

Soil carbon cycling and sequestration in a seasonally saturated wetland receiving agricultural runoff

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Abstract. The fate of organic carbon (C) lost by erosion is not well understood in agricultural settings. Recent models suggest that wetlands and other small water bodies may serve as important long-term sinks of eroded C, receiving ~30% of all eroded material in the US. To better understand the role of seasonally-saturated wetlands in sequestering eroded C, we examined the spatial and temporal dynamics of C and sediment accumulation in a 13-year-old constructed wetland used to treat agricultural runoff. The fate of C sequestered within deposited sediment was modeled using point-sampling, remote sensing, and geostatistics. Using a spatially-explicit sampling design, annual net rates of sedimentation and above-ground biomass were measured during two contrasting years (vegetated (2004) vs. non-vegetated (2005)), followed by collection of sediment cores to the antecedent soil layer, representing 13 years of sediment and C accumulation. We documented high annual variation in the relative contribution of endogenous and exogenous C sources, as well as absolute rates of sediment and C deposition. This annual variation, however, was muted in the long-term (13 yr) sediment record, which showed consistent vertical patterns of uniform C distribution ($\sim 14 \text{ g kg}^{-1}$) and $\delta^{13}\text{C}$ signatures in high depositional environments. This was in contrast to low depositional environments which had high levels of surface C enrichment ($20\text{--}35 \text{ g kg}^{-1}$) underlain by C depleted ($5\text{--}10 \text{ g kg}^{-1}$) sediments and an increasing $\delta^{13}\text{C}$ signature with depth indicating increased decomposition. These results highlight the importance of sedimentation in physically protecting soil organic carbon and its role in controlling the long-term C concentration of seasonally-saturated wetland soils. While significant enrichment of surface sediments with endogenous C occurred in newly deposited sediment (i.e., 125 kg m^{-2} in 2004), fluctuating

cycles of flooding and drying maintained the long-term C concentration at the same level as inflowing sediment (i.e., 14 g kg^{-1}), indicating no additional long-term storage of endogenous C. These results demonstrate that constructed flow-through wetlands can serve as important sinks for eroded C and sediment in agricultural landscapes, however, additional C sequestration via enrichment from endogenous sources may be limited in seasonally-saturated wetlands due to rapid decomposition during drying cycles.

1 Introduction

Organic carbon (C) sequestration in the terrestrial biosphere has become an important research topic due to growing interest in mediating anthropogenic impacts to climate change (Schlesinger, 1999; Lal, 2004a, b; Berhe et al., 2007). Global C inventories estimate that between ~ 0.5 and 2 Gt C yr^{-1} are being sequestered and not accounted for in identified C reservoirs (Stallard, 1998), with much of this “missing” C thought to reside as soil organic carbon (SOC) (Smith et al., 2001, 2005). Several studies indicate that the sink/source dynamics of terrestrial ecosystems have substantially changed within the last century with a transition from a C source to sink occurring during the 1930s (Bruno and Joos, 1997; Joos and Bruno, 1998). This source to sink transition is coincident with an era of soil erosion associated with agriculture, resulting in the redistribution of an unknown quantity of SOC into depositional areas within the terrestrial ecosystem (McCarty and Ritchie, 2002).

Previous global C modeling estimates have overestimated the magnitude of terrestrial C exported to oceans, implicitly assuming an equilibrium-erosion model in which sediment and C are mobilized from uplands and delivered directly to the ocean (Mulholland, 1981; Mulholland and Elwood, 1982; Kempe, 1984). Recent studies, however, highlight the potential role of small water bodies (e.g. water catchment



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reservoirs, farm ponds, and wetlands) for capturing eroded sediment and C within watersheds (Smith et al., 2002; Renwick et al., 2005). As a result, current SOC models are being updated to reflect the significance of wetlands and other landscape depressions as soil C sinks (Stallard, 1998). An estimated 2.6 million small (surface areas smaller than approx. 1 ha.), artificial water bodies are scattered across the continental US. These water bodies are estimated to receive one third of all eroded materials in the US (Smith et al., 2002).

An estimated 6.8 M ha of wetlands, representing 15 % of all wetlands in the US, exist in agricultural landscapes (US Department of Agriculture, 2009). Restored and constructed wetlands within agricultural landscapes have been proven successful in mitigating the loss of eroded sediment and C (Braskerud, 2001; Jordan et al., 2003; O'Geen et al., 2007; Maynard et al., 2009). As a result, deposition of eroded sediment in wetlands has been proposed as a potential "missing sink" in the global C cycle (Stallard, 1998; Smith et al., 2001; McCarty and Ritchie, 2002). However, debate has revolved around the fate of eroded C in agricultural landscapes and the role small sediment sinks play in sequestering eroded C (Jacinthe and Lal, 2001; Smith et al., 2001; Lal, 2003; Renwick et al., 2004; Smith et al., 2005; Van Oost et al., 2007; Harden et al., 2008; Lal and Pimentel, 2008; Van Oost et al., 2008). Considerable uncertainty concerning rates and locations of terrestrial sedimentation exists due to the lack of good methods for tracking soil redistribution and sedimentation in terrestrial ecosystems (McCarty and Ritchie, 2002).

Wetlands record temporal fluctuations of material fluxes in their sediments. Deciphering information embedded in sedimentary profiles can provide valuable insight into past environmental changes from decadal to millennial time scales. Sediment profiles from constructed wetlands offer a "snapshot" of land-use effects on a sub-decadal scale, providing information on the fate of eroded C within human-altered landscapes. Although there has been an increase in modeling efforts to examine the role of wetlands in terrestrial C capture (Smith et al., 2001, 2002), there is a paucity of field-based studies examining the fate of eroded C in wetlands with which to constrain modeling results (McCarty and Ritchie, 2002; Bedard-Haughn et al., 2006; McCarty et al., 2009).

The conversion of floodplain agro-ecosystems into constructed wetlands is becoming a common management practice to promote wildlife habitat, flood protection and water quality improvement. In California's Central Valley, constructed and restored wetlands are commonly used to treat agricultural runoff. There are currently 83 000 ha of managed wetlands in the valley, representing a 46 % increase since 1990 (56 700 ha in 1990) (Central Valley Joint Venture, 2006). The majority of managed wetlands in this region are seasonally-saturated (87 %, ~72 000 ha) and receive high annual loads of nutrients, sediment, and organic carbon. Although the fate of organic C in transported sediments is

unclear, it is known that once organic C reaches subaqueous depositional areas, rates of organic matter (OM) decomposition are greatly suppressed (Brinson et al., 1981). In addition, once deposited, OM associated with sediment may become physically protected (i.e., aggregate formation and burial), further slowing rates of oxidative loss (Harden et al., 1999; Liu et al., 2003). Thus, C accumulation in small subaqueous environments may have a significant effect on C storage within agricultural watersheds. However, little is known about the fate of eroded C sequestered in seasonally-saturated wetlands within agricultural landscapes. The main goal of this research was to assess the fate of eroded C deposited in a small seasonally-saturated constructed wetland through quantifying sources and fluxes of organic C.

Organic C inputs to wetland systems originate from both exogenous (terrestrial plant debris and eroded soil material) and endogenous (i.e., plankton and aquatic macrophytes) sources. Constructed wetlands receiving agricultural runoff have the potential to sequester exogenous and endogenous C through processes such as sedimentation and in-situ primary production. To address the relative importance of endogenous and exogenous C sources on long-term C sequestration dynamics, we quantified spatial and temporal variation in C pools in a seasonally-saturated constructed wetland. Specific objectives were to: (i) evaluate the efficiency of the wetland to trap sediment and organic material entering the wetland, (ii) examine annual variability in C sources, and (iii) evaluate the potential for long-term C storage in seasonally-saturated wetland sediments.

2 Material and methods

2.1 Study site

This study was conducted at a 13-year-old constructed wetland located on the west side of the San Joaquin River in California's Central Valley. The site was once part of the historic river floodplain that was converted to agriculture in the 1930s and then restored into a wetland in the early 1990s. The study area experiences hot dry summers (mean summer temperature = 24 °C) and cool moist winters (mean winter temperature = 8 °C) with a mean annual precipitation of 28 cm. The wetland is seasonally-saturated, receiving agricultural runoff from flood and furrow irrigation during the summer (May–September), when most seasonal wetlands in California are dry, and rain and flood events in the winter and early spring. This results in a hydroperiod of 9 to 11 months each year. The wetland receives agricultural runoff from approximately 2300 ha of irrigated land that dominantly supports row and nut crops.

The wetland has a surface area of 7.3 ha with a long (850 m) and narrow (85 m) design and an average water depth of ~0.6 m (Fig. 1). The location of the wetland outflow changed between years, with the outflow located at

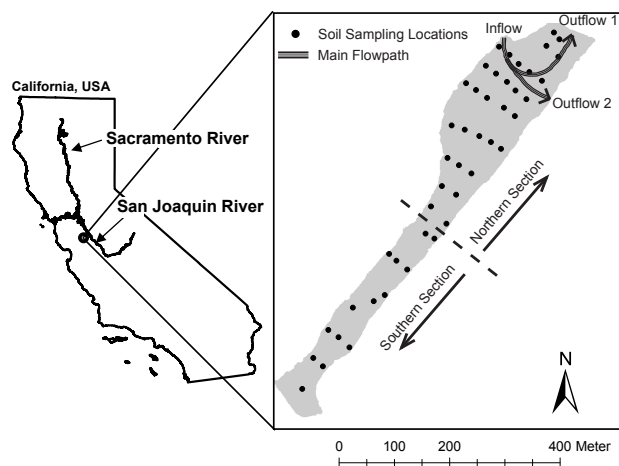


Fig. 1. Schematic of study site, sampling locations, inflow and outflow locations, and main flow-path.

Outflow-1 in 2004 and at Outflow-2 in 2005 (Fig. 1). Due to the close proximity of inflow and outflow structures in the northern portion of the wetland, a hydrologic disconnection exists between the northern and southern sections (Fig. 1). Additionally, due to the close proximity of Outflows 1 and 2, differences in wetland hydrodynamics between years were assumed to be minimal.

Variation in the timing of spring flooding can dramatically affect vegetation dynamics through its effect on the germination of emergent macrophytes. The dominant vegetation species at the site is pale smartweed (*Polygonum lapathifolium*), which requires a spring dry period for germination to occur. Since its construction in 1993, the wetland has oscillated between vegetated (i.e., >70% plant cover) and non-vegetated (i.e., <10% plant cover) states, with vegetated years in 1994, 1996, 1999, 2003, and 2004; and non-vegetated years in 1995, 1998, 2000, 2001, 2002, and 2005. The wetland was drained in 1993 during initial construction and in 1997 and 2006 following severe flooding (Fig. 2). This type of annual variation in vegetation dynamics is common in floodplain wetlands of this region.

2.2 Wetland water analysis

Weekly grab samples (2L) were collected in acid-washed polyethylene bottles from inflow and outflow locations during the 2004 and 2005 irrigation seasons (May–September) (2004: $n = 19$; 2005: $n = 16$). Chlorophyll-*a* (Chl-*a*) was measured from a 200–600 mL subsample using ethanol extraction and standard fluorometry techniques (Greenberg et al., 1985). Chlorophyll-*a* values were converted to algal-carbon using a C:Chl ratio of 40 (Lehman et al., 2004). Dissolved organic carbon (DOC) was measured following filtration through a 0.45 μm polycarbonate membrane filter (Millipore) using a Dohrmann UV enhanced-persulfate TOC

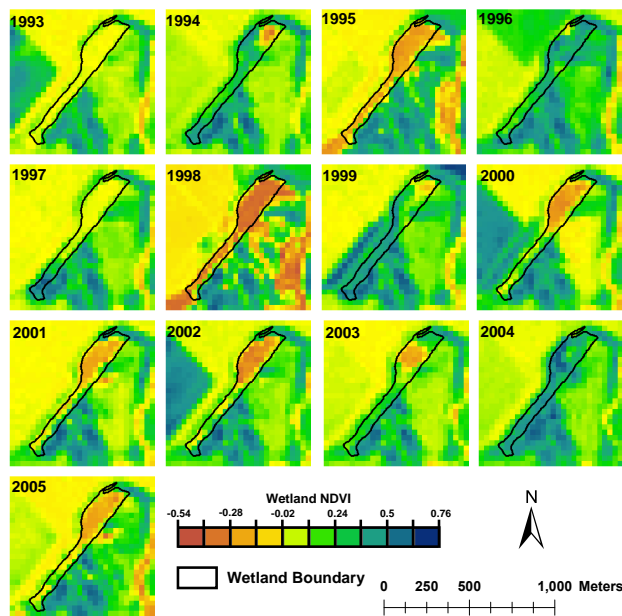


Fig. 2. Multi-temporal images (1993–2005; acquired during the month of July) of wetland NDVI, derived from Landsat TM imagery. Low values (i.e., -0.5 ; red) indicate open water, while high values (i.e., 0.75 ; blue) indicate dense vegetation. The wetland was vegetated in 1994, 1996, 1999, 2003, and 2004; non-vegetated in 1995, 1998, 2000, 2001, 2002, and 2005; and drained (i.e., bare soil) in 1993 during initial construction and in 1997 following a severe flood.

analyzer (Phoenix 8000) with a limit of detection (LOD) of $\sim 0.10 \text{ mg L}^{-1}$. Total suspended solids (TSS) was measured from a 300–800 mL subsample (depending on turbidity) by filtering through a 0.45 μm pre-combusted, pre-weighed glass fiber filter (Millipore) (LOD $\sim 0.5 \text{ mg L}^{-1}$). The filter was dried at 60°C for 24 h and weighed again, the difference giving the mass of sediment in the water sample. The filter was further combusted at 550°C for 3 h with the difference in mass giving the volatile suspended solids (VSS) (i.e., OM fraction). Particulate organic carbon (POC), comprising suspended soil organic matter (SOM), algae-C and particulate plant matter, was calculated by dry combustion of TSS samples with a Carlo Erba C/N analyzer. For ^{13}C and ^{15}N analysis of suspended sediment, seasonal composite samples of TSS were obtained by aggregating a 1 L subsample from each weekly grab sample of inflow and outflow water in 2004 ($n = 19$) and 2005 ($n = 14$). Composite water samples were allowed to settle for 48 h at 4°C or until all particles had settled out of solution. Water was then decanted until only a small concentrated aliquot of suspension remained. The suspension was centrifuged at 2500 rpm for 15 min, the supernatant decanted, and the solids collected after air drying (Sharpley et al., 1991).

A water budget for the wetland was obtained in 2005, but not in 2004 due to problems with sensor installation. In 2005, flow measurements were taken every 15 min using ISCO (ISCO, Lincoln, NE) area-velocity meters installed in inlet and outlet pipes. Due to the absence of vegetation in 2005, an evaporation rate was calculated using a mass transfer evaporation equation (Dunne and Leopold, 1978), using data obtained from a local weather station (Patterson, CA) (CIMIS, 2005). There was no precipitation during the summer study period in either year. Seepage was calculated as the difference between inflow and outflow plus evaporation (Seepage = Inflow – [Outflow + Evaporation]). Based upon the 2005 water budget, evaporation accounted for 3% and seepage accounted for 36% of the water budget (See Table S1). Due to the absence of a water budget for 2004, we present water column C constituents both in terms of concentration (2004 and 2005) and seasonal load (2005). However, due to water losses from evapotranspiration and seepage (~40%), seasonal retention efficiencies based on reduction in load will be approximately 40% greater than percent decrease in concentration. Constituent loads in 2005 were calculated using the period-weighted approach with weekly constituent concentration and weekly water flux (Moldan and Cerny, 1994).

2.3 Wetland sediment analysis

Net sedimentation rates were measured during the 2004 and 2005 irrigation seasons using 30 × 30 cm sedimentation plates (Pasternack and Brush, 1996). Plates were installed in May before the irrigation season wet up and collected following wetland dry down. A total of 50 sediment plates were installed along transects running northwest to southeast (Fig. 1). The sampling design approximated that of a non-aligned grid, which captured the spatial variability at scales greater than 10 m. Sediment samples were oven dried at 60 °C for 48 h and weighed to give a dry weight per unit area. Samples were passed through a 2 mm sieve to remove coarse fragments and macro-OM. Total carbon (TC) and total nitrogen (TN) were analyzed by dry combustion with a Carlo Erba C/N analyzer. We verified that the samples contained no detectable carbonates, thus TC was considered a measure of organic C.

In the spring of 2006, sediment was sampled to assess the spatial distribution of sediment accumulation since 1993 in the northern half of the wetland. At a total of 58 locations, soils were excavated by hand auger to the antecedent soil layer to record the depth of sediment accumulation since 1993. The antecedent layer was identified by an abrupt textural discontinuity between the original surface (fine/medium sand) deposited by flooding of the San Joaquin River in 1993 and more recent sediment (clay loam) supplied by the wetland input. At 36 of these sampling locations, intact sediment cores were collected to the antecedent layer, sectioned at 2.5 cm increments, and analyzed for TC and TN ($n = 322$).

Bulk density measurements were taken at 15 locations using the core method (Grossman and Reinsch, 2002). To assess the potential for methanogenesis within the wetland, redox potential was measured at two depths (2.5 and 10 cm) at four locations within the wetland. Measurements were taken in triplicate at each depth and recorded continuously at 30 min intervals from 25 August to 5 October 2005. Redox potential was measured using platinum electrodes and calomel reference electrodes interfaced to a datalogger.

2.4 Wetland vegetation analysis

Above-ground biomass sampling was conducted in the fall of 2004, with samples taken adjacent to each sediment plate. Samples were collected using a 0.5 × 0.5 m quadrat. All surface organic material was oven dried (60 °C), weighed and analyzed for TC and TN. Biomass samples were not collected in 2005 due to the absence of wetland vegetation as a result of early spring flooding.

Airborne remotely sensed imagery of the wetland was obtained on two dates, 18 June 2004 and 19 June 2005, which represented peak standing biomass. The imagery was acquired using the HyMap airborne sensor operated by HyVista Corporation (Sydney, Australia) (Cocks et al., 1998). HyMap hyperspectral imagery collects data over 126 spectral bands ranging from 0.450 to 2.500 μm with a bandwidth of 0.015 to 0.020 μm and spatial resolution of 3 m.

Organic C in above-ground biomass was modeled using point quadrat sampling of standing vegetation in 2004 and airborne hyperspectral imagery. A regression kriging procedure was conducted; regressing measured C accumulation to Red Edge Normalized Difference Vegetation Index (NDVI 705). NDVI 705 is a modification of the traditional broadband Normalized Difference Vegetation Index, which uses bands along the red edge (0.680 to 0.780 μm) instead of the main absorption and reflection peaks. NDVI 705 was calculated as:

$$\text{NDVI}_{705} = (\rho_{750} - \rho_{705}) / (\rho_{750} + \rho_{705}) \quad (1)$$

where ρ_{750} is the spectral band at 750 μm and ρ_{705} is the spectral band at 705 μm.

Organic C in below-ground biomass was estimated using a shoot:root ratio of 0.23 ± 0.15 ($\bar{x} \pm \text{SD}$), which was established at a nearby constructed wetland dominated by pale smartweed (*Polygonum lapathifolium*) (Unpublished data, 2007). The ratio was calculated from above- and below-ground biomass measurements taken at five locations within the wetland. Above-ground biomass was sampled using the method outlined above. Below-ground biomass was determined by taking three cores within each quadrat sampled to a depth of 15 cm. All root biomass from each core was separated, dried at 60 °C, and weighed. The average root weight of the three cores was used to estimate the below-ground biomass for each quadrat.

A subset of sediment ($n = 20$, 2004; $n = 20$, 2005) and vegetation ($n = 18$, 2004) samples, and seasonal composite samples of suspended sediment were analyzed for ^{13}C and ^{15}N using a PDZ Europa ANCA-GSL elemental analyzer interfaced to a PDZ Europa 20–20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK).

2.5 Geostatistical analyses

Geostatistics were used to model the spatial distribution of wetland sediment and vegetation. Two different kriging methods were used in the interpolation of sediment and vegetation properties: ordinary kriging (OK) (Goovaerts, 1999) and regression kriging (RK) (Hengl et al., 2007). Ordinary kriging was used to model the spatial distribution of total organic C (g m^{-2}), net sedimentation (kg m^{-2}), sediment depth (cm), and C/N ratio in 2004 and 2005. A three dimensional OK procedure was used to model the C concentration (g kg^{-1}) in sediment accumulated since the wetland was constructed in 1993. Regression kriging was used to interpolate the spatial distribution of above-ground biomass C (g m^{-2}), using quadrat point data and remotely sensed data as an auxiliary, spatially continuous predictor variable. All variables were interpolated to a 1 m^2 grid cell size. All statistical and geostatistical analyses were conducted using R software (R Development Core Team, 2005). Kriging analysis was performed using the “gstat” package (Pebesma, 2004). Variogram fitting was optimized using the “automap” package (Hiemstra et al., 2009). Statistical differences were tested using a paired non-parametric Wilcoxon Rank Sum Test and statistical differences were tested at the $p = 0.05$ confidence level.

3 Results

3.1 Carbon in the water column

The fate of organic C in the water column was assessed through measurements of DOC, POC, Chl-*a* (a bio-indicator of algae), and TSS concentration at inflow/outflow locations in 2004 and 2005. Constituent loads were calculated at inflow/outflow locations in 2005 (Table 1). Water losses from seepage and evapotranspiration accounted for 36 and 3 % of total inflow in 2005, respectively; thus water column retention efficiencies calculated from C loads were higher than reductions in concentration in 2005. This trend likely occurred in 2004 as well, due to the high percentage of water lost via seepage. Thus, in terms of the efficacy of the wetland to sequester eroded C, reductions in concentration represent a conservative measure of trapping efficiency. Calculations of C retention efficiencies, however, do not account for gaseous C losses or dissolved C exiting the wetland via seepage.

There were no clear temporal trends in DOC inflow or outflow waters during either irrigation season (Fig. 3) and no significant difference between inflow and outflow DOC

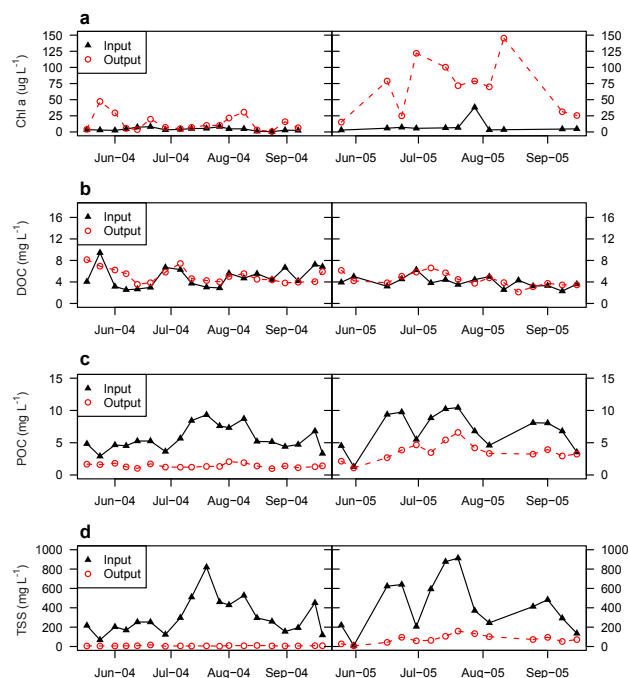


Fig. 3. Inflow and outflow wetland water column concentrations of (a) chlorophyll-*a*, (b) dissolved organic carbon, (c) particulate organic carbon, and (d) total suspended solids in 2004 and 2005.

concentrations in either 2004 or 2005 (Table 1). However, in terms of seasonal load, there was a reduction in water column DOC of 1200 kg yr^{-1} (32 %) in 2005 corresponding roughly to the percent hydrologic water loss via seepage (36 %). The wetland was a sink for POC, with consistently lower POC concentrations at the outflow relative to inflow in 2004 and 2005 (Fig. 3). Average POC concentration was $5.7 \pm 1.9 \text{ mg L}^{-1}$ (mean \pm standard deviation) in inflow and $1.4 \pm 0.3 \text{ mg L}^{-1}$ in outflow water in 2004, and $7.0 \pm 2.8 \text{ mg L}^{-1}$ in inflow and $3.6 \pm 1.4 \text{ mg L}^{-1}$ in outflow water in 2005. Corresponding reduction in seasonal POC concentrations were 75 % and 48 % for 2004 and 2005, respectively (Table 1). Seasonal reduction in POC load was 4400 kg yr^{-1} (67 %) in 2005.

Constructed wetlands have the potential to serve as bioreactors for algae when hydraulic residence times are long and nutrient levels are high. Chl-*a* was used as a proxy for algal biomass in the water column. Trends in Chl-*a* concentration were variable, particularly for the outflow (Fig. 3). In 2004 and 2005, average Chl-*a* concentrations were low at the inflow (2004: $4.2 \pm 2.3 \text{ µg L}^{-1}$; 2005: $8.0 \pm 10.1 \text{ µg L}^{-1}$) and increased significantly at the outflow (2004: $13.5 \pm 12.6 \text{ µg L}^{-1}$; 2005: $69.5 \pm 42.4 \text{ µg L}^{-1}$) (Table 1). When considering seasonal averages, the wetland was a major source of algae, increasing concentrations over two fold in 2004 and almost 8 fold in 2005 (Table 1). In terms of seasonal load, the wetland exported 42.6 kg yr^{-1} of Chl-*a*, or

Table 1. Seasonal mean concentration of C constituents at inflow and outflow locations in 2004 and 2005 (mean \pm standard deviation).

| | Dissolved Organic Carbon DOC | | Particulate Organic Carbon POC | | Chlorophyll- <i>a</i> Chl- <i>a</i> | | Total Suspended Solids TSS | |
|-----------------------------------|---------------------------------|---------------------|-----------------------------------|---------------------|--|---------------------|-------------------------------|---------------------|
| | mg L ⁻¹ | kg yr ⁻¹ | mg L ⁻¹ | kg yr ⁻¹ | μ g L ⁻¹ | kg yr ⁻¹ | mg L ⁻¹ | kg yr ⁻¹ |
| 2004 | | | | | | | | |
| Inflow | 4.9 \pm 1.9 | NA | 5.7 \pm 1.9 | NA | 4.2 \pm 2.3 | NA | 305 \pm 185 | NA |
| Outflow | 5.1 \pm 1.3 | NA | 1.4 \pm 0.3 | NA | 13.5 \pm 12.6 | NA | 7 \pm 3 | NA |
| Retention Efficiency [†] | -4 % (ns) | NA | 75 % (**) | NA | -221 % (**) | NA | 98 % (**) | NA |
| 2005 | | | | | | | | |
| Inflow | 4.0 \pm 1.0 | 3700 | 7.0 \pm 2.8 | 6600 | 8.0 \pm 10.1 | 7.9 | 430 \pm 271 | 405 000 |
| Outflow | 4.4 \pm 1.2 | 2500 | 3.6 \pm 1.4 | 2200 | 69.5 \pm 42.4 | 42.6 | 78 \pm 41 | 47 000 |
| Retention Efficiency [†] | -10 % (ns) | 32 % | 48 % (**) | 67 % | -769 % (**) | -438 % | 82 % (**) | 88 % |

[†]Retention efficiencies are calculated as the percent reduction in seasonal mean concentration or seasonal mean load between inflow and outflow locations. Significance level between inflow and outflow mean concentrations is given in parenthesis. ns = not significant, * = significant at $P < 0.05$, ** = significant at $P < 0.01$.

when converted to C units a total of 1700 kg yr⁻¹ of algal C, which comprised 36 % of all C exported from the wetland.

Mean TSS concentration in outflow water was lower than inflow water over both irrigation seasons (Table 1). TSS concentration was 305 \pm 185 mg L⁻¹ at the inflow and 7 \pm 3 mg L⁻¹ at the outflow in 2004, and 430 \pm 271 mg L⁻¹ at the inflow and 78 \pm 41 mg L⁻¹ at the outflow in 2005 (Table 1). Corresponding seasonal reduction in TSS concentrations were 98 % and 82 % in 2004 and 2005, respectively (Table 1). Seasonal reduction in TSS load was 358 000 kg yr⁻¹ (88 %) in 2005.

3.2 Carbon in wetland sediments

Analysis of sediment plates was used to understand the role of sedimentation on C dynamics. In 2004, spatial trends in sediment and C deposition were highest near the input, and decreased along the flow path towards the outputs (Figs. 4a and b). Almost all sediment and C accumulation was confined to the northern half of the wetland where the inlet and outlets are located. Sediment and C deposition rates were higher in 2005, with spatial trends in sediment and C deposition highest near the input and outputs (northern section) and in the southern end of the wetland. A zone of low deposition was present in the center of the wetland (Figs. 4c and d).

Average sediment accumulation rate nearly quadrupled in 2005 relative to 2004, with mean rates of 2.7 kg m⁻² y⁻¹ (range: 0.4–11.1 kg m⁻² y⁻¹) in 2004 and 10.0 kg m⁻² y⁻¹ (range: 0.01–97.4 kg m⁻² y⁻¹) in 2005 (Table 2). However, the sediment C accumulation rate, averaged for the entire wetland, was similar between years, with rates of 0.21 kg m⁻² y⁻¹ (range: 0.07–0.39 kg m⁻² y⁻¹) in 2004 and 0.25 kg m⁻² y⁻¹ (range: 0.01–0.70 kg m⁻² y⁻¹) in 2005 (Table 2). Mean organic C concentration of TSS entering the wetland was 14.6 and 13.2 g kg⁻¹ in 2004 and 2005, respectively (Table 3).

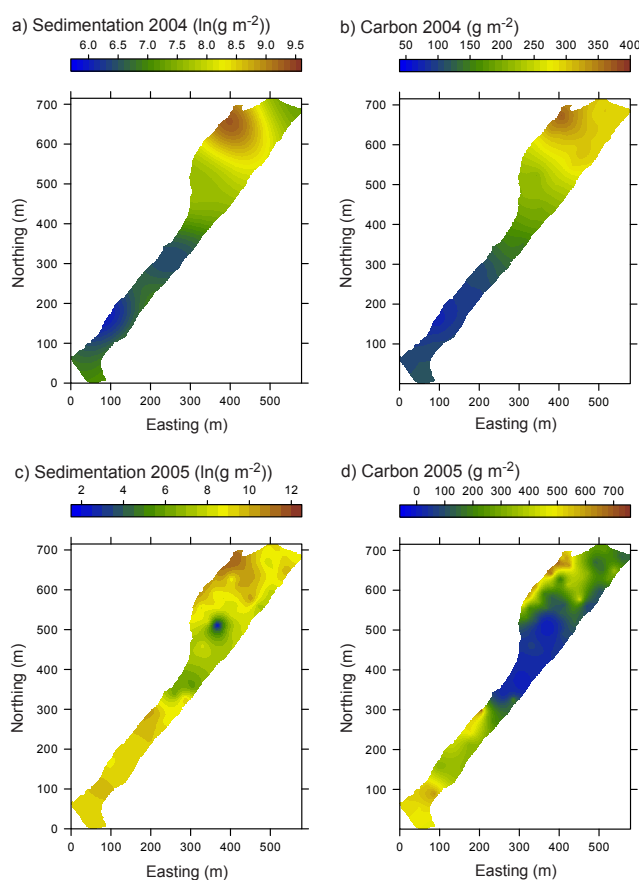


Fig. 4. Interpolation maps of sedimentation, (a and c) and sediment carbon (b and d) in 2004 and 2005, respectively. Maps are displayed using different scales in 2004 and 2005 to most clearly display gradients of C and sediment deposition across the wetland during each year.

Table 2. Annual sediment and C loads and accumulation rates for seasonally submerged soils in 2004 and 2005 for the whole wetland.

| | Entire Wetland | | Northern Wetland Section | |
|-------------------|------------------------|--|--------------------------|--|
| | Annual Load | Average Accumulation Rate | Annual Load | Average Accumulation Rate |
| | kg yr ⁻¹ | kg m ⁻² yr ⁻¹ | kg yr ⁻¹ | kg m ⁻² yr ⁻¹ |
| 2004 | | | | |
| Sedimentation | 197 800 | 2.7 | 181 200 | 3.5 |
| Sediment Carbon | 15 100 | 0.210 | 13 700 | 0.252 |
| Vegetation Carbon | | | | |
| Above Ground | 15 800 | 0.218 | 11 300 | 0.219 |
| Below Ground† | 3700 | 0.051 | 2600 | 0.051 |
| 2005 | | | | |
| Sedimentation | 724 400 | 10.0 | 474 500 | 9.2 |
| Sediment Carbon | 18 000 | 0.249 | 9300 | 0.179 |
| Vegetation Carbon | NA | NA | NA | NA |
| 13 yr | kg 13 yr ⁻¹ | kg m ⁻² 13 yr ⁻¹ | kg 13 yr ⁻¹ | kg m ⁻² 13 yr ⁻¹ |
| Sedimentation | NA | NA | 11 067 000 | 214 |
| Sediment Carbon | NA | NA | 156 000 | 3.0 |

†Below ground biomass was estimated using a shoot:root ratio established from field measurements at an adjacent site.

NA = not applicable due to lack of vegetation in 2005.

3.3 Carbon in emergent vegetation

The spatial distribution of NDVI 705 values in 2004 indicated a heterogeneous pattern of vegetation cover ranging from small sections of open water to areas of dense vegetation (i.e., ~100 % cover). Values of NDVI 705 ranged from 0, indicating open water, to 0.6, indicating dense vegetation (Fig. 5a). The northern section of the wetland contained both a large open water environment, as well as some of the densest areas of plant cover (Fig. 5). The correlation between above-ground biomass C (g m⁻²) and the corresponding NDVI 705 value was weak, but highly significant ($r^2 = 0.25$, $p < 0.001$), and when incorporated into the regression kriging model, produced an interpolated surface with lower prediction error relative to biomass C modeled with ordinary kriging (RMSE: OK = 125.1, RK = 121.1) (Fig. 5b). The mean organic C concentration of vegetation in above-ground biomass was 251 ± 9.6 g kg⁻¹ in 2004. The average C accumulation rate from vegetation in 2004 was 0.218 kg m⁻² y⁻¹ for above-ground biomass and 0.051 kg m⁻² y⁻¹ for below ground biomass (Table 2, see Fig. S3 for kriging standard error).

3.4 Potential for methanogenesis

Methane is an important greenhouse gas, with a global warming potential (GWP) of 62 relative to 1 for CO₂ (20 year potential) (Shine et al., 2005), and thus high production of CH₄ may offset the potential benefits of wetland C sequestration. Reduction of CO₂ and production of CH₄ is predicted to occur in the Eh range of -250 to -350 mV (Mitsch

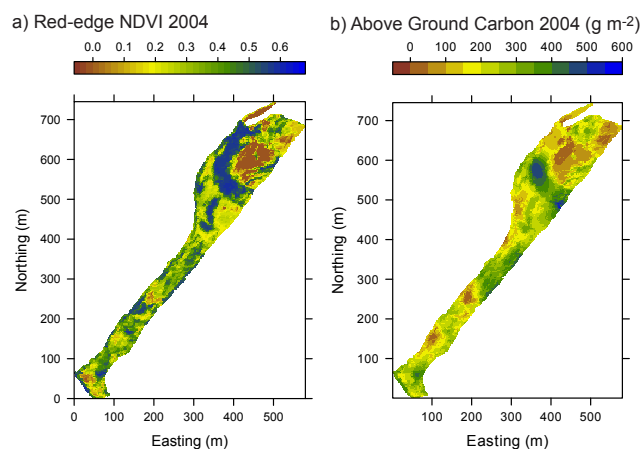


Fig. 5. Maps of (a) Red-edge NDVI in 2004, and (b) regression kriging map of above-ground carbon in 2004.

and Gosselink, 2000). Eh values at our site ranged from 0 to -250 mV, with most values between -100 and -200 mV (Fig. S2). This Eh range, combined with high sulfate concentrations in inflow water, indicates that the wetland soil was likely poised at sulfate reducing conditions. This was further confirmed by the presence of iron monosulfide masses throughout the soil matrix. Consequently, methanogenesis was not likely an important process influencing C cycling within this wetland, although methane production may occur in reduced micro-sites within the soil matrix.

3.5 Sources of carbon

Stable isotopes of C and N from different wetland OM inputs were analyzed and used in conjunction with C:N ratios to identify end-member sources of OM. There are four dominant OM end-member groups in flow-through wetlands: imported terrestrial plant material, imported SOM, plankton, and aquatic macrophytes (vascular aquatic plants) (Kendall et al., 2001).

The isotopic composition of wetland OM can reflect the relative proportion of exogenous terrestrial OM (predominantly derived from C3 plant detritus and C3 plant-dominated soils) and endogenous OM (derived from plankton, aquatic macrophytes and benthic biota). Values of $\delta^{13}\text{C}$ ranged from -31 to -26 ‰, with all input C sources generally falling within the range of the four potential end-member sources (Table 3). There was a decrease in the $\delta^{13}\text{C}$ value of TSS from inflow (-26.9 ‰) to outflow (-28.2 ‰) in 2004, and from inflow (-26.3 ‰) to outflow (-28.1 ‰) in 2005 (Table 3, Figs. 6a and b). This also corresponded with an increase in the $\delta^{15}\text{N}$ in both years: Inflow (7.3 ‰) vs. outflow (10.0 ‰) in 2004 and inflow (6.7 ‰) vs. outflow (8.9 ‰) in 2005 (Table 3). The average $\delta^{13}\text{C}$ value of wetland sediment was -28.47 ‰ in 2004, which was similar to the $\delta^{13}\text{C}$ value of vegetation (-28.8 ‰) and TSS in outflow (-28.2 ‰) that year. In 2005, the average $\delta^{13}\text{C}$ value of wetland sediment (-28.0 ‰) and TSS in outflow (-28.1 ‰) were similar to 2004 (Table 3, Fig. 6a).

C:N ratios of wetland sediment were also used to identify OM sources (Figs. 7a and b). Nonvascular plants such as algae contain low C:N ratios (between 4 and 10), whereas vascular plants (terrestrial plants and aquatic macrophytes), which contain cellulose, have higher C:N ratios (≥ 20) (Meyers and Ishiwatari, 1993). C:N ratios of inflowing and outflowing TSS were similar in 2004, with ratios of 9.1 and 9.2 at inflow and outflow, respectively. In contrast, the C:N ratio of outflowing TSS (7.9) in 2005 decreased relative to inflowing TSS (9.3) suggesting a greater contribution of algal biomass to the C stock of the system. In both years, C accumulation was greatest near the inflow, due to high sediment accumulation and the addition of exogenous OM. The spatial patterns of C:N ratios differed between years, indicating potentially different sources of OM. In 2004, the average C:N ratio of sediment for the entire wetland was 9.9 (range: 7.2 to 12.8, $n = 48$), with scattered zones of high C:N around the outflows and in small patches in the middle and southern portions of the wetland (Fig. 7a). In 2005, C:N ratios were lower with an average of 7.2 (range: 3.8 to 10.5, $n = 68$), with higher C:N ratios present towards the southern end of the wetland (Fig. 7b).

To further elucidate the relationship between OM input sources, we plotted $\delta^{13}\text{C}$ vs. C:N ratio (Fig. 6b). The most distinct grouping was aquatic vegetation from 2004 due to a wide range in C:N ratios. All other groups fell within a narrow range of C:N values (6 to 13), but had a wide range of

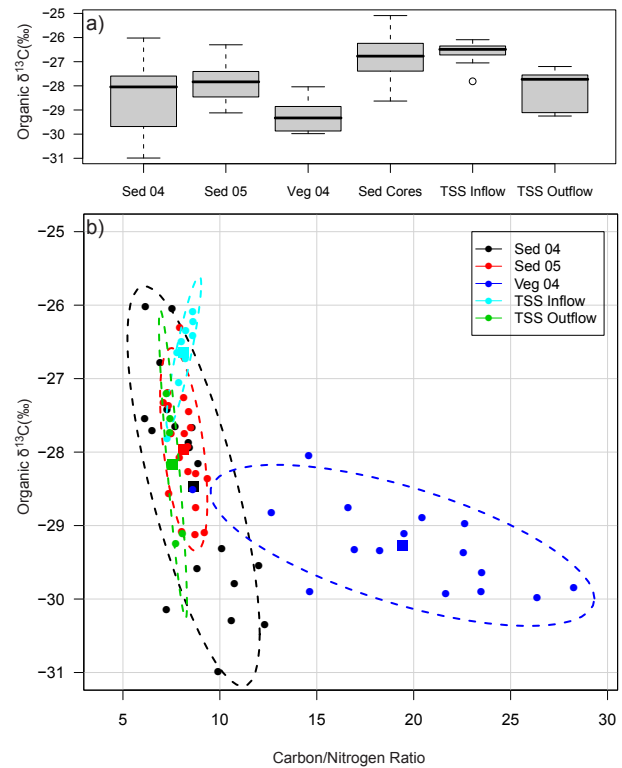


Fig. 6. Boxplot of $\delta^{13}\text{C}$ (a) and xy-plot of $\delta^{13}\text{C}$ vs. C:N ratio (b) for different wetland carbon sources. The middle of each boxplot indicates the median value. The upper and lower edges of each boxplot indicate the 75th and 25th percentiles, respectively. The ends of the vertical lines indicate the minimum and maximum data values. Points outside of the vertical lines indicate outliers. The ellipsoids in (b) represent 80% confidence intervals.

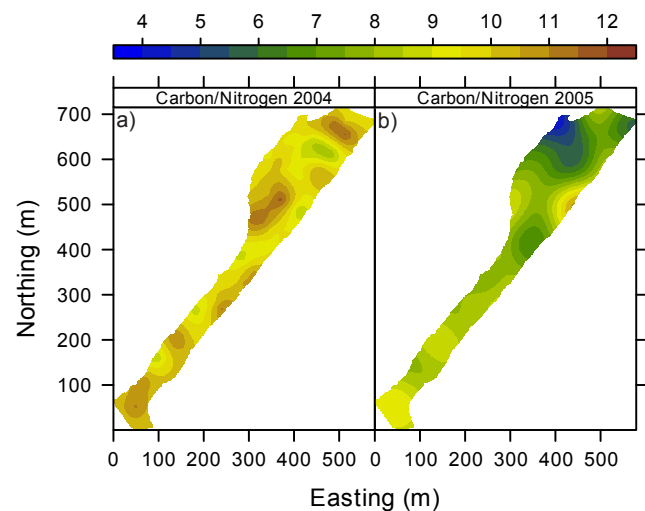


Fig. 7. Interpolation map showing the C:N ratios in (a) 2004 and (b) 2005.

Table 3. Total carbon, total nitrogen, C:N ratio, $\delta^{13}\text{C}$, and $\delta^{15}\text{N}$ for suspended sediment, sediment, and vegetation in 2004, 2005, and a 13-year average for the whole wetland.

| | Total Carbon (g kg^{-1}) | Total Nitrogen (g kg^{-1}) | C:N Ratio | $\delta^{13}\text{C}$ | $\delta^{15}\text{N}$ |
|---------------|--|--|-----------|-----------------------|-----------------------|
| 2004 | | | | | |
| Inflow TSS | 14.6 | 1.6 | 9.1 | -26.9 | 7.3 |
| Outflow TSS | 75.5 | 8.2 | 9.2 | -28.2 | 10.0 |
| Sediment | 125.2 | 12.4 | 9.9 | -28.5 | 8.3 |
| Vegetation | 251.0 | 16.0 | 16.6 | -28.8 | 7.6 |
| 2005 | | | | | |
| Inflow TSS | 13.2 | 1.4 | 9.3 | -26.3 | 6.7 |
| Outflow TSS | 25.6 | 3.2 | 7.9 | -28.1 | 8.9 |
| Sediment | 27.4 | 3.7 | 7.2 | -28.0 | 6.5 |
| Vegetation | NA | NA | NA | NA | NA |
| 13-yr-average | | | | | |
| Sediment | 14.1 | 1.55 | 9.1 | -26.9 | 5.5 |

NA = not applicable due to lack of vegetation in 2005.

$\delta^{13}\text{C}$ values (-31 to -25 ‰). Sediment samples from 2004 had a wider range of $\delta^{13}\text{C}$ and C:N values than 2005.

3.6 Long-term carbon storage

Long-term C storage (i.e., 13-year) was assessed through intensive sampling of the northern section of the wetland, which represents the area of most active sediment deposition. The depth of sediment accumulation since wetland construction in 1993 was modeled using ordinary kriging (Fig. 8). The distribution of long-term sediment accumulation shows the highest rates of accumulation close to the inflow and along the northwestern edge, moderate accumulation towards outflows, and low rates of accumulation in the wetland center. Three-dimensional ordinary kriging was used to model sediment C in the x, y, and z directions. Bulk density measurements taken at different locations and depths within the wetland were similar, showing minimal variation. The average bulk density was $1.24 \pm 0.13 \text{ g cm}^{-3}$, which was used to calculate the 13-year sediment load and 13-year C load in the northern section of the wetland (Table 2). The 13-year sediment and C accumulation rates were $214 \text{ kg m}^{-2} \text{ 13 yr}^{-1}$ ($16.5 \text{ kg m}^{-2} \text{ yr}^{-1}$) and $3.0 \text{ kg m}^{-2} \text{ 13 yr}^{-1}$ ($0.23 \text{ kg m}^{-2} \text{ yr}^{-1}$), respectively (Table 2).

Sedimentation exhibited a strong spatial gradient, with decreasing rates of deposition extending away from the main flow-path and towards the southern end of the wetland. Spatial patterns of C within the different depositional environments are presented via four, 2-D cross-sections of the 3-D interpolation. Each cross section runs from west to east, showing the distribution of C with depth (Fig. 9, see Fig. 8 for location of cross sections). Cross Sect. 1 is located in an area where sedimentation was highest and runs from the input

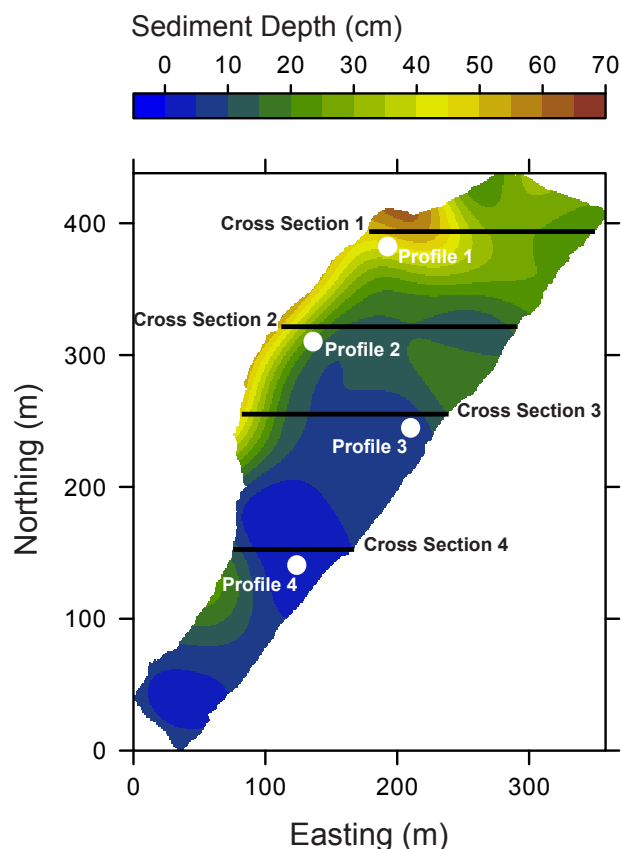


Fig. 8. Interpolation map showing the depth of sediment accumulation over 13 years in the northern section of the wetland, and sampling locations for sediment cross sections (1–4) and soil profiles (1–4).

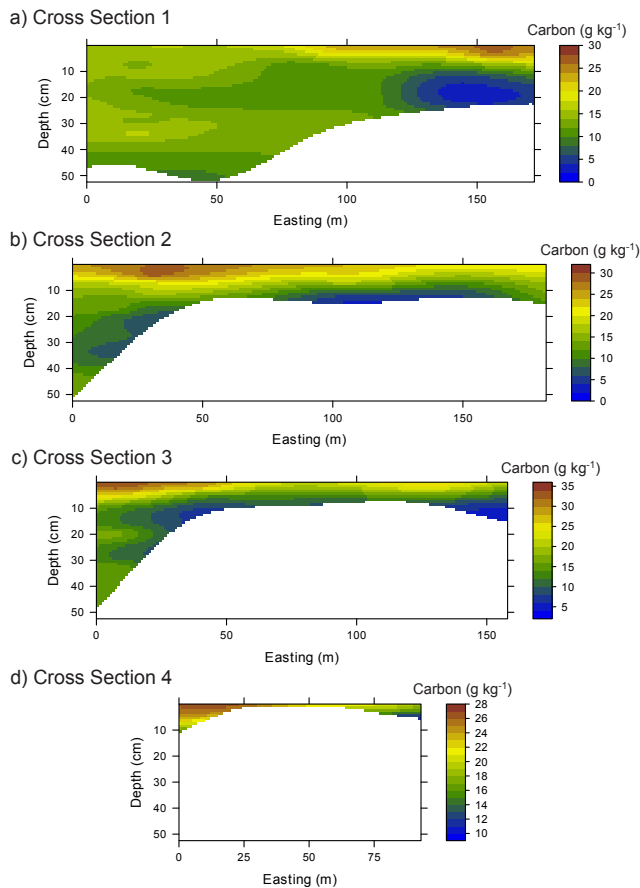


Fig. 9. Maps showing vertical cross-section of sediment carbon concentration along four transects running west to east. See Fig. 8 for cross section locations.

towards the output. In the area proximal to the input along cross section 1 (0 and 50 m), C concentration was uniform with depth ranging from 10 to 15 g kg^{-1} to 50 cm (Fig. 9a). With increasing distance from the input (125 to 175 m), sediment thickness decreased (i.e., ~ 20 cm) and SOC decreased with depth from 25 to 30 g kg^{-1} in the surface layer to 3 to 5 g kg^{-1} in deeper layers. In cross sections 2 and 3, there was a trend of high C concentration in the surface layer (25 to 35 g kg^{-1}), which decreased with depth (5 to 15 g kg^{-1}) (Figs. 9b and c). Cross Sect. 4 was located in a zone of low sedimentation, where sediment thickness above the antecedent layer ranged from 2–10 cm (Fig. 9d). Carbon concentration was high in this region and decreased with increasing distance to the east, ranging from 18 to 28 g kg^{-1} in the west (0–25 m) to 10 to 18 g kg^{-1} along the eastern end of the transect (70–90 m).

Representative soil profiles were chosen adjacent to each of the four cross-sections, representing three distinct depositional environments (Fig. 10). Soil profile 1 is located in a zone of high sediment deposition, profiles 2 and 3 in a zone of moderate sediment deposition, and profile 4 in zones of

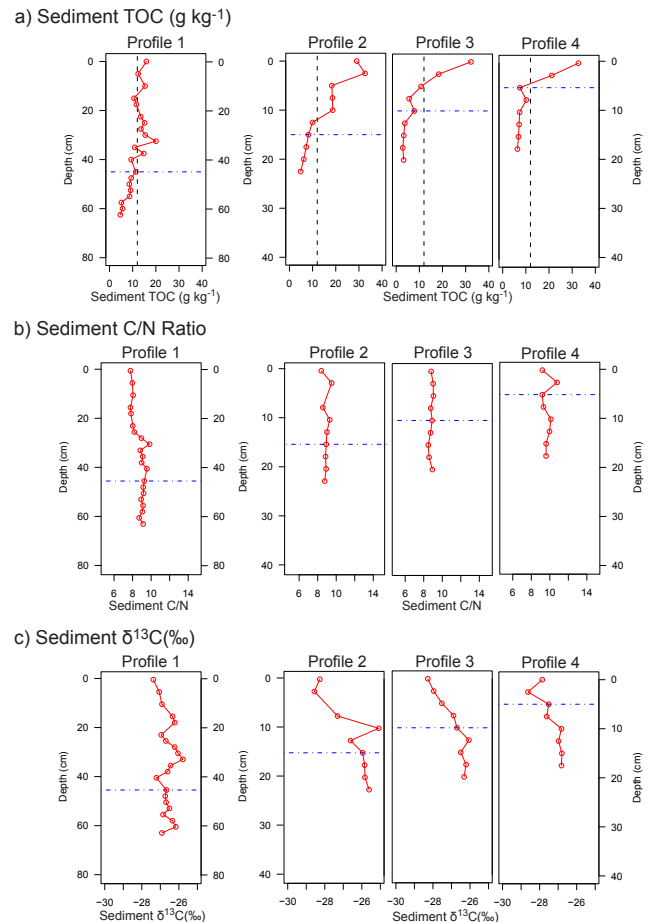


Fig. 10. Four sediment profiles of (a) sediment total organic carbon, (b) sediment carbon to nitrogen ratio (C:N), and (c) sediment $\delta^{13}\text{C}$, sampled at 2.5 cm intervals. The horizontal dashed line represents the depth of the antecedent (1993) soil layer. The vertical dashed line represents the average carbon concentration of inflowing sediment.

low sediment deposition. Soil profile 1 was located adjacent to the inflow and had a sediment depth of 43 cm. The organic C (OC) concentration was similar to that of inflowing sediment (14 g kg^{-1}). In contrast, soil profiles 2, 3, and 4, with sediment depths that ranged from 5 to 15 cm, showed substantial enrichment of C in the surface layers ranging from 20 to 35 g kg^{-1} . These high surface concentrations, however, abruptly decreased with depth to levels below the C concentration of the inflowing TSS. The C:N ratio was generally constant with depth in each of the four profiles, with values that ranged from 8 to 10. In soil profile 1, $\delta^{13}\text{C}$ was generally uniform with depth, ranging from -27 to -26 ‰. In profiles 2, 3, and 4, there was a general increase in $\delta^{13}\text{C}$ values with depth.

4 Discussion

4.1 Wetland carbon sequestration

Recent models have proposed a conceptual relationship between soil erosion, C sequestration, and net primary productivity, whereby erosion and redistribution of soil within the terrestrial biosphere may establish states of ecosystem disequilibria that may promote C sequestration (Stallard, 1998; Harden et al., 1999; McCarty and Ritchie, 2002). This concept was originally proposed by Stallard (1998) based upon two main hypotheses: (i) a significant proportion of eroded C in terrestrial landscapes is redistributed and buried in depositional sinks, rather than exported to the ocean; and (ii) eroded SOC is replaced by newly fixed SOC at erosional sites. This conceptual model addresses eroding landscapes, but does not account for C dynamics in depositional environments. In wetland ecosystems, the burial of sediment with a C concentration below the wetland's organic C equilibrium will promote C sequestration via endogenous enrichment (McCarty and Ritchie, 2002; McCarty et al., 2009). Several factors dictate the pedogenic equilibrium for C storage in wetland soils, including: net primary productivity, OM quality (i.e., lignin, cellulose, carbohydrates), soil properties (i.e., texture, bulk density, mineralogy), climatic variables (i.e., temperature, wetland hydroperiod), and anthropogenic forcing (i.e., nutrient, sediment and C loading). Thus, wetland C sequestration is determined by the rate and concentration of both exogenous C deposition and endogenous C inputs, with both sources constrained by the pedogenic equilibrium for OC storage in wetland soil. In seasonally-saturated wetlands, the pedogenic equilibrium for OC storage is largely controlled by the interaction between the wetland hydroperiod (i.e., frequency, duration and depth of flooding) and the rate of sedimentation. In general, wetlands subjected to long dry-down periods experience high rates of OM decomposition, although wetlands that experience high rates of sedimentation typically have lower rates of OM decomposition due to the physical protection of deposited C as its buried deeper in the profile where anaerobic conditions are present (Viollier et al., 2000).

In agricultural landscapes, constructed wetlands have been shown to serve as important sinks for C through their retention of sediment and associated OM (Johnston, 1991). The efficiency of wetlands to retain inflowing sediment and C and the resulting rates of deposition, are dependent upon several factors including: watershed size, land use, wetland size and design, sediment load, and water influx. Our study wetland was highly effective at reducing POC and TSS concentrations in the water column in both 2004 and 2005 (Figs. 3c and d, Table 1) and when evaluated in terms of seasonal load, was highly efficient at trapping sediment (82 %) and POC (67 %) in 2005 (Table 1). These findings are consistent with other studies evaluating the efficacy of constructed wetlands to improve the quality of surface waters in agricultural

landscapes (Johnston, 1991; Braskerud, 2001; Jordan et al., 2003; O'Geen et al., 2007; Maynard et al., 2009). The trapping of sediment and C from surface waters has been cited as one of the most important benefits of constructed wetlands treating agricultural runoff (O'Geen et al., 2007; Maynard et al., 2009), with reported retention efficiencies ranging from 77 to 100 % removal of TSS (Johnston, 1991; Hey et al., 1994; Downer and Myers, 1995; Mitsch et al., 1995; Nairn and Mitsch, 1999; Maynard et al., 2009), and 30 to 71 % removal of OC (Kadlec and Knight, 1996; Jordan et al., 2003). DOC was a small component of the wetland C budget, comprising $\sim 20\%$ (1200 kg yr^{-1}) of inflow/outflow water column OC retention in 2005. However, when accounting for the water loss via seepage (36 %), the net retention of DOC within the wetland was likely negligible. Although we did not directly measure gaseous carbon losses, Eh measurements indicate that methane production was not likely to occur at appreciable rates. Production of CO_2 via water column and benthic respiration was not quantified in this study, however, $\delta^{13}\text{C}$ sediment profiles showed high rates of OM decomposition in the low depositional environments.

The close proximity of inflow and outflow water control structures was a dominant factor controlling C and sediment depositional patterns within the wetland. This was illustrated in 2004 and 2005 where the highest rates of sedimentation occurred along the main flow path during both years (Figs. 1 and 4). The presence and distribution of emergent vegetation also played an important role in influencing sedimentation patterns as illustrated by the contrasting patterns and rates between 2004 (vegetated) and 2005 (non-vegetated). In 2004, high rates of sedimentation were confined to the area proximal to the inflow, where vegetative cover was most dense. Emergent vegetation is known to increase sedimentation by slowing water velocities, providing a substrate for particle adhesion, and preventing re-suspension (Braskerud, 2001). In contrast, sediment accumulation in 2005 was dispersed throughout the wetland due to the absence of emergent vegetation, allowing sediment to remain in suspension over greater distances and increasing the wetland floor's susceptibility to re-suspension (Fig. 4c). Multi-temporal Landsat imaging of the wetland revealed a high degree of annual variation in vegetation dynamics (vegetated=5 years, non-vegetated = 6 years, drained = 2 years) since its initial construction in 1993 (Fig. 2). Thus, our accounting of carbon dynamics during 2004 and 2005 likely accounts for the typical annual variation in carbon sources and fluxes.

In addition to capturing inflowing sediment and C, wetlands are also highly productive ecosystems capable of producing and incorporating large amounts of biomass into the soil (Brinson et al., 1981). Sequestration of endogenous C inputs is particularly pronounced in constructed wetlands that receive agricultural runoff due to elevated nutrient concentrations, resulting in increased net primary productivity (Aerts et al., 1999; Bedford et al., 1999). This was demonstrated

by both high aquatic macrophyte productivity in 2004 and high algal productivity in 2005. In 2004, the presence of dense vegetation provided high amounts of endogenous OM in areas outside the main zone of deposition, producing C enriched sediment with average concentrations of 125 g kg^{-1} (range: 18 to 369 g kg^{-1} , $n = 48$) (Table 3, Fig. S1). Temporal trends in [Chl-*a*] in 2004 showed that initial outflow [Chl-*a*] increased 15 fold, yet over time, as emergent vegetation established, [Chl-*a*] in outflow water decreased to 35 % of inflow levels likely due to shading by the plant canopy (Fig. 3). In 2005, vegetation failed to establish due to early spring flooding resulting in elevated [Chl-*a*] at the outflow throughout the season (Fig. 3). Thus, the absence of aquatic macrophytes resulted in lower deposited sediment C (average: 27 g kg^{-1} , range: 7 to 52 g kg^{-1} , $n = 68$) relative to 2004, despite elevated [Chl-*a*] (Fig. S1). The C content of sediment in 2005, however, was higher than that of inflowing sediment ($\sim 14 \text{ g kg}^{-1}$), indicating substantial endogenous C enrichment. In 2004, despite receiving less than one third the rate of sediment deposition ($2.7 \text{ kg m}^{-2} \text{ yr}^{-1}$ in 2004 vs. $10.0 \text{ kg m}^{-2} \text{ yr}^{-1}$ in 2005), enrichment of sediment with endogenous C from aquatic macrophytes resulted in a similar rate of sediment C accumulation to that of 2005 ($0.21 \text{ kg m}^{-2} \text{ yr}^{-1}$ in 2004 vs. $0.25 \text{ kg m}^{-2} \text{ yr}^{-1}$ in 2005) (Table 2).

4.2 Sources of wetland carbon

This study measured the isotopic and elemental composition of all OM inputs within the wetland to understand the relative importance of exogenous vs. endogenous C inputs on long-term C sequestration. With the exception of aquatic macrophytes, we did not explicitly measure the composition of potential end-members. Therefore, we used published values of OM sources for constraining our results.

Aquatic plants, including both plankton and aquatic macrophytes, primarily derive their C from dissolved inorganic C (DIC) (Hillaire-Marcel, 1986), which can vary widely in the water column resulting in an isotopic composition that is less predictable than terrestrial organic matter sources. Plankton, which in our system was dominated by algae, has an average $\delta^{13}\text{C}$ value of -30‰ , while aquatic macrophytes have $\delta^{13}\text{C}$ values ranging between -27 and -20‰ (Kendall et al., 2001). The $\delta^{13}\text{C}$ signature of macrophytes and algae can often be differentiated based on their differing ranges (macrophytes: -27 to -20‰ ; algae: -30‰), however, in this study the $\delta^{13}\text{C}$ signature of macrophytes was low (-30 to -28‰), thus preventing differentiation from algal sources (Fig. 6a). Due to the wide range of processes affecting $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values and the overlapping range of isotopic values for OM sources, C:N ratios serve as a better indicator of OM source (Kendall et al., 2001). In general, aquatic (endogenous) OM sources are more sensitive to microbial degradation than terrestrial (exogenous) OM sources (Wetzel, 1992). Consequently, wetland soils

often retain a large and relatively unreactive fraction of terrestrial OM. During early diagenesis, microbial degradation can modify the bulk C isotopic content of OM, potentially masking the original source signature. However, several lake studies have found that burial of OM appears to stabilize OM C:N ratios (Ishiwatari et al., 1977; Ertel and Hedges, 1985; Talbot and Johannessen, 1992).

Average C:N values of inflowing sediment were similar between years indicating similar OM sources (i.e., SOM, particulate plant matter), with values of 9.1 and 9.3 in 2004 and 2005, respectively. In contrast, average C:N values in outflowing sediment differed between years with values of 9.2 and 7.9 in 2004 and 2005, respectively. The lower average C:N ratio in 2005 was likely due to the large contribution of algal sources, whereas in 2004, low algal productivity resulted in maintenance of the source signal of inflowing sediment. In 2004, the average C:N ratio of deposited sediment was slightly elevated when compared to that of inflowing sediment (9.9 C:N sediment vs. 9.1 C:N inflowing TSS) due to the addition of OM from aquatic vegetation (16.6 C:N) (Table 3). In contrast, sediment deposited in 2005 had a lower average C:N ratio relative to inflowing sediment (7.2 C:N sediment vs. 9.3 C:N inflowing TSS) due to the contribution of algal sources (4–9 C:N).

Further insight into the origin of OM can be obtained by comparing the elemental and isotopic values of end-members with observed data. This type of analysis is based on the observation that freshwater plankton generally have C:N and/or $\delta^{13}\text{C}$ values that are considerably lower than terrestrial or other aquatic plants (Dunne and Leopold, 1978; Hamilton and Lewis Jr, 1992; Schlacher and Wooldridge, 1996). The $\delta^{13}\text{C}$ and C:N values from most OM inputs appear to plot within a broad mixing “zone” between the planktonic end-member and the overlapping range of values for aquatic plants and/or SOM (Fig. 6b). Aquatic vegetation plotted far to the right of all other OM sources and was therefore likely altered during the 1–3 month dry-down period as a result of rapid decomposition and leaching. All other C sources plot close together indicating similar origin, likely dominated by SOM mixed with lesser amounts of plankton and aquatic vegetation.

Thus, spatial patterns of C accumulation were dependant on the addition of both exogenous and endogenous sources of OM. In terms of concentration (g kg^{-1}), the concentration of C in 2004 was lowest at the inflow and along the main flow path, and highest at outflow locations and at the far reaches of the wetland where water levels were shallow and emergent vegetation was most dense (Fig. S1). This indicates that areas high in endogenous OM provide higher amounts of C per unit mass than areas high in exogenous sources, further demonstrated by the negative correlation between C concentration and sediment deposition ($r^2 = 0.47$, $p < 0.001$). Due to the absence of vegetation in 2005, the negative correlation between C concentration and sediment deposition was weaker relative to 2004 ($r^2 = 0.25$, $p < 0.001$), indicating

the increasing importance of exogenous OM associated with eroded sediment as a C source (Figs. 4 and S1). However, higher sediment C concentrations relative to inflowing sediment C and lower C:N ratios in 2005, indicate that algae was an important source of C in deposited sediment.

4.3 Long-term carbon storage in wetland sediments

An estimated 45 million ha of wetlands exist in the United States, with 15 % of these wetlands located in agricultural watersheds (6.8 Mha total agricultural wetlands) (US Department of Agriculture, 2009). These 6.8 Mha of agricultural wetlands experience high rates of sediment and C deposition and increased net primary productivity ensuing from nutrient excesses (Sanchez-Carrillo et al., 2011) resulting in elevated C-storage rates relative to natural pristine wetlands. The long-term average (13 years) annual sedimentation rate in the northern section of our wetland was $16.5 \text{ kg m}^{-2} \text{ yr}^{-1}$, which was appreciably higher than sedimentation rates of $3.5 \text{ kg m}^{-2} \text{ yr}^{-1}$ in 2004 and $9.2 \text{ kg m}^{-2} \text{ yr}^{-1}$ in 2005 (Table 2). Studies examining sedimentation dynamics in constructed wetlands have shown that newly constructed wetlands have higher rates of sedimentation than older wetlands (Fennessy et al., 1994; Braskerud, 2001; Craft et al., 2003). This is largely due to the effects of long-term sedimentation on the wetland's hydrodynamics and hydraulic efficiency (Persson et al., 1999). As wetlands begin to fill up with sediment they become channelized and less efficient in retaining inflowing sediment and carbon. In agricultural landscapes, rates of wetland sedimentation can be high, resulting in the rapid filling of these systems. Consequently, to maintain their C and sediment sink capacity, these systems require regular maintenance which includes the dredging and excavation of deposited sediment. Thus the long-term fate of eroded carbon is ultimately dependent upon what happens to the excavated sediment, e.g., whether it is reapplied to adjacent agricultural fields resulting in further disturbance and oxidation, or mounded to create and fortify levees resulting in its burial and physical protection. Although our wetland system was 13 yrs-old at the completion of this study, it maintained a high retention capacity for inflowing sediment and carbon. When viewed in terms of inflow and outflow TSS concentrations, the wetland had 98 and 82 % water column retention efficiency in 2004 and 2005, indicating its strong sink potential. Thus the dominant reason why observed sediment accumulation rates were lower than the long-term average is likely due to higher inflowing sediment loads in previous years. This is supported by the high annual variability in sediment loading observed between years ($197\,800 \text{ kg yr}^{-1}$ in 2004; $724\,400 \text{ kg yr}^{-1}$ in 2005). The long-term average annual C accumulation rate in the active deposition zone (i.e., northern section) was $0.231 \text{ kg C m}^{-2} \text{ yr}^{-1}$ (13-year average), which was lower than the total C accumulation rate in 2004 ($0.522 \text{ kg C m}^{-2} \text{ yr}^{-1}$:

$0.252 \text{ kg C m}^{-2} \text{ yr}^{-1}$ sediment C + $0.219 \text{ kg C m}^{-2} \text{ yr}^{-1}$ above-ground C + $0.051 \text{ kg C m}^{-2} \text{ yr}^{-1}$ below-ground C), but higher than in 2005 ($0.179 \text{ kg C m}^{-2} \text{ yr}^{-1}$) (Table 2). These rates of C accumulation are similar to those reported by McCarty and Richie (2002) who evaluated the role of organic wetlands in sequestering eroded C in an agricultural landscape. They reported annual rates of C storage ranging from 0.160 – $0.220 \text{ kg C m}^{-2} \text{ yr}^{-1}$. In another study examining mineral wetlands in an agricultural watershed, average rates of sediment and C accumulation during a ten year period ranged from 4.5 to $4.9 \text{ kg m}^{-2} \text{ yr}^{-1}$ for sediment and 0.152 to $0.166 \text{ kg m}^{-2} \text{ yr}^{-1}$ for C (Anderson and Mitsch, 2006). These rates are significantly higher than rates of C accumulation in natural organic wetlands, which range from $0.029 \text{ kg C m}^{-2} \text{ yr}^{-1}$ (Gorham, 1991) to $0.043 \text{ kg C m}^{-2} \text{ yr}^{-1}$ (Mitsch and Wu, 1995); as well as rates of sediment and C accumulation in natural mineral wetlands, with rates of $0.118 \text{ kg m}^{-2} \text{ yr}^{-1}$ for sediment and $0.020 \text{ kg m}^{-2} \text{ yr}^{-1}$ for C based on a 30-year average (Craft and Casey, 2000).

Despite significant enrichment of newly deposited sediment (i.e., 125 g kg^{-1} in 2004, 27 g kg^{-1} in 2005; Table 3) with endogenous C (e.g., vegetation/algal C inputs), the average long-term C concentration of the wetland sediment (pedogenic organic C equilibrium) was 14 g kg^{-1} which was the same as inflowing sediment (Table 3). This indicates that substantial decomposition occurs within the wetland, likely during the 1–3 month dry-down period in mid spring. Several studies examining permanently saturated mineral wetlands report higher average C concentrations (Anderson and Mitsch, 2006: 37 g C kg^{-1} ; Craft and Casey, 2000: 25 – 100 g C kg^{-1}). The decomposition of OM affects its isotopic and elemental composition, where the percentage of C and N decrease disproportionately during decomposition and the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values increase with progressive decomposition (Macko et al., 1993; Balesdent and Mariotti, 1996; Yoneyama, 1996). The C:N ratio was similar with depth in all four profiles, indicating little to no alteration in the C:N signature. In profile 1 (northern section), high rates of sedimentation limit OM decomposition as C is buried below the aerobic region of the soil surface (~ 1 – 5 cm). This is reflected in the $\delta^{13}\text{C}$ profile, which showed only slight fluctuations with depth. In contrast, profiles 2, 3 and 4 have lower rates of sedimentation, resulting in higher rates of decomposition. This was reflected in the $\delta^{13}\text{C}$ signatures for these profiles which showed a gradual increase with depth indicating increasing levels of OM decomposition (Fig. 10). Due to the close proximity of inflow and outflow control structures in this wetland, significant hydrological short-circuiting occurred resulting in highly variable patterns and rates of sedimentation, which in turn affected the degree of C stabilization via burial across the wetland. Although high rates of sedimentation stabilized the exogenous carbon entering the wetland, these sites where extremely low in endogenous C enrichment resulting in low carbon concentrations

(i.e., 14 g kg^{-1}). In contrast, low depositional environments where highly enriched in endogenous C but experienced high rates of decomposition. Thus we conclude that there exists an optimal balance between sediment deposition and endogenous C enrichment that may promote a higher pedogenic organic C equilibrium. Through optimizing wetland designs to promote a more even distribution of sediment deposition, higher rates of sedimentation can occur in areas with high endogenous C productivity, thus stabilizing this carbon via burial and promoting a higher pedogenic organic C equilibrium in seasonally-saturated wetland soils.

5 Conclusions

The conversion of flood plain agro-ecosystems to flow-through wetlands is becoming a popular land-use practice nationwide, yet little information exists to document how these systems function as C sinks, particularly in Mediterranean climates where constructed wetlands dry out in late winter and spring. This study shows that constructed flow-through wetlands can play an important role in the storage of eroded C. The wetland in this study experienced higher annual rates of sediment and C accumulation relative to other published studies; however, the long-term C concentration for this site (14 g kg^{-1}) was lower than most other mineral wetlands, likely a result of aerobic decomposition during the 1–3 month dry-down period and the low carbon content of farmed soils in California's Central Valley (i.e., 0.25 to 12.5 g kg^{-1}). However, given the short time frame for this study (i.e., 13 yrs) and the high degree of annual variation, a pedogenic organic C equilibrium for the wetland soil may not have been reached. This study calculated a wetland C budget during a vegetated and non-vegetated year, two conditions that represent the annual variation in endogenous C inputs. This annual variation, however, was muted in the long-term (13 yr) sediment record, which showed consistent vertical patterns across depositional environments. While high surface C concentrations were present in the distal regions of the wetland where sedimentation rates were low, there was a systematic decrease in C concentration and increase in $\delta^{13}\text{C}$ signature with depth, indicating increasing decomposition. Thus, despite significant annual endogenous C additions in surface sediment, high rates of decomposition may limit any long-term endogenous sequestration particularly in areas where sedimentation is low or highly variable. Furthermore, given that the long-term sediment C concentration was similar to the C concentration in inflowing TSS, it seems reasonable to conclude that in the span of 13 yrs there was no significant additional long-term storage of endogenous C. However, through optimizing wetland designs to facilitate a more uniformly thick depositional zone, a higher pedogenic organic C equilibrium may be established in seasonally-saturated wetlands. This study shows that the C storage capacity of seasonally-saturated wetlands is highly

sensitive to changes in agricultural and wetland management practices. Additionally, climate change may have a profound effect on ephemeral wetland systems, where changes in wetting and drying cycles may result in dramatic shifts in their pedogenic organic C equilibrium.

Supplementary material related to this

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