Agriculture, Ecosystems and Environment 179 (2013) 1–10

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

The role of irrigation runoff and winter rainfall on dissolved organic carbon loads in an agricultural watershed

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ARTICLE INFO

Article history:
Received 26 February 2013
Received in revised form 5 July 2013
Accepted 15 July 2013

Keywords:
DOC
Agriculture
Watershed
Flood irrigation

ABSTRACT

We investigated the role of land use/land cover and agriculture practices on stream dissolved organic carbon (DOC) dynamics in the Willow Slough watershed (WSW) from 2006 to 2008. The 415 km^2 watershed in the northern Central Valley, California is covered by 31% of native vegetation and the remaining 69% of agricultural fields (primarily alfalfa, tomatoes, and rice). Stream discharge and weekly DOC concentrations were measured at eight nested subwatersheds to estimate the DOC loads and yields (loads/area) using the USGS developed stream load estimation model, LOADEST. Stream DOC concentrations peaked at 18.9 mg L^{-1} during summer irrigation in the subwatershed with the highest percentage of agricultural land use, demonstrating the strong influence of agricultural activities on summer DOC dynamics. These high concentrations contributed to DOC yields increasing up to 1.29 g m^{-2} during the 6 month period of intensive agricultural activity. The high DOC yields from the most agricultural subwatershed during the summer irrigation period was similar throughout the study, suggesting that summer DOC loads from irrigation runoff would not change significantly in the absence of major changes in crops or irrigation practices. In contrast, annual DOC yields varied from 0.89 to 1.68 g m^{-2} yr^{-1} for the most agricultural watershed due to differences in winter precipitation. This suggests that variability in the annual DOC yields will be largely determined by the winter precipitation, which can vary significantly from year to year. Changes in precipitation patterns and intensities as well as agricultural practices have potential to considerably alter the DOC dynamics.

1. Introduction

River water chemistry represents an integration of many terrestrial and aquatic biogeochemical processes in watersheds (Cole et al., 2007) and linkages among watershed hydrology, water quality, and human-driven changes in land use/land cover have been the focus of many studies (Raymond et al., 2008; Chen and Driscoll, 2009; Wilson and Xenopoulos, 2009). In particular, agricultural land use and associated practices such as irrigation, fertilization, liming, and crop rotations have the potential to greatly alter water budgets and surface water chemistry (Oh and Raymond, 2006; Royer et al., 2006; Raymond et al., 2008).

Riverine DOC concentrations and loads have been studied extensively due to the quantitative importance of DOC in regional and global carbon budgets (Cole et al., 2007; Raymond and Oh, 2007), in food web for aquatic biota (Stepanauskas et al., 2005), and in the transport of toxic metals (Ravichandran, 2004). In addition, DOC impacts drinking water quality due to the potential formation of carcinogenic by-products such as trihalomethanes (THMs) and haloacetic acids (HAAs) during water disinfection (Xie, 2004). Thus, the California state government recommended maximum DOC concentration of 3 mg L^{-1} in order to more effectively manage associated disinfection byproduct (DBP) concentrations in surface water used for drinking water (CALFED, 2000; Chomycia et al., 2008). Although the newly formed THMs could be removed through coagulation, sedimentation, or filtration at later stages of water treatment (Xie, 2004), reducing the concentrations of DOC and DBP precursors from source water can be an improved

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http://dx.doi.org/10.1016/j.agee.2013.07.004

management option. Therefore, understanding the riverine DOC dynamics and its sources in California is crucial to assess drinking water management scenarios given that water runoff from the upstream Sacramento and San Joaquin Rivers are the dominant sources to the Delta and drinking water intakes (Jassby and Cloern, 2000).

Many factors affect watershed DOC dynamics including hydrological flow paths (Lewis and Grant, 1979; McGlynn and McDonnell, 2003), storm events (Hinton et al., 1997; Saraceno et al., 2009), in-stream processes (Stepanauskas et al., 2005), wetland area (Eckhardt and Moore, 1990), and human land use/land cover (Sickman et al., 2007, 2010; Chen and Driscoll, 2009). In particular, agricultural land use has been recognized as a significant source of DOC and influences DOC characteristics such as chemical composition and lability (Dalzell et al., 2005; Hernes et al., 2008; Chen and Driscoll, 2009; Wilson and Xenopoulos, 2009; Sickman et al., 2010). However, the role of specific crop types and agricultural practices associated with the crop on stream DOC dynamics is not clear, particularly in watersheds in Mediterranean climates such as California's Central Valley where intensive irrigation practices ranging from drip to flood irrigation (Cooley et al., 2009) could significantly affect the production and transport of DOC to surface waters and downstream ecosystems. Agricultural land use in the Central Valley of California provides vital crop production in the U.S. and has received considerable attention for impacts of upstream agricultural land use on water quality in the Sacramento River/San Joaquin River Delta ecosystem (Stepanauskas et al., 2005; Krupa et al., 2012). We examined the impact of agricultural land use on DOC concentrations and loads from the Willow Slough watershed, a 415 km^2 agricultural watershed in the northern Central Valley, California. The objectives of this study were to (i) examine the temporal and spatial variability in DOC concentrations and loads from eight nested watersheds, (ii) assess the relative contribution of winter storm events on watershed DOC export, and (iii) infer from our study the potential role of agricultural watersheds on DOC dynamics of the large Sacramento River Basin. Given the reliance on surface water export from the Sacramento River/San Joaquin River Delta system for the drinking water needs of nearly 25 million people in California, understanding linkages between agricultural water use and water quality are critical to ecosystem and human health.

2. Methods

2.1. Site description

The Willow Slough Watershed (WSW) is located near Davis, California and the longitude and latitude of the mouth of WSW are 38.60° and −121.75° (Fig. 1a). The watershed includes the hilly inner Coast Range in the west and flat alluvial plains in the east (Florsheim et al., 2011). The inner Coast Range (mean slope = 25%) in the west covers about a third of the watershed area where relatively well-drained, coarse textured soils are developed with more poorly drained, fine textured soils in the alluvial fans and flood plains (mean slope = 1%) in the east (Florsheim et al., 2011). The soils data were extracted from the Soil Survey Geographic (SSURGO) database (http://soils.usda.gov/survey/geography/ssurgo/) and the gridded SSURGO database (http://soils.usda.gov/survey/geography/ssurgo/description_gssurgo.html) to identify the soil series and estimate the soil organic carbon content of the WSW. The soils of the WSW demonstrated a variety of weathering stage from relatively new entisols and inceptisols to advanced weathering stage of alfisols and vertisols. The most prevalent soil series occupying 20% of the watershed area was Capay series (*fine, smectitic, thermic Typic Haploxererts*) followed by Marvin (*Haploxeralfs*), Brentwood (*Haploxerepts*), and Tehama series (*Haploxeralfs*) that covered 8%, 7%, and 7% of the watershed, respectively. The soil organic carbon (SOC) content at 0–30 cm of depths was relatively large in the low lying agricultural part of the watershed (up to ~6.5 kg m^{-2}) whereas the SOC content was low in the western hilly area (Fig. 2).

The mean annual precipitation of the entire WSW was 572 mm (median = 552 mm) per water year (from October to September) for 113 years (10/01/1895–09/30/2008) which was estimated using the PRISM data set (http://www.prism.oregonstate.edu/). Annual rainfall ranged from ~450 mm in the eastern part of the watershed to ~860 mm in the hilly Coast Range, with 95% of rainfall occurring between October and April. The rainfall in water years from 2006 to 2008 was 896, 311, and 503 mm per water year, respectively, which corresponded to 8th, 106th, and 66th wettest years among the 113 water years, thus providing an excellent opportunity to compare water and DOC budgets during extreme and average precipitation years.

Agricultural cropland is the dominant land use/land cover of the watershed (63%), followed by grassland (21%) and natural shrubland (8%; Table 1), which was quantified using GIS with National Land Cover Dataset 2001 (http://www.mrlc.gov/). Field observations were coupled with GIS data of crop types to quantify the distribution of individual crops in the watershed. Alfalfa (*Medicago sativa*) and tomato (*Lycopersicon esculentum*) were the two most prevalent crops, covering about 28% and 14% of the agricultural lands of WSW, respectively (Fig. 3). Other significant crops included grass for forage (13%), orchards (10%), and rice (*Oryza sativa*, 7%) (Fig. 3).

A total of eight gauging stations including the entire watershed (Fig. 1) were monitored for discharge at 15 min intervals and coupled with weekly and storm event discrete sampling for DOC concentrations (Table 1). The watersheds are nested such that the entire WSW includes two large subwatersheds, W2 and W3 (Fig. 1b and c), and W2 includes subwatersheds W6 (which includes subwatershed W4) and W8, whereas W3 includes W7 (which includes W5) (Fig. 1).

2.2. Sample collection and analysis

Water samples from the eight watersheds were collected weekly during baseflow, as well as more intensively during several high flow rainfall-runoff events. Stream DOC concentrations from the eight watersheds were monitored in 2006 while DOC concentrations from the entire watershed (W1) and the W8 subwatershed were also monitored in 2007 (Fig. 4). 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 μm glass-fiber filters, Advantec MFS, Inc.), with DOC samples acidified to pH ~2 and refrigerated until analysis (within 7 days). DOC concentrations were measured with a Shimadzu TOC-5000A high temperature catalytic oxidation analyzer measuring non-purgeable organic carbon. The mean of 3–5 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. Reported values were corrected for the instrument blank, which was measured at the time of analysis.

2.3. Flow monitoring and DOC load calculations

Flow was also monitored at eight gauging stations within the watershed. Each station was located near a bridge and included a pressure transducer (In-Situ Inc., Fort Collins, CO) that recorded water levels at 15 min intervals, and a staff gauge. When water levels were sufficiently low, flow was

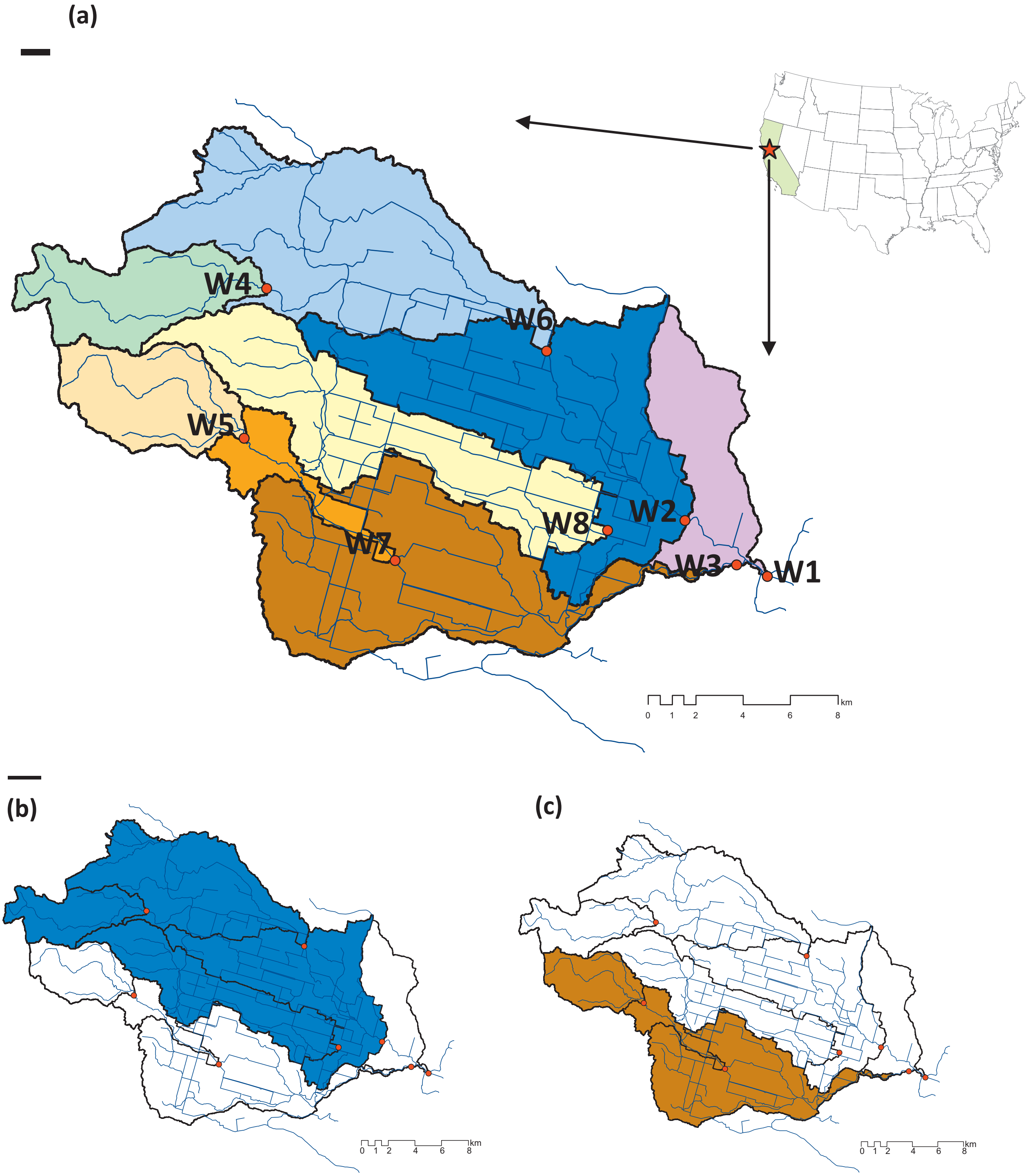

Fig. 1. (a) Subwatersheds of the entire Willow Slough Watershed (WSW = W1) where watershed ID's (W1–W8) are presented at the gauging stations. The two large subwatersheds, (b) upper Willow Slough (W2) and (c) Dry Slough (W3) include the smaller subwatersheds (W2 > W6 > W4; W2 > W8; W3 > W7 > W5). The red dots are locations of gauging stations where weekly stream water chemistry and daily discharge data have been monitored. Blue lines are streams and irrigation channels and black lines are boundaries of watersheds. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

measured along a set stream cross-section with the SonTeck flowtracker (www.sontek.com/flowtracker.php). Stage-discharge relationships were determined across flow conditions to estimate continuous flow records for the study period.

Daily DOC load was estimated using LOADEST model developed by the US Geological Survey (USGS) (Runkel et al., 2004), in which the daily DOC load was estimated with daily discharge data using the relationship between discharge and load. Among the automatically-selectable nine models in LOADEST (Runkel et al., 2004), the simplest model was selected:

$$\ln(\text{Load}) = a_0 + a_1 \ln Q$$

where a_0 and a_1 are coefficients, and lnQ is ln(stream flow) – center of ln(stream flow). This conservative model was selected because the load can be significantly overestimated with other models, especially models with temporal terms when a significant trend

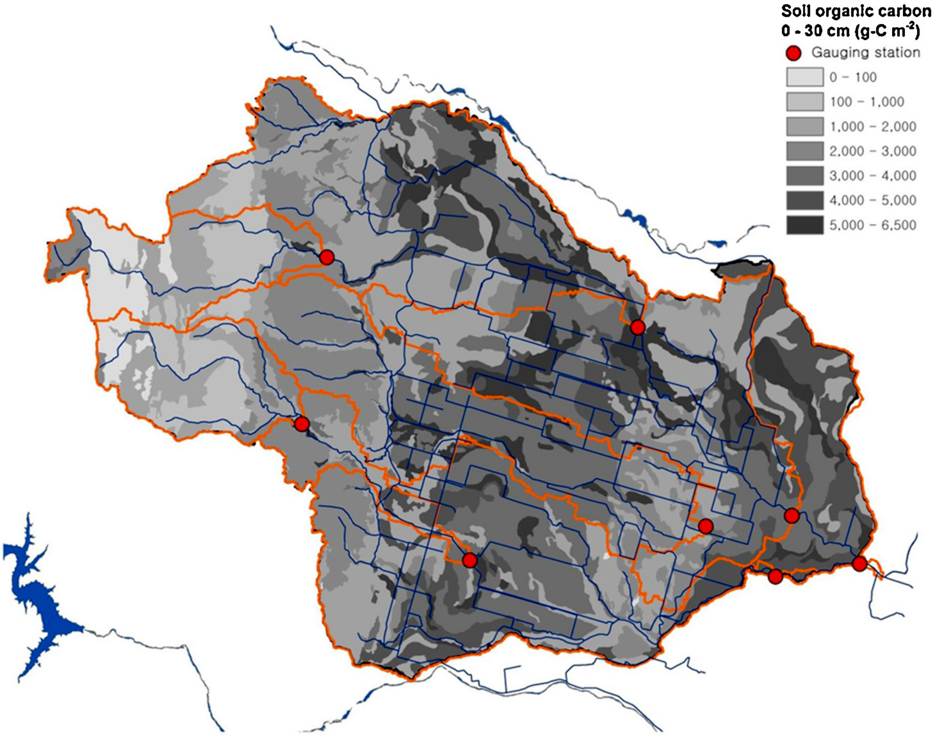

Fig. 2. Soil organic carbon content of the WSW at 0–30 cm of depths (data source: USDA gridded SURRGO database).

exists in the calibration data and the period of daily discharge data is extended beyond the period of concentration data. In many subwatersheds, the period of concentration data are shorter than the period of daily discharge (Table 1), and we used the conservative model to prevent overestimation of daily DOC loads. We also estimated the daily load of DOC at the mouth of watershed where the most complete data set of both concentration and discharge are available, using the automatically selected model to compare with the results of the conservative model.

The calibration data for LOADEST were prepared for two separate seasons, summer growing (from May to October) and winter dormant (November to April) seasons from February 2006 to April 2008, and LOADEST was run separately for each 6-month period with daily discharge. LOADEST outputs (or daily loads) were summed to calculate monthly, seasonal, and annual loads. Although the choice of the two seasons (from November to October for a full year) does not correspond to the traditional water year (from October to September), we used the two 6-month seasons for all watersheds because analysis of monthly precipitation showed that precipitation was negligible from May to October and coincided with the delivery of low DOC irrigation water in May from Clear Lake located ~70 km northwest of the WSW. The lack of weekly DOC data for 2007 and 2008 in six subwatersheds, W2 to W7 (Table 1), did not allow for the proper calibration of a LOADEST model for these sites. Instead, DOC fluxes were estimated as the

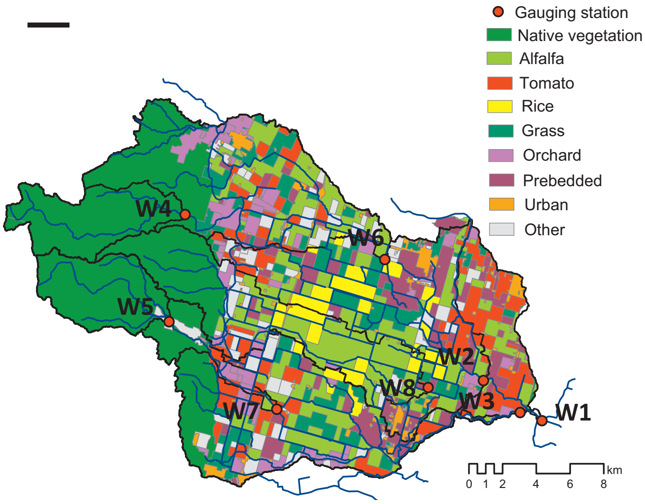

Fig. 3. The map of land use type within the WSW.

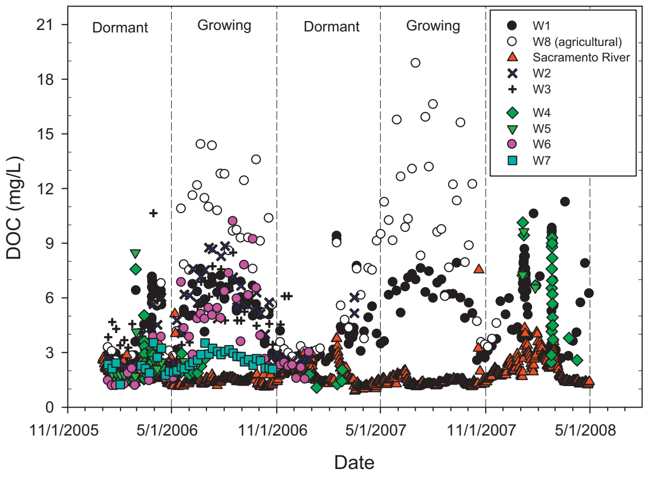

Fig. 4. The weekly and storm DOC concentrations of the subwatersheds within the Willow Slough Watershed, showing high [DOC] during summer irrigation periods and winter storms. The white circles are [DOC] at W8, the most agricultural subwatershed (Fig. 3) and the red triangles are [DOC] at the main stream of Sacramento River. The vertical dashed lines divide seasons, summer irrigated, growing season (May–October) and winter non-irrigated, dormant season (November to April).

Table 1
Area, data collection period for LOADEST runs, and land use/land cover (%) of the subwatersheds of WSW. Land use/land cover of the subwatersheds was quantified using National Land Cover Dataset (2001).

Watershed ID	Name	Area (km^2)	[DOC] (From)	[DOC] (To)	Discharge (From)	Discharge (To)
W1	Willow Slough watershed mouth at Highway 113	415.3	2/26/2006	5/14/2008	2/22/2006	5/16/2008
W2	Willow Slough at Road 98	261.6	2/14/2006	12/27/2006	2/10/2006	5/15/2008
W3	Dry Slough at Road 98	122.2	4/27/2006	11/21/2006	4/27/2006	5/15/2008
W4	Cottonwood Creek at Yolo County	30.3	1/24/2006	2/23/2007 (and 1/4/2008-4/8/2008)	12/7/2006	5/16/2008
W5	Chickahominy Slough on Road 29	27.8	2/14/2006	6/7/2006 (and 1/4/2008-1/26/2008)	2/10/2006	5/16/2008
W6	Willow Slough on Road 93	115.5	3/23/2006	12/27/2006	3/22/2006	4/11/2008
W7	Walnut Canal at Buckeye Road	40.6	1/10/2006	10/24/2006	12/28/2006	5/15/2008
W8	Union School Slough at Road 96	62.6	3/30/2006	11/12/2007	3/23/2006	5/16/2008

Watershed ID	Water	Developed	Barren	Forest	Natural Shrubland	Grasslands	Agriculture	Wetlands
W1	0.0	5.2	0.3	2.2	7.8	21.4	62.9	0.2
W2	0.0	5.4	0.3	2.2	8.2	20.6	63.2	0.2
W3	0.1	3.8	0.4	2.6	9.1	28.7	55.2	0.1
W4	0.0	0.5	0.0	15.5	52.1	31.8	0.0	0.0
W5	0.0	0.1	0.0	11.1	38.7	50.1	0.0	0.0
W6	0.0	5.7	0.3	4.8	17.3	26.3	45.7	0.0
W7	0.0	0.6	0.0	7.8	27.4	52.5	11.6	0.0
W8	0.0	2.9	0.4	0.5	2.2	31.5	62.3	0.1

product of mean DOC concentration for each 6-month period from 2006 and the seasonal sum of stream discharge for comparison.

The DOC yield (load per unit area) and water yield (water discharge per unit area) allow for a comparison among watersheds of different sizes in our study. In order to calculate summer DOC and water yields, the area of nested headwater catchments that lacked measurable discharge during the growing season was subtracted from the larger watershed areas, instead calculating yields using the areas where water was supplied through irrigation channels and groundwater extraction. These areas correspond to the areas of all crops and land use except native vegetation of Fig. 2. However, winter and annual DOC and water yields were calculated using watershed areas that include the headwater catchments since there was runoff during that period. The calculated DOC and water yields were correlated with the percentage of each crop species to infer possible roles of crop type and irrigation management on constituent and water transport.

Water and DOC budgets for subwatersheds were also used to investigate the contribution of large storm events toward the annual watershed DOC budget. We defined large storms as any days with daily discharge larger than the mean +3 standard deviation of daily discharge during the study period. The DOC load and water discharge of large storms was extracted from LOADEST runs to calculate the contribution of DOC loads by strong storms and water discharge to annual DOC loads and water release from the watershed.

3. Results and discussion

3.1. Temporal and spatial variations of DOC concentrations

DOC responded strongly to summer irrigation periods, with elevated concentrations at all locations of the agricultural Willow Slough watershed, suggesting strong linkages between stream DOC concentrations and agricultural activities (Fig. 4). DOC concentrations at the watershed mouth (W1) ranged from 2.0 to 11.2 mg L^{-1}, with highest concentrations observed during the prolonged summer irrigation period and during short-duration winter storms (Fig. 4). Highest DOC concentrations were measured at a small intensive agricultural subwatershed (W8; 18.9 mg L^{-1}), with both W8 and the two largest subwatersheds (W2 and W3) showing seasonality similar to the watershed mouth, W1 (Fig. 4). In contrast, weekly baseflow DOC concentrations of grassland headwater sites (W4 and W5) were relatively low (1.1 to 3.8 mg L^{-1}) when streamflow occurred in winter, with higher values (up to 10.1 mg L^{-1}) measured during short-duration winter storm events (Fig. 4).

Previous studies have shown that the primary source of DOC during the summer irrigation period is terrestrial vascular plants rather than algal production as evidenced by lignin moiety analysis and optical properties in water samples (Hernes et al., 2008). Leaching from crops and aquatic macrophytes can directly increase the DOC concentrations during irrigated season, demonstrated by an incubation experiment where 9% to 26% of total plant carbon was solubilized in 4 h (Pellerin et al., 2010). Desorption from sediments can be another source of increased DOC concentrations at the WSW, suggested by a relatively strong correlation between lignin concentration and total suspended sediments (Hernes et al., 2008).

The temporal variation in DOC concentrations in the WSW differs from that of the main stem Sacramento River (http://cdec.water.ca.gov/cgi-progs/staMeta?station_id=SRH), which was relatively constant at ~2 mg L^{-1} except a few peaks at ~4 mg L^{-1} during winter storms (Fig. 4). While the Sacramento River is influenced by agriculture with its ~8000 km^2 drainage area, the large inflow of low DOC runoff from the Sierra Nevada to the Sacramento River likely limits any seasonal increases in summer DOC concentrations as observed in the WSW.

In a relatively small watershed like Willow Slough, the rapid and direct coupling between the activation of hydrologic flow paths and DOC transport to the stream results in subsequent discharge and DOC flux over relatively short time-scales (Hernes et al., 2008; Saraceno et al., 2009). In the winter, this results in rapid runoff from a number of sources ranging from steep grassland headwater catchments with relatively low DOC water to agricultural fields with higher DOC concentrations. In the summer, flood irrigation of alfalfa and orchard grass results in the direct contact of irrigation water with soils and plant material, resulting in a large yield of DOC when drained. This is particularly true for the sites with highest DOC concentrations, which tend to be dominated by alfalfa. The soil organic carbon content was relatively high in the agricultural regions (Fig. 2), suggesting that flood irrigated alfalfa fields can work as a temporary wetland, resulting in increased DOC concentrations in flood irrigated fields and ditches.

The combination of crop type and/or land cover can also have a large effect on DOC composition in watershed runoff (Eckard et al.,

Table 2
Mean daily DOC load for each season with 95% confidence intervals estimated using the LOADEST. Note that only subwatersheds with more than 160 daily discharge data were run. The units are kg day^{-1}.

Period	Season	Watershed	Number of days	Mean load	Lower (95% C.I.)	Upper (95% C.I.)	Std. error prediction	Std. error
5/2006–10/2006	Summer	1	184	1137	1043	1237	49	42
5/2006–10/2006	Summer	2	184	716	623	819	50	47
5/2006–10/2006	Summer	3	181	243	200	291	23	22
5/2006–10/2006	Summer	6	184	287	226	359	34	31
5/2006–10/2006	Summer	8	184	280	244	319	19	17
11/2006–4/2007	Winter	1	181	125	107	146	10	4
11/2006–4/2007	Winter	2	181	92	77	110	9	7
11/2006–4/2007	Winter	6	179	33	23	45	5	4
11/2006–4/2007	Winter	8	169	27	21	34	3	3
5/2007–10/2007	Summer	1	184	787	725	853	33	26
5/2007–10/2007	Summer	2	184	536	466	613	38	35
5/2007–10/2007	Summer	3	174	267	219	324	27	25
5/2007–10/2007	Summer	8	183	291	253	333	21	18
11/2007–4/2008	Winter	1	182	1426	1091	1832	189	78
11/2007–4/2008	Winter	2	163	781	556	1066	131	115
11/2007–4/2008	Winter	6	162	151	98	222	32	28
11/2007–4/2008	Winter	8	177	292	187	435	64	56

2007). For example, an analysis on DOC composition using lignin phenols suggested that the source of winter baseflow DOC at the watershed mouth (WSW) is highly processed, aromatic compounds presumably originated from deeper soil horizons while DOC during winter storms is more strongly influenced by grassland headwater runoff (Hernes et al., 2008). The lignin phenol analysis and SUVA$_{254}$ suggested that DOC during summer irrigation period is geochemically distinct from both the winter baseflow and winter storms (Hernes et al., 2008), demonstrating that one of the major sources of summer DOC could be the leached carbon from relatively shallow, organic carbon-rich surface flow paths. Irrigation of these flooded crops also results in extended contact between the incoming water and soils, which results in a greater desorption of DOC from soils. However, across the entire Sacramento Valley, all the agricultural irrigation practices as well as winter storms occur at different times with different intensities, and thus pulses and spikes in DOC concentrations that we observed in the WSW are dampened and integrated with pulses and spikes from every other watershed.

3.2. *Temporal and spatial variations of DOC loads and yields.*

Estimated daily DOC loads at the mouth of WSW varied from 4.4 kg day^{-1} during winter base flow to as large as 43.6 × 10^3 kg day^{-1} during a winter storm. While DOC concentrations were elevated during storm flow (Fig. 4), loads measured during our study were dominantly controlled by water discharge (Fig. 5) as reported in other agricultural watersheds (Dalzell et al., 2007). This large variation in daily DOC loads due to winter storms is reflected in the mean daily DOC load for each season (Table 2). For example, the mean daily DOC loads at the mouth of WSW for the dry 2007 winter (294 mm of rain) and relatively wet 2008 winter (464 mm of rain) differed by an order of magnitude, from 125 to 1426 kg day^{-1} with a large 95% confidence interval during the 2008 winter (Table 2). Similarly, large differences in mean daily DOC loads between the dry 2007 winter and wet 2008 winter were observed for the other subwatersheds (Table 2). For comparison, the mean DOC loads at the mouth of WSW during 2006 and 2007 summer were comparable (1137 and 787 kg day^{-1}, respectively), with relatively narrow confidence intervals for both years.

Since DOC loads can increase as watershed area increases, DOC yields were used to compare the release of DOC among the nested watersheds (Table 3). The DOC yield during 2006 summer growing season ranged from 0.01 g m^{-2} at headwater streams to 1.25 g m^{-2} at the most intensive agricultural subwatershed, W8 (Table 3). A similar range of DOC yield was observed during 2007 summer, from 0 to 1.29 g m^{-2} except for W7 with the highest DOC yield (6.01 g m^{-2}).

While summer water and DOC yields are driven almost entirely by irrigation water runoff which is re-used during downstream transport and therefore resulting in relatively low runoff from the watershed as a whole, winter yields are highly dependent on precipitation. The winter precipitation of the entire WSW was 294 and 464 mm for Nov., 2006–Apr., 2007, and Nov., 2007–Apr., 2008, respectively. Estimated winter discharge from the entire WSW was 12 and 99 mm for the same period, respectively, hence corresponding discharge: precipitation (D:P) ratios were 0.04 and 0.21 for each winter, demonstrating a large variation of D:P ratio depending on precipitation received. The higher D:P ratio in the wetter year suggests that soils are more saturated with water, with the implication that DOC stored in surface soil horizons can be more easily released to streams, increasing the watershed DOC yield (Raymond and Oh, 2007; Hernes et al., 2008).

The large variation of winter water yield drives winter DOC yield, which ranged from negligible for many subwatersheds during Nov., 2006–Apr., 2007, to as large as 0.83 g m^{-2} during Nov., 2007–Apr., 2008 at W8, which was still lower than summer DOC yield in spite of a few storms. However, winter DOC yields could

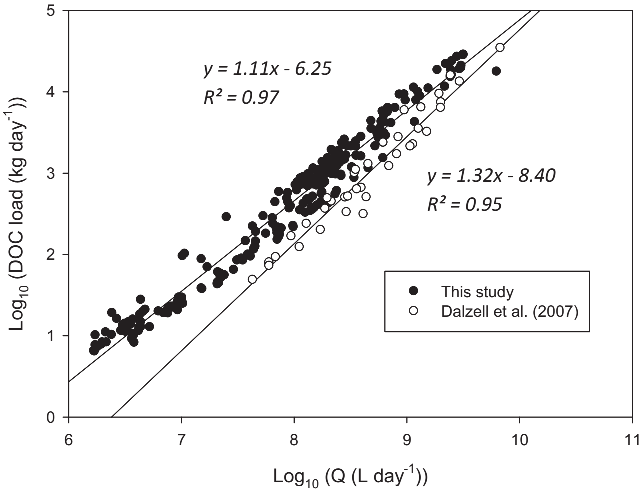

Fig. 5. Relationship between log-transformed DOC load vs. log-transformed discharge (Q) at the mouth of the WSW (closed circles) and at the mouth of a Midwestern agricultural watershed (open circles) (Dalzell et al., 2007).

Table 3

Water discharge (Q) and DOC loads and yields from the Willow Slough watershed from May 2006 to Apr. 2008. The DOC loads were estimated using the LOADEST for summer and winter separately (see Section 2) and combined for the annual export when both concentration and daily discharge data were available for the calibrating days. For those watersheds for which LOADEST could not run, DOC loads were estimated by multiplying the mean [DOC] of the season and discharge. $N(Q)$: Number of days for daily discharge, NA = not available.

Season	ID	Period	Q (m^3)	$N(Q)$	LOADEST DOC (kg)	Area (km^2)	(mean [DOC] × Q) DOC (kg)	Q (mm)	DOC yield (g m^{-2})
Summer	W1	5/2006–10/2006	3.63×10^7	184	2.09×10^5	288.27	1.98×10^5	126	0.73
Summer	W2	5/2006–10/2006	2.12×10^7	184	1.32×10^5	182.42	1.30×10^5	116	0.72
Summer	W3	5/2006–10/2006	8.94×10^6	184	4.39×10^4	74.30	4.67×10^4	120	0.59
Summer	W4	5/2006–10/2006	NA	NA	NA	30.34	NA	NA	NA
Summer	W5	5/2006–10/2006	1.76×10^5	184	NA	27.84	3.93×10^2	6	0.01
Summer	W6	5/2006–10/2006	9.28×10^6	184	5.28×10^4	57.95	4.79×10^4	160	0.91
Summer	W7	5/2006–10/2006	NA	NA	NA	5.63	NA	NA	NA
Summer	W8	5/2006–10/2006	4.60×10^6	184	5.14×10^4	41.20	4.61×10^4	112	1.25
Winter	W1	11/2006–4/2007	4.87×10^6	181	2.26×10^4	415.56	1.78×10^4	12	0.05
Winter	W2	11/2006–4/2007	5.28×10^6	181	1.67×10^4	261.77	1.65×10^4	20	0.06
Winter	W3	11/2006–4/2007	2.59×10^6	181	NA	122.24	1.44×10^4	21	0.12
Winter	W4	11/2006–4/2007	8.72×10^3	144	NA	30.34	12	0	0.00
Winter	W5	11/2006–4/2007	0	181	NA	27.84	0	0	0.00
Winter	W6	11/2006–4/2007	2.27×10^6	181	5.88×10^3	115.54	4.96×10^3	20	0.05
Winter	W7	11/2006–4/2007	3.43×10^6	123	NA	40.65	NA	84	NA
Winter	W8	11/2006–4/2007	1.01×10^6	181	4.54×10^3	62.61	4.68×10^3	16	0.07
Annual	W1	5/2006–4/2007	4.12×10^7	365	2.32×10^5	415.56	2.16×10^5	99	0.56
Annual	W2	5/2006–4/2007	2.65×10^7	365	1.48×10^5	261.77	1.47×10^5	101	0.57
Annual	W3	5/2006–4/2007	1.15×10^7	365	NA	122.24	6.11×10^4	94	0.50
Annual	W4	5/2006–4/2007	NA	NA	NA	30.34	12	NA	NA
Annual	W5	5/2006–4/2007	1.76×10^5	365	NA	27.84	393	6	0.01
Annual	W6	5/2006–4/2007	1.15×10^7	365	5.87×10^4	115.54	5.28×10^4	100	0.51
Annual	W7	5/2006–4/2007	NA	NA	NA	40.65	NA	NA	NA
Annual	W8	5/2006–4/2007	5.60×10^6	365	5.60×10^4	62.61	5.07×10^4	90	0.89
Season	ID	Period	Q (m^3)	$N(Q)$	LOADEST DOC (kg)	Area (km^2)	(mean [DOC] × Q) DOC (kg)	Q (mm)	DOC yield (g m^{-2})
Summer	W1	5/2007–10/2007	2.59×10^7	184	1.45×10^5	288.27	1.51×10^5	90	0.50
Summer	W2	5/2007–10/2007	1.67×10^7	184	9.86×10^4	182.42	1.02×10^5[a]	92	0.54 [a]
Summer	W3	5/2007–10/2007	9.47×10^6	184	4.65×10^4	74.30	4.95×10^4[a]	127	0.63[a]
Summer	W4	5/2007–10/2007	0	184	NA	30.34	0[a]	0	0.00[a]
Summer	W5	5/2007–10/2007	0	184	NA	27.84	0[a]	0	0.00[a]
Summer	W6	5/2007–10/2007	5.56×10^6	184	NA	57.95	2.87×10^4[a]	96	0.49[a]
Summer	W7	5/2007–10/2007	1.28×10^7	184	NA	5.63	3.38×10^4[a]	2281	6.01[a]
Summer	W8	5/2007–10/2007	4.72×10^6	184	5.33×10^4	41.20	5.02×10^4	115	1.29
Winter	W1	11/2007–4/2008	4.10×10^7	182	2.60×10^5	415.56	1.98×10^5	99	0.62
Winter	W2	11/2007–4/2008	3.34×10^7	182	1.27×10^5	261.77	1.07×10^5	127	0.49
Winter	W3	11/2007–4/2008	1.24×10^7	182	NA	122.24	5.62×10^4[b]	101	0.46[b]
Winter	W4	11/2007–4/2008	4.79×10^6	182	NA	30.34	8.50×10^3[b]	158	0.28[b]
Winter	W5	11/2007–4/2008	3.77×10^6	182	NA	27.84	7.53×10^3[b]	135	0.27[b]
Winter	W6	11/2007–4/2008	8.74×10^6	162	2.44×10^4	115.54	1.95×10^4	76	0.21
Winter	W7	11/2007–4/2008	5.47×10^6	182	NA	40.65	1.35×10^4[b]	135	0.33[b]
Winter	W8	11/2007–4/2008	1.16×10^7	182	5.17×10^4	62.61	3.98×10^4	185	0.83
Annual	W1	5/2007–4/2008	6.69×10^7	366	4.04×10^5	415.56	3.49×10^5	161	0.97
Annual	W2	5/2007–4/2008	5.01×10^7	366	2.26×10^5	261.77	2.09×10^5	191	0.86
Annual	W3	5/2007–4/2008	2.19×10^7	366	NA	122.24	1.06×10^5	179	0.86
Annual	W4	5/2007–4/2008	4.79×10^6	366	NA	30.34	8.50×10^3	158	0.28
Annual	W5	5/2007–4/2008	3.77×10^6	366	NA	27.84	7.53×10^3	135	0.27
Annual	W6	5/2007–4/2008	1.43×10^7	346	NA	115.54	4.82×10^4	124	0.42
Annual	W7	5/2007–4/2008	1.83×10^7	366	NA	40.65	4.73×10^4	450	1.16
Annual	W8	5/2007–4/2008	1.63×10^7	366	1.05×10^5	62.61	9.00×10^4	260	1.68

[a] Assuming the same mean summer [DOC] as 2006 summer.

[b] Assuming the same mean winter [DOC] as 2006/02–2006/04 (this period was selected instead of 2006/11–2007/04 because 2007 winter was dry in terms of precipitation).

surpass the current estimates in particularly wet years. The annual DOC yield, which was calculated by summing the summer and winter DOC flux divided by un-adjusted watershed area ranged from 0.01 g m^{-2} yr^{-1} at head water streams for a dry year up to 1.68 g m^{-2} yr^{-1} at W8 (Table 3).

Although annual DOC yields can be calculated for the periods from November of the previous year to October of the current year, two time frames (May 2006 to Apr. 2007 and May 2007 to Apr. 2008) were selected in order to estimate annual DOC yields for the two full years (Fig. 4). The annual DOC yields of WSW were 0.56 and 0.97 g m^{-2} yr^{-1} for May 2006–Apr. 2007 and May 2007–Apr. 2008, respectively. Agricultural watersheds in the Midwestern U.S. showed generally comparable DOC yields. For example, DOC yields of 1.95 and 1.41 g m^{-2} yr^{-1} were reported in an Ohio River Basin agricultural watershed that was >80% row crop (Dalzell et al., 2007). Similarly, mean DOC yields of 1.10 and 0.90 g m^{-2} yr^{-1} were reported for other agricultural watersheds in the Ohio River Basin with similar size (481 and 365 km^2 for Embarras River watershed and Lake Fork Kaskaskia River) to our study site (Royer and David, 2005).

A few studies have been conducted on DOC yields in the Mediterranean climate of the Central Valley of California (Kratzer

Table 4
Contribution of strong winter storms (>mean + 3 s.d.) on DOC load and discharge (*Q*) from the Willow Slough watersheds.

ID	Period	Number of strong storm days	Storm DOC load (kg)	Storm discharge (m^3)	DOC load (kg)	Discharge (m^3)	Storm contribution (DOC load)	Storm contribution (*Q*)
W1	11/2006–04/2007	3	3.71×10^3	7.04×10^5	2.26×10^4	4.87×10^6	0.16	0.14
W2	11/2006–04/2007	1	670	1.99×10^5	1.67×10^4	5.28×10^6	0.04	0.04
W6	11/2006–04/2007	4	3.42×10^3	1.24×10^6	5.88×10^3	2.27×10^6	0.58	0.55
W8	11/2006–04/2007	4	764	1.70×10^5	4.54×10^3	1.01×10^6	0.17	0.17
W1	11/2007–04/2008	4	1.25×10^5	1.74×10^7	2.60×10^5	4.10×10^7	0.48	0.43
W2	11/2007–04/2008	3	4.71×10^4	1.10×10^7	1.27×10^5	3.34×10^7	0.37	0.33
W6	11/2007–04/2008	4	1.31×10^4	4.49×10^6	2.44×10^4	8.75×10^6	0.54	0.51
W8	11/2007–04/2008	4	1.99×10^4	4.50×10^6	5.17×10^4	1.16×10^7	0.39	0.39

et al., 2004; Chow et al., 2007; Saleh et al., 2007). During 1995–1998 water years, the DOC yield of 10 major subwatersheds of the Sacramento River Basin varied from 0.75 to 11.24 g m^{-2} yr^{-1} (Saleh et al., 2007). Among them, the two subwatersheds with the most agricultural land use/land cover were Colusa Basin Drain and Sacramento Slough where 47% and 62% of areas are categorized as agricultural land use by 2001 NLCD, respectively, both comparable to WSW at 63% of agricultural coverage. However, there is a large difference in DOC yield among the watersheds. The DOC yields of Colusa Basin Drain and Sacramento Slough where flood irrigation is practiced for rice production (Ruark et al., 2010) were 3.14 and 11.24 g m^{-2} yr^{-1} for 1995–1998 and 1997–1998 water years, respectively (Saleh et al., 2007), 1–2 orders of magnitude higher than annual DOC yield of the WSW during our study period (Table 3). The highest DOC yield from the most agricultural subwatershed (W8) in our study was 0.89 and 1.68 g m^{-2} yr^{-1} (Table 3), demonstrating higher DOC release than the integrated signal at the watershed mouth, but still significantly lower than that observed at other sites in previous years.

The water years from 1995 to 1999 are all defined as wet years for Sacramento Valley while 2007 and 2008 are defined as dry and critical years (http://cdec.water.ca.gov/cgi-progs/iodir/wsihist). Therefore, the DOC yield of the WSW could have been higher in a wet year presumably as a result of higher D:P ratios. The difference in DOC yields among the watersheds can be explained by a large difference in riverine discharge, with the D:P ratio of Sacramento Slough close to 1. Therefore, for about the same percentage of agricultural land use/land cover, other factors such as agricultural irrigation practices, precipitation intensity and amount, or agricultural practices specific for the crop can be important for generating runoff. This occurs despite higher mean summer DOC concentrations in WSW (mean = 5.63 mg L^{-1}) versus a mean summer DOC concentrations of 4.82 and 3.03 mg L^{-1} for Colusa Basin Drain and Sacramento Slough, respectively (Chow et al., 2007; Saleh et al., 2007).

3.3. *Contribution of winter storms to DOC concentrations and yields*

Winter DOC loads were strongly influenced by total precipitation because irrigation contributed minimally to the winter watershed DOC budget. An estimated total of 260×10^6 g DOC was exported from the WSW in winter of 2008 while only 23×10^6 g DOC was released from the WSW during the winter of 2007 (Table 3), demonstrating more than an order of magnitude difference depending on winter precipitation. This is in contrast to summer DOC concentrations and loads, which were driven by irrigation needs, not greatly influenced by precipitation, and resulted in a total of 209×10^6 g and 145×10^6 g of stream DOC export from the entire WSW during summers of 2006 and 2007, respectively (Table 3). The similar DOC exports during summer irrigation periods regardless of wet or dry year indicates that the annual water need for agriculture in the Mediterranean climate is relatively consistent.

Large differences among winter DOC fluxes demonstrate the strong influence of seasonal storm events. During a dry year (Nov. 2006 to Apr. 2007), three strong storm days during this period still contributed 16% and 14% of winter DOC flux and winter water flow, respectively, for the entire WSW (Table 4). Precipitation during the 2008 winter season (Nov. 2007 to Apr. 2008) was approximately 50% higher than in 2007 (464 mm), and four strong storm days contributed 48% and 43% of winter DOC flux and water flow, respectively, in WSW (Table 4). This amount is still considerable in annual DOC and water budgets, corresponding to 31% and 26% of annual DOC load and water flow, respectively, for May 2007 to Apr. 2008.

Large contributions of strong storms on annual DOC export has been reported for a variety of ecosystems (Hinton et al., 1997; Dalzell et al., 2005; Yoon and Raymond, 2012) as well as rice fields in northern California (Ruark et al., 2010). The rice field DOC study was conducted from Apr. 2006 to Mar. 2008, providing an opportunity to compare DOC yields of two different crop systems for similar precipitation conditions. Willow Slough DOC yields during winters of 2006–2008 also suggested that winter storms could be an important factor in watershed DOC budget in agricultural watersheds located in a Mediterranean climate. However, while the summer DOC yields of the rice field study ranged from 0.37 to 3.46 g m^{-2} for April–September which is comparable to our summer DOC yield (~0 to 1.29 g m^{-2}, Table 3), the winter DOC yields were much larger than those of WSW, ranging from 0 to as high as 20.2 g m^{-2} during October–March (Ruark et al., 2010). The high DOC yields were due to both high DOC concentrations with an average of ~30 mg L^{-1} during October–November (up to ~80 mg L^{-1}) by straw-incorporation practices and water yields up to 1306 mm during October–March. The large water yield, 1306 mm, during Oct. 2006 to Mar. 2007 is surprising considering that the precipitation was only 245 mm for the period (Ruark et al., 2010), suggesting that rice cropping involves intense water management.

3.4. *The role of agricultural land use on stream DOC concentrations and loads*

A variety of land use/land cover including cropland, wetlands, and urban areas have been shown to affect riverine DOC concentration and loads (Eckhardt and Moore, 1990; Mulholland, 1997; Sickman et al., 2007; Chen and Driscoll, 2009). In particular, wetlands or poorly drained soils can be a significant factor in controlling watershed DOC concentrations. In the WSW, the wetland coverage was less than 0.3% in all the subwatersheds, whereas agricultural land use covered 63% of subwatershed areas (Table 1). However, poorly drained soil can be a result of agricultural irrigation practices, making the separation between the two variables difficult especially for crops that need long- or short-term flood irrigation such as rice and alfalfa (Cooley et al., 2009).

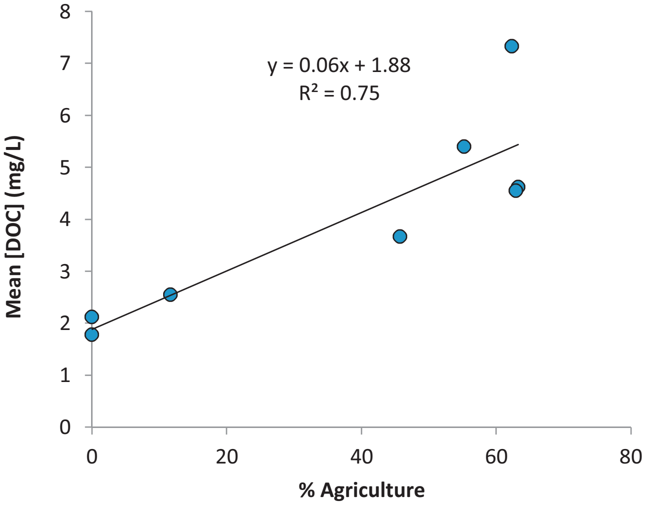

Fig. 6. The relationship between mean DOC concentrations and percentage covered by agricultural land use of eight watersheds of WSW. The mean [DOC] is the average of growing (May, 2006–Oct., 2006) and dormant (Nov., 2006–Apr., 2007) seasons. For watersheds, W5 and W7, [DOC] data for Jan., 2006–Apr. 2006 are used instead, due to the lack of [DOC] data for Nov., 2006–Apr., 2007.

We observed a positive correlation between annual mean DOC concentration and percentage of agricultural land in the nested study watersheds (Fig. 6). Agricultural activities in WSW require active irrigation throughout nearly the entire summer growing season, which may in part explain differences in the timing of peak DOC concentrations between WSW and other agricultural watersheds which receive rainfall throughout the year (Royer and David, 2005; Dalzell et al., 2007). For example, low summer discharge in agricultural watersheds in the Great Lake region resulted in a concentration effect on DOC that was more pronounced (to ~25 mg L^{-1}) due to low volume of water (Chen and Driscoll, 2009). Similarly, The DOC concentrations also increased at very low flows (<1 $m^3 s^{-1}$) in agricultural watersheds in Illinois, suggesting that in situ primary production became significant, particularly in the summer (Royer and David, 2005). In WSW, re-used water during summer flood irrigation may result in the leaching of organic carbon from the surface soil with high organic matter (Hernes et al., 2008). In addition, the role of algae in contributing to elevated summer DOC concentrations in WSW is light-limited due to high suspended sediment loads during irrigation (Hernes et al., 2008). Therefore, the relationship between annual mean DOC concentrations and agricultural land use suggests that a variety of agricultural activities can increase DOC concentrations, although the mechanism might be different depending on irrigation methods and hydrology of the region.

Multiple terrestrial DOC sources can contribute to stream DOC including crop field runoff, sediment carbon desorption, and plant leachate (Hernes et al., 2008; Pellerin et al., 2010). More than 80% of field crops in California are flood irrigated (Cooley et al., 2009) including alfalfa and rice, and thus the field could act as a temporary wetland releasing DOC from soils and plant residue to flooded water until the irrigated water is discharged to the stream. This transient flood period and low irrigation water discharge can result in high DOC concentrations for several months (Fig. 4). Considering that the observed DOC yield in our study (63% agricultural land, Table 1) was only about 20% of that predicted for a 100% agricultural watershed in the Great Lake region (Chen and Driscoll, 2009), agricultural lands may have a large range of DOC yields. Even still, due to the relatively low discharge, the DOC yields of the WSW was lower by about an order of magnitude than forested watersheds containing natural wetlands (Aitkenhead and McDowell, 2000). This suggests that carbon loss potential through the DOC pathway is limited (Kronholm and Capel, 2012) despite the large soil organic carbon storage (Fig. 2).

4. Regional implications and conclusions

This study clearly demonstrates the potential impact of agriculture on river biogeochemistry with DOC concentrations during the summer irrigation period reaching up to 18.9 mg L^{-1} from most agricultural subwatershed (Fig. 4). Similar patterns of high summer DOC concentrations were observed throughout the watershed, but lower peak concentrations at the mouth (~10 mg L^{-1}) suggest a dilution with lower DOC irrigation water or the greater relative contribution of DOC source such as row crop runoff (Fig. 4). This pattern of high summer DOC concentrations was not observed during the irrigation season for the Sacramento River, which received runoff from agricultural regions in the northern Central Valley. The DOC concentration from the Sacramento River was relatively constant with an average of 1.8 mg L^{-1} during summers of 2008 and 2009 (Fig. 4), suggesting that high DOC concentrations from agricultural fields was diluted with a large input of water from other non-agricultural regions of the Sacramento River Basin, especially snow melted water from the Sierra Mountains and release from numerous large reservoirs.

The disconnect in DOC maxima between small agricultural watersheds and large basins presents a conundrum on the efficacy of reducing DOC in the Sacramento River by decreasing DOC from agricultural fields. The area of the Sacramento River Basin above Freeport, CA which is located near the mouth of the entire basin is ~60,000 km^2 (Saleh et al., 2007) and agricultural land use covers 12% of the basin (with 2001 NLCD data), thus agricultural land occupies ~7200 km^2. Assuming summer DOC and water yield of agricultural lands in the basin is similar to those of WSW, 4.6 × 10^9 g of DOC would be exported from agricultural fields to the Sacramento River. This is consistent with estimates of ~2.1 × 10^9 g DOC derived from Sacramento Slough and Colusa Basin Drain data (Saleh et al., 2007), which constitute about half of agricultural lands in the Sacramento River Basin.

Assuming summer mean Sacramento River DOC of 1.77 mg L^{-1} of (Fig. 4) and using USGS discharge data (an average of 8.64 km^3 for summer 6 months during 2007–2008), the DOC load from the Sacramento River Basin was estimated to be 15.3 × 10^9 g per summer 6 months. Thus, DOC load from non-agricultural lands in the Sacramento River Basin is estimated to be 10.7 × 10^9 g. Although the impacts on the Sacramento River DOC concentrations would be limited even if the DOC concentrations from the agricultural fields are reduced by half due to the small coverage of agricultural land use, it is noteworthy that only 12% of agricultural land use within the Sacramento River Basin can contribute 30% of regional DOC loads.

Hydrology and flow paths strongly influence seasonal and annual DOC loads from the WSW in the Mediterranean climate. While DOC dynamics during winter baseflow and summer irrigation periods appear to be highly repetitive, the relative importance of winter storms for annual DOC export from the watershed varied significantly from year to year depending on winter precipitation. Considering that one of the key DOC sources of the WSW appears to be desorption from sediments and release from agricultural soils, changes in precipitation patterns and intensities as well as agricultural practices have potential to significantly alter the DOC dynamics.

Acknowledgments

We thank JohnFranco Saraceno, Jeanette Wrysinski, Frank Anderson for sample collection and Kathryn Crepeau, Will

Kerlin, and Cathleen Roush for lab analyses. We also thank Tamara Kraus and two anonymous reviewers for comments on an earlier draft of this manuscript. This work was funded by a grant from the California Bay Delta Authority Drinking Water Program and partial support to N.-H. Oh from Research Settlement Fund for the new faculty of SNU.

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