compositionally there are important distinctions as well.

### 3.2. Temporal trends in lignin phenols

The presence of lignin in any organic matter pool is an unambiguous indicator of a vascular plant source to that pool. In addition, syringyl phenols, S, are unique indicators of angiosperm tissues, cinnamyl phenols, C, are unique indicators of nonwoody tissues, while vanillyl phenols, V,

are present in all lignin (Hedges and Mann, 1979). Therefore, plots in S:V vs. C:V space can be used to distinguish between woody and nonwoody angiosperm and gymnosperm sources. In this study, all samples are fairly tightly clustered within the nonwoody angiosperm region of the plot (Fig. 3), indicating a fairly uniform source. This is not unexpected, as the entire watershed is dominated by nonwoody angiosperm vegetation, whether natural or as crops.

Previous studies in large rivers have demonstrated annual or seasonal variation in riverine lignin concentrations. For instance, annual measurements of lignin phenols in the lower Mississippi River from 1990 to 1993 yielded lignin concentrations from 12 to 37  $\mu\text{g L}^{-1}$  (Benner and Opsahl, 2001). Seasonal measurements near the mouth of the Yukon River from 2003 to 2005 showed variation from 2 to 74  $\mu\text{g L}^{-1}$  (Spencer et al., in press), while the Sacramento River varied seasonally from 3 to 14  $\mu\text{g L}^{-1}$  from late 1999 to early 2001 (Eckard et al., 2007). In this study, our

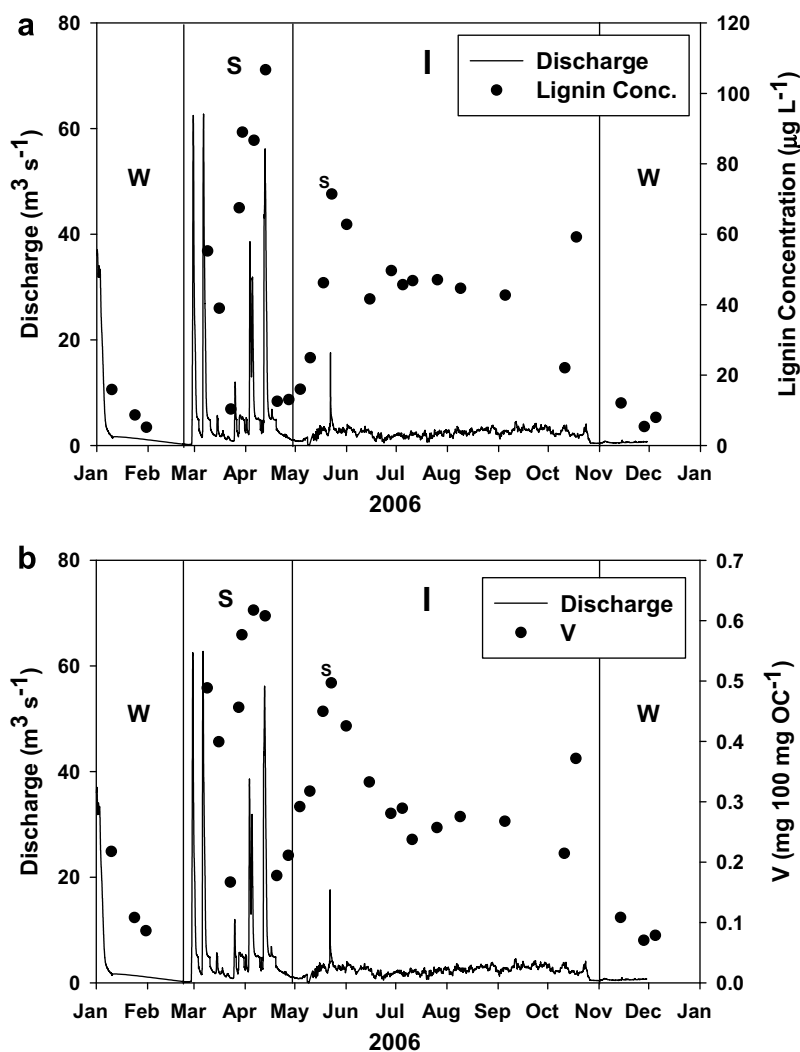


Fig. 4. Relationship between discharge and (a) lignin concentration, and (b) carbon-normalized yields of vanillyl phenols. Only the vanillyl phenols in carbon-normalized yields were included due to variable sources and preferential degradation of syringyl and cinnamyl phenols (Hernes et al., 2007). Portions of the year dominated by winter baseflow are denoted by “W”, storm-influenced by “S”, and summer irrigation by “I”.

higher frequency sampling yielded concentrations ranging from 5 to 107  $\mu\text{g L}^{-1}$  with an average of 40  $\mu\text{g L}^{-1}$  (Fig. 4a), demonstrating that not only are small agricultural watersheds in the Sacramento River valley like Willow Slough potentially significant sources of DOC to the Sacramento River, this DOC also contains considerably higher loads of vascular plant material. As with regional DOC concentrations, the lignin concentrations in Willow Slough are most comparable to agricultural island drains in the Delta, which ranged from 15 to 103  $\mu\text{g L}^{-1}$  (Eckard et al., 2007). A similar sample set from the Big Pine Creek watershed in Indiana (>80% row crop agriculture, no irrigation) also yielded comparable lignin concentrations (estimated at 2–100  $\mu\text{g L}^{-1}$ ) over the course of a year (Dalzell et al., 2007). The implications are that small agricultural watersheds have the capability of exerting considerable influence on mainstem DOC compositions.

Carbon-normalized yields of dissolved lignin phenols can be used to estimate the relative contributions of vascular plant sources to Willow Slough DOC, with higher yields indicative of a greater proportion of vascular plant carbon. A particular point of interest for this study is the source of high DOC concentrations during summer irrigation. If flows from fields do not greatly increase DOC loadings into Willow Slough (relative to incoming DOC loads to fields), then alternate sources must be investigated, including *in situ* algal and plant production (similar to the agricultural systems in Royer and David, 2005) as well as desorption from sediments. Across the hydrograph, carbon-normalized yields of the vanillyl component of lignin, V, ranged from 0.07 to 0.62 mg 100 mg  $\text{OC}^{-1}$  (Fig. 4b). Only vanillyl phenols were included in this analysis due to significant variation in sources and diagenesis of syringyl and cinnamyl phenols relative to vanillyl phenols (Hedges and Mann, 1979; Hernes et al., 2007; Opsahl and Benner, 1995). The highest V values—and therefore the highest vascular plant contributions—occurred during storms, the lowest during winter base-

flow, while the summer irrigation values are only slightly lower than storm values. In essence, carbon-normalized lignin yields mirror and are consistent with  $S_{290-350}$  measurements, indicating higher polyphenolic lignin content in conjunction with greater aromaticity and higher molecular weight DOC during storm and irrigation-influenced hydrologic regimes. Thus, carbon-normalized lignin yields would seem to indicate that the source of the high DOC concentrations during summer irrigation is not algal-derived (3- to 10-fold higher suspended sediments in summer than in winter would seem to preclude significant light penetration), but more likely vascular plant carbon from sources other than irrigation return waters.

Relationships between lignin and suspended particulates hint at one potential driver for the lignin component of DOC. We observed a strong correlation ( $r^2 = 0.79$ ) between lignin concentration and total suspended sediments (Fig. 5), suggesting that lignin concentrations could be controlled in part by partitioning between the solid and dissolved phase. Hernes et al. (2007) and Aufdenkampe et al. (2001) both demonstrated that riverine DOC compositions at the molecular level can largely be explained by sorptive partitioning; this study indicates that DOC loading might be linked to particulates as well. Relationships between DOC and total suspended solids, however, were much weaker than for lignin ( $r^2 = 0.42$ , plot not shown), indicating that this mechanism might only be significant for certain DOC components. In addition, the timing of the suspended sediment and lignin peak concentrations occurred 1–2 months sooner than the peak summer DOC concentrations, further demonstrating that not all DOC components are linked to suspended sediments. Riverine ecosystem function is highly dependent on DOC concentrations and compositions (Findlay and Sinsabaugh, 2003), and one implication of this finding is that agricultural practices that mobilize large amounts of sediments could have far-reaching effects to downstream systems, with the Delta as one example of an impacted system in the California central valley.

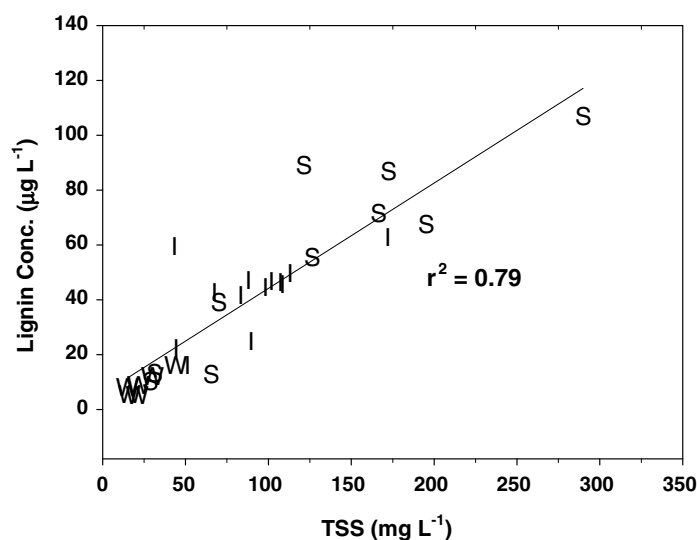


Fig. 5. Relationship between lignin concentration and total suspended sediments (TSS) for all samples.



### 3.3. Lignin compositional relationships to hydrologic flow regimes

In addition to source information, lignin compositional parameters also record diagenetic processing due to the slightly different structures and reactivities of the various lignin monomers. Preferential degradation of aldehydes relative to acids is well-documented in decomposition studies (Hedges et al., 1988; Hernes and Benner, 2003; Opsahl and Benner, 1995) and has led to the general use of vanillic acid to vanillin ratios, (Ad:Al)v, and syringic acid to syringaldehyde, (Ad:Al)s, as relative indicators of the degradation state of different organic matter pools. However, more recent experiments indicate that phase changes such as leaching and sorption result in considerable fractionation of lignin parameters, thus highlighting the importance of restricting comparisons of relative degradation to samples of the same phase (Hernes et al., 2007). In this study, dissolved (Ad:Al)s vs. (Ad:Al)v reveals very intriguing source information, as the composition of winter baseflow samples are readily distinguishable from irrigation and storm samples (Fig. 6a). These compositional differences are even more pronounced in the ketone fraction of lignin, as ratios of vanillic acid to acetovanillone, (Ad:Kn)v, provide greater separation of winter baseflow from storm and irrigation samples (Fig. 6b).

Differences in these lignin parameters emphasize the importance of hydrologic flowpaths toward determining DOC compositions. Observed S:V and C:V ratios (Fig. 3) suggest that the original source of the organic matter in our study is similar, but that winter baseflow samples are more highly processed by either sorption/desorption or by degradation. Such processing is entirely consistent with organic matter deeper in the soil column, which is the likely source of vascular plant material during winter baseflow. Indeed, the strong linear regressions between (Ad:Al)v and (Ad:Al)s for each hydrologic regime would seem to indicate that degradation is an important process in this system, whether as microbial degradation in soils or as photooxidation within the stream channel itself. Both (Ad:Al)v and (Ad:Al)s have been shown to increase significantly with photooxidation (Hernes and Benner, 2003). Conversely, S:V has been shown to decrease with photooxidation (Hernes and Benner, 2003; Opsahl and Benner, 1998), and the relationship between (Ad:Al)v and S:V for the winter baseflow samples is intriguingly consistent with photooxidation (Fig. 6c), whereas storm and irrigation samples show no relationship (plot not shown).

### 3.4. Lignin concentration and carbon-normalized yield relationships to optical measurements

Measurement of molecular biomarkers such as lignin are invaluable in carbon cycling studies in both freshwater and marine systems due to the unambiguous information that they can provide about sources and diagenesis. However, the cost and complexity of making biomarker measurements can be prohibitive in attempting to achieve the spatial and temporal resolution required to adequately characterize dynamic systems. One method of extending

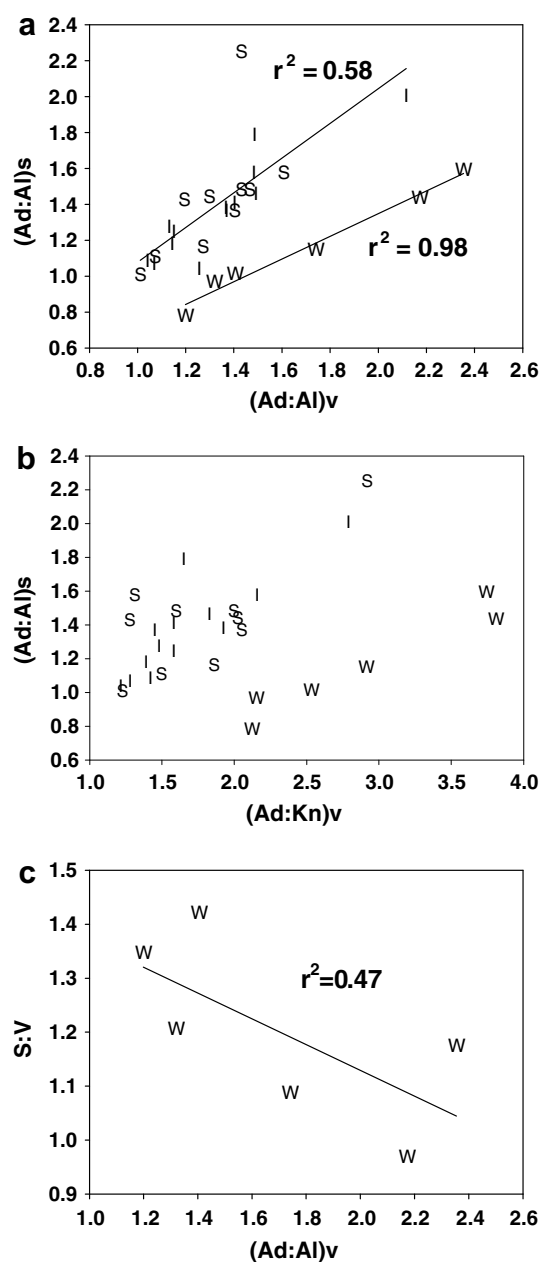


Fig. 6. Lignin compositional relationships to flow regimes, as evidenced by (a) syringic acid to syringaldehyde ratio, (Ad:Al)s, vs. vanillic acid to vanillin ratio, (Ad:Al)v, (b) (Ad:Al)s vs. vanillic acid to acetovanillone ratio, (Ad:Kn)v, and (c) S:V vs. (Ad:Al)v for winter baseflow samples.

biomarker coverage is to develop optical proxies for biomarker concentrations and compositions. For instance, the strong relationship between lignin concentration and the absorption coefficient at 350 nm,  $a_{350}$ , observed in the plume waters of the Mississippi River plume in the spring of 2000 (Hernes and Benner, 2003) was later coupled to satellite absorption measurements to generate a map of lignin concentration, and hence terrigenous DOC, throughout the Gulf of Mexico (Mannino et al., 2007). Such a relationship in marine systems makes intuitive sense, given that it essen-

tially represents a dilution series of lignin-rich waters with lignin-poor water. In this study,  $a_{350}$  varied from 2.58 to 26.25  $\text{m}^{-1}$  (Table 1), and the linear relationship between  $a_{350}$  and lignin concentration was strong ( $r^2 = 0.83$ ; Fig. 7a), indicating a robustness for  $a_{350}$ /lignin concentration relationships even in freshwater systems in which all water sources contain significant concentrations of lignin.

As a direct measure of aromatic carbon, lignin measurements can be compared to optical proxies for aromaticity, namely  $S_{290-350}$  and  $\text{SUVA}_{254}$ . Linear correlations between carbon-normalized lignin and  $S_{290-350}$  ( $r^2 = 0.54$ ; plot not shown) and  $\text{SUVA}_{254}$  ( $r^2 = 0.57$ ; Fig. 7b) are not as strong as for  $a_{350}$  vs. lignin concentrations. CDOM compositional related measurements are typically independent of CDOM concentration (Del Vecchio and Blough, 2004) and so the relationships described here show that lignin is an important component of the dissolved aromatic carbon pool and a central driver behind CDOM compositional measurements.  $\text{SUVA}_{254}$  vs.  $\Lambda_8$  highlights the compositional differ-

ences between the three flow regimes, which plot nearly independent of each other (Fig. 7b). The only exceptions are three storm season samples that also contained low suspended sediments and thus are similar in that regard to winter baseflow.

As a whole, UV-vis data have the most predictive power for lignin concentrations, but less so for lignin compositional information. In contrast, recent efforts at modeling lignin compositional parameters such as  $\Lambda_8$ , S:V, and C:V ratios with fluorescence excitation emissions data have demonstrated strong predictive capability ( $r^2 = 0.86$ , 0.85, and 0.87, respectively) (Hernes et al., 2006). Hence, it appears that not surprisingly, the best coverage can be obtained with multiple analytical tools.

### 3.5. Agricultural impacts on DOC cycling

Understanding anthropogenic impacts on DOC cycling at the watershed and sub-watershed scale is an enormous

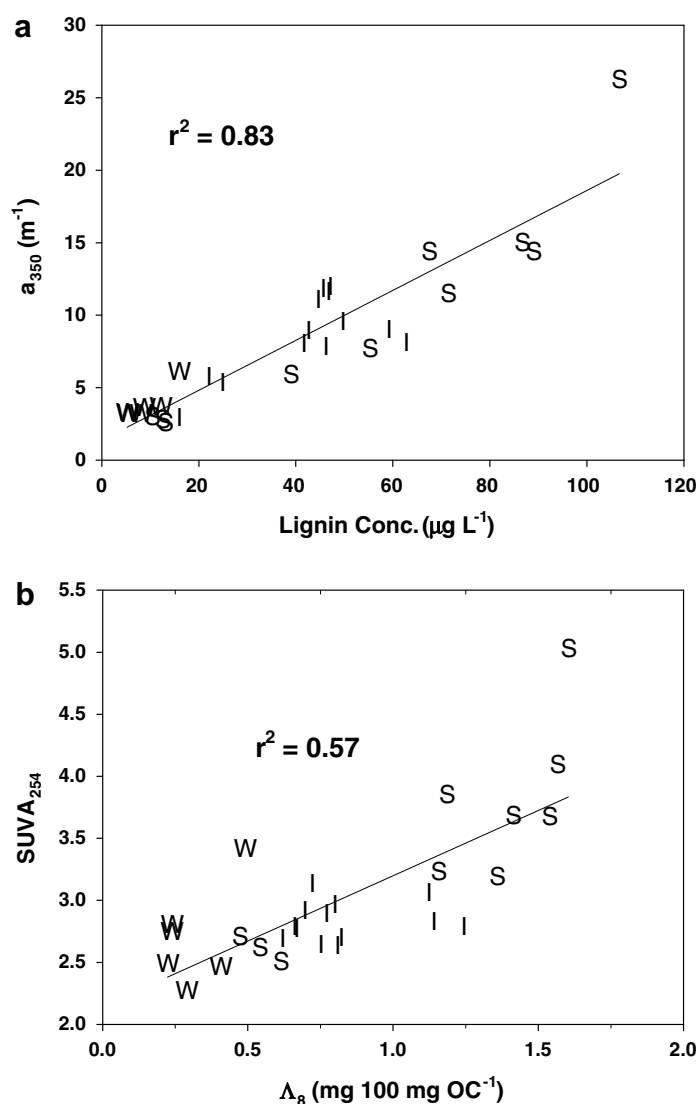


Fig. 7. Relationships between optical properties and lignin. (a) Absorption coefficient at 350 nm vs. lignin concentrations. (b) Specific UV absorbance at 254 nm ( $\text{SUVA}_{254}$ ) vs. carbon-normalized yields of lignin.

challenge. This study demonstrates that DOC concentration and composition are significantly altered by the practice of irrigation, and in part this appears to be driven by hydrologic flow regimes that may not have natural analogs. Based on the strong linear relationship between suspended sediments and lignin concentrations, we hypothesize that DOC compositions might be highly sensitive to agricultural practices and erosive processes that increase the sediment load in streams and rivers. Ultimately, agricultural changes to natural DOC cycling in sub-watersheds like Willow Slough are transmitted downstream to potentially sensitive ecosystems like the Sacramento River/San Joaquin River Delta and San Francisco Bay estuary. Conventional wisdom suggests that mobilization of larger amounts of SOM/vascular plant material will not necessarily support a larger foodweb due to limited bioavailability. However, sorption studies indicate that DOC that looks degraded at the molecular level may, in fact, be relatively fresh material that only appears degraded due to sorptive fractionation (Aufdenkampe et al., 2001; Hernes et al., 2007). Hence, it is paramount to determine the source of increased vascular plant materials, whether from fresh plant leachates or mobilized from aged and degraded SOM pools. Understanding the full impact of sub-watersheds like Willow Slough on the entire watershed will require careful attention to scaling, and one potential tool to help with scaling efforts is the use of rapid and inexpensive optical measurements (Spencer et al., 2007b) that have demonstrated strong relationships with molecular biomarkers such as lignin.

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