



DOM composition in an agricultural watershed: Assessing patterns and variability in the context of spatial scales

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Abstract

Willow Slough, a seasonally irrigated agricultural watershed in the Sacramento River valley, California, was sampled synoptically in order to investigate the extent to which dissolved organic carbon (DOC) concentrations and compositions from throughout the catchment are represented at the mouth. DOC concentrations ranged from 1.8 to 13.9 mg L⁻¹, with the lowest values in headwater 1st and 2nd order streams, and the highest values associated with flood irrigation. Carbon-normalized vanillyl phenols varied from 0.05 to 0.67 mg 100 mg OC⁻¹ (0.37 mean), indicative of considerable contributions from vascular plants. DOC concentrations and compositions at the mouth appear to be primarily influenced by land use (agriculture) in the lower reaches, and therefore very little of the headwater chemistry (1st and 2nd order streams) can be discerned from the chemistry at or near the mouth (3rd and 4th order streams), indicating the need for synoptic sampling to capture the breadth of organic carbon cycling within a catchment. Field sampling during irrigation showed the large impact that flood irrigation can have on DOC concentrations and compositions, likely a primary cause of significantly elevated Willow Slough DOC concentrations during the summer irrigation season. Optical proxies exhibited varying degrees of correlation with chemical measurements, with strongest relationships to DOC and dissolved lignin ($r^2 = 0.95$ and 0.73 , respectively) and weaker relationships to carbon-normalized lignin yields and C:V (r^2 from 0.31 to 0.42). Demonstrating the importance of matching scale to processes, we found no relationship between dissolved lignin concentrations and total suspended sediments (TSS) across all sites, in contrast to the strong relationship observed in weekly samples at the mouth. As DOC concentrations and compositions at the mouth of Willow Slough are closely tied to anthropogenic activities within the catchment, future changes in land-use driven by climate change, water availability, and economic pressures on crop types will also bring about changes in the overall biogeochemistry.

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1. INTRODUCTION

Agriculture in the contiguous United States accounts for 54% of land use (Nickerson et al., 2011), with much located in fluvial settings. As such, agricultural land use exerts a dominant impact on river biogeochemistry that will

continue to evolve with conversion of agricultural land for urbanization, increasing demand for food due to population growth, increasing demand for biofuel feedstock, changes in management practices due to environmental stewardship, changes in soil chemistry due to agricultural practices, and changes due to climate change.

Our ability to forecast changing river biogeochemistry due to changes in agricultural practices and land use is contingent on establishing a baseline understanding of sources and processing within agricultural catchments at multiple

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temporal and spatial scales. The Central Valley of California constitutes one of the most dynamic agricultural systems in the world, with <1% of the agricultural land in the United States producing 8% by value of the nation's agricultural output. The Central Valley has already experienced significant environmental degradation from ~150 years of agricultural practices and land-use changes, and has the potential to be a canary in the coal mine for impacts from climate change and tipping points related to unsustainable practices. Rivers capture snapshot signals of all processes within a catchment through DOC and inorganic concentrations and compositions, and therefore are likely to respond quickly to such changes.

Of the various dissolved constituents in rivers, DOC is arguably the most dynamic in terms of ecosystem function, sources, and reactivity. DOC is the base of the microbial foodweb, a driver of photochemical reactions, actively partitions between the dissolved and particulate phase, contains millions of unique compounds with reactivities of microseconds to decades, and constitutes a major flux of terrigenous carbon to marine systems (Findlay and Sinsabaugh, 2003). In more recent years, DOC has become a drinking water constituent of concern due to its propensity to form EPA-regulated carcinogens upon disinfection for drinking water purposes. In natural systems, increases in DOC concentration over base flow values are most commonly correlated to increases in discharge, with the conceptual model that conditions resulting in increased discharge elevate hydrologic flowpaths within the soil column through organic rich surface soil and litter layers, and connect previously isolated wetlands to discharge channels. In essence, water at high discharge flows through organic-rich soils closer to the surface compared to organic-poor soils at depth during baseflow conditions (Lewis and Grant, 1979; McGlynn and McDonnell, 2003). Agricultural land use with irrigation systems has the potential to disrupt this pattern because by design, hydrologic flowpaths through litter layers and shallow soils in the rooting zone are favored. In contrast, agricultural lands that use tile drains to lower the water table divert hydrologic flow through deeper soils and may decrease DOC concentrations (Dalzell et al., 2011).

This study is a companion to a time-series study of a typical agricultural catchment (Willow Slough) in the Sacramento River valley (Hernes et al., 2008). The previous study took advantage of the integrative nature of riverine constituents by analyzing DOC, molecular-level lignin (a unique tracer of vascular plant organic carbon sources), and UV/visible absorbance on a weekly basis at the mouth of the study catchment. The most significant findings were 2-fold: (1) elevated DOC concentrations were measured during the low-flow irrigation season that runs counter to the more typical pattern of elevation in DOC concentration associated with increases in discharge, and (2) a strong correlation was observed between dissolved lignin concentration and total suspended sediment (TSS) indicative of active partitioning between the dissolved and particulate phase (Hernes et al., 2008). The former demonstrated the impact of agricultural systems on DOC concentrations, but the focus on sampling at the mouth did not allow for establishing linkages between specific land-use/management practices and

elevated DOC. The latter demonstrated the potential for sedimentary loads to impact DOC compositions on the timescale of up to a week (i.e. the average transit time for headwaters to reach the mouth), but left unresolved whether this process is significant at smaller spatial scales. The current study emphasizes a synoptic approach to characterizing the catchment, with an emphasis on understanding how relationships between DOC concentrations and compositions varied spatially throughout the catchment, how those in turn compared to observations at the mouth, and whether relationships between DOC and ancillary measurements (TSS and UV/visible absorbance) were consistent at all spatial scales within the study catchment. The latter is an emerging issue in river biogeochemistry, as prior studies generally focus on either high order rivers or small headwater catchments, but rarely both at the same time, hence functional and interpretive relationships between the two are poorly constrained. This study involved sampling from the field scale, as well as 1st, 2nd, 3rd, and 4th order streams in the Willow Slough catchment during three different hydrologic regimes in an effort to bridge a significant gap in the literature.

2. METHODS

2.1. Willow Slough sampling scheme

Willow Slough is an agricultural catchment in the Sacramento River Valley in California (Fig. 1), with an area of 425 km² and a range of land uses representative of the Central Valley. Approximately 30% of the catchment contains natural vegetation, predominantly the upper, western portion of the catchment that drains the Coast Range. The remaining 70%, 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 catchment are saline indicating high water table conditions. Average annual precipitation in the study area varies from 18 inches in the lower eastern end of the catchment to 34 inches in the Coast Range (Jones and Stokes Associates Inc, 1996) and occurs primarily from November to April. In summer months, irrigation supplies up to 42 additional inches of water in the agricultural portions (Borcalli and Associates, 2000).

Synoptic stream sampling used a nested approach that focused on two primary sub-watersheds that discharge at the mouth, including Willow Slough (WS), which drains the northern catchment, and Dry Slough (DS), which drains the south (Fig. 1). Willow Slough in turn can be subdivided into Willow Slough north (WSN) and Union School Slough (USS) (Fig. 1), the latter which drains the central part of the catchment. WSN and DS are also fed by Cottonwood Slough and Chickahominy Slough, respectively, from the headwaters in the foothills. Baseflow at the mouth is <1 cubic meters per second (cms), with values as low as 0.2 cms, while discharge during spring storms can be >60 cms. Summer irrigation flows are typically 1.5 to

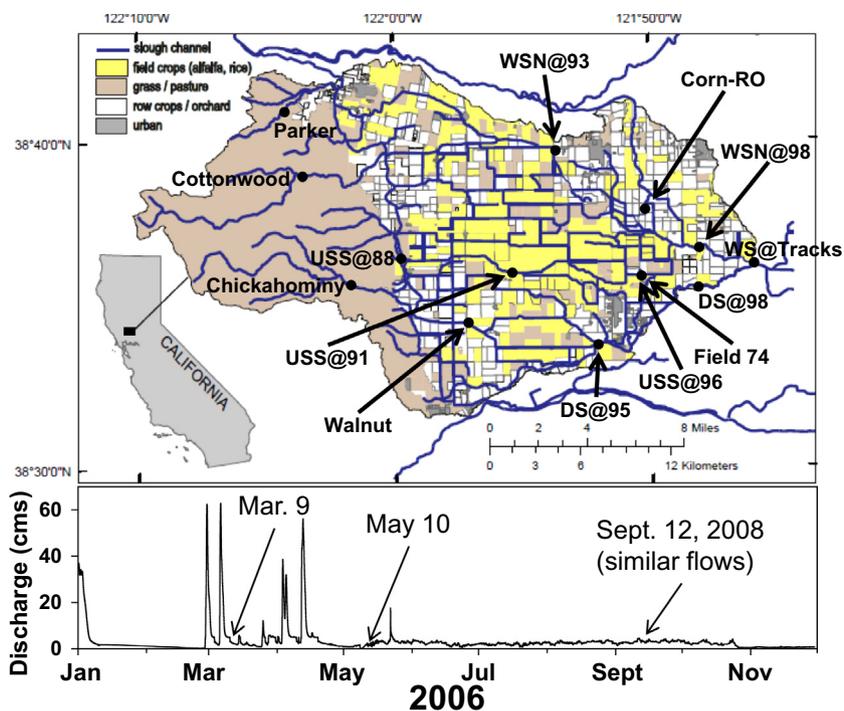


Fig. 1. Map of the Willow Slough watershed with sampling locations indicated by black dots and names corresponding to Table 1. Field 74 and USS@96 are both located under the same dot. Appended to the bottom of the map is a hydrograph for 2006 with sampling dates noted. Sampling conditions for Sept. 2008 were very similar to that shown for Sept. 2006.

4 cms. In general, 2–3 additional upstream sampling locations were included in each sub-watershed to capture contributions from the upper basin dominated by pasture and grasslands, as well as an area of the watershed with intensive flood irrigation for rice and alfalfa. Incoming irrigation water (if present) and the integrated chemistry at the watershed mouth was also sampled during synoptic sampling. Sampling dates were chosen to capture spring/storm-influenced samples in the absence of irrigation (3/9/2006), at the start of the growing season with the onset of irrigation (primarily surface water irrigation, 5/10/2006), and toward the end of the growing season just prior to irrigation reduction (increased contributions from groundwater irrigation, 9/12/2008). Two field samplings were conducted to investigate the impact of land use and irrigation practices on lignin composition and concentration. On 7/24/2007, samples were collected at the inlet and outlet from a furrow-irrigated corn field within the Willow Slough North subcatchment. On 9/30/2007, samples were collected from a flood-irrigated orchard grass field within the USS subcatchment, and included an inlet sample, outlet samples from the eastern and western parts of the field, and a settling pond where the two outlets co-mingled before discharging into USS.

2.2. Water sample collection and processing

All water samples were collected manually from the center of the channel, then returned to the laboratory and immediately filtered (pre-combusted 0.3 μm glass-fiber

filters), with DOC samples acidified (pH \sim 2) and refrigerated until analysis, and lignin samples frozen until analysis. Measurements of total suspended sediments (TSS) were determined gravimetrically on filters (Clesceri et al., 1998).

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 three to five injections of 100 μl is reported for every sample and precision, described as the coefficient of variance (C.V.), was $<2\%$ for the replicate injections. A minimum of 10% of samples were run in duplicate with a requirement of $<5\%$ C.V. Accuracy was verified by inclusion of a standard reference material (caffeine) in every batch at a concentration within 20% of the DOC concentrations in samples in a similar matrix. 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 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, λ_{ref} is a reference wavelength and S is the slope fitting parameter. S was calculated over the wavelength ranges 275–295 nm and 350–400 nm, with the spectral slope ratio, S_R , calculated as the ratio of $S_{275-295}$ to $S_{350-400}$ (Helms et al., 2008).

2.4. Lignin analyses

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 ~3 mL. The concentrate was then transferred to monel reaction vessels (Prime Focus, Inc.) and dried under vacuum centrifugation in preparation for lignin analysis. Lignin analyses were carried out by CuO oxidation following a modified version of that outlined by Hedges and Ertel (1982) and Spencer et al. (2010a). Following oxidation in 8% NaOH in the presence of excess CuO at 155 °C for three hours, samples were acidified and extracted three times with ethyl acetate. Excess solvent was evaporated under a gentle stream of ultrapure nitrogen. Samples were then stored frozen until analysis. Lignin phenols were trimethylsilyl derivatized using bis-trimethylsilyltrifluoroacetylacetamide (BSTFA); separation of phenols was achieved using an Agilent 6890 gas chromatograph fitted with a DB5-MS capillary column (30 m, 0.25 mm inner diameter, J&W Scientific) and equipped with an Agilent 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). Samples were analyzed by GC–MS in batches of twelve with calibration curves generated before and after each batch. All samples were quantified by both calibration curves, and reported values are averages of the two values weighted according to relative sequential proximity to either curve (Spencer et al., 2010a). Sensitivity analyses of the calibration curves indicated that optimal quantification is achieved with a vanillin to internal standard response ratio of 2:1 to 4:1, which corresponds to an amount ratio of 1:1 to 2:1. 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 ten 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 compounds never exceeded 5% of the Willow Slough yields (average 1.3%).

3. RESULTS

3.1. Hydrologic flows

Relative contributions of the two main sub-catchments, WS and DS, to discharge were variable among the sampling dates. On 3/9/2006, flows from these sub-catchments accounted for approximately 60% (5% from USS) and 40%, respectively, of the 5 cms discharge observed at the mouth. Sampling on 3/9/2006 was 72 h removed from a peak discharge of 62 cms during a spring storm, but over the prior 24 h, flows were within 20% of that measured on 3/9/2006, indicating that the catchment had largely returned to pre-storm hydrologic conditions. On 5/10/2006, WS and DS flows accounted for approximately 55% (15% from USS) and 45%, respectively, of the discharge at the mouth. As irrigation season starts, flows can vary considerably as irrigation water demand is met by import of water into the Willow Slough catchment, and ground water pumping. Flows on 5/10/2006 varied from 1 to 2 cms. On 9/12/2008, WS and DS flows accounted for approximately 65% (15% from USS) and 35% of the discharge at the mouth of the Willow Slough catchment, which was approximately 3 cms.

3.2. DOC concentrations, TSS, and optical characterization

DOC concentrations across all samples ranged from 1.1 mg L⁻¹ to >13 mg L⁻¹ (median 3.9 mg L⁻¹), with 9/12/2008 samples roughly 2- to 3-fold higher than the other two sampling periods (Tables 1 and 2). In general, concentrations increased from headwaters toward the mouth within each sub-catchment for all sample dates. In the field runoff samples that were measured for lignin, DOC concentrations were uniformly higher in the outflow than the inflow, increasing from 3.35 mg L⁻¹ to 11.94 mg L⁻¹ and 8.52 mg L⁻¹ in the flood irrigation field (further increasing to 12.16 mg L⁻¹ in the combined settling pond), and furrow irrigation DOC concentrations increased from 7.69 to 10.98 mg L⁻¹ (Table 2). These values are generally representative of values seen in a larger study of several different fields, and time series measurements within the fields (Hernes et al., 2010).

Total suspended sediment concentrations within the sloughs ranged from <10 mg L⁻¹ in headwater catchments to 189.2 mg L⁻¹ in Dry Slough during the storm-influenced sampling period. TSS was lowest during the 9/12/2008 sampling period. In field samples, flood irrigation resulted in a net loss of sediments, as TSS decreased from 67.5 mg L⁻¹ to concentrations <25 mg L⁻¹ in the outflows, while furrow irrigation elevated sediment concentrations, with TSS increasing from 42.3 mg L⁻¹ to over 1 g L⁻¹ (Table 2).

As expected, the absorption coefficient at 350 nm, a_{350} , varied in proportion to DOC concentrations, (Fig 3; Table 1). Carbon-normalized absorbance in the UV range has been correlated to aromaticity (Traina et al., 1990), and UV absorbance at 254 nm normalized to DOC concentrations, SUVA₂₅₄, in this study ranged from 2.40 L mg⁻¹ m⁻¹ in a headwater sample, Cottonwood Slough on 3/9/2006, to 3.79 L mg⁻¹ m⁻¹ in Dry Slough during the same period

Table 1

Select lignin and optical parameters from three synoptic samplings of the Willow Slough watershed. Gaps in the data are a result of either samples not being collected on a given day, samples lost during analysis (USS at 91 and Walnut on 9/12/2008), or samples whose total lignin content did not meet our 1000 ng threshold for inclusion (primarily headwaters).

3/9/2006													
Willow Slough north	Order	DOC	TSS	a_{350}	SUVA ₂₅₄	$S_{275-295}$	$S_{350-400}$	S_R	A_8	Σ_8	S:V	C:V	(Ad:Al) _v
Parker	1	3.93	6.5	6.23	3.06	16.29	19.62	0.83	0.83	32.5	1.09	0.31	2.71
Cottonwood	2	2.07	48.3	2.52	2.40	15.21	18.61	0.82	0.12	2.6	1.13	0.58	2.75
93	3	2.05	216.5	2.68	2.74	15.88	15.15	1.05	0.63	12.9	2.21	0.11	1.30
98	4	3.96	104.0	8.12	3.20	14.22	13.65	1.04	1.29	51.1	1.27	0.61	1.22
Mouth Tracks	4	3.55	118.2	7.84	3.69	14.42	16.82	0.86	1.41	50.0	1.52	0.90	1.64
Weighted average		4.09	124.1	8.74	3.34	14.09	14.17	1.00	1.41	58.1	1.31	0.69	1.19
Union School Slough													
88	2	4.96	42.8	11.96	4.06	14.41	17.72	0.81	1.66	82.2	1.27	0.50	1.96
91	3	3.25	35.1	6.02	3.31	14.36	18.92	0.76	1.22	39.6	1.42	0.56	2.87
96	3												
Dry Slough													
Chickahominy	2	1.99	32.4	3.76	3.16	14.30	15.40	0.93	0.81	16.1	1.06	0.57	2.97
Walnut	2	2.28	28.9	3.54	2.93	16.57	19.84	0.84	0.80	18.2	0.96	0.45	1.99
95	3	3.52	189.2	8.11	3.79	14.30	17.31	0.83	2.29	80.8	1.43	0.97	2.90
98	3	4.28	154.1	9.66	3.55	13.89	14.96	0.93	1.60	68.5	1.38	0.82	1.15
5/10/2006													
Willow Slough north													
Parker	1												
Cottonwood	2												
93	3												
98	4	4.77	106.0	8.49	2.43	13.18	22.83	0.58	1.22	58.1	0.73	0.63	1.13
Mouth Tracks	4	3.12	89.5	5.43	2.98	14.59	19.09	0.76	0.80	25.0	0.86	0.66	1.49
Weighted average		3.80	110.0	6.66	2.66	14.22	19.60	0.76	1.02	41.2	0.89	0.61	1.29
Union School Slough													
88	2	1.84	23.3	2.30	2.54	17.89	17.50	1.02	0.35	6.5	0.74	0.08	1.05
91	3	2.69	32.7	5.05	2.98	14.95	19.15	0.78	1.33	35.8	1.10	0.67	1.47
96	3	4.15	47.1	8.44	3.48	14.71	18.41	0.80	1.83	76.1	1.24	0.87	1.18
Dry Slough													
Chickahominy	2	1.80	1.1	2.33	2.51	15.97	17.96	0.89	0.44	7.9	0.87	0.29	0.73
Walnut	2	2.01	32.7	2.56	2.57	16.91	16.51	1.02	0.64	12.9	1.10	0.38	1.78
95	3	1.89	107.4	3.13	3.16	16.17	15.40	1.05	0.85	16.1	1.05	0.54	1.27
98	3	2.61	114.8	4.43	2.93	15.50	15.65	0.99	0.79	20.6	1.08	0.59	1.48
9/12/2008													
Willow Slough north													
Parker	1												
Cottonwood	2												
93	3	7.35	20.2						0.69	50.4	0.72	0.17	0.51
98	4	8.75	49.9						0.51	44.5	0.87	0.27	0.63
Mouth Tracks	4	7.94	56.3						0.59	47.1	0.78	0.23	0.53
Weighted average		8.37	68.5						0.57	47.4	0.88	0.26	0.60
Union School Slough													
88	2												
91	3												
96	3	13.09	21.4						0.96	125.3	1.04	0.42	0.67
Dry Slough													
Chickahominy	2												
Walnut	2												
95	3												
98	3	7.66	103.2						0.69	52.8	0.89	0.25	0.55

Abbreviations: DOC, dissolved organic carbon; TSS, total suspended sediment; a_{350} , absorption coefficient at 350 nm; SUVA₂₅₄, carbon-specific UV absorbance at 254 nm; $S_{275-295}$, spectral slope between 275 and 295 nm, multiplied by 1000; $S_{350-400}$, spectral slope between 350 and 400 nm, multiplied by 1000; S_R , ratio of $S_{275-295}$ and $S_{350-400}$; A_8 , sum of carbon-normalized yields of eight measured lignin phenols; Σ_8 , sum of concentrations of eight measured lignin phenols; S:V, ratio of total syringyl phenols to total vanillyl phenols; C:V, ratio of total cinnamyl phenols to total vanillyl phenols; (Ad:Al)_v, ratio of vanillic acid to vanillin.

Table 2
Select lignin and optical parameters from field runoff studies.

	Irrigation	DOC	TSS	a_{350}	SUVA ₂₅₄	$S_{275-295}$	$S_{350-400}$	S_R	A_8	Σ_8	S:V	C:V	(Ad:Al) _v
Field 74 Inflow	Flood	3.35	67.5	4.12	2.09	17.88	13.67	1.31	0.46	15.3	0.91	0.49	1.30
E74 Outflow	Flood	11.94	12.4	20.13	2.55	13.65	15.11	0.90	1.60	191.7	1.27	0.68	1.07
W74 Outflow	Flood	8.52	6.3	15.23	2.76	13.81	15.11	0.91	1.75	149.5	1.40	0.59	0.80
Field 74 Settling Pond	Flood	12.16	23.1	20.56	2.57	13.88	15.29	0.91	1.41	171.5	1.22	0.56	1.15
Corn-RO Inflow	Furrow	7.69	42.3	11.25	2.38	14.88	15.81	0.94	0.69	53.4	1.11	0.40	0.90
Corn-RO Outflow	Furrow	10.98	1017.0	20.68	2.85	13.76	15.81	0.87	0.55	60.4	0.90	0.29	1.10

Abbreviations: DOC, dissolved organic carbon; TSS, total suspended sediment; a_{350} , absorption coefficient at 350 nm; SUVA₂₅₄, carbon-specific UV absorbance at 254 nm; $S_{275-295}$, spectral slope between 275 and 295 nm, multiplied by 1000; $S_{350-400}$, spectral slope between 350 and 400 nm, multiplied by 1000; S_R , ratio of $S_{275-295}$ and $S_{350-400}$; A_8 , sum of carbon-normalized yields of eight measured lignin phenols; Σ_8 , sum of concentrations of eight measured lignin phenols; S:V, ratio of total syringyl phenols to total vanillyl phenols; C:V, ratio of total cinnamyl phenols to total vanillyl phenols; (Ad:Al)_v, ratio of vanillic acid to vanillin.

(Table 1), indicating highly aromatic material. Values were higher during the spring-influenced period, 3.31 L mg⁻¹ m⁻¹ on average, than during summer irrigation, 2.84 L mg⁻¹ m⁻¹ (Table 1).

Spectral slopes and spectral slope ratios have been linked to low vs. high molecular weight DOM (Helms et al., 2008). In this study, $S_{275-295}$ ranged from 13.2 to 17.9 nm⁻¹, $S_{350-400}$ ranged from 13.6 to 22.8 nm⁻¹ and S_R varied from 0.58 to 1.31 with no clear trends between sampling periods (Table 1).

3.3. Lignin concentrations and compositions

Within the two primary sub-catchments, significant differences exist in lignin concentration along the drainage flowpath. For example, on 3/9/2006 lignin concentrations varied from 2.6 µg L⁻¹ in the foothills to 51.1 µg L⁻¹ near the mouth in the WSN subdrainage, from 39.6 to 82.2 µg L⁻¹ from the foothills to the confluence in the USS tributary to WSN, and 16.1 µg L⁻¹ in the foothills to 80.8 µg L⁻¹ near the mouth in the DS sub-catchment (Table 1). The concentration at the mouth was 50 µg L⁻¹, which represents an integration of all sources and processes within the sub-catchments. On 5/10/2006, concentrations ranged from 6.5 µg L⁻¹ to 76.1 µg L⁻¹ among the sub-catchments (25 µg L⁻¹ at the mouth), representing baseflow conditions. The highest lignin concentrations were measured during summer irrigation on 9/12/2008, ranging from 44.5 µg L⁻¹ to 125.3 µg L⁻¹ among all sites (47.1 µg L⁻¹ at the mouth).

Carbon-normalized yields of lignin, A_8 , an indicator of the relative contributions of vascular plant sources to the total carbon, varied from 0.12 mg 100 mg OC⁻¹ in the headwaters to 2.29 mg 100 mg OC⁻¹ in Dry Slough during the spring sampling (Table 1). In general, A_8 progressively decreased from spring through summer to fall and was higher in USS and DS than WSN (Table 1).

Lignin compositional information can be used to decipher source and processing information. While vanillyl phenols (V) are present in all vascular plant tissues, syringyl phenols (S) are only present in angiosperms, and cinnamyl phenols (C) are only present in nonwoody tissues (Hedges and Mann, 1979), hence plots of S:V vs. C:V differentiate between angiosperm vs. gymnosperm sources and woody

vs. nonwoody tissues. In this watershed, angiosperm sources are dominant, and dissolved lignin composition was consistent with primarily nonwoody tissues (Table 1, Fig. 2). Spring samples from March in general had higher S:V ratios (average = 1.34, $n = 11$) than summer irrigation samplings (average = 0.91, $n = 14$), and somewhat higher C:V ratios (0.58 vs. 0.44) (Fig. 2). Increased acid:aldehyde ratios are generally indicative of greater relative degradation in samples with physical connectivity. In this study, ratios of vanillic acid to vanillin, Ad:Al_v, ranged from 0.51 to 2.97 with generally higher values in the headwaters. Seasonally, the fall irrigation samples from September had by far the lowest Ad:Al_v values, with an average of 0.58 ($n = 5$) compared to irrigation onset in May (1.25; $n = 9$) and spring samples from March (2.13; $n = 11$).

Field irrigation practices had variable effects on lignin concentrations. While lignin concentrations only increased by ~10% in the furrow-irrigated field from 53.4 µg L⁻¹ to 60.4 µg L⁻¹, concentrations increased dramatically in the flood-irrigated fields, from 15.3 µg L⁻¹ at the inlet to as high as 191.7 µg L⁻¹ at the outlet (Table 2). In the field runoff study, A_8 values increased 3 to 4-fold between inflow and outflow for flood irrigation (0.46 mg 100 mg OC⁻¹ increasing to 1.41–1.75 mg 100 mg OC⁻¹), while decreasing slightly between inflow (0.69 mg 100 mg OC⁻¹) and outflow (0.55 mg 100 mg OC⁻¹) in the furrow irrigation samples.

Lignin compositional parameters for irrigation runoff samples were most similar to May samplings, with an average S:V = 1.13, C:V = 0.50, and Ad:Al_v of 1.05 (Table 2). As with A_8 values, compositional parameters trended the opposite direction between inflow and outflow for flood vs. furrow irrigation. Whereas flood irrigation exhibited increases in S:V and C:V with a decrease in Ad:Al_v between inflow and outflow, the furrow irrigation samples indicated a decrease in S:V and C:V while Ad:Al_v increased.

4. DISCUSSION

4.1. DOC concentration and composition as a function of stream order

Although river DOC signatures represent an integrated signal of all catchment sources and processing, not all sources and processes are equally represented, as the

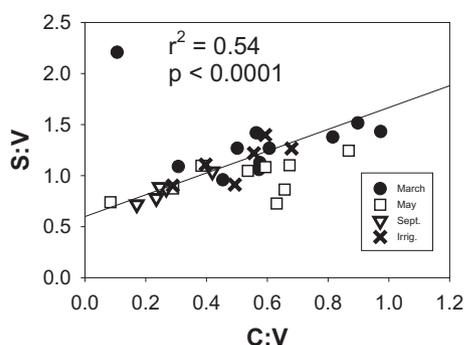


Fig. 2. Plot of S:V vs. C:V for all samples.

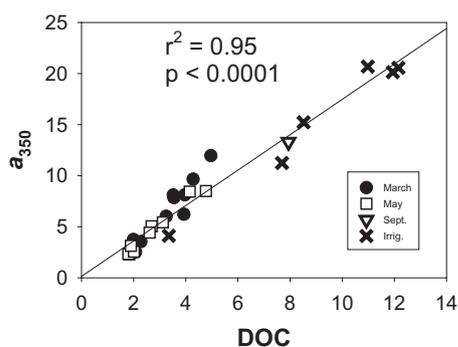


Fig. 3. Relationship between the absorption coefficient at 350 nm vs. DOC for all samples.

riparian zone has a stronger influence on river chemistry than more distant areas (Findlay et al., 2001), and DOC from local landscape features can overwhelm the upstream signature (Eckard et al., 2007; Kraus et al., 2008; Dalzell et al., 2011). Averages across the entire data set by stream order, while not a perfect representation of spatial scales or loads, clearly demonstrates the extent to which headwater signatures (often represented by 1st, 2nd, and 3rd order streams, but in this study better represented by 1st and 2nd order) are “overwritten” as they merge into 3rd and 4th order streams (Table 3). Of the various bulk, optical, and lignin parameters measured or calculated in this study, concentrations (or indications of concentrations like a_{350}) all exhibited statistically significant differences between the 1st and 2nd order streams combined and either 3rd and 4th combined or just 4th order streams, while indicators of composition were much less likely to show statistically significant differences, with the notable exceptions of spectral slope between 275 and 295 nm, $S_{275-295}$, and the lignin (Ad:Al)_v parameter (Table 3). The systematic increase in DOC concentration with higher stream order is consistent with that observed in a midwestern agricultural catchment/basin (Dalzell et al., 2011). It is rather surprising that more compositional differences are not evident, as the significant increase in concentrations, and hence loads, at the 3rd and 4th order sites must come from different local (agricultural) sources compared to headwater DOC, which stems primarily from native grasslands. In essence, the

lignin source signatures are nearly identical, the proportion of DOC that is made up of lignin and aromatic compounds is similar, but the (Ad:Al)_v and $S_{275-295}$ parameters (both higher in the headwaters) are consistent with DOC in the headwaters that is more heavily processed, although notably, increased (Ad:Al)_v in DOC has not been observed in microbial incubations (Hernes and Benner, 2003; Pellerin et al., 2010). However, at least in this catchment it is apparent that headwater DOC dynamics cannot be inferred from DOC concentrations and compositions measured at the mouth, despite the integrative nature of the latter. As with Eckard et al. (2007), we would conclude that riverine DOC biogeochemistry must be interpreted within the context of local landscape features.

4.2. Land use as a determinant of lignin concentrations and compositions

Increases in DOC concentrations tied to anthropogenic activities are well-documented in both urban (Sickman et al., 2007) and agricultural settings (Royer and David, 2005; Dalzell et al., 2007; Hernes et al., 2008). Whereas in most natural systems DOC concentration are positively correlated to discharge (with significant wetland coverage or discharge <1 cms as typical exceptions, Eckhardt and Moore, 1990; Royer and David, 2005), we have previously documented that the high DOC concentrations at the mouth of Willow Slough occur in conjunction with relatively low discharge associated with summer irrigation (Hernes et al., 2008). Our synoptic and field runoff data suggest that DOC runoff from irrigated agricultural sub-watersheds (3.0–13.0 mg L⁻¹) could be largely responsible for the high DOC concentrations during summer, while greater relative contributions of DOC from headwater sites result in lower DOC concentrations during winter baseflow periods (1.8–2.0 mg L⁻¹). Our results clearly indicate that agricultural impacts are non-uniform, and highly dependent on the effects of different irrigation methods as well as cropping type. For example, the highest DOC concentration measured occurred in Union School Slough (USS), the sub-catchment with the highest proportion of agricultural land subject to flood irrigation (see Fig. 1). Even within the same crops, differing management practices can have a large impact. For example, rice fields in nearby watersheds that incorporate straw into the soil export water with DOC concentrations 50–500% greater during winter flooding and early growing season than fields that have had the straw burned off (Ruark et al., 2010).

Lignin concentrations and compositions—and by inference any number of dissolved organic constituents—are also tied to land use. Lignin concentrations increased ~10-fold between inflow and outflow in the flood-irrigated field 74, and by 13% in the furrow-irrigated corn field (Table 2), demonstrating net export of lignin from agricultural fields. However, changes in carbon-normalized yields clearly indicate differential impacts on the overall DOC composition, as the proportion of lignin increased 3- to 4-fold in flood-irrigated field 74 (0.46 mg 100 mg OC⁻¹ increasing to 1.60 and 1.75 mg 100 mg OC⁻¹), but decreased by ~20% in the corn field (Table 2), suggesting

Table 3

Bulk, lignin and optical averages by stream order. *p*-Values calculated by Mann Whitney *U*.

Order	DOC	TSS	a_{350}	SUVA ₂₅₄	$S_{275-295}$	$S_{350-400}$	S_R	A_8	Σ_8	S:V	C:V	(Ad:Al) _v
1&2	2.61	26.99	4.40	2.90	15.94	17.89	0.90	0.71	22.36	1.03	0.40	1.99
3	4.78	94.69	5.94	3.24	14.97	16.87	0.90	1.17	52.63	1.23	0.54	1.40
4	5.35	87.33	7.47	3.07	14.10	18.10	0.81	0.97	45.97	1.00	0.55	1.11
1&2 v 3&4 <i>p</i> -value	0.013	0.002	0.047	0.135	0.025	0.384	0.678	0.086	0.009	0.669	0.157	0.049
1&2 v 4 <i>p</i> -value	0.02	0.001	0.073	0.57	0.048	1	0.57	0.345	0.029	0.573	0.228	0.043

Abbreviations: DOC, dissolved organic carbon; TSS, total suspended sediment; a_{350} , absorption coefficient at 350 nm; SUVA₂₅₄, carbon-specific UV absorbance at 254 nm; $S_{275-295}$, spectral slope between 275 and 295 nm, multiplied by 1000; $S_{350-400}$, spectral slope between 350 and 400 nm, multiplied by 1000; S_R , ratio of $S_{275-295}$ and $S_{350-400}$; A_8 , sum of carbon-normalized yields of eight measured lignin phenols; Σ_8 , sum of concentrations of eight measured lignin phenols; S:V, ratio of total syringyl phenols to total vanillyl phenols; C:V, ratio of total cinnamyl phenols to total vanillyl phenols; (Ad:Al)_v, ratio of vanillic acid to vanillin.

that a larger proportion of other biochemicals is added in corn fields.

The overall dominance by angiosperm vegetation in the WS catchment (oak savannah and grasslands in the headwaters, orchards, alfalfa, grasses, and other angiosperm crops in the eastern two thirds) is reflected in lignin compositional parameters, as all samples contained a significant component of syringyl phenols and in general were consistent with nonwoody tissues at various stages of degradation (Fig. 2). The positive S:V intercept highlighted by linear regression is suggestive that cinnamyl phenols are degraded preferentially to syringyl phenols, which makes intuitive sense when considering that the most likely syringyl-rich, cinnamyl-free endmember would be wood. This is also consistent with the previous finding that cinnamyl phenols are frequently ester-bound to lignin polymers as opposed to incorporation through C–C or ether linkages (Opsahl and Benner, 1995). Identifying trends between sampling dates is complicated by the small number of samples for each date, but Sept. samples plotting farther to the left on the degradation trajectory than March or May is consistent with the tail end of the summer growing season when many crops are harvested and grasslands are parched from summer heat. Similar to carbon-normalized lignin yield differences in the irrigation samples, trends between the inflow and outflow in S:V and C:V in the corn field are opposite of the flood irrigation field. Namely, outflow samples from the flood irrigated field contained fresher signatures with higher S:V and C:V values (20–50% greater) than inflow, while S:V and C:V exported from corn fields appeared more degraded (20–25% lower) than inflows (Table 2). This difference could result from direct leaching of DOC from live and senescent plant materials in flood irrigation vs. leaching of degraded soil organic matter during furrow irrigation. This interpretation is also supported by acid:aldehyde ratios, which were lower in flood irrigation outflows than inflows, but higher in the furrow-irrigated corn field outflow than inflow.

4.3. Optical relationships to lignin concentrations and compositions

CDOM absorbance is largely governed by aromatic, phenolic, and other unsaturated organic compounds, therefore if polyphenolic lignin is representative of these

compounds, strong correlations between lignin concentrations and compositions and various optical measurements are expected. Strong linear relationships between lignin concentration and the absorption coefficient at 350 nm have previously been demonstrated in other riverine systems for sampling at the mouth (Hernes and Benner, 2003; Hernes et al., 2008; Spencer et al., 2009). This study extends this relationship in river systems down to the field scale, indicating that the relationship is likely controlled by source contributions rather than environmental processing such as photolysis or microbial degradation (Fig. 4a).

Various parameters generated from CDOM spectra have been linked to compositional characteristics of the CDOM fraction. The spectral slope, $S_{275-295}$, is typically used as a relative indicator of molecular size, with higher $S_{275-295}$ associated with lower molecular weight CDOM and lower $S_{275-295}$ with higher molecular weight CDOM (Helms et al., 2008). Dalzell et al. (2011) observed increasing molecular weight (via size exclusion chromatography) with increasing stream order and DOC concentration in a midwestern agricultural basin and attributed the increase in downstream DOC concentration to more terrestrial sources as opposed to microbial DOC that can dominate in headwater baseflow. In this study, we found a weak ($r^2 = 0.30$) but significant ($p = 0.004$) relationship between $S_{275-295}$ and DOC concentration (plot not shown) that similarly indicates increasing molecular weight with increasing DOC concentration. Lignin data in our previous study indicated that increases in DOC concentration over baseflow were driven by vascular plant sources, and hence an inverse correlation between $S_{275-295}$ (as a proxy for molecular weight) to polymeric lignin is intuitive (Fig. 4b). Although it is unlikely that lignin polymers alone are abundant enough to drive this trend, they clearly mark the presence of other high molecular weight compounds associated with a higher proportion of vascular plant source materials. Further insight into the relationship between $S_{275-295}$ and lignin is evident by a significant, but weaker, negative correlation between $S_{275-295}$ and C:V (Fig. 4c). If C:V is a proxy for the degradation state of lignin in this system, then higher C:V ratios would imply fresher lignin and presumably a higher degree of polymerization, hence higher molecular weight. Diagenesis preferentially removes cinnamyl phenols relative to vanillyl phenols (Opsahl and Benner, 1995), hence C:V decreases as lignin polyphenols are degraded, producing

lower molecular weight material. One interpretation, then, would be that the relationship between $S_{275-295}$ and carbon-normalized lignin yields is driven by degradation more than source in this agricultural system.

Finally, carbon-normalized UV absorbance has been previously correlated to aromaticity (Traina et al., 1990), and therefore would be expected to correlate to carbon-normalized aromatic lignin. We found a significant positive correlation between the two (Fig. 4c), although lignin only explains 42% of SUVA₂₅₄, again indicating the presence of another significant and variable source of aromatic or unsaturated dissolved organic compounds.

4.4. The sum is more predictable than the parts – except when it is not

It is apparent from various river biogeochemistry studies that scale can be a significant factor in determining what is observed. For example, higher order rivers capture signals integrated over a larger area and time than small order streams, and by smoothing out variability, fairly robust relationships can emerge. In this study, the correlation between a_{350} and DOC is robust across all scales (Fig. 3) and compares well to the a_{350} vs. DOC correlation observed at the mouth in the companion study (Hernes et al., 2008), and in fact, to high order rivers at all latitudes (Hernes and Benner, 2003; Spencer et al., 2009, 2010b). Relationships between UV absorbance and DOC in low order headwater streams are much less common in the literature. However, two such examples for a 1st order stream at Hubbard Brook and a moorland catchment in the UK (Spencer et al., 2012; Stutter et al., 2012) indicate that such relationships are likely common at all scales.

Unlike the robust relationships for a_{350} and DOC at all scales in Willow Slough, dissolved lignin concentration vs. TSS proved to be highly dependent on scale, with a strong correlation at the mouth ($r^2 = 0.79$; Hernes et al., 2008), but essentially no relationship at smaller scales from this synoptic study (Fig. 5). If this relationship is driven by sorptive partitioning (Hernes et al., 2007), then the presence or absence of this relationship is dependent on sufficient contact time, and the implication is that at least one week (total transit time in Willow Slough) is needed in order to equilibrate. If the relationship is driven by coupled sediment/DOC sources, then the relationship at the mouth may be driven by local landscape features that override the headwater signatures.

Another demonstration of the dependence of observations on scale is shown in the relationship between carbon-normalized lignin yields and C:V, for which there was no significant correlation at the mouth ($r^2 = 0.05$), but in this synoptic study throughout the catchment, we observed a positive correlation between these two lignin parameters that was highly significant (Fig. 6). Further, the positive trend is apparent when considering any of the March, May, or September samples by themselves, and does not appear to be driven by location. Interestingly, this trend was also significant ($r^2 = 0.69$) for high-molecular weight DOC in the agricultural Big Pine Creek catchment (865 km²) in Indiana during a synoptic study that incorporated both flood stage and baseflow (regression generated from Table 6 in Dalzell et al., 2005). Similar to the relationship between C:V and $S_{275-295}$, this is likely driven by degradation, as both carbon-normalized yields and C:V would be expected to decrease with increasing degradation. The fact that this trend is not exhibited in the time-series mouth

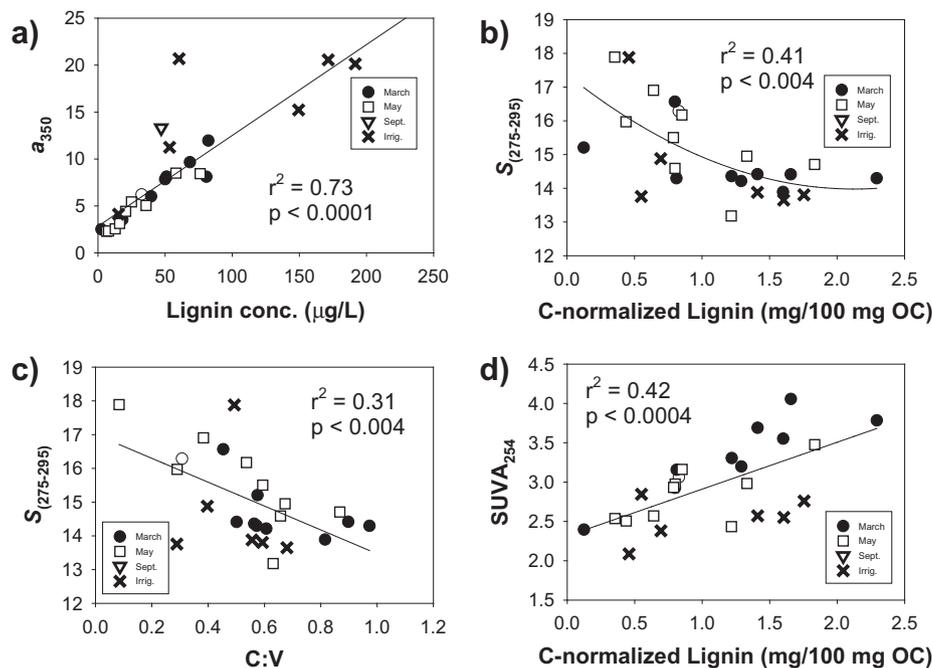


Fig. 4. Relationship between optical measurements and lignin measurements for all samples, including (a) the absorption coefficient at 350 nm and lignin concentration, (b) the spectral slope between 275 and 295 nm multiplied by 1000, $S_{275-295}$, and carbon-normalized lignin yields, (c) $S_{275-295}$ and C:V, and (d) SUVA₂₅₄ and carbon-normalized lignin yields.

samples suggests that the degradation signature is imprinted primarily in the soils. In other words, synoptic sampling captures the degradation signature closer to the source, whereas DOC at the mouth has had greater opportunity for in situ processing or the addition of lignin-free DOC via primary production.

Factors that contribute to differences in DOC signatures and correlations at different scales include contact time with particulate materials of bed sediments (sorption/desorption), photooxidation or photosynthesis, local sources of DOC that vary greatly from reach to reach (see Dalzell et al., 2011, for another example of this in an agricultural setting), variable contributions of sediments depending on local land-use and landscape features, and gaining and losing reaches that involve DOC exchange with groundwater reservoirs. Comparison of synoptic samples with mouth samples clearly indicate that both temporal and spatial sampling at multiple scales are necessary to capture all the dynamics of carbon sources and cycling in a catchment.

4.5. Integrated signals: predicted vs. measured

In the absence of in situ processing or additional sources, DOC concentrations and compositions at the mouth of Willow Slough could be expected to equal the discharge-weighted average of WSN and DS at road 98. Weighted averages are reported just below the mouth/tracks sample for all three time periods in Table 1. Several notable differences exist between the “predicted” and measured concentrations and compositions, including an average decrease in DOC concentration of $\sim 0.5 \text{ mg L}^{-1}$ across the three sampling periods, an average decrease in TSS of $\sim 13 \text{ mg L}^{-1}$, lignin concentrations decreasing 14% in March, 40% in May, but similar to predictions in September, and carbon-normalized lignin yields that were similar to predictions in March and September, but 22% lower in May (Table 1). In general, measured values lower than predicted values can be explained by groundwater input that is lower in concentrations of DOC or TSS (Deverall et al., 2010), as the lower stretches of WS were observed to be gaining reaches. Transit times between road 98 and the mouth are less than a half day, limiting the opportunity for extensive DOC processing.

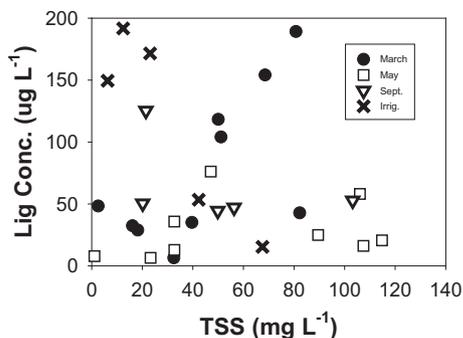


Fig. 5. Relationship between lignin concentration and total suspended sediments (TSS) for all samples.

In general, river biogeochemistry has been shifting away from the “pipe-flow” model for transport of dissolved constituents, correctly recognizing that in situ processes and sources can profoundly impact DOM and nutrient concentrations and compositions. However, this example indicates that for short enough reaches, “pipe-flow” may be a reasonable approximation.

4.6. Linking process with scale

This study, in combination with other Willow Slough studies (Hernes et al., 2008; Saraceno et al., 2009; Pellerin et al., 2010; Florsheim et al., 2011), demonstrates the importance of identifying appropriate temporal and spatial scales to investigate specific processes. Discretizing river systems by stream order is just one effort at trying to identify scales that are relevant for study. For example, degradation studies are challenging within Willow Slough due to short transit times, therefore microbial (Pellerin et al., 2010) and photochemical degradation are best investigated with controlled incubations, or perhaps rivers that are 5th order or higher. Partitioning between the dissolved and particulate phases appears to be important on time and length scales of the entire Willow Slough catchment (3rd/4th order streams and higher) (Hernes et al., 2008), but not at the sub-catchment scale. In river systems of any size, high resolution sampling during storms (Saraceno et al., 2009) or spring flush events in temperate and polar climates (Spencer et al., 2008; Strohmeier et al., 2013) are critical toward capturing threshold events that contribute a significant fraction of the annual loads. This study demonstrates the importance of understanding field-scale processes toward DOC concentrations and compositions at the mouth in an agricultural catchment, which arguably runs counter to our earlier findings that small-scale processes in the 1st and 2nd order are not well-represented by compositions and concentrations at the mouth (4th order), and perhaps indicates that certain state factors (elevation, vegetation, climate) must be considered in addition to stream order.

Global change is driven by climate change, population increase, and land use change. Particularly in agricultural systems, the latter is often an accommodation to climate and population drivers. In the Central Valley, for example, greater unpredictability in water availability from year to

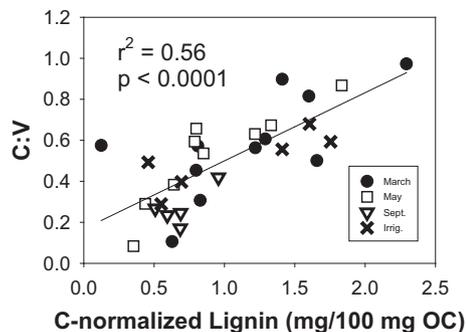


Fig. 6. Relationships between C:V and carbon-normalized lignin yields for all samples.

year due to greater extremes in annual precipitation and smaller snowpack is likely to induce changes in cropping systems and therefore irrigation practices. Population dynamics and economics continually change the economic value of crops, thereby also driving changes in cropping systems. Greater use of flood irrigation would increase the baseline for DOC export, while reductions due to water scarcity would lead to decreases. Accompanying changes in DOC composition and reactivity will in turn impact the ecology of everything downstream. The cumulative effects of heavily disturbed agricultural systems in the Central Valley have already exerted considerable pressure on the ecology of the Sacramento River/San Joaquin River Delta (the Delta) and San Francisco Bay Estuary (SFBE), and the uncertainty in how climate change and population dynamics will impact Central Valley agriculture in the future is one of several factors that make the future ecology of the Delta and SFBE less predictable.

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