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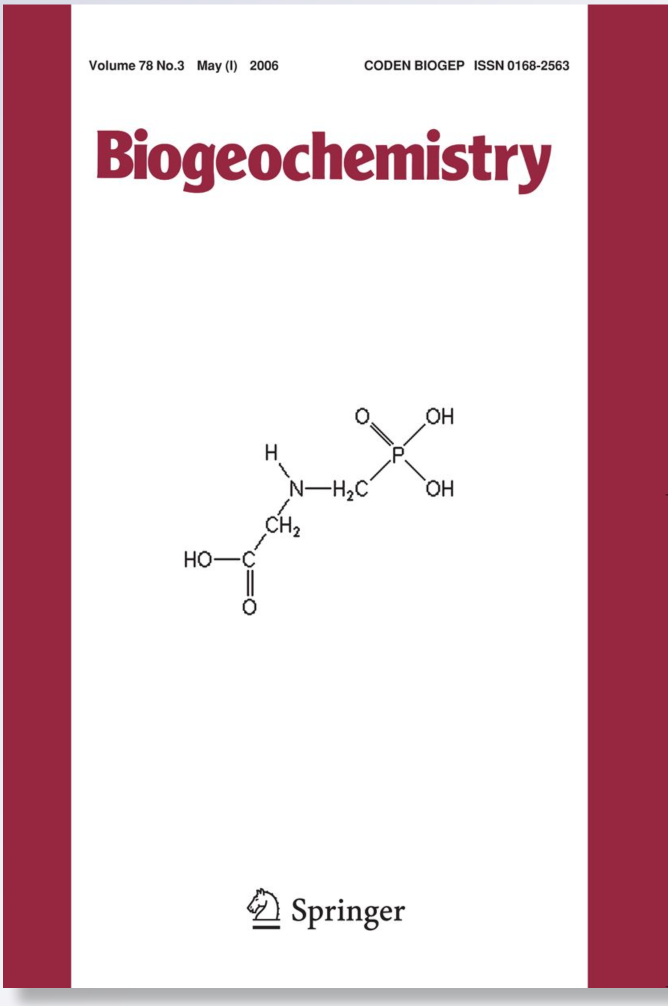

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Controls on dissolved organic carbon composition and export from rice-dominated systems

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Abstract Rice field outflow can contain high concentrations of dissolved organic carbon (DOC), which plays a crucial role in drinking water quality and aquatic ecosystem processes. This study examined the relationship between potential determining factors (i.e. rice area, outflow, drainwater reuse, soil properties, and time, measured as the day in the growing season) and the concentration and composition of DOC exported from 11 rice-dominated subwatersheds. Samples were collected from subwatershed inflow and outflow every 1–2 weeks from May through September 2008 and analyzed for DOC concentration, trihalomethane formation potential (THMFP), and also specific ultraviolet absorbance ($SUVA_{254}$) and the spectral slope parameter (S), which are indicators of DOC composition. Concentrations of DOC across all subwatersheds and sampling dates ranged from 1.56 to 14.43 mg L^{-1} (mean = 4.32 mg L^{-1}). Linear mixed effects (LME) analysis indicated that DOC concentration decreased over time, and that THMFP, and DOC and THM flux, decreased over time, but increased with outflow. LME analysis of the $SUVA_{254}$ and S parameters indicated that the fraction of aromatic DOC moieties increased with time, outflow, and reuse. Additionally, apparent peaks in DOC concentrations, THMFP, and $SUVA_{254}$ coincided with the onsets of flooding and draining. Lastly, subwatersheds with outflow less than approximately 4,700 m^3 ha^{-1} behaved as sinks of DOC. Our findings suggest that water management factors such as outflow, reuse, and discrete irrigation events, all of which vary over the course of the growing season, were the dominant determinants of DOC concentration and composition.

Keywords Agriculture · Rice · Dissolved organic carbon · Dissolved organic matter · Trihalomethanes

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Introduction

Dissolved organic carbon (DOC) plays a critical role in many ecosystem processes. The composition and concentration of DOC influence water quality, nutrient cycling, ecosystem respiration, and metal toxicity (Mulholland 2003). There are two sources of DOC to waterways: (i) internally produced sources derived from macrophytes and algae, which typically are low molecular weight, non-aromatic compounds (Bertilsson and Jones 2003) and (ii) terrestrially derived sources from plants, dissolved atmospheric dust, and soil organic matter, which tend to be high molecular weight, aromatic compounds (Aitkenhead-Peterson et al. 2003). In addition to its role in ecosystem processes, DOC can have impacts on human health, as it has been found to be a major precursor in the formation of carcinogenic and mutanogenic disinfection byproducts (Reckhow et al. 1990; Rook 1976, 1977). Trihalomethanes (THMs) are the most common form of disinfection byproducts, and are created during the chlorination of water in the drinking water treatment process (Dodds and King 2001; Nieuwenhuijsen et al. 2000). In response to this drinking water quality threat, the California Bay-Delta Authority (CALFED), whose mission is to improve the state's water supply and the ecological health of the Sacramento-San Joaquin River Delta, has efforts currently underway to define official drinking water standards and recommends that water treatment plants begin to remove DOC when concentrations exceed 3 mg L^{-1} (CALFED 2007).

Agriculture is now one of the dominant forms of land use on Earth, with croplands and pasture making up approximately 40% of the Earth's surface (Foley et al. 2005). Agricultural practices have been shown to impact the timing and magnitude of DOC export and biochemical composition in watersheds, because the water used for irrigation (i) flows over soil surfaces, which are relatively rich in organic matter, (ii) changes soils moisture conditions (Dalzell et al. 2005; Hernes et al. 2008; Wilson and Xenopolous 2009), and (iii) alters hydrologic flow regimes (Coe et al. 2009; Costa et al. 2003; Hernes et al. 2008). During the past 40 years there has been an ~70% increase in irrigated cropland area worldwide (Foley et al. 2005; Gleick 2003), making it crucial to understand how DOC exported from agricultural watersheds is impacting downstream ecosystems and what ramifications this poses for drinking water quality.

Rice is one of the most important irrigated crops on Earth. This staple grain is eaten by about 3 billion people (Bouman et al. 2007) and provides 20% of the World's dietary energy supply, compared to 19% for wheat and 5% for maize (FAO 2004). In 2009, 161 million ha of land (an area comparable to the size of Alaska) were used for rice cultivation (FAOSTAT 2009). Most rice is grown under submerged conditions, which provides several environmental benefits, including non-chemical weed control, increased water percolation and groundwater recharge, and flood control during heavy rains. In many countries, this system requires rice to receive up to two to three times more water than other irrigated crops, and it is estimated that irrigated rice receives one-fourth to one-third of the World's developed freshwater resources (Bouman et al. 2007). However, depending on local and regional water use practices, a variable fraction of rice water is reused in downstream areas, with estimates of 15–29% (Hafeez et al. 2007; Zulu et al. 1996).

The United States is the 12th largest producer of rice in the World, and in 2009, 1.3 million ha of land were employed in rice production (FAOSTAT 2009). Currently, approximately 200,000 ha of land in the Sacramento Valley are used to grow rice, and these areas drain into the Sacramento River (CDFA 2009). The Sacramento River is a source of drinking water for the city of Sacramento, and can provide up to 92% of freshwater inputs to the Sacramento-San Joaquin Delta (Kraus et al. 2008), which itself is a source of drinking water for over 22 million people throughout California.

Irrigation water in the Sacramento Valley drains from fields into small drainage canals, which drain into a series of progressively larger canals and/or natural creeks. This system of canals and creeks make up subwatersheds, similar to the concept of hydrologic watersheds (CH2MHILL 2003). The climate is characterized by hot, dry summers, which means that the subwatersheds are virtually dry throughout the growing season (May through September). Due to the dry summer climate and the highly managed, irrigated nature of most Sacramento Valley agriculture, water management practices are the dominant influence on water and DOC dynamics throughout the growing season (Hernes et al. 2008).

Flow-through water management is the most common practice in California rice agriculture. In this system, parallel earthen berms divide a rice field into several basins. Irrigation water enters the field through one or two inlet points at the top basin and then flows through the basins sequentially via weir boxes. Excess water leaves the field through one or more weirs at the bottom basin. At the start of the growing season in late April/early May, the fields are flooded and seeding takes place. For an approximately 40 day period after the initial flooding, fields are often drained and reflooded to promote seedling establishment and/or to allow for herbicide application. After this 40 day establishment period, maintenance flow begins, lasting from June through mid-August, when water levels are maintained at a depth of 10–13 cm by the steady addition of water through the inlets. Beginning in mid-August thru September, inputs into rice fields are stopped and the fields are drained completely to allow for harvest.

In California, rice cultivation consumes comparable quantities of water to other commonly grown crops (Hill et al. 2006). However, rice agriculture has a strong influence on drainwater flows relative to other crops because flow-through irrigation requires more water to enter a field than is actually utilized by the rice crop, and because the primary goal of irrigation in non-rice crops is water infiltration into the soil, whereas the goal of irrigation in rice is limited infiltration and high surface water flows (CH2MHILL 2003).

The mechanisms of water loss in all agricultural fields are evapotranspiration, percolation, seepage and drain outflow (Bouman et al. 2007). Approximately half of the water added to a California rice field is lost through evapotranspiration (Hill et al. 2006). The rate of seepage (the lateral flow of water, which may lead to the transportation of the water to drains) and percolation (the downward flow of water, leading to groundwater replenishment) is generally low in Sacramento Valley rice growing regions relative to non-rice agricultural areas due to high soil clay content (40–60%) and, in some rice soils, additionally due to the presence of a cemented soil layer (Hill et al. 2006). Because of the nature of these soils, surface flow paths dominate in rice fields, and this causes surface drainage to account for the majority of water loss that is not due to evapotranspiration. Furthermore, because water that travels via seepage and percolation comes into contact with deeper soils horizons that have low organic matter content and high DOC sorption capacity (Aitkenhead-Peterson et al. 2003), rice field contributions of DOC to surface water flows are likely to be higher relative to other forms of agriculture due to greater rice water contact with primarily surface soil horizons.

At the watershed scale, within both rice and non-rice agricultural areas, the primary sources of DOC in subwatershed outflow are (i) DOC in input waters and (ii) terrestrial inputs via water that has passed through soil, thereby coming into contact with soil organic matter and/or plant residues (Aitkenhead-Peterson et al. 2003). Rice straw residues are a potentially important DOC source, as Ruark et al. (2010) found that the burning of rice straw in the winter, versus the widespread practice of rice straw incorporation into the soil by plowing, significantly lowered DOC concentration and flux in rice field outflow. This is also important to the THMFP of DOC leaving these systems, because vascular plant materials are highly aromatic DOC sources (Hernes et al. 2008; Spencer et al. 2009, 2010).

Rice fields are comparable to wetlands in terms of high surface runoff (Aitkenhead-Peterson et al. 2003), however, unlike wetlands, which are characterized by the accumulation of organic matter (Faulkner and Richardson 1989), rice fields experience annual harvesting similar to non-rice crops. Both rice and non-rice Sacramento Valley soils have 1–2% organic matter in the surface horizon (Hill et al. 2006). As a result of these characteristics, rice fields are unique, a land use in between dry land forms of agriculture and wetlands.

In order to fully understand the impacts of rice-dominated areas on downstream water quality, it is important to understand the biochemical composition of dissolved organic matter (DOM) being released from rice-dominated watersheds. DOC is the carbon component of DOM, and the propensity of DOC to react with chlorine and form THMs has been found to increase with increasing DOM aromaticity (Chow et al. 2005). DOM composition is dependent on which organic matter pools are acting as DOM sources, on soil microbial and sorption processes, and on watershed hydrology (Hood et al. 2006). Numerous studies have used chromophoric DOM (CDOM) parameters, such as specific ultraviolet absorbance ($SUVA_{254}$) at 254 nm, the spectral slope parameter (S), and the spectral slope ratio (S_R), as indicators of DOM molecular characteristics (Helms et al. 2008; Spencer et al. 2010; Stedmon et al. 2000). The percent aromatic carbon of DOM has been found to be closely and positively correlated with $SUVA_{254}$ (Weishaar et al. 2003). Spectral slope and the spectral slope ratio have been found to be inversely correlated with both percent aromatic carbon and molecular weight (Blough and Del Vecchio 2002; Helms et al. 2008).

The goals of this study were (i) to quantify DOC and THM concentration, flux, and CDOM parameter dynamics over the course of the rice growing season and (ii) to generate multivariate models using linear mixed effect (LME) analysis, which identify and quantify the relationships between subwatershed characteristics, time (e.g. the progression of the growing season, measured as the day of the year), and DOC and THM concentration and flux and CDOM parameters. The subwatershed characteristics considered were soil properties (e.g. soil order, clay and organic matter content), water management and irrigation practices (e.g. water reuse, inflow and outflow rates), and the presence of other crops and/or land uses within the subwatersheds (e.g. orchards, wetlands, urban areas).

Materials and methods

Study area

The Glenn-Colusa Irrigation District (GCID) is located northwest of Sacramento and is the largest irrigation district in the Sacramento Valley, California (Fig. 1). It contains 11 subwatersheds ranging from 700 to 5,100 ha in size (Table 1; Fig. 1). The climate is Mediterranean, with a mean annual precipitation of 45 cm that occurs primarily from November through April (Glenn County 1993). During the growing season, the primary source of water to the GCID is the Sacramento River; groundwater, natural stream inputs, and inputs from neighboring irrigation districts are negligible (CH2MHILL 2003).

The GCID is located between the California Coast Range and the Sacramento River, which results in a west to east drainage pattern across subwatersheds. The Main Canal receives all of its water from the Sacramento River and moves water north to south along the western edge of the district (Fig. 1). Water from the Main Canal is delivered throughout the subwatersheds via a network of lateral canals. Once the water is used in an agricultural field, it enters a network of drainage canals, from which the water can be reused, before eventually emptying into the Colusa Basin Drain (Fig. 1). The Colusa Basin Drain begins in the GCID and transports drainwater south from over 400,000 ha of agricultural land before discharging into the Sacramento River (Department of Water Resources 2008). The quantity and timing of the use of water by the GCID significantly influence both flow in the Sacramento River and agricultural return flows to the Colusa Basin Drain (CH2MHILL 2003).

Water reuse is the practice of diverting agricultural return water from a drainage canal into a lateral canal, which allows the diverted water to be reused by growers. Water reuse activities within GCID subwatersheds take three forms: (i) water is reused within the subwatershed from which it came, (ii) water is added to a lateral within one subwatershed from another subwatershed, and (iii) water is sent to areas outside the subwatershed from which it came. The estimates of reuse that fell under categories (i) and (ii) were added together for each subwatershed to form a variable called internal reuse. The estimate of reuse that fell under category (iii) was called reuse out. Reuse out removes water before it can reach a subwatershed outlet point, causing a loss of information on that water's quantity and quality impacts at the sampling site. As a result, reuse out was treated as a random confounding variable whenever it occurred in a subwatershed, as described in the statistical analysis.

Subwatershed soils are dominated by Alfisols and Mollisols in the north and Vertisols in the south. The percent clay and percent soil organic matter of the top soil horizons range from 31 to 47%, and from 1.5 to 2.6%, respectively. The subwatersheds are dominated by soils classified as either poorly drained or somewhat poorly drained under the National Soils Survey Handbook (Natural Resources Conservation Service 2009). The percent area of each subwatershed that is used for rice agriculture ranges from 42 to 95%. The other forms of agriculture found in the GCID are diverse, and include alfalfa, almond and walnut orchards, corn, beans, onions, oats, safflower, sunflower, tomatoes, wheat, and pasture (GCID 2009).

The Sacramento National Wildlife Refuge, which consists of manmade wetlands managed by the U.S. Fish and Wildlife Service, is located within the Logan Creek subwatershed (Fig. 1). It obtains its water through the Main Canal, however it does not receive a significant amount of water during the rice growing season (U.S. Fish and Wildlife Service, personal communication), and was therefore not considered part of the Logan Creek irrigated subwatershed area (Table 1).

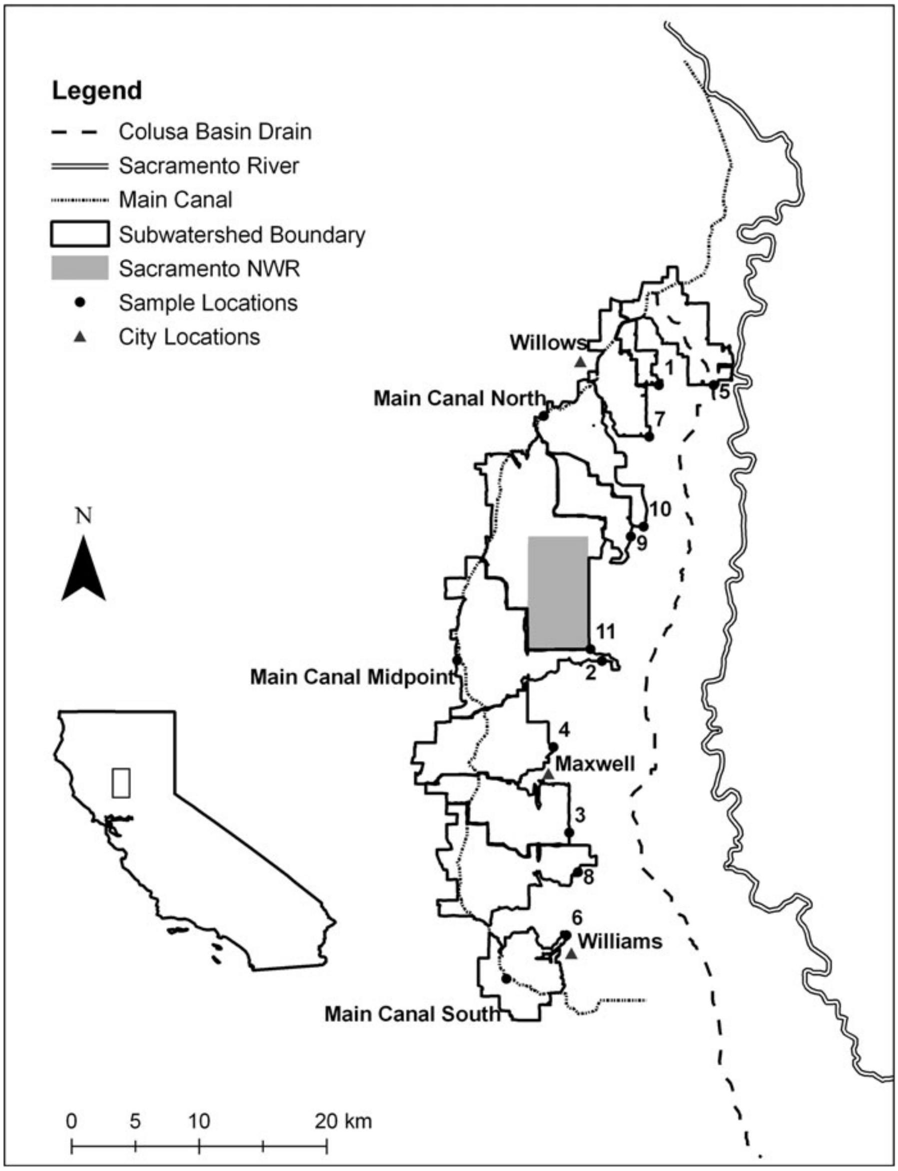

Fig. 1 GCID subwatersheds and sample locations (*black dots*). Water travels from north to south in the Sacramento River, in the Main Canal, and in the Colusa Basin Drain. GCID water is pumped into the northernmost section of the Main Canal from the Sacramento River and is delivered to subwatersheds via the Main Canal as it travels south. Drains within each subwatershed carry water from west to east to primary outlet points. Subwatershed outflow then enters the Colusa Basin Drain and is discharged back to the Sacramento River. The Sacramento National Wildlife Refuge (NWR) is located within the Logan Creek subwatershed. The *numbers* at the sample locations correspond to the Subwatershed IDs in Table 1

Sample collection and analyses

Sampling occurred every 1–2 weeks throughout the 2008 growing season, with more frequent sampling occurring during the establishment and drain periods. The first sampling event was May 8 and the final sampling event was September 25, 2008. During each sampling event, grab samples were collected at about 20 cm below the water surface from 11 subwatershed outlets and from a northern, midpoint, and southern location along the Main Canal (Fig. 1). Over the entire growing season, a total of 15 samples were collected from each subwatershed outlet and from each Main Canal location, with the exception of the midpoint Main Canal location, from which 11 samples were collected due to site inaccessibility, and with the exception of Salt Creek Weir, from which 11 samples were collected due to sampling at this site starting in June as a result of new information being obtained from the GCID (GCID staff, personal communication). A given sampling event would begin in the morning of each day and end in the evening.

On August 12, 2009, diurnal sampling occurred in the Colusa Basin Drain, and the Salt Creek Weir and

Table 1 Summary of subwatershed characteristics

Site name	Bondurant	Hunter Creek	Kuhl	Stone Corral	2047 Sidds	Salt Creek Weir	Drain 55	Section 25	Salmon Hole	Willow Creek	Logan Creek
Subwatershed ID	1	2	3	4	5	6	7	8	9	10	11
Outflow (m^3 ha^{-1})	15174	11481	10685	10516	10210	8394	4893	4185	2756	2127	1116
Net DOC load (kg ha^{-1})	14.6	38.8	34.4	10.6	18.3	11.9	−4.4	−2.4	0.1	−6.4	−8.7
Internal reuse (m^3 ha^{-1})	3922	913	3043	308	3020	1340	2651	167	4679	3047	2114
Reuse out (m^3 ha^{-1})	1461	0	0	1579	0	0	0	2939	0	3750	0
Inflow (m^3 ha^{-1})	25752	14951	18484	17984	21894	15317	19917	21052	11446	13828	14962
Irrigated area (ha)	696	5120	3683	3635	2945	2894	2395	4616	2073	3079	4462
Total area (ha)	697	5238	3821	4347	2971	3041	2416	4915	2086	3114	9696
% Irrigated	100	98	96	84	99	95	99	94	99	99	46
% Rice	86	78	81	47	80	42	89	84	95	94	82
% Vertisols	13	69	67	59	11	82	6	78	61	35	67
% SOM	2.57	1.57	2.26	1.68	1.79	1.97	1.77	2.32	1.73	1.58	1.52

Flow, net DOC loads, and reuse quantities represent the sum over the entire growing season, normalized by irrigated subwatershed area. % Rice, % Vertisols, and % Irrigated indicate the fraction of the total subwatershed area containing these properties. % Soil organic matter (SOM) indicates the average SOM content of the top horizon of subwatershed soils. The order of the subwatersheds is from the highest to lowest total outflow per hectare. During the growing season, 11 samples were collected from Salt Creek Weir and 15 samples were collected at each of the other subwatersheds

Logan Creek subwatersheds, to determine whether DOC concentration and biochemical quality varied significantly over the course of a day. Two water samples were collected in the morning, noon, and evening at each site.

Water samples were stored on ice and in the dark and subsequently filtered on return to the laboratory through a 0.45 μm filter (Millipore). After filtering, a portion of each sample was allowed to reach room temperature and analyzed for UV–Visible absorbance from 200 to 800 nm in a 10 mm quartz cuvette via a Shimadzu UV-1700 spectrophotometer.

The remaining filtered sample was stored frozen (−20°C) in the dark. DOC concentration was measured on acidified samples (pH 2 with 12 N HCl) with a Shimadzu TOC-V_{CSH} analyzer via the non-purgeable organic carbon method. All DOC data are the mean of 3–5 replicate injections for which the coefficient of variance (c.v.) was always less than 2%. DOC results were referenced against certified reference materials obtained from the Rosenstiel School of Marine and Atmospheric Science, University of Miami, USA and were found to always be within ±5%.

The spectral slope parameter was calculated for the 290–350 nm ($S_{290–350}$), 275–295 nm ($S_{275–295}$), and 350–400 nm ($S_{350–400}$) wavelength ranges. The spectral slopes were calculated by applying a non-linear exponential function regression to the absorbance spectrum over these ranges (Helms et al. 2008; Stedmon et al. 2000). The three ranges were selected because Helms et al. (2008) highlighted that, in a broad study of S for a range of DOM sources, the first derivative of the natural log spectra showed the greatest variation in the 275–295 and 350–400 ranges, and Spencer et al. (2007a) found 290–350 to allow discrimination of a wide variety of DOM sources. Lastly, the spectral slope ratio (S_R) was calculated as the ratio of $S_{275–295}$ to $S_{350–400}$ as this has also been linked to DOM sources and processing (Helms et al. 2008).

$SUVA_{254}$ values were calculated by dividing UV absorbance at a wavelength of 254 nm (a_{254}) by DOC concentration (mg L^{-1}) (Weishaar et al. 2003). a_{254} was also used in the estimation of the trihalomethane formation potential (THMFP) of the samples. a_{254} has been shown in a number of studies to have a strong linear correlation with THMFP (Chow et al. 2007, 2008; Fujii et al. 1998). However, the slope of the relationship between a_{254} and THMFP can vary between different water sources because, although a_{254} is indicative of aromaticity, differences in the specific chemical structures of DOM can cause variations in the propensity of the aromatic fraction to react with chlorine (Chow et al. 2008; Korshin et al. 1997; Weishaar et al. 2003). The THMFP analysis was conducted for samples collected from all sites on June 11 and September 10 in order to test the efficacy of a_{254} as an indicator of THMFP across the 11 different subwatersheds over the course of the growing season.

The THMFP method developed by the California Department of Water Resources at the Bryte Laboratory was used in this study (Crepeau et al. 2004). The THMFP analysis was performed immediately after sample filtration. First, the samples were diluted to DOC concentrations of 1–5 mg L^{-1}. The pH was then adjusted to 8.3 through the addition of H_3BO_3 and NaOH buffers. The samples were chlorinated with 4–6% NaOCl in order to have a concentration of available chlorine of 120–130 mg L^{-1}. The samples were then sealed in containers without headspace and stored for 7 days in a dark room at 20°C. After this time period, the chlorine was neutralized using Na_2SO_3 solution. The samples were then sent to Test America in Colton, California, and analyzed for THM concentrations by modified US EPA Method 524.2.

Subwatershed characteristics data

The GCID provided GIS data that delineated all of the agricultural fields within each subwatershed, the type of agriculture occurring on each field, the area of each field, and whether or not the field was irrigated (GCID staff, personal communication). ArcGIS 8.3 Desktop GIS (ESRI 2002) software tools and the GCID data were then used to calculate the total subwatershed areas, total irrigated subwatershed areas, the percent area of each subwatershed that was irrigated, and the percent area of each subwatershed that was used for the various forms of agriculture that were present during the 2008 growing season (Table 1).

Data from the GCID (GCID staff, personal communication) and GIS tools (ESRI 2002) were also used to estimate daily inflow, outflow, and reuse of water for each subwatershed. The GCID uses weirs at 10 sites and a staff gauge at one site to estimate daily subwatershed outflow. For inflow, the GCID data included information on the location of all laterals along the Main Canal, estimates of the amount of water added to each lateral from the Main Canal made using daily meter measurements, and spatial data regarding the layout of each lateral canal within each subwatershed. For reuse, the GCID data included information on the locations of the pumps and weirs used for drainwater reuse, the location and layout of the laterals to which they divert water, and the associated daily measurements of reuse diversions at each pump and weir. Because lateral canals cross subwatershed boundaries, estimates of the amount of water delivered by a lateral to a particular subwatershed were made by estimating the fraction of the total length of a lateral that is located within a given subwatershed and multiplying this by the total daily input of water into that lateral. Similarly, drainwater reuse estimates were made by estimating the fraction of the total length of a lateral downstream of a reuse pump or weir that is located within a given subwatershed and multiplying this by the total daily reuse measured at the pump or weir.

Inflow and outflow fluxes of DOC and THM occurring in each subwatershed on the day of a given sampling event were calculated by multiplying inflow and outflow DOC and THM concentrations by inflow and outflow measurements, respectively. Because of the low variation in DOC concentration across Main Canal sampling locations, inflow concentrations for a given sampling event were estimated by averaging the values of the Main Canal samples collected during that event. Flux values were then normalized by dividing absolute flux by the irrigated area of each subwatershed.

LoadRunner software was used to estimate daily inflow and outflow DOC flux for each subwatershed on days when concentrations were not measured, based on the daily inflow and outflow data provided by the GCID (Booth et al. 2007). LoadRunner uses LOADEST (Runkel et al. 2004) to apply the Maximum Likelihood Estimation (MLE) statistical method to concentration and flow data. This method centers the flow and concentration data to eliminate colinearity. Further, it uses the Akaike Information Criterion (AIC) to select one of nine predefined regression models that best fits the data. The coefficient of variation is presented in the model output and is an estimation of error for the fluxes calculated. Additionally, the output provides the r^2 of the MLE, residuals data, and serial correlation of residuals data, in order to verify that the model is valid and that the data are normally distributed.

LOADEST requires 12 measurements of concentration and flow per site. To calculate daily outflow DOC flux, 15 measurements of DOC concentration, and 15 corresponding measurements of outflow, were entered into LoadRunner for each subwatershed. In order to account for 11 concentration measurements taken at Salt Creek weir, the concentration at a sampling site downstream of the weir was used as the estimate of a 12th DOC concentration for the May 26, 2008 sampling event. A similar process was performed to calculate the daily inflow DOC flux from Main Canal deliveries. The concentration and flow values used were the 15 measurements of average Main Canal DOC concentration, and the corresponding 15 measurements of inflow for each subwatershed.

The r^2 of the regression of observed flux values versus the flux values predicted by LoadRunner were 0.94 and 0.90 for inflow and outflow flux, respectively (Online Resource 1). The estimations of the daily flux values were then summed to determine the total growing season DOC loads that entered and left each subwatershed. Lastly, the entry load was subtracted from the outflow load to obtain an estimate of the net DOC growing season load produced by each subwatershed (Table 1).

The towns of Maxwell, Williams, and Willows are located within the GCID (Fig. 1), but towns were not included in irrigated subwatershed areas because there were no storm events during the growing season. The only potential influence of the towns on DOC was through treated wastewater inputs. Williams wastewater is not discharged into any of the subwatersheds after treatment. Maxwell wastewater enters the drainage system in the middle of the Kuhl subwatershed. Willows wastewater goes through tertiary treatment and is added to a lateral for agricultural use within the Willow Creek subwatershed.

Soils data was obtained from the Soil Survey Geographic (SSURGO) database (Soil Survey Staff 2009). R statistical software (R Development Core Team 2009) and GIS tools (ESRI 2002) were utilized to estimate the percent area of each soil order within a subwatershed. The average percent clay and percent organic matter contents in the top subwatershed soil horizons were also estimated. This was done by taking the area weighted average of the surface horizon clay and organic matter values of all the soil map units located within each subwatershed.

Statistical analyses

LME regression analysis (Pinheiro and Bates 2000; Zuur et al. 2009) was used to identify and quantify relationships between the subwatershed characteristic and sampling date independent variables and the DOC and THM concentration and flux and CDOM parameter response variables (Table 2). The analysis of data with LME has been performed in studies with similar longitudinal (measured over time) and cross-sectional (monitoring of multiple locations) data structure. This method allows for the robust, simultaneous assessment of relationships between response variables and environmental factors, while accounting for the repeated measures embedded in the data structure (Ahearn et al. 2005; Tate et al. 2003).

Data analysis was carried out using S-PLUS software (S-PLUS 2001). Separate statistical models were developed for DOC concentration, THMFP, DOC and THM flux normalized by irrigated subwatershed area (DOC flux per ha and THM flux per ha, respectively), $SUVA_{254}$, S_R, $S_{275–295}$, $S_{290–350}$, and $S_{350–400}$ (Table 2). DOC and THM flux per ha models used the flux values measured during each sampling event and not the estimates obtained from LoadRunner. For all analyses, sample site (subwatershed) identity was treated as a random effect grouping variable to account for autocorrelation introduced by repeated measures at each sampling location. Additionally, reuse out was added as a random effect variable to adjust for the diversion of water upstream of sampling locations.

Fixed effect independent variables for all initial models were time (day of the growing season, measured as Julian day), outflow, irrigated area, % rice, % vertisols, % surface horizon soil organic matter, and internal reuse. The following interactions were also included: outflow $\times$ time, irrigated area $\times$ time, % rice $\times$ time, and % rice $\times$ irrigated area. Measurements of inflow and % clay were not included because these factors were collinear with outflow (Pearson $r = 0.50$) and % vertisols (Pearson $r = 0.70$), respectively.

In the case of the DOC and THM flux per ha models, irrigated area and its interactions were removed from the initial model because these two response variables are already normalized by this factor. In order for independent variable units to be consistent with the normalized flux units, the internal

Table 2 Results of LME analyses for DOC concentration and flux, THMFP and THM flux, $SUVA_{254}$, and spectral slope ($S_{275-295}$ and $S_{290-350}$)

Response variable	LME model coefficients ± standard error						Goodness-of-fit[c]		
	Time[a]	Outflow[b]	Internal reuse[b]	Time × outflow[b]	Intercept	AIC	r^2	Slope	Intercept
ln DOC (mg L^{-1})	−0.006 ± 0.0004	–	–	–	2.592 ± 0.104	0.71	0.80	0.79	0.29
ln THMFP (mg L^{-1})	−0.003 ± −0.0003	0.091 ± 0.025	–	–	6.729 ± 0.129	32	0.72	0.70	1.89
DOC flux (g day^{-1} ha^{-1})	−0.259 ± 0.139	7.541 ± 0.665	–	−0.019 ± 0.003	75.422 ± 35.132	1722	0.90	0.89	19.17
THM flux (g day^{-1} ha^{-1})	−0.065 ± 0.011	0.511 ± 0.026	–	–	14.880 ± 4.540	1083	0.90	0.89	2.66
$SUVA_{254}$ (L mg C^{-1} m^{-1})	0.006 ± 0.0005	0.093 ± 0.020	0.195 ± 0.062	–	1.245 ± 0.123	113	0.53	0.51	1.34
$S_{275-295}$ ($\times 10^{-3}$ nm^{-1})	−0.013 ± 0.002	0.768 ± 0.247	−0.624 ± 0.192	−0.006 ± 0.001	18.416 ± 0.501	427	0.53	0.58	6.13
$S_{290-350}$($\times 10^{-3}$ nm^{-1})	−0.021 ± 0.002	−0.350 ± 0.070	–	–	19.945 ± 0.371	461	0.59	0.57	6.51

DOC concentration and THMFP data were natural log transformed in order to meet the normality assumption. There were 160 measurements used for each LME analysis and goodness-of-fit estimation. The '–' indicates that the variable was not significant ($p > 0.05$) or that the variable raised the model AIC. The '±' indicates standard error of the coefficient

[a] Time is the day in the growing season measured as Julian day

[b] DOC flux per ha and THM flux per ha analyses were performed using outflow and reuse values that were normalized by irrigated area with units of (m^3 day^{-1} ha^{-1}). For all other analyses, outflow and reuse units were (m^3 s^{-1})

[c] Results of the linear regression of the observed data versus the values predicted by the LME model. The goodness-of-fit of an ideal model would have an r^2 and slope equal to 1, and an intercept equal to zero

reuse, reuse out, and outflow variables used in the initial model were also normalized by irrigated area.

Final models were created using a two-part backwards stepping approach. First, insignificant variables ($p > 0.05$) were removed if they were not part of a significant interaction. Second, significant ($p < 0.05$) variables that raised the AIC were removed. This was done in order to create significant, parsimonious models. The r^2, slope, and intercept values obtained from the simple linear regression of the observed data versus the values predicted by the LME models were used as indicators of the model goodness-of-fit (Table 2).

The assumptions of homogeneity of variance and normality were checked by evaluation of graphs of: (i) residuals versus fitted values, (ii) predicted versus observed values, and (iii) normal quantile–quantile plots of the residuals. DOC concentration and THMFP data did not meet the assumption of normality and were natural log transformed.

The same backwards stepping approach and assumption testing procedures were used to create an LME model for the relationship between a_{254} and THMFP. The data for this analysis involved the repeated sampling of both the Main Canal and subwatershed outlet locations. To account for this, sampling location identity was added to the model as a random grouping variable. THMFP was the response variable, and a_{254}, sampling event date, and the a_{254} × sampling event date interaction were fixed independent variables.

The analysis of the diurnal sampling data was performed by developing LME models for DOC concentration and CDOM parameter response variables. In these models, sampling location was a random effect grouping variable, and time of day (morning, noon, and evening) was a fixed independent categorical variable.

Results

DOC and THM concentration and flux and CDOM parameter dynamics

There were no known significant variations from typical climate, and agricultural and water management practices during the 2008 growing season (GCID staff, personal communication). Furthermore, DOC concentration patterns were similar among subwatersheds (Online Resource 2) and consistent with patterns measured in the sampling of drainage canals performed by Ruark et al. (2010) during the 2006 and 2007 growing seasons. This implies that the 2008 growing season was likely representative of normal conditions.

Important soil and agricultural characteristics and water management practices investigated in this study are presented in Table 1. Figure 2 shows the distributions of the concentration, flux, flow, internal reuse, and CDOM parameters collected for each subwatershed. DOC concentrations across all subwatersheds and sampling dates ranged from 1.56 to 14.43 mg L^{-1}, with a mean of 4.32 mg L^{-1} (SE ± 0.17 mg L^{-1}). $SUVA_{254}$ across all subwatersheds and sampling dates ranged from 1.65 to 4.02 L mg C^{-1} m^{-1}, with a mean of 2.73 L mg C^{-1} m^{-1} (SE ± 0.03 L mg C^{-1} m^{-1}). DOC concentrations across all Main Canal locations and sampling dates ranged from 0.82 to 1.67 mg L^{-1}, with a mean of 1.18 mg L^{-1} (SE ± 0.03 mg L^{-1}). $SUVA_{254}$ across all Main Canal locations and sampling dates ranged from 1.98 to 3.66 L mg C^{-1} m^{-1}, with a mean of 2.53 L mg C^{-1} m^{-1} (SE ± 0.06 L mg C^{-1} m^{-1}). A Tukey test did not detect a significant difference ($p > 0.05$) in the DOC concentration and

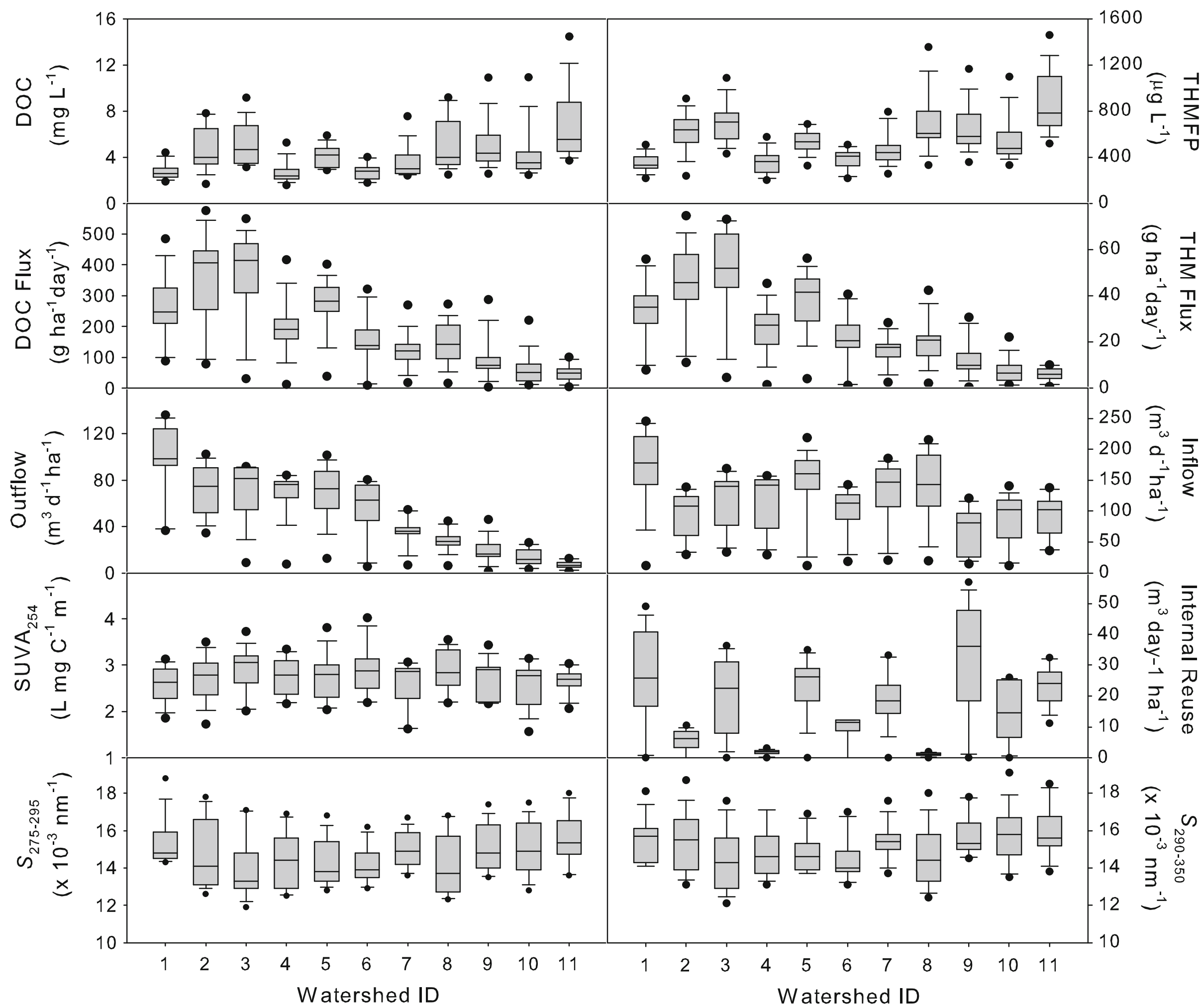

Fig. 2 Boxplots representing the distributions of DOC concentration and flux, THMFP and THM flux, $SUVA_{254}$, spectral slope ($S_{275-295}$ and $S_{290-350}$), flows, and internal reuse measured for each subwatershed. The *whiskers* are the upper 90% and lower 10%, the *boxes* are the upper 75% and lower 25%, and the *line* is the median value. Subwatersheds are ordered from the most to the least total growing season outflow per hectare

CDOM parameters between the northern, midpoint, and southern sampling locations. Simple linear regression showed that there was no significant relationship between DOC concentration and time in the Main Canal ($p > 0.05$). Simple linear regression indicated that SUVA decreased over the course of the growing season in the Main Canal ($p = 0.01$), however the slope of the relationship is near zero (*slope coefficient* = −0.003).

CDOM parameters are characterized by small variation between subwatersheds relative to DOC and THM concentration and flux (Fig. 2). Variations over time in DOC concentration and flux, flow, internal reuse, and select CDOM parameters measured in one representative subwatershed (Subwatershed ID 3 in Fig. 1) are presented in Fig. 3. This subwatershed showed similar trends in DOC quantity and quality, and inflow and outflow, as other subwatersheds, and also exhibited relatively average values for all parameters measured (Subwatershed ID 3 in Fig. 1) (Online Resource 2). DOC flux patterns followed outflow more closely than they did concentration both across and within subwatersheds (Figs. 2, 3). Furthermore, apparent increases in DOC, THMFP, and $SUVA_{254}$ values, and corresponding decreases in $S_{275–295}$ and $S_{290–350}$, coincided with the onsets of the establishment and drain periods (Fig. 3; Online Resource 2). Overall, as the growing season progressed, DOC concentration, THMFP, $S_{275–295}$ and $S_{290–350}$ gradually decreased over time, while $SUVA_{254}$ gradually increased over time (Fig. 3).

The relationship between net DOC load per ha and total outflow per ha produced by each subwatershed over the entire growing season was investigated using simple linear regression on the natural log transformed data (Fig. 4a; Table 1). The results show that there is a strong correlation between the net growing season DOC load and the total growing season outflow calculated for the 11 subwatersheds ($r^2 = 0.86$; $p < 0.0001$) (Fig. 4a). The linear regression indicates that net DOC loads are zero when total growing season outflow is approximately 4,700 $m^3\ ha^{-1}$. Net DOC loads ranged from −8.7 to 38.8 kg ha^{-1} (Fig. 4b; Table 1).

There was a strong correlation between THMFP and a_{254} ($r^2 = 0.99$; $p < 0.0001$), with no difference in the slope of the relationship between the June 11 and September 10 sampling events. This suggests that the linear relationship between THMFP and a_{254} is constant across sample sites and throughout the growing season. The LME analysis of the diurnal sampling event showed no significant difference in DOC concentration or CDOM parameters between the morning and noon, morning and evening, and noon and evening sampling times ($p > 0.05$).

LME analysis identification and quantification of significant factors driving subwatershed DOC and THM dynamics

The models for $S_{350–400}$ and S_R had very low r^2 values ($r^2 = 0.15$ and $r^2 = 0.25$, respectively), and for this reason the data and models for these factors are not included (Table 2). As in a simple linear regression, the coefficients of the fixed effect independent variables presented in Table 2 represent the magnitude of the relationship between the independent and response variable and whether the relationship is a positive or negative correlation.

DOC flux per ha was predicted by a combination of time, outflow, and time × outflow interaction (Table 2). The equation for this LME model is (DOC flux per ha) = 75.4 + −0.259*Time + 7.541*Outflow + −0.019*(Time × Outflow) (Table 2). The goodness-of-fit parameters show that this model has an r^2 and slope close to 1, and an intercept value that is relatively small compared to the magnitude of the range in DOC flux per ha (Fig. 2). This indicates that the model explains a large portion of the variation in DOC flux per ha leaving each subwatershed.

Because the nature of an interaction is difficult to discern by looking only at the coefficients of a linear equation, the LME model of the response of DOC flux per ha to variations in time and outflow (Table 2) is depicted in Fig. 5a. DOC flux per ha tends to increase with increased outflow per ha, but the magnitude of that increase diminishes as the growing season progresses (Fig. 5a).

The LME models for THM flux per ha and THMFP indicate that both factors increase with outflow and decrease over time. DOC concentration showed no significant response to outflow, but was similarly found to decrease over time. $SUVA_{254}$ was found to increase with time, outflow, and internal reuse. $S_{290–250}$ was found to decrease with both time and outflow. $S_{275–295}$ was predicted by time, outflow, internal reuse, and time × outflow. It was found to decrease with all three individual variables, but the

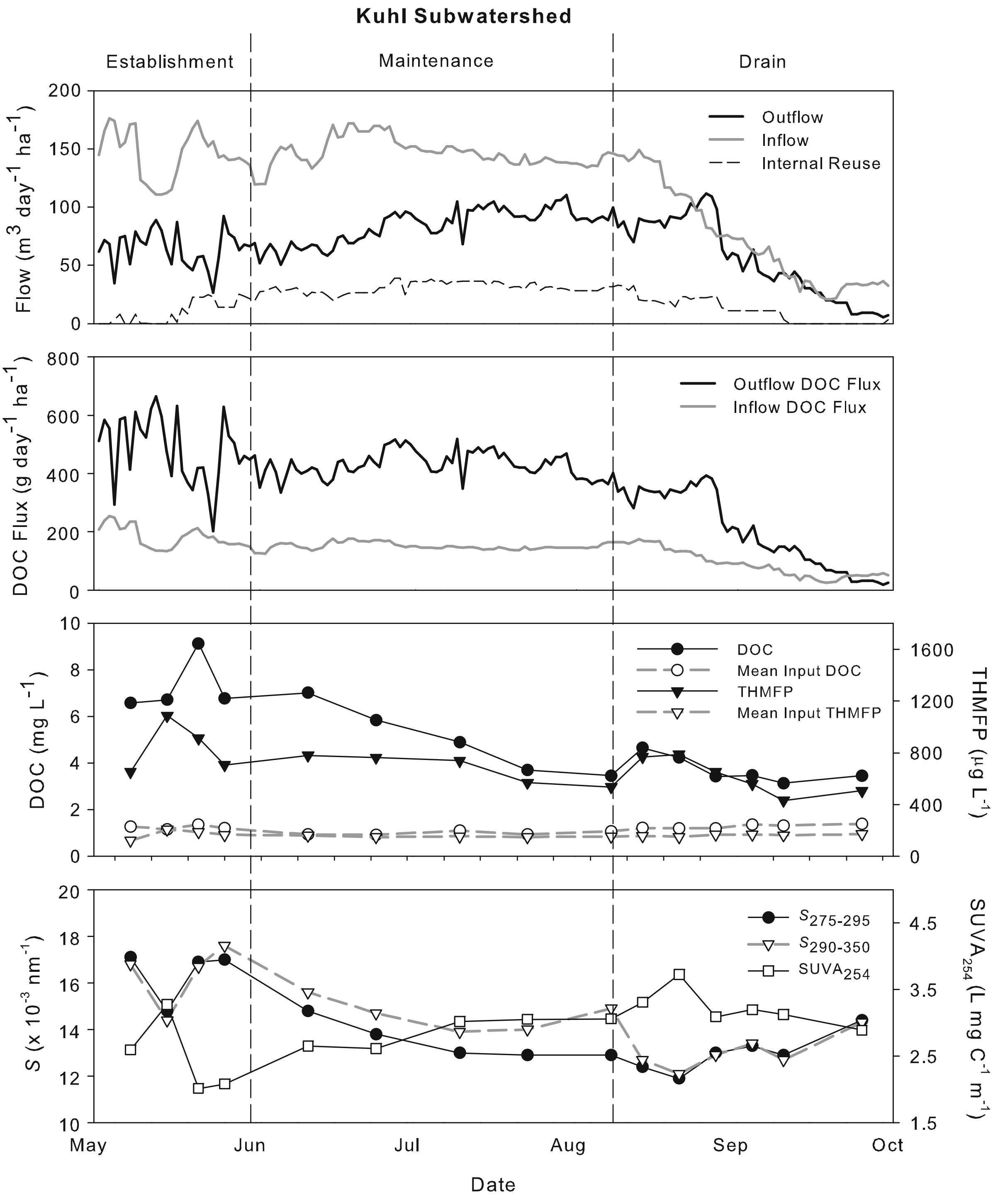

Fig. 3 Flow, internal reuse, DOC concentration and flux, THMFP, $SUVA_{254}$, and spectral slope ($S_{275–295}$ and $S_{290–350}$) data obtained over the course of the growing season for the Kuhl subwatershed. Additionally, the average DOC and THMFP values of the three Main Canal sampling locations for each sampling event are included in the third panel. The standard error values for these measurements were too small to be visible in the figure. The DOC and THMFP standard errors of all Main Canal samples were 0.03 mg L^{-1} and 10.07 µg L^{-1}, respectively. The *dashed vertical lines* indicate the estimated establishment, maintenance, and drain periods occurring within the rice growing season in 2008

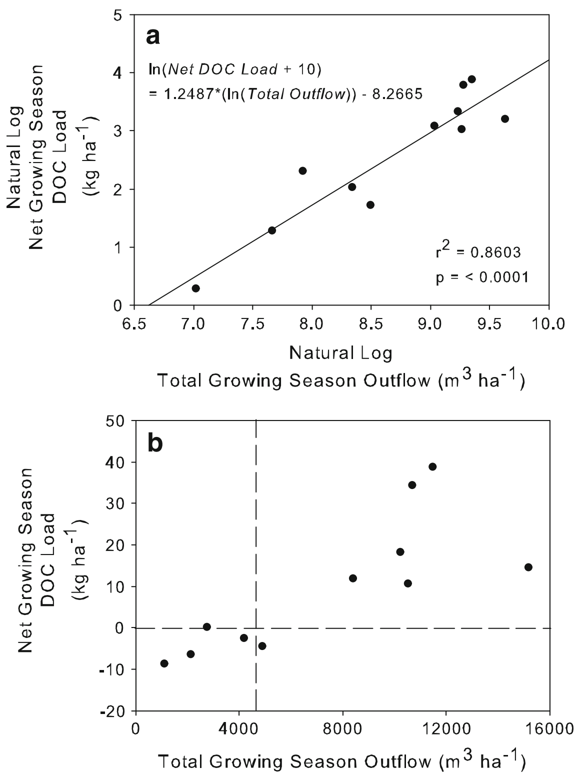

Fig. 4 **a** Results of the linear regression of total outflow versus the net dissolved organic carbon (DOC) load generated by each subwatershed over the course of the growing season. The data was natural log transformed to meet the assumption of homogeneity of variance. **b** Total growing season outflow versus net DOC load. The *dashed lines* indicate the total outflow amount, estimated from the linear regression presented in Fig. 4a, that results in zero net DOC flux. Parameter data can be found in Table 1

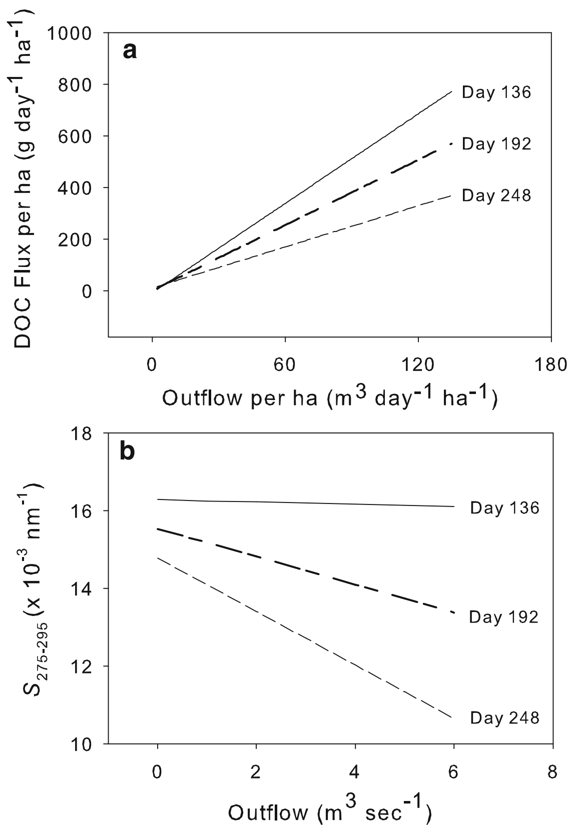

Fig. 5 **a** Graphical depiction of the relationship between DOC flux per ha and the time × outflow interaction, predicted by the LME model. Hypothetical values of time and outflow were used as inputs into the model. **b** Graphical depiction of the relationship between spectral slope ($S_{275–295}$) and the time × outflow interaction, predicted by the LME model. Hypothetical values of time, outflow, and internal reuse (which was assumed constant at 0.5 m^3 s^{-1}) were used as inputs into the model. The goodness-of-fit parameters of both LME models are presented in Table 2

time × outflow interaction indicates that as the growing season progressed, $S_{275–295}$ decreased more in high outflow than low outflow systems (Fig. 5b). In general, the LME models for the CDOM parameters had much lower r^2 and slope values than the flux and concentration models (Table 2). This is likely due to the low variation in CDOM parameters between subwatersheds (Fig. 2).

Discussion

General DOC trends in rice dominated subwatersheds

Across subwatersheds, the water inflow averaged 17,600 m^3 ha^{-1} and the outflow averaged 7,400 m^3 ha^{-1}. These values are consistent with field scale measurements of inflow and outflow in California rice agriculture (Hill et al. 2006). When compared to other Sacramento Valley watersheds, the average growing season DOC concentration (4.35 mg L^{-1}) measured in the GCID subwatersheds was greater than the annual average concentration of 2.02 mg L^{-1} detected in the Sacramento River, but similar to the annual average concentration of 4.74 mg L^{-1} measured in the Colusa Basin Drain (Chow et al. 2007) and the average growing season concentration of 5.28 mg L^{-1} measured in the Willow Slough watershed (Hernes et al. 2008), both of which are dominated by outflow from agriculturally dominated areas and both of which drain into the Sacramento River. All of the watershed scale concentrations are lower than the annual median DOC concentration of 9.5 mg L^{-1} that was measured over the course of 2 years in California rice field outlets (Ruark et al. 2010). The variation in DOC concentration among field and watershed systems highlights the need for research to characterize the response of DOC dynamics to agricultural irrigation activities at multiple scales.

The similarity among subwatersheds in $SUVA_{254}$, $S_{275–295}$ and $S_{290–350}$ (Fig. 2) implies that, despite variations in percent rice area, the dominant source of drainwater in all subwatersheds is rice water, simply because of the large amount of surface water inputs that rice produces relative to other crops. This dominance of rice water may also explain why, in all of the LME models, % rice was not detected as a significant driving factor.

Although soil properties have been found to influence DOC in watershed runoff (McDowell and Likens 1988; Moore 1989; Moore and Jackson 1989; Nelson et al. 1993), in this study soil properties were not a significant influence in any of the LME models. This is most likely due to rice field management causing such an intense disturbance and change in the soil, that soil differences prior to rice cultivation are masked by the strength of anthropogenic management effects (Kogel-Knabner et al. 2010).

LME models of DOC and THM concentration and flux

The LME analysis of DOC and THM flux per ha indicates that greater outflow is able to mobilize more DOC from these systems (Fig. 5a; Table 2). This is consistent with the results of studies of DOC export from California rice fields (Ruark et al. 2010), studies of agricultural subwatersheds, both in California and the Midwest (Dalzell et al. 2005, 2007; Hernes et al. 2008), and studies of natural watersheds (Raymond and Saiers 2010), all of which found that outflow was the primary factor controlling DOC flux.

There are two possible mechanisms that allow higher flow to mobilize a greater quantity of DOC out of rice field soils. First, studies have shown that higher outflow is able to flush more of the DOC adsorbed on soil aggregate surfaces and contained in soil micropores (Hood et al. 2006; Jardine et al. 1990; Kalbitz et al. 2000). Second, higher flow rates have been found to cause a decrease in the contact time between water and soils, allowing for less DOC adsorption and microbial degradation (Kalbitz et al. 2000).

The DOC and THM concentration and flux per ha were also found to be driven by time, with all of these variables decreasing over the course of the growing season (Fig. 3; Online Resource 2). This is likely a result of the depletion of the pool of available DOC over time by the constant flow of water through the rice fields, an example of supply limited dynamics (Chow et al. 2009; Hood et al. 2006; Sanderman et al. 2009; Spencer et al. 2010). This depletion is also the most probable cause for the decreased response over time of DOC flux per ha to increased outflow per ha (Fig. 5a).

The lack of a significant relationship between DOC concentration and outflow is different from many forested and agricultural watershed studies (Dalzell et al. 2007; Mulholland 2003). This is likely because this study did not include short duration hydrologic events (e.g. storms, freshets), and peaks in discharge due to short high intensity events are most often what drive corresponding peaks in DOC concentration (Mulholland 2003). Furthermore, strong DOC–discharge relationships apply primarily to well-drained soils (Mulholland 2003). Streams draining areas with predominantly surface flowpaths, which is the case in California rice fields, have poor DOC concentration and discharge relationships, due to the predominance of surface flow paths depleting the DOC in surface horizons (Mulholland 2003), leading to a hysteresis effect (Boyer et al. 1997; Hornberger et al. 1994).

LME models of CDOM parameters

All three CDOM parameters ($SUVA_{254}$ $S_{275–295}$ and $S_{290–350}$) indicate a significant increase in the fraction of aromatic and high molecular weight moieties over the course of the growing season. This shift in DOM biochemical composition may be due to two possible mechanisms, which are not mutually exclusive. First, non-aromatic compounds tend to be more hydrophilic than aromatic compounds (Benner 2003), therefore dissolving more easily in water, while hydrophobic, high molecular weight, and/or more aromatic DOM tend to be preferentially adsorbed onto soil aggregates (Gu et al. 1995; Kalbitz et al. 2000; McKnight et al. 1992; Meier et al. 2004). The likely result of this fractionation of DOM over time is that the organic matter that remains in rice fields becomes relatively enriched in aromatic moieties of DOM. Second, microbes tend to preferentially degrade non-aromatic compounds, especially under the anaerobic conditions typically occurring in irrigated rice systems, which can also result in a relative enrichment in the aromatic fraction of DOM (Cleveland et al. 2004; Kalbitz et al. 2003a, b; Marschner and Kalbitz 2003).

The dependence of biochemical composition on internal reuse detected by the $SUVA_{254}$ and $S_{275-295}$ parameters is closely related to the processes occurring over time discussed above. Reuse increases the residence time of water in the subwatersheds, thereby effectively acting to increase the magnitude of preferential microbial degradation and mobilization of non-aromatic DOM.

All three CDOM parameters indicate that outflow is correlated with changes in DOM quality (Table 2; Fig. 5b). The processes responsible for these trends are likely due to the combination of higher outflow removing greater amounts of the DOM sorbed onto soils and at the same time allowing less time for DOM sorption to occur. As discussed previously, DOM that sorbs onto soil tends to be more aromatic. Therefore, in addition to removing more DOC, greater outflow likely decreases the amount of preferential aromatic sorption to the soil and increases the relative fraction of aromatic moieties of DOM being mobilized from the soil.

The interaction between time and outflow detected by $S_{275-295}$ indicates that the magnitude of the outflow leaving subwatersheds has a smaller influence on DOM quality earlier in the growing season (Fig. 5b). The most probable mechanism behind this interaction is that early in the growing season, the preferential removal of non-aromatic moieties has had little time to occur (i.e. low hydrologic throughput), but as the growing season progresses, higher outflow systems experience greater DOM fractionation and therefore greater enrichment in aromatic DOM moieties.

Variations in DOM composition are likely responsible for THMFP being predicted by both time and outflow, while DOC concentration is predicted only by time. The positive correlation between THMFP and outflow is most likely driven by the positive correlation between percent aromatic DOM moieties and outflow, as THMFP has been found to increase with DOM aromaticity (Chow et al. 2005).

The LME model for $S_{275-295}$ detected a greater number of significant variables than the $S_{290-350}$ and $SUVA_{254}$ models (Table 2). The apparent sensitivity of this CDOM parameter to changes in DOM quality is consistent with previous work, which has found that this narrow wavelength range within the UV is highly sensitive to shifts in DOM properties (Helms et al. 2008; Spencer et al. 2009). Because the $S_{275-295}$ LME model was driven by all of the same determining factors as the $SUVA_{254}$ model, and additionally it was able to detect a significant time $\times$ outflow interaction, $S_{275-295}$ is a potentially useful and simple measurement that can be used as an alternative and/or supplement to $SUVA_{254}$ measurements. Unlike $SUVA_{254}$, spectral slope has the benefit of being a measurement that can be taken instantly in the field using in situ instruments, which allows for real time monitoring (Belzile et al. 2006; Saraceno et al. 2009; Spencer et al. 2007b). It should be noted that although the $S_{275-295}$ parameter was the most sensitive in this study, other studies, performed in larger watersheds and across seasons, found that the S_R, $S_{350-400}$, and $S_{290-350}$ measurements were also highly sensitive to changes in DOM quality (Helms et al. 2008; Hernes et al. 2008; Spencer et al. 2009, 2010). This implies that studies utilizing CDOM parameters as indicators of DOM biochemical composition would benefit from calculating a range of CDOM parameters and then determining which is the most responsive to the specific systems and time scales under investigation.

Apparent peaks in DOC concentration and quality during establishment and drainage activities

There are apparent, short-term peaks in DOC concentration, THMFP, and $SUVA_{254}$, and corresponding dips in $S_{275-295}$ and $S_{290-350}$, that coincide with the periods of the growing season when the onset of flooding (May) and onset of draining (late August thru early September) primarily occur (Fig. 3; Online Resource 2). Ruark et al. (2010) also found peaks in DOC concentration, both in rice field outlet and drainage canal measurements, which coincided with these events. The timing of these peaks implies that they are a signature of rice field flooding and draining, however the sampling frequency in this study resulted in only one, sometimes two, samples being collected for a given peak, the low resolution thereby preventing a statistical analysis of these events. As a result, the peaks and their potential causes are treated qualitatively in the following discussion.

The apparent changes in DOC concentration, THMFP, and CDOM parameters that coincide with the onset of flooding have been observed to be common in terrestrial systems that are subject to wet–dry cycles (Lundquist et al. 1999; Tipping et al. 1999). Assuming that the onset of flooding is the cause of the early peaks, several mechanisms may be responsible for the dynamics in DOC concentration and composition observed during this period: (i) during the dry period decreased microbial utilization limits the depletion of organic matter, (ii) the rewetting of the fields disturbs soil structure, thereby causing a release of previously sorbed and protected organic matter, and (iii) because rice straw is the primary organic matter input into these soils, much of the organic matter that accumulates at the soil surface is highly aromatic vascular plant derived material. This accumulated material would be readily mobilized upon initial contact with water, which could thereby cause an increase in DOC, THMFP, and $SUVA_{254}$, and a concurrent decrease in $S_{275-295}$ and $S_{290-350}$, as observed in Fig. 3.

The apparent increases in DOC concentration and THMFP that coincide with the onset of draining could potentially be due to the sharp increase in the flow rate of water across fields during the drain period relative to the maintenance flow period. The drain period involves the quick release of water so that fields can dry and support the machinery required to harvest rice. Increases in DOC concentration due to events that cause sharp increases in overland flow have been observed in many systems (Chow et al. 2009; Dalzell et al. 2005; Hood et al. 2006; Moore 1989). The mechanisms behind such a change in concentration most likely involve increased mobilization, and decreased sorption in response to greater outflow, which were discussed previously. Another potential mechanism is that increased flow causes the mobilization of DOC from new source pools (Dalzell et al. 2005; Hood et al. 2006; Sanderman et al. 2009). However, this is unlikely to be a mechanism in the rice-dominated subwatersheds because no new areas are being irrigated during the draining period and because the nature of the soils restricts changes in the depth of flow of water (Hill et al. 2006).

During the onset of draining, CDOM parameters indicate that there are apparent increases in aromatic DOM moieties. This is consistent with other studies, which found high flow events are commonly associated with increases in DOM aromaticity (Dalzell et al. 2005; Hood et al. 2006; Sanderman et al. 2009; Spencer et al. 2010). Such variations are potentially driven by the mobilization of previously untapped DOM sorbed onto soil aggregates and by the lack of time for preferential DOM adsorption, with both of these processes resulting in an increase in DOM aromaticity (Dalzell et al. 2005; Hood et al. 2006; Sanderman et al. 2009). Additionally, DOM that was previously unable to be mobilized is older, as it was retained in the fields until the end of the growing season. This implies that it may have experienced greater microbial degradation, which, as discussed earlier, tends to increase DOM aromaticity.

The apparent changes in DOC concentration, THMFP, and CDOM parameters that coincide with the onsets of flooding and draining (Fig. 3) indicate that further studies with greater sampling frequency during key irrigation events are needed for a complete understanding of the factors that drive DOC export and quality patterns in rice agricultural systems.

Management implications

In California, urban expansion is driving the need for greater amounts of clean drinking water, and simultaneously, there is an increasing demand by the public for the development of agricultural production methods with minimal environmental impacts (Hill et al. 2006). The results of this study indicate that the reduction of DOC flux and control of DOM composition can be largely achieved by reducing outflow in rice-dominated systems. Outflow can be managed at a number of scales: field, irrigation district and/or subdistrict, or regional. Certainly in this study, water in several subwatersheds was managed in such a way that these areas acted as sinks for DOC rather than sources. Water management to control or restrict outflow at these scales is not a new concept and such practices have been implemented as part of strategies to reduce herbicide runoff from rice fields. Practices can range from having no outflow from a field to reusing water at the field, farm, or irrigation district scale (Hill et al. 1991). The costs to implement such practices can be minimal, as in the case of simply not allowing water to drain from a field, or they can be high, as in the case for developing the infrastructure for water reuse at irrigation district or regional scales. The implementation of new practices at any scale needs to consider the downstream impacts on growers who are dependent on drainage water for irrigation. Also, the implementation of outflow control should consider the timing of the release of water, as impacts are likely to be greatest when downstream flows are low. Lastly, the LME results for this study indicate that reuse can increase the relative aromatic content of DOM. Consequently, this practice should be undertaken only with consideration of the risks that changes in DOM biochemical composition may have on THMFP. It is clear that as agricultural land use continues to grow, further work is required to evaluate the downstream impacts with respect to DOM dynamics under different management systems versus comparable natural systems.

Conclusions

Multiple studies of agricultural watersheds have concluded that irrigation flows create patterns in DOC removal that are very different than what would occur under natural conditions (Dalzell et al. 2005, 2007; Hernes et al. 2008). The large quantity of surface water produced by rice agriculture relative to other crops results in a high potential of rice activities to impact downstream ecosystems and beneficial downstream uses, such as drinking water extraction. The results of the LME analysis in this study illustrate that outflow and internal drainwater reuse rates in rice-dominated subwatersheds are the primary drivers of carbon biogeochemical dynamics within these systems. Furthermore, the coincidence of peaks in DOC concentration, THMFP, and $SUVA_{254}$ with the onsets of flooding and draining, indicate that future studies of rice systems are needed to quantify the impacts of specific irrigation activities, particularly as studies of natural systems have found that short term events affecting water flow can have particularly significant effects on DOC dynamics (Hood et al. 2006; Fellman et al. 2009; Spencer et al. 2009, 2010).

The variations in DOC and THM concentrations and fluxes and in CDOM parameters that occur throughout the rice growing season are likely driven by a combination of mechanisms, which include water management activity impacts on: (i) the extent to which sorption/desorption occur and the degree to which this causes DOM fractionation, (ii) the extent of microbial degradation and its concurrent impact on DOM biochemical composition, (iii) the extent of DOM mobilization from soil micropores, (iv) the release of protected DOM due to the breakup of soil structure, (v) the total supply of organic matter available to be mobilized, and (vi) surface accumulation of organic matter. This study also found that the influence of outflow decreases with the progression of the growing season (Fig. 5a, b), which indicates that, in order to understand DOM dynamics in agricultural systems, it is crucial to consider the period of time over which a practice occurs in addition to simply considering the magnitude of its occurrence.

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