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# Organic Carbon and Disinfection Byproduct Precursor Loads from a Constructed, Non-Tidal Wetland in California's Sacramento-San Joaquin Delta

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## ABSTRACT

Wetland restoration on peat islands in the Sacramento-San Joaquin Delta will change the quality of island drainage waters entering the Delta, a primary source of drinking water in California. Peat island drainage waters contain high concentrations of dissolved and particulate organic carbon (DOC and POC) and organic precursors to drinking water disinfection byproducts, such as trihalomethanes (THMs). We quantified the net loads of DOC, POC, and THM-precursors from a constructed subsidence mitigation wetland on Twitchell Island in the Delta to determine the change in drainage water quality that may be caused by conversion of agricultural land on peat islands to permanently flooded, non-tidal wetlands. Creation of permanently flooded wetlands halts oxidative loss of the peat soils and thereby may mitigate the extensive land-surface subsidence of the islands that threatens levee stability in the Delta. Net loads from the wetland were dominated by DOC flushed from the oxidized shallow peat soil layer by seepage flow out of the wetland. The permanently flooded conditions in the overlying wetland resulted in a gradual evolution to anaerobic conditions in the shallow soil layer and a concomitant decrease in the amount of DOC mobilized from the soil. The seepage flow could be minimized by reducing the hydraulic gradient between the wetland and the adjacent drainage ditch. Estimates of net loads from the wetland assuming efflux of surface water only were comparable in magnitude to net loads from nearby agricultural fields, but the wetland and agricultural net loads had opposite seasonal variations. Wetland surface water net loads of DOC, POC, and THM-precursors were lower during the winter months when the greatest amounts of water are available for diversion from the Delta to drinking water reservoirs.

## KEYWORDS

wetland restoration, organic carbon, drinking water quality, disinfection byproducts, organic soils, peat, Sacramento-San Joaquin Delta, Twitchell Island

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## INTRODUCTION

For over a century, subsidence of peat soils has led to an increasing need for subsurface drainage on over 60 islands and tracts in California's Sacramento-San Joaquin Delta (hereafter referred to as the "Delta", Figure 1A, B). Cultivation of the Delta's peat soils began in the late 1800s, as Delta marshes were drained and leveed to utilize the nutrient-rich soils for agriculture. Subsidence occurs on these islands because drainage of the marsh soil leads to changes in the decomposition pathway. Under the saturated conditions under which the Delta's soils formed, organic matter from plants decays slowly and builds up the land surface. Under the drained conditions required for agricultural use, decomposition increases because oxygen is introduced to the matrix and the organic matter is converted to carbon dioxide and released as gas, leaving behind an altered soil matrix lower in organic content (oxidized peat). These same factors remain the primary cause of subsidence today (Deverel and Rojstaczer 1996).

Land subsidence is a major concern in the Delta because land-surface elevations of some Delta islands have subsided by as much as six meters below sea level, resulting in serious threats to levee stability (Weir 1950; Rojstaczer et al. 1991, Prokopovich 1985). Levee failures would lead to increased salinities in the Delta, threatening the source of drinking water of 23 million people. One strategy to increase levee stability on the deeply subsided Delta islands would be to construct wetlands on the subsided soils. Construction of wetlands would restore the island soils to their original, flooded conditions, thus eliminating the opportunity for aerobic decomposition and leading to the buildup of new marsh soils. Raising the islands' water table would also reduce the hydraulic gradient across the levees, creating a more stable condition. Because many Delta islands are so deeply subsided, the construction of tidal wetlands is infeasible. As a solution to this challenge, the construction of non-tidal wetlands within islands' levees has been proposed.

To help guide this effort, the California Department of Water Resources (DWR), Reclamation District 1601, the U.S. Geological Survey (USGS) and HydroFocus, Inc. constructed two pilot-scale wetlands on Twitchell Island, a deeply subsided island, to investigate different management approaches to mitigate deep subsidence using non-tidal wetlands. The permanently flooded wetlands resulted in a net carbon gain, reversing the effects of subsidence (Miller et al. 2000; Fujii et al. 2006); however, evidence from other studies indicated that persistent flooding of shallow, highly oxidized organic soils can result in high dissolved organic carbon (DOC) concentrations in drainage water relative to conventional agricultural drainage (Deverel and Rojstaczer 1996). These results suggested that flooding organic Delta soils to create wetlands for subsidence mitigation may contribute to high DOC loads entering Delta waterways.

Organic carbon (OC) loads are a concern because high concentrations of OC can impair drinking water quality and increase treatment costs for water treatment facilities. Organic carbon reacts with disinfectants (primarily chlorine) added during drinking water treatment to form undesirable disinfection byproducts, including trihalomethanes (THMs). The concentrations of THMs and several other disinfection byproducts in finished drinking water are regulated because of their potential carcinogenic and mutagenic impacts on human health (U.S.EPA 1998). The amount of THM formed during water treatment depends on both the concentration and the compositional nature of the DOC. The propensity of DOC to form THMs varies by more than a factor of five per unit carbon (Weishaar et al. 2003; Fram et al. 1999; Fujii et al. 1998). Chlorination experiments with simple organic molecules suggest that many substituted aromatic structures may serve as THM-precursor sites within DOC (Rook 1977; Reckhow and Singer 1985; Gallard and von Gunten 2002). THM formation is generally correlated with aromaticity (often measured by UV absorbance) (Edzwald et al. 1985; Weishaar et al. 2003), although the degree of scatter in the data indicates that other compositional factors are also important in controlling THM formation (Weishaar et al. 2003; Fram et al. 1999; Fujii et al. 1998).

Previous studies of DOC released from Delta peat soils have shown that the compositional nature of the DOC and its propensity to form THMs vary strongly with the initial composition of the peat soil, the extent of decomposition of soil organic matter and the decomposition environment. Fujii et al. (1998) compared

DOC in pore-water from shallow, variably saturated, oxidized peat soils to DOC in pore-water from deep, saturated, anoxic peat soils in an agricultural field on Twitchell Island. Although both pore-waters had high DOC concentrations, the DOC from the deeper soil was significantly more aromatic, as measured by UV absorbance, and had a higher abundance of the hydrophobic fraction of the DOC, suggesting that oxidation state during soil decomposition affected the composition of the DOC. Deverel and Rojstaczer (1996) reported a similar pattern on the scale of whole island drainage. Drainage from islands where deep water levels were consistently maintained had lower DOC concentrations with higher hydrophobic fractions than drainage from islands where water levels fluctuated into the highly decomposed and oxidized shallow peat soil. Fleck et al. (2004) compared DOC extracted from shallower and deeper soil horizons in two environments (a constructed wetland, and two agricultural fields) on Twitchell Island, and found that the prior history of the soil (length of time since first agricultural use, abundance of new organic carbon inputs, and oxidation state) all affected the DOC concentration, aromaticity, and propensity to form THMs. In particular, the DOC with the highest propensity to form THMs came from new sediment accumulating in the constructed wetland, suggesting that wetlands restored on peat soils may release DOC with a higher THM formation potential per unit carbon than the DOC released from peat soils under agricultural management. Although a lot has been learned about DOC concentrations and its compositional nature in Delta agricultural lands and constructed wetlands, the loads of DOC and THM-precursors released from these systems have been insufficiently quantified.

In this paper, we evaluate the hydrologic and geochemical processes controlling concentrations and chemical characteristics of dissolved and particulate organic carbon (DOC and POC) and THM-precursors in a pilot-scale wetland on Twitchell Island in the Delta. We determine a water budget for the wetland, calculate net loads of organic carbon exported from the wetland, and estimate the change in these loads as the wetland matures. We then compare net organic carbon loads from the wetland to net organic carbon loads determined for agricultural fields on Twitchell Island by Deverel et al. (2007). Finally, we assess the potential effects of wetland restoration on water quality of peat island drainage waters.

## Site Description

As part of a cooperative study between the California Department of Water Resources (DWR) and the USGS to study the potential use of wetland restoration for subsidence mitigation on deeply subsided islands, two wetland ponds were constructed on Twitchell Island (38° 06’25” N, 121° 38’49” W, Figure 1). East Pond and West Pond are each flow-through, impounded wetlands constructed by enclosing a formerly drained agricultural field with a berm of native soils (Figure 2a). Although two wetlands were constructed, only East Pond was monitored for water quality.

East Pond has a surface area of 2.42 hectares. Water was supplied to the ponds from the nearby San Joaquin River using a gravity siphon. Water flowed

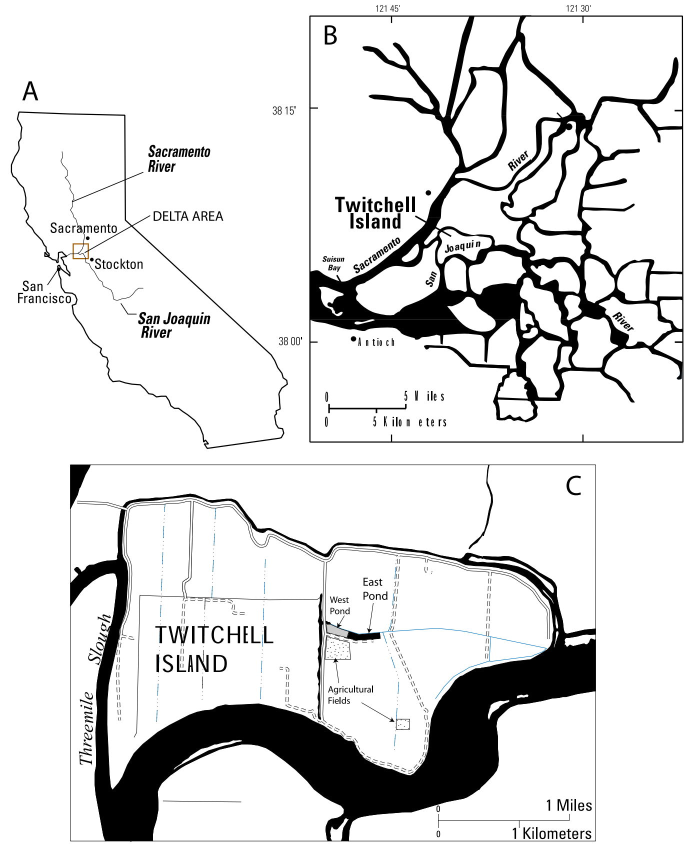


**Figure 1.** Location of A) the Sacramento-San Joaquin Delta within California, B) Twitchell Island within the Delta, and C) the constructed wetlands and agricultural fields under study on Twitchell Island.

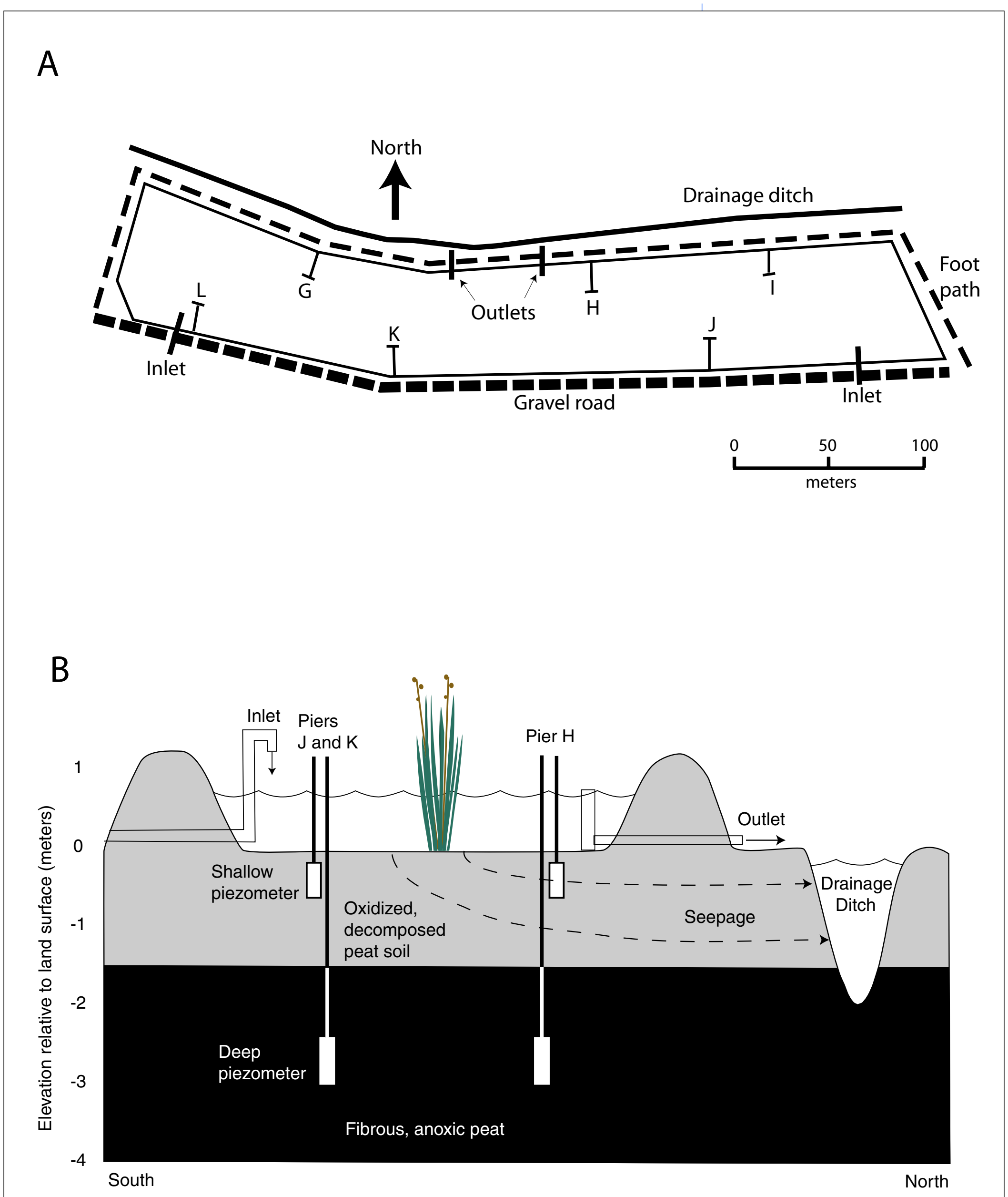


**Figure 2.** Location of the sampling sites in East Pond, Twitchell Island in (A) map view and (B) cross-section. Cross-section drawn to scale vertically, but horizontal scale is arbitrary.

continuously into the ponds via two inlet pipes on the south side of each pond. Two spillways along the northern edge of each pond controlled water depth. The spillways lead to pipes that convey the water through the berm to the drainage ditch on the north side of the pond. The pond water level was above the water level in the ditch, creating a hydraulic gradient toward the ditch through the soils underlying the pond (Figure 2b). Inflow and outflow rates were controlled to maintain a constant water depth of 60 cm in East Pond. Monitoring wells were installed at several sites in East Pond. Instruments were deployed in East Pond inlet pipes and spillways to gather data for water budget calculations. A water budget was calculated only for East Pond.

East Pond is underlain by approximately 4.5 m of organic soils (Figure 2b). The upper 1.5 m of soil has undergone repeated and extended drainage events due to long-term cultivation practices, subjecting the soil organic matter to aerobic decomposition, markedly altering its structure and reactivity from its pre-cultivated properties (Gamble et al. 2003; Fleck et al. 2004). The lower 3 m of soil are below the minimum drainage elevation for the island and therefore retain the relatively unaltered properties of naturally occurring anoxic, fibrous peat. Chemically-reduced blue clay, sand, and silt layers underlie the organic soils. Cores from an agricultural field adjacent to the ponds were used to measure hydraulic conductivities in both organic soil layers (T. Mathany, U.S. Geological Survey, unpub. data). The shallow organic soil layer showed horizontal conductivities ranging from 250 to 4,100 cm day$^{-1}$. The deeper organic soil layer showed significantly lower horizontal conductivities, ranging from 1.35 to 1.50 cm day$^{-1}$. Vertical conductivities were 10 and 3 times lower than horizontal conductivities for the shallow and deep layers, respectively. Gamble et al. (2003) estimated average hydraulic conductivity in the deep soil layer between 0.3 and 21 cm day-1 using data from slug tests conducted in East Pond monitoring wells. Groundwater flow directions are primarily lateral from the pond to the adjacent drainage ditch, and upward from the sand and silt layers into the organic soils. The broader hydrogeologic framework for the study area is described in greater detail in Burow et al. (2005), Gamble et al. (2003), and Deverel et al. (2007).

Approximately one percent (1%) of East Pond was planted with tules (*Schoenoplectus acutus*) just prior to initial flooding in October 1997, and by mid-2002, emergent wetland vegetation had spread over 50% of the pond (R. Miller, U.S. Geological Survey, written comm., 2005). This emergent vegetation consisted of about 11% tules and 89% cattails *(Typha latifolia, T. domingensis, T. angustifolia*). Open water areas of the pond contained submerged aquatic vegetation, primarily pondweed (*Potamogeton sp.*), milfoil (*Myriophyllum sp.*) and coontail (*Ceratophyllum sp.*). Wind sheltered areas were covered by duckweed (*Lemna sp.*) and water fern (*Azolla sp.*). Algae (primarily unidentified filamentous charophytes) grew in the water column of the open water areas throughout the year, with blooms occurring primarily in spring and fall. All marsh plants identified at the site are common in the Delta (nomenclature follows Hickman 1993).

## FIELD AND LABORATORY METHODS

### Water Budget

Detailed descriptions of the methods used to monitor water flows in and out of East Pond are given in Gamble et al. (2003). Water flow was metered at the east and west inlets (Figure 2a) using McCrometer propeller-type flow meters in 16-cm-diameter polyvinyl chloride supply pipes. Surface discharge from the pond was gauged at the east and west outlets (Figure 2a) using Parshall flumes installed at the exit to the outlet pipes that flow into the drainage ditch.

Precipitation records from a weather station maintained on Twitchell Island by DWR were obtained for the study period through the California Irrigation Management Information System (CIMIS) automated data system. Precipitation was converted to a volumetric inflow to the pond by multiplying precipitation depth by the pond area.

Water flux out of the pond from evaporation and uptake by plants was computed as evapotranspiration (ET). Actual ET is estimated by multiplying the reference ET (ETo) by a crop coefficient. Based on the proportion of the pond covered by emergent vegetation and variations in shading during the annual cycle of vegetation growth and senescence, the crop coefficient was estimated to be between 0.97 and 1.05 (similar to the estimate made by Gamble et al. 2003). Because the range of crop coefficients resulted in less than a 2% change in the overall water budget, a simplified crop coefficient of 1.0 was used. Daily totals were estimated by summing the hourly ETo values obtained from the DWR weather station through CIMIS. Similar to precipitation, the ET estimate was converted to volumetric outflow from the pond by multiplying ET by the pond area.

Subsurface flow, or seepage, was determined as the difference between the inflow (surface inlets and precipitation), and the outflow (surface outlets and ET). From 1997 through 2000, wetland water levels fluctuated due to breaks in inflow supply, development of boils in the berm, and island flooding. A water budget was computed for the period October 2001 through February 2003 because pond depth was maintained within +/- 1 cm of 62 cm, except for a one-week period in April 2002 when the inflow was temporarily interrupted. Changes in pond storage over the study period were negligible, and continuous electronic data were available for both inlets and both outlets.

### Water Sampling

Surface water samples were collected on two schedules: 1) Samples from Pier H (north side of pond), Pier K (south side of the pond), and the inlet and outlets of East Pond were collected semi-annually from October 1997 through July 2003 (Figure 2a); and 2) Samples from the inlet and outlets of the East Pond were collected weekly from July 2001 through March 2003. Ground water samples were collected at Piers H, J, and K at the same time as the surface water samples in schedule 1.

Semi-annual surface-water samples from Piers H and K were collected at mid-depth in the water column and samples from the inlet and outlet were collected as water exited the pipes. Groundwater was sampled from paired piezometers, screened at depths of 15-60 cm (shallow piezometer, SP), and 2.4-3.0 m (deep piezometer, DP), at Piers H, J, and K (Figure 2a, b). Piezometers at Pier I were not sampled because the site was strongly disturbed by invasive repairs to the adjacent berm after a large boil developed in 2000.

Samples were collected from the piezometers using a peristaltic pump and Teflon or C-flex tubing. Three casing volumes of water were purged from each well prior to sample collection. Dissolved oxygen, Pt-electrode redox potential, temperature, specific conductance, and pH were measured in the field using a YSI (MODEL 600XL, YSI Environmental, Yellow Springs, Ohio) fitted with a flow-through chamber. Samples for laboratory analysis were collected after the field parameters had stabilized (indicated by successive readings not changing by more than about 5 percent over a 4-minute period). Semi-annual field samples were pressure-filtered in the field through 0.45-micron pore-size filters using a plate filter (0.45 um filter) or Gelman capsule filter. Filters were rinsed with 1 L of organic-free deionized water followed by 1 L of sample water before collection of the filtered sample (or filtrate).

All samples collected for DOC concentration, UV absorbance spectra, and THM formation potential analysis were collected in clean 125 L amber glass bottles. Filtrate samples for DOC fractionation and isolation analysis, were collected in 11.4 L, stainless steel containers. Sample containers for filtrates were rinsed three times with filtered sample water before the sample was collected. Method blanks were collected to assure that filtering and field-sampling equipment were not an unintended source of DOC (or other contaminants) to the study samples. Method blanks were required to have a DOC concentration of < 0.2 mg L-1. All samples were placed on ice for transit to the lab, refrigerated at 4o C and analyzed as described below within 14 days of collection.

Weekly surface water samples were collected in clean 1-L amber glass bottles directly from the center of the water flow. Samples were immediately placed on ice, returned to the lab, refrigerated at 4° C, and filtered within 24 hours.

### Laboratory Procedures

Samples collected semi-annually were analyzed for DOC concentration, ultraviolet adsorption at 254 nanometers (UVA254), THM formation potential, and for DOC fractionation and isolation. DOC concentration was measured by high-temperature catalytic combustion using a Shimadzu TOC-5000A total organic carbon analyzer (Bird et al. 2003). UVA254 was measured using a spectrophotometer (Model UV/Vis Lambda 3B, Perkin-Elmer) with a 1cm path length quartz glass sample cuvette. Samples with UVA254 greater than 1.2 cm-1 were diluted and reanalyzed.

Abundance of THM-precursors was assessed by measuring the total THM formation potential (THMFP) using a modified versions of U.S. EPA Methods 502.2 and 510.1 as described by Crepeau et al. (2004). THMFP is the amount of THMs formed by chlorination of a water sample under specified laboratory conditions. For this method, chlorination conditions are defined as: reactivity-based chlorine dosing (concentration of chlorine added equaled 3-4 times the DOC plus 10 times the NH3-N concentrations in a sample diluted to a DOC concentration of approximately 2 mg $L^{-1}$), a 7 day reaction time, pH buffered at 8.3, temperature held at 25°C, and residual free chlorine concentration at the end of the reaction time restricted to 2-4 mg $L^{-1}$. THM formation from DOC depends strongly on chlorination conditions, thus the concentrations of THM-precursors estimated from our measured THMFP values may not represent the abundance of THM-precursor sites in the DOC that may react under different chlorination conditions. However, because all water samples in this study were chlorinated under the same conditions, the estimated concentrations of THM-precursors can be meaningfully compared.

Two indicators of DOC compositional nature were calculated from the analytical measurements. Specific ultraviolet absorbance at 254 nanometers ($SUVA_{254}$) in units of L $mg^{-1}$ $m^{-1}$ was calculated by normalizing the $UVA_{254}$ to DOC concentration. Higher $SUVA_{254}$ values indicate a higher proportion of aromatic carbon in the DOC (Chin et al. 1994). Specific trihalomethane formation potential (STHMFP, in units of mmol THM per mol DOC) was calculated by normalizing THMFP to DOC concentration, in molar units. STHMFP indicates the number of carbon atoms per 1,000 carbon atoms in the DOC that react to form a THM under the specified chlorination conditions.

DOC compositional nature was also assessed by fractionating the DOC using column chromatography with XAD-8 and XAD-4 non-ionic resins (Aiken et al. 1992; Fujii et al. 1998). XAD fractionation separates the DOC into five operationally defined fractions: hydrophobic, transphilic, and hydrophilic acids, and hydrophobic and transphilic neutrals. For this study, only the percentages of the DOC in the hydrophobic acid (HPOA) and transphilic acid (TPIA) fractions, the fractions eluted from the XAD-8 and XAD-4 resins with base, respectively, were quantified. Most of the remaining DOC comprised hydrophilic acids, the fraction not retained on either column, as the neutral fractions generally constitute a minor portion of DOC. A detailed description of the physical and chemical properties of these resins and the operationally defined fractions are given by Aiken et al. (1992).

Samples collected weekly were analyzed for DOC, POC, and total suspended solids (TSS), THMFP, and $UVA_{254}$. Samples for DOC, THMFP, and $UVA_{254}$ analyses were gravity-filtered using Teflon filter towers and 47-mm, baked, 0.3_m pore size glass-fiber filters. All filtration was conducted within 24 hours of sample collection. Filtered samples were refrigerated at 4° C and analyzed within 7 days. Filters and bottles were pre-baked at 450° C for four hours. DOC concentration and THMFP were measured as already described. $UVA_{254}$ was measured on a Varian-Cary Bio300 scanning spectrophotometer with a 1 cm path length in quartz glass cells. Samples for TSS and POC were vacuum-filtered through 25-mm, pre-baked, 0.7µm-pore size, glass fiber filters. Filters for POC analysis were wrapped in aluminum foil and frozen until analyzed. POC was determined using a Perkin-Elmer CHNSO Analyzer according to USGS methods adapted from U.S. EPA method 440 (U.S. EPA 1997), and TSS was measured gravimetrically. All filter pore sizes are nominal and tests showed no differences between DOC or POC measurements for the different filters.

## RESULTS

### Wetland Water Budget

The daily records of water flux into and out of the wetland from 2001-2003 are illustrated in Figure 3. The data were smoothed using a 13-day running average to match the residence time of the pond. The

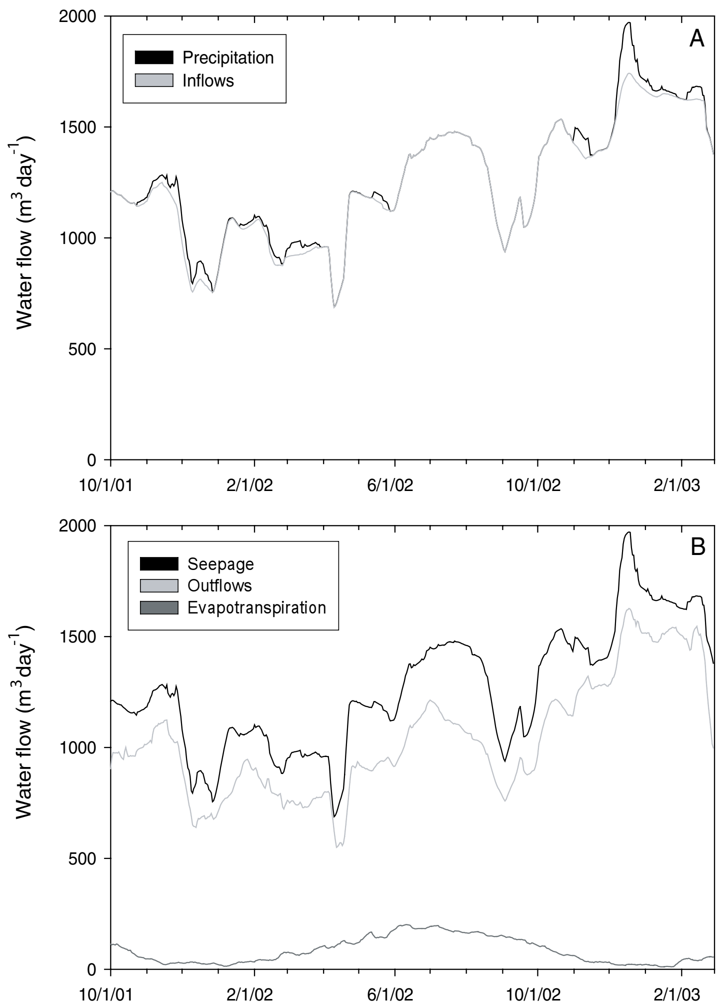


**Figure 3.** Water fluxes (A) into and (B) out of East Pond, October 2001 through February 2003. Precipitation, inflows, outflows, and evapotranspiration are based on average daily volumes for the pond. Seepage is calculated by difference. Data plotted as 13-day running averages.

surface inlets are the dominant water flux into the pond, ranging from 95-100% of the water flux throughout the year. Precipitation into the pond accounted for the remaining 0-5% of the total influx. To maintain constant water depth and residence time in the pond, the surface inlet flow rate ranged from a minimum of 750 $m^3$ $day^{-1}$, to a maximum of 1600 $m^3$ $day^{-1}$ (Figure 3a). Water flux into the pond from precipitation occurred almost entirely in the months of November through March.

The surface outlets accounted for 65-80% of the outward flux, with combined outflow rate between 600 and 1600 $m^3$ $day^{-1}$ (Figure 3b). ET was at a maximum in the summer with a rate of 200 $m^3$ $day^{-1}$ in July compared to 30 $m^3$ $day^{-1}$ in December and January. Seepage accounted for approximately 10-25% of the outward flux of water and the majority of daily seepage rates were between 100 and 350 $m^3$ $day^{-1}$. Greater seepage tended to occur when inflow rates were increasing or high, and during large precipitation events.

## Surface-Water Chemistry

### DOC Concentrations and Compositional Characteristics

The chemistry of the inlet water was seasonally variable. DOC concentrations were approximately 1.5 mg $L^{-1}$ in the summer months (mid-May through mid-November) and increased to maximum concentrations of over 4 mg $L^{-1}$ in January (Figure 4a). These concentrations closely reflected the DOC concentrations for Sacramento River at Freeport in both magnitude and temporal trends and were lower than concentrations measured in the San Joaquin River near Vernalis (http://ca.water.usgs.gov/archive/waterdata/). This is consistent with data indicating that the Sacramento River is the dominant water source in the reach of the San Joaquin River south of Twitchell Island where the siphon feeding the inflow to the ponds is located (J.R. Burau, U.S. Geological Survey, pers. comm.).

Water leaving the pond via the surface outlets exhibited different DOC trends from the inlet. Outlet waters had significantly higher DOC than inlet waters (t-test of difference between two means, $p<0.00005$) and exhibited less seasonal variation (Figure 4a). DOC concentrations in outlet waters ranged between 2.6 and 5.9 mg $L^{-1}$, with most of the high values occurring from January through June.

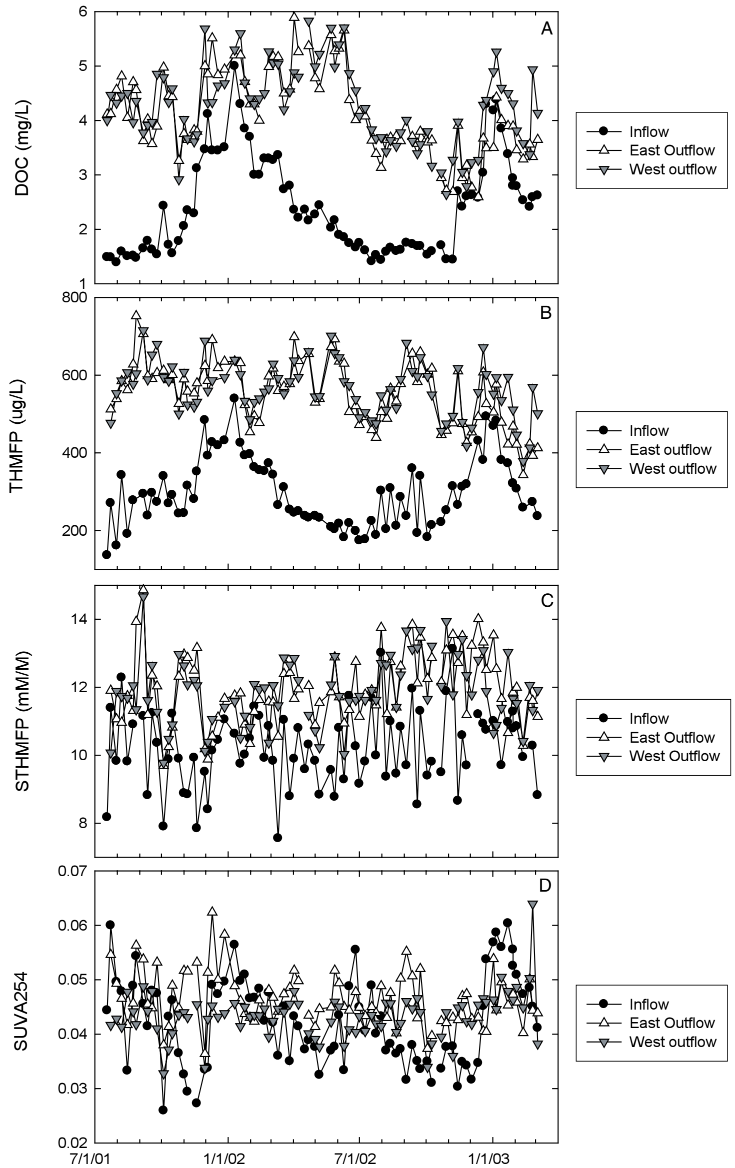


**Figure 4A-D.** Weekly data for dissolved constituents in samples collected from the Inflow and Outflows of East Pond, July 2001 through March 2003.

The compositional characteristics of the DOC in the inlet and outlets waters were also markedly different. STHMFP of outlet waters ranged from 9.7 to 14.8 mmol mol-1 (median = 11.8 mmol mol-1) and was significantly greater than STHMFP of inlet waters, which ranged from 7.5 to 13.0 mmol mol-1 (median =

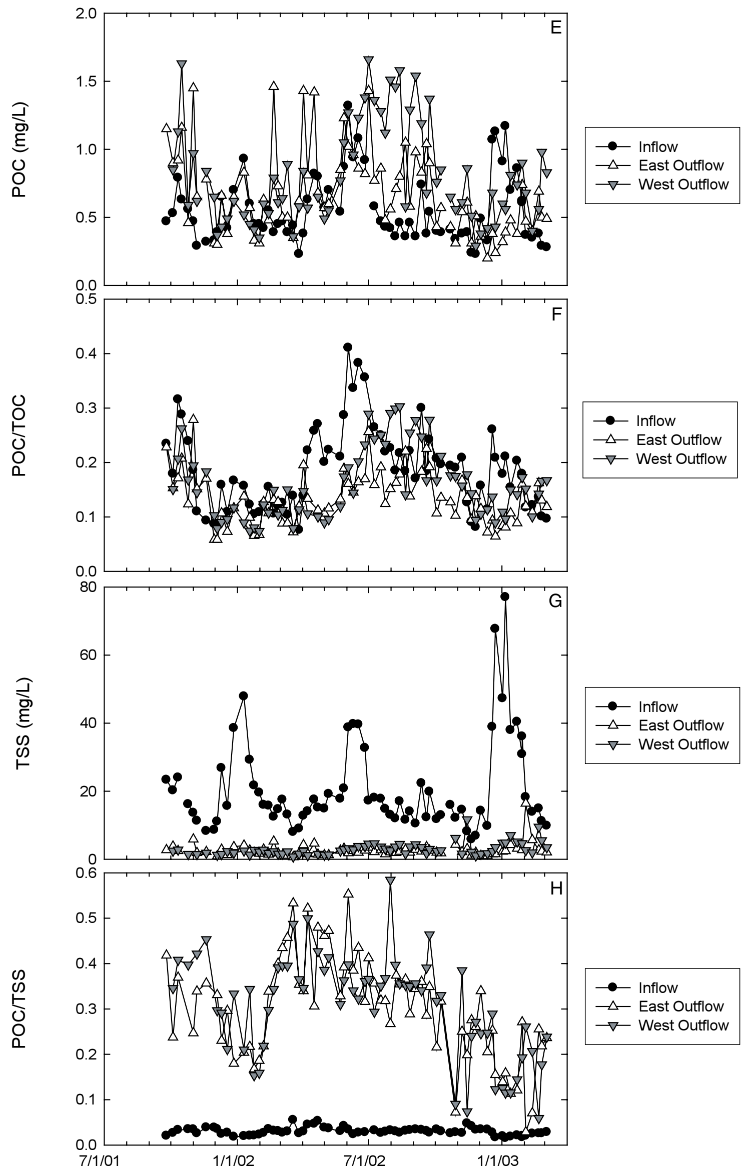


**Figure 4E-H.** Weekly data for particulate constituents in samples collected from the Inflow and Outflows of East Pond, July 2001 through March 2003.

10.0) (t-test of difference between two means; $p < 0.00005$). The inlet and outlet waters had different $SUVA_{254}$ values. Mass-weighted annual mean $SUVA_{254}$ values for the inlet and outlet waters were 0.0418 and 0.0432 L mg$^{-1}$ cm$^{-1}$, respectively. The outlet waters showed no seasonal pattern; whereas the inlet waters had a winter and a summer peak in $SUVA_{254}$, roughly corresponding to the timing of the TSS peaks in the inlet water (Figure 4d, g).

Significant spatial and temporal variability were observed within East Pond surface waters. Between 2001 and 2003, when water levels were maintained at the desired depth, DOC concentrations in Pier K surface water (K-SW), was higher in summer than winter (7.3 mg L$^{-1}$ and 5.2 mg L$^{-1}$ respectively), yet no seasonal trend was apparent in Pier H surface water (H-SW) (4.1 mg L$^{-1}$ in summer and 4.4 mg L$^{-1}$ in winter). DOC concentrations in H-SW compares well to outlet concentrations for the dates sampled, whereas K-SW showed elevated DOC relative to the outlets during the summer months (Figure 5a). These trends were variable in years when water levels and supply were not maintained (data not shown). Seasonal trends in dissolved oxygen were the reverse of the DOC trend. K-SW had DO concentrations less than 1 mg L$^{-1}$ year-round, whereas H-SW was only anoxic during the summer months.

K-SW was different from other surface waters in all three measures of DOC compositional quality (Figure 5b-d). Percentage of HPoA fraction of DOC in K-SW waters (about 55%) was greater than the percentage in the inlet waters (about 45%). The percentage of HPoA fraction in the outlet waters (about 50%) was between concentrations of the inlet water and K-SW (Figure 5b). The mass-weighted annual mean $SUVA_{254}$ values of the outlet waters were greater than the $SUVA_{254}$ of the inlet waters. $SUVA_{254}$ values for the K-SW site were even greater (Figure 5c). However, while K-SW STHMFP values were greater than the mass-weighted annual mean inlet STHMFP, they were less than the mass-weighted annual mean outlet STHMFP (Figure 5d). Although data are limited, there were no apparent seasonal trends in any of the compositional quality parameters at K-SW or H-SW sites.

### POC Concentrations and Compositional Characteristics

POC concentrations in the inlet waters ranged between 0.23 and 1.32 mg L$^{-1}$ and showed both winter and summer peaks that coincided with peaks in TSS (Figure 4e, g). For the inlet waters, the percent of the TOC in the particulate fraction (POC/TOC) ranged from 8 to 41%, with maximum values occurring during the summer months when DOC concentrations were low (Figure 4f). POC concentrations in outlet waters ranged from 0.20 to 3.85 mg L$^{-1}$, with the highest concentra-

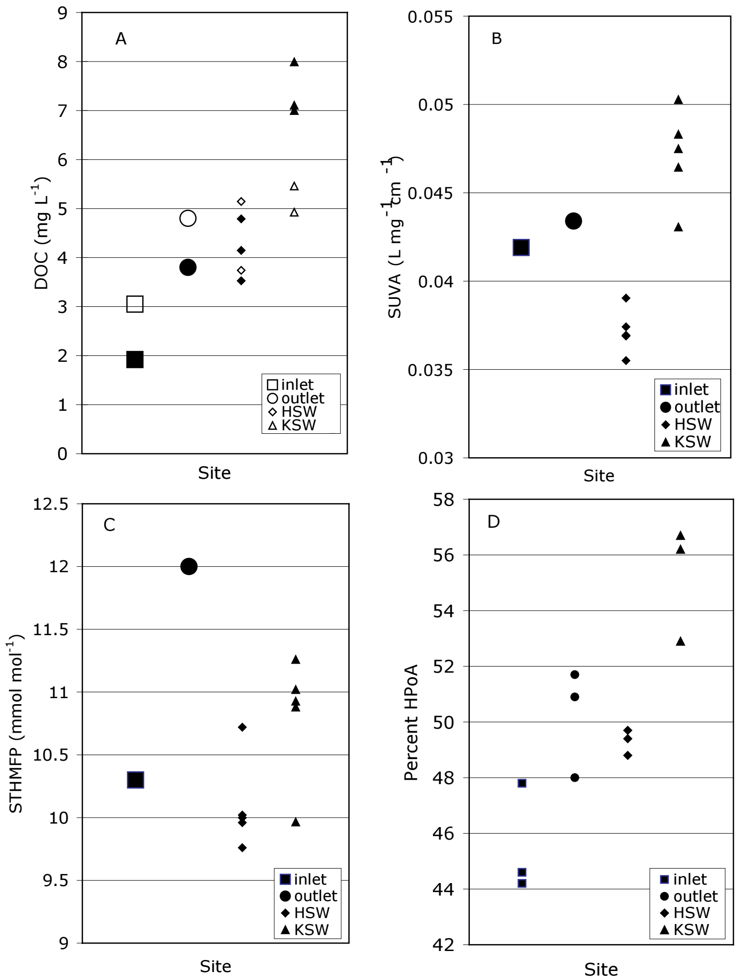


**Figure 5.** Comparison of (A) DOC concentrations, (B) $SUVA_{254}$, (C) STHMFP, and (D) percent HPoA in surface water from inflow, outflows, Pier H, and Pier K. For figure 5A, open symbols are winter and filled symbols are summer data.

tions occurring between June and October (Figure 4e), corresponding to the time when algal growth in the pond was greatest (R. Miller, U.S. Geological Survey, written comm., 2005). For the outlet waters, POC constituted between 7 and 34% of the TOC, again with greatest contribution in the summer months (Figure 4f).

The suspended solids entering East Pond were quite different from the suspended solids leaving. TSS concentrations in inlet waters ranged from 6 to 77 mg $L^{-1}$ with both winter and summer peaks; whereas, TSS concentrations in the outlet waters were nearly always below 4 mg $L^{-1}$ and showed no seasonal pattern (Figure 4g).

## Ground-Water Chemistry

Spatial and temporal trends were observed in the DOC concentrations of pore-waters, measured in piezometers installed at the sampling piers. The primary differences occurred in the vertical dimension as DOC concentrations differed greatly between the two soil layers. DOC concentrations measured in the shallow-soil-layer-pore-waters at Piers H, J, and K (H-SP, J-SP, K-SP, respectively) ranged between 15 and 200 mg $L^{-1}$. Concentrations in the deep-soil-layer-pore-waters (H-DP, J-DP, K-DP) were much lower, ranging between 10 and 40 mg $L^{-1}$, and much less variable (Figure 6a). The variability within the shallow soil concentrations reflects the temporal trends in the shallow pore-waters. DOC concentrations at K-SP and J-SP increase between 1997 and 1999, plateau between 1999 and 2001 and decrease to remain relatively stable between 2001and 2003. In contrast, H-SP concentrations decreased throughout the record. The temporal trends resulted in K-SP having the highest concentrations and H-SP the lowest throughout the entire study, except after initial flooding of the wetland when all three were similar. The temporal trend in DOC concentration in the deep pore layers was less apparent. All sites were elevated immediately following wetland establishment, then stabilized at lower concentrations for the remainder of the study.

The DOC quality parameters, $SUVA_{254}$ and STHMFP, also varied spatially and temporally but not in the same manner as DOC. $SUVA_{254}$ values were typically higher in the deep pore-waters from 1997 to 2000, but generally reversed that trend by 2002, despite high variability in deep pore-waters (Figure 6b). This reversal was the result of a general increase in $SUVA_{254}$ values in the shallow pore-waters from 1997 through 2003, while the deep pore-waters showed no such increase over the same time period. The $SUVA_{254}$ from H-SP was always higher than K-SP for every sample date. Pore-waters typically had higher $SUVA_{254}$ values than the pond surface water. STHMFP values were highly variable throughout the record (Figure 6c). Variations in analytical procedure between 1997 and 2000 cannot be ruled out as a cause for the trends in that portion of the data record, and are therefore excluded from data analyses. Analytical procedures were standardized for

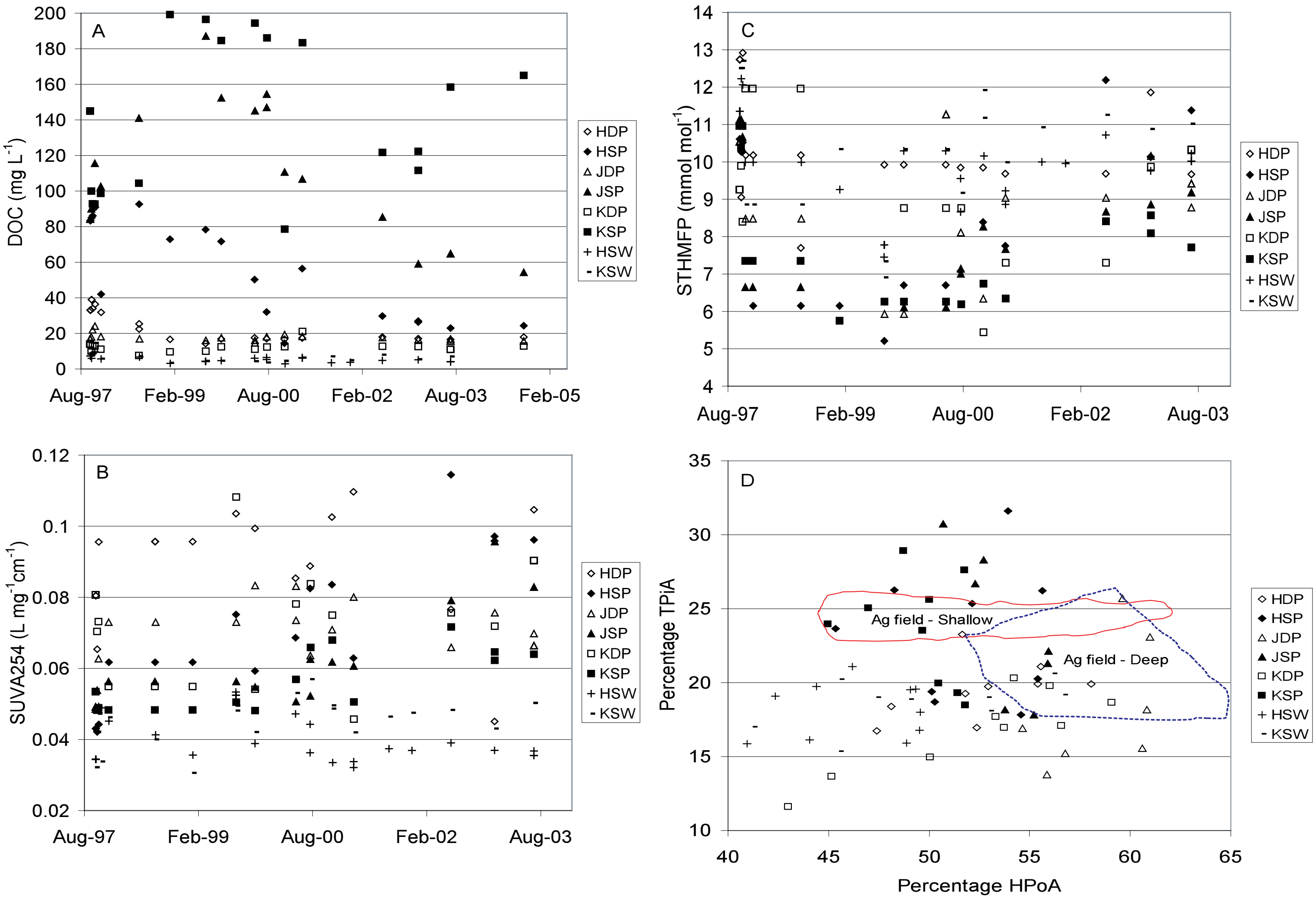


**Figure 6A-D.** Comparison of water quality for pore-waters from deep (DP) and shallow (SP) piezometers at Piers H, J, and K in 1999-2002. Results are presented for (A) DOC concentrations, (B) $SUVA_{254}$, (C) STHMFP, (D) DOC fractionation results, and (E) specific conductance *(next page)*. In figure 6D, the range of DOC fractionation results from pore-waters in shallow and deep soil layers in Twitchell Island agricultural fields are provided for comparison (Deverel et al. 2007).

2000 through 2003 and could not responsible for variations during that period. Between 2000 and 2003 the shallow pore-water STHMFP increased systematically. By 2003 there were no significant differences between mean values of shallow and deep pore-water STHMFP (Figure 6c).

DOC in H-SP, J-SP, and K-SP from 1998 through 2003 generally contained a higher proportion of the TPiA fraction and a lower proportion of the HPoA fraction than pore-waters from the deep piezometers (Figure 6d). Because DOC concentrations in shallow pore-waters were so much higher than in deep pore-waters, directional flow from the shallow to deep soil layer would have resulted in pore-waters with similar DOC compositional characteristics, but this was not the case. DOC from shallow soil pore-waters of agricultural fields nearly always had lower HPoA and greater TPiA percentages, than DOC from pore-waters in deeper soils (Deverel et al. 2007; Figure 6d). The similarity in DOC quality of wetland soil layers and soil layers of drained fields indicates that pre-inundation soil characteristics dominantly affect the current pore-water DOC character, despite six years of permanent flooding

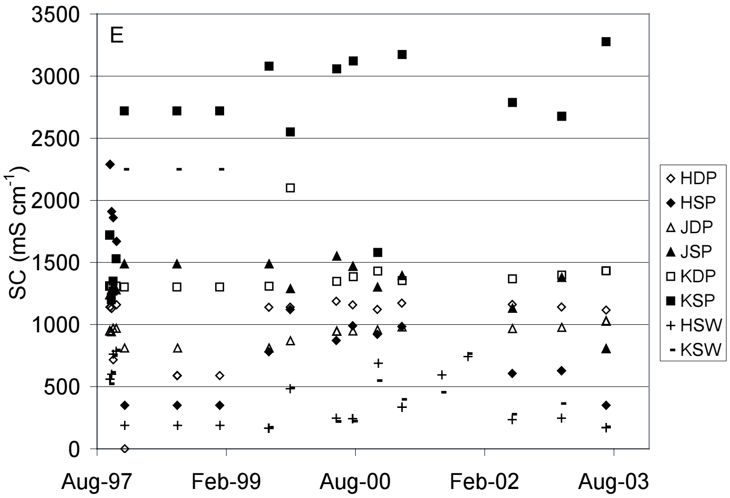


**Figure 6E.** Comparison of water quality for pore-waters from deep (DP) and shallow (SP) piezometers at Piers H, J, and K in 1999-2002. Results are presented for (A) DOC concentrations, (B) $SUVA_{254}$, (C) STHMFP, (D) DOC fractionation results *(previous page)*, and (E) specific conductance. In figure 6D, the range of DOC fractionation results from pore-waters in shallow and deep soil layers in Twitchell Island agricultural fields are provided for comparison (Deverel et al. 2007).

for wetland restoration. Apparently, the shift from aerobic to anaerobic conditions after permanent flooding did not change the $HP_oA$- $TP_iA$ character of the DOC in shallow soil water.

Specific conductances of shallow and deep soil layer pore-waters were also different. In general, the specific conductances of the shallow soil pore-waters at each pier were greater than those of the deep soil pore-waters for most sampling times (Figure 6e). The main exception to this trend was Pier H, where the deep soil pore-waters (H-DP) had consistently greater specific conductance than the shallow soil pore-waters (H-SP) after 1998.

## DISCUSSION

### Conceptual Models

#### Surface Water DOC

The change in DOC concentrations between the inlet and outlet indicate that the wetland is contributing DOC to the surface water environment. The increase in THMFP between the inlet and outlet waters was due both to an increase in DOC and an increase in STHMFP contributed by the wetland, suggesting that the processes that contribute DOC to the surface water contribute a type of DOC that is highly reactive in forming THMs. The higher THM formation in outlet water compared to inlet water has also been observed in other constructed wetlands (Rostad et al. 2000). The differences in the temporal trends between inlet and outlet suggest different mechanisms are responsible for the differences in composition. The DOC peak in the inlet water corresponds to the annual winter DOC peak observed in the Sacramento and San Joaquin Rivers and the Delta channels. This may represent initial flushing of watershed soils at the onset of the rainy season. The DOC trend in the outlet waters reflects *in situ* wetland processes. For instance, DOC in the water column is derived primarily from algal production, plant exudates, and diffusion from the soil-water interface. The greatest challenge is decoupling which process, or what combination of processes, dominates in a specific system. Identifying the mechanism that contributes DOC with high reactivity is important to understand and manage wetlands that will be constructed in the future.

The spatial variability in surface water data provides insight into the nature of wetland-derived DOC. Pier K is located in an isolated corner of the pond where its distance from preferred flow paths between pond inlets and outlets, combined with thick vegetation at this location, are likely to limit water exchange with the rest of the pond (Figure 2a). Pier H, on the other hand, has less dense vegetation, and is closer to the east outlet, so surface water continuously flows past this location. Dissolved oxygen data support these inferences about flow patterns in the pond. Well-aerated inlet water replenished dissolved oxygen in the water column at Pier H. At Pier K, oxygen consumption in the summer increased due to microbial activity, and out-paced oxygen replenishment. Pier K never received sufficient input of well-oxygenated inlet water to replenish dissolved oxygen in the water column. It is likely that these flow conditions resulted in a much longer residence time for water in the vicinity of Pier K, compared to water in the vicinity of Pier H or at the outlets. Thus, it can be deduced that K-SW contains a large proportion of wetland-derived DOC.

Observations at Pier K can provide evidence for certain mechanisms that would drive high DOC and STHMFP, however, decoupling the mechanisms at Pier K is difficult. While no measurements were taken, it is assumed that algal production at Pier K is limited because thick vegetation shades the water and reduces light availability at the site. The large difference between STHMFP in the surface waters and shallow pore-waters at Pier K suggests that diffusion from the soil is unlikely to be the dominant source of DOC in surface waters. The low STHMFP in the shallow soils at Pier K also suggests that anaerobic conditions are not the sole cause of increased reactivity in wetland-derived DOC, because the pore-waters are at least as deficient in DO as the surface waters. That leaves DOC derived from plants as the most likely source of the DOC at Pier K. The release of DOC from either live plants or plant remains at Pier K is the likely source of the highly reactive DOC in East Pond surface waters. Fresh plant remains have been identified as a source of THM-reactive DOC in other locations as well (Fram et al. 2001; Rostad et al. 2000).

The temporal variability in the surface water data provides another line of evidence for vegetation being the source of the highly reactive DOC in pond exit waters. Although the algal contribution at Pier K was assumed to be low because of thick vegetation, East Pond has significant open water areas where algae thrive. Outlet water particles are predominantly algal derived (see next section), suggesting that algae production in open water areas could be a significant contributor to the overall DOC found in East Pond surface water outlet samples. The primary evidence against algae being the dominant DOC contributor at the outlet is timing. Outlet DOC is elevated from January through July. In contrast, East Pond algal blooms occur primarily in the late spring and early autumn. $SUVA_{254}$ is also lower in H-SW compared to K-SW, agreeing with low $SUVA_{254}$ measurements typical of algal derived DOC. That the H-SW $SUVA_{254}$ concentration is lower than the concentration of $SUVA_{254}$ at the outlets suggests that other sources contribute a greater proportion of DOC to the outlet waters than algae. These inconsistencies lend credibility to the theory that algal production is not the dominant DOC source in East Pond.

Temporal variability in outlet DOC concentrations suggests that plant materials are the dominant source of DOC to East Pond surface waters. This supports our contention (from our analysis of Pier K data) that plant materials were the dominant source of DOC at Pier K. Plant senescence and deposition into the pond begins in fall and early winter. Microbial activity increases with temperature. Microbial populations in the East Pond were related to DOC extracted from the soils (Bossio et al. 2006). Assuming that low winter temperatures and physical plant structure cause a lag between initial plant material deposition and decomposer growth, the timing of DOC production from plant materials that causes elevated DOC concentrations in the outlets coincide well. East Pond DOC production in January is low with elevated concentrations of outlet water similar to concentrations of inlet waters. Lower temperatures in the winter months may also suppress microbial degradation of DOC, thus leaving higher DOC concentrations in the water. The inlet concentrations drop quickly in spring when temperatures increase. The East Pond then contributes more DOC to outlet waters, keeping outlet concentrations high through summer. By autumn, there may be little plant material remaining that would act as a good substrate for DOC production, thus lowering DOC production at a time when DOC decomposition is greatest and resulting in the lowering of DOC concentrations during the late summer and autumn months. Measured bacterial abundance in outlet waters was four times greater in July than in February (Stepanauskaus et al. 2003). This condition would persist until the next time of plant senescence and plant material input.

It is important to note that seasonal variations in THMFP in both the inlet and outlet waters were less pronounced than the variations in DOC, primarily because of the effect of bromide, not DOC composition. Bromide concentrations in the San Joaquin River at Twitchell Island are greater in August through November because low summer river flows permit tidal mixing to extend further upstream. Bromide reacts rapidly with chlorine to produce reactive bromine species that react with DOC to form THMs even more efficiently than the reactive chlorine species

(Symons et al. 1993). Bromine has more than twice the atomic mass of chlorine; thus, brominated THM molecules result in higher mass concentrations of THMs. The effect is greatest in inlet water in the summer because this is where bromide concentrations are highest and DOC concentrations are the lowest, resulting in formation of fewer THM molecules that contain a higher proportion of bromine.

In summary, our conceptual model for DOC production in the surface waters is as follows: the primary DOC source in East Pond surface water is derived from plant remains that are deposited in winter and decomposed under anaerobic conditions in spring and summer. The DOC produced is highly reactive in forming THMs and thus poses an increased risk to drinking water relative to agricultural management. There is a wealth of supporting evidence in both spatial and temporal trends for vegetative material as the dominant source of DOC in overlying waters, although algal contribution cannot be ignored. More research is necessary to determine the effect of different water management strategies on DOC contribution from the different sources.

#### Surface Water POC

The TSS peaks in the inlet water were likely due to mobilization of watershed soils during the winter rainy and summer irrigation seasons and/or bed sediment resuspension in the river channel. Composition of the suspended solids in the inlet water was nearly constant at 88% ash and 3% POC, suggesting the same source year-round. The mean atomic carbon-to-nitrogen ratio (C/N) of the inlet particulate organic matter was 9, which is consistent with watershed soil organic matter source (Kendall et al. 2001). The composition of the suspended solids leaving East Pond ranged from a median of 27% ash and 36% organic carbon in the summer months, to a median of 43% ash and 26% organic carbon in the winter months, indicating that the outlet water TSS contained a much larger fraction of organic matter than the inlet water TSS, and that the fraction of organic matter in the outlet water TSS was largest in the summer months. Furthermore, the mean atomic C/N of the outlet water TSS organic matter was 7, with no systematic seasonal variation, suggesting that the organic component was algal and microbial material, rather than terrestrial or aquatic plant debris (Kendall et al. 2001).

In short, East Pond efficiently trapped incoming riverine sediment high in mineral composition but added algal and microbial particles high in organic matter to the outflow. Data indicate that the mechanisms in East Pond that lead to POC generation are different than those generating DOC, as algae appeared a minor contributor to the dissolved fraction. Mechanisms controlling algal and microbial production will govern POC dynamics in constructed, flow-through wetlands like East Pond. The conversion of mineral particles to organic particles as water passes through the wetland may be of significance to water treatment facilities that do not remove particles prior to disinfection. The organic particles can contribute a large portion of the disinfection byproducts if they are not removed (Fram et al. 2001).

#### Groundwater DOC

We hypothesize that the DOC concentrations in the soil pore-waters underlying East Pond reflect the historic drainage conditions caused by the previous agricultural operations on Twitchell Island, despite six years of wetland establishment. DOC concentrations in shallow soil and deep pore-waters mirror the concentrations in the same soil layers in nearby agricultural fields. DOC concentrations in pore-waters from agricultural fields on Twitchell Island were between 40 and 120 mg $L^{-1}$ at depths shallower than 2 m, and between 5 and 40 mg $L^{-1}$ at depths greater than 2 m (Deverel et al. 2007). Although Fujii et al. (1998) reported high DOC concentrations in deep peat, the deep wells measured in that study were in close proximity to the drainage ditch. This proximity to the ditch would likely include the deep wells in the drainage area above the hydrostatic surface, resulting in the deep peat at this location to have undergone significant oxidation and alteration compared to deep peat not impacted by drains (the majority of the deep peat on the island). The fraction of TPiA and HPoA in the pore-waters underlying East Pond also mirror those of the pore-waters underlying the nearby agricultural fields, suggesting the source of the DOC is likely to be the same under the wetland as in the agricultural fields.

These data suggest that the concentration of East Pond pore-water DOC is derived from mechanisms incurred during the historic drainage of the surface soil layer during agricultural production. This large DOC reservoir is present despite six years of wetland flooding. Equilibrium studies of the Delta's altered peat soil (shallow soil layer) confirm the presence of a large reservoir of readily soluble DOC (Aguilar and Thibodeaux 2005). Mathany (U.S. Geological Survey, unpub. data) also identified a large DOC reservoir in the shallow soil layer through core flushing studies. It is possible that other sources of DOC, such as plant exudates, detritus and upwelling, may contribute DOC to the shallow soil pore-waters under the wetland, but the high concentrations associated with the shallow pore-waters are unique to highly impacted organic soils.

We further hypothesize that the conditions brought on by construction of the wetland have increased the reactivity of the pore-water DOC with respect to disinfection byproduct formation, through the establishment of anaerobic conditions that alter the composition of the DOC. Although DOC concentrations in pore-waters reflect the previous agricultural management of the shallow soils, STHMFP in pore-waters of the wetland shallow soil layer are markedly higher than those under agricultural management. This increase may be related to an increase in DOC aromaticity. Following construction of East Pond, the shallow soil pore-waters were low in both SUVA254, a common indicator of aromaticity, and STHMFP, similar to values found in shallow agricultural soils (Fujii et al. 1998; Fleck, et al. 2004; Deverel et al. 2007). However, after the wetland was established, both measurements rose throughout the record as anaerobic conditions began to dominate. This trend is consistent with an increase DOC aromaticity associated with flooded conditions (Sihombing et al. 1991). However, the HPoA of the shallow pore-water, another indicator of aromaticity, did not increase after wetland establishment suggesting that aromaticity is not increasing under wetland conditions.

The assumption that higher $SUVA_{254}$ of the deep soil pore-waters reflects an increase in DOC aromaticity may be erroneous in this system. Unfortunately, the origin of high $SUVA_{254}$ values can be ambiguous in systems containing high concentrations of dissolved iron because iron also absorbs UV light at 254 nanometers (Weishaar et al. 2003). Pore-waters from the deep soil layer in the field adjacent to East Pond contained 4 to 21 mg $L^{-1}$ dissolved iron (Fujii et al. 1998), and $SUVA_{254}$was positively correlated with iron concentration normalized to DOC concentration. Because dissolved iron concentrations were not measured in this study, it cannot be determined whether the increases in $SUVA_{254}$ were caused by higher normalized iron concentration or by more aromatic composition of DOC in anaerobic pore-waters that also contained high iron concentrations. Regardless of which mechanism leads to higher $SUVA_{254}$, the increase reflects a general response to anaerobic conditions which leads to higher STHMFP, but it is unclear what compositional changes have occurred under anaerobic conditions that result in the higher STHMFP.

#### Groundwater Hydrology

The groundwater flow path from the pond is important because of the large difference in composition between the shallow and deep pore-waters. Seepage of water from the pond through the soil matrix constituted 10-25% of the water flow out of the pond; thus the composition of the seepage water will strongly affect calculations of DOC and THM-precursor loads from the pond. This is particularly true for a wetland constructed on a subsided island encircled by agricultural fields with low drain elevations maintained by off-island pumping. This specific condition results in a hydraulic gradient between the constructed wetland and the island drain, which results in water being driven from the wetland towards the drain.

The spatial and temporal variability in pore-waters supports the hypothesis that water from the pond seeped into the shallow soil layer and flowed north towards the ditch (Figure 2b). DOC concentrations in H-SP on the north side of the pond decreased systematically from 88 mg $L^{-1}$ in 1997 to 23 mg $L^{-1}$ in 2003, and specific conductance decreased somewhat less systematically from approximately 2,000 to 500µS $cm^{-1}$ (Figure 6a, e)—in both cases approaching the values in surface water from the pond. Laboratory column studies in which core samples were flushed with inlet water showed that high DOC concentrations measured in pore-water in the shallow peat soils were eventually reduced to close to inlet water DOC concentrations by continuous passage of inlet water through the core (T. Mathany, U.S. Geological Survey, pers. comm.). Soil compaction beneath the well-maintained road on the south side of the pond likely restricted flow through the shallow soil layer out the south side of the pond compared to the foot trail on the north side of the pond. Therefore, the south side would experience less leaching of the soils and thus would possess pore-water characteristics more closely related to past conditions (K-SP, J-SP) while pore-water composition in the north side soils (H-SP) would approach the composition of the pond water (Figure 6). Furthermore, the fact that J-DP, K-DP, and H-DP had relatively constant but different specific conductivities from 1997-2003 implies that negligible horizontal flow occurred within the deep soil layer.

The differences in DOC concentrations, DOC quality indicators, and specific conductances between pore-waters in the shallow and deep soil layers indicate that the deep soil layer was hydrologically isolated from the shallow soil layer and the pond throughout the course of the study. This hydrologic isolation is a result of the historic agricultural drainage on the wetland site which caused decomposition of the peat soil which damages the soil structure and results in an increase in hydraulic conductivity in the shallow soil layer. The increased hydraulic conductivities in the shallow soil layer controls the flow path of seepage water from the wetland. These inferences are consistent with the very low vertical and horizontal hydraulic conductivities measured in the deep soil compared to the shallow soil. However, these inferences conflict with the flow paths suggested by Burow et al. (2005) and Gamble et al. (2003) for this same study site. Based on modeling of pore-water temperature profiles, Burow et al. (2005) proposed that water seeped through the shallow soil layer to the deep soil layer and flow to the adjacent ditch was primarily through the deep soil layer.

The discrepancies between the flow paths suggested in this study and those presented in Burow et al. (2005) are due in large part to the difficulties in using temperature as a tracer in peat dominated systems. Burow et al. (2005) provided the best possible model with the data available at the time of publication, unfortunately the study lacked appropriate considerations for heat conduction in saturated black soils exposed to long periods of direct sun. Temperature data from wells in the agricultural fields on Twitchell Island showed similar temperature trends to East Pond wells, discounting the underlying assumption of the model that the temperature trends in wetland wells reflected surface water movement from the pond through the shallow soil layer and into the deeper peat layer (S.J. Deverel, Hydrofocus Inc., pers. comm.). The lack of these data at the time of model development and publication resulted in inappropriate model boundary conditions being applied to the model. Furthermore, Burow et al. (2005) acknowledged using higher conductivities for the deeper soils relative to the shallow soils despite field data showing the opposite conditions (Burow et al. 2005; Gamble et al. 2003). Their explanation was that their values were within literature values. However, newly reported data further support evidence of higher conductivities in the surface soils compared to the deep peat layer through direct measurements (T. Mathany, U.S. Geological Survey, unpub. data; Deverel et al. 2007). We contend that the sum of all the data reported for Twitchell Island are better represented by our proposed flow model compared to the one proposed by Burow et al. (2005).

## Load Calculations

### Net Loads in 2002

To evaluate the impact of constructed wetlands on water quality in Delta channels, net loads of DOC, TOC, and THM-precursors from the wetland must be calculated and compared to net loads from agricultural fields on the peat islands. Daily loads for the wetland were calculated using the mean daily water flows for inlet, outlet, and seepage from the water budget (Figure 3). The measured DOC, POC, and THM-precursor concentrations in the weekly inlet and outlet samples were assumed to represent the mean concentrations on the day of sampling (Figure 4a, b, e), and values for all the other days were calculated by interpolation between the measured data. Concentrations of DOC, POC, and THM-precursors in precipitation were not measured as part of this study but the contribution of precipitation to the total water influx is very small (Figure 3), resulting in a negligible load from precipitation (< 1%) even if concentrations in the precipitation reach 10 mg $L^{-1}$, higher than any reported concentrations for precipitation in open systems of which the authors are aware. For this reason, the contribution of precipitation to the flux was not included in the calculations. Water lost to evapotranspiration was assumed to have concentrations of zero. The composition of the seepage flow was assumed equal to the composition of pore-water in the shallow soil layer on the north side of the pond (H-SP). In mid-2002, H-SP contained approximately 25 mg $L^{-1}$ DOC (Figure 6a), 2700µg $L^{-1}$ THMFP, and had an STHMFP of approximately 10 mmol mol-1. POC was assumed to be 15% of DOC. The mean net daily loads were calculated as follows:

$$\text{measured daily net export load} = \frac{F_I C_I - F_O C_O - F_S C_S}{A} \quad (1)$$

where A is surface area of pond, F is water flux in L $day^{-1}$, C is concentration in mg $L^{-1}$ or µg $L^{-1}$, and the subscripts I, O, and S, refer to inlet, outlet, and seepage, respectively.

Because the hydraulic gradient between the pond and the ditch that induced the seepage flow was particular to the design of this wetland, daily net loads were also calculated assuming all the flow occurred as surface flow through the pond outlets (i.e., no seepage):

$$\text{no-seepage daily net export load} = \frac{F_I C_I - (F_O + F_S) C_O}{A} \quad (2)$$

Measured and no-seepage daily net loads were averaged over one month periods to yield monthly mean daily net loads. Monthly mean daily net loads for East Pond in 2002 are plotted in Figure 7 and compared to monthly mean daily net loads from agricultural fields on Twitchell Island (Deverel et al. 2007). It is unclear what effect no-seepage hydrologic conditions would have on surface water concentrations and loads but a recent study showed that increasing surface water residence times and restricting subsurface flows from rice fields resulted in higher concentrations in surface waters but no significant increase in DOC loads because of the reduction in flow (P.M. Bachand, Bachand and Associates, written comm. 2006).

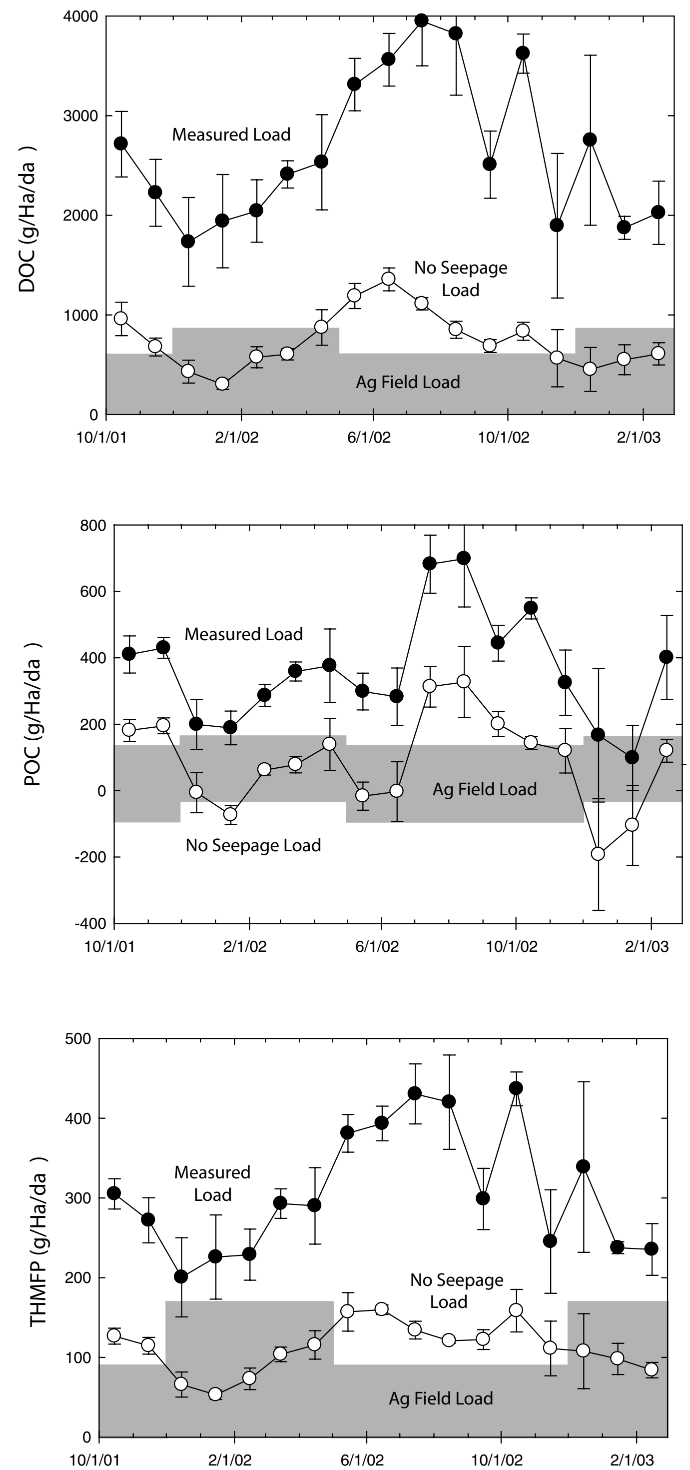


**Figure 7.** Calculated monthly loads from East Pond for (A) DOC, (B) POC, and (C) THM-precursors (measured as THMFP). Agricultural field loads are from Deverel et al. 2007, and the shading encompasses the mean and one-standard deviation from the mean for three fields on Twitchell Island.

Measured monthly mean daily net loads for DOC, POC, and THM-precursors from East Pond were much higher than loads calculated assuming no seepage (i.e., only surface water efflux) (Figure 7). The difference between the measured and no-seepage loads was greatest in July, August, October, and December 2002, all months with high, and steady or increasing inflow rates (Figure 3). The no-seepage loads for all three constituents were similar in magnitude to the loads emitted from Twitchell Island agricultural fields, although the patterns of seasonal variation in loads from East Pond and from the fields were opposite.

The measured and no-seepage loads from East Pond followed similar patterns of seasonal variation, except for the four months with greatest seepage. Net DOC loads were smallest in the winter months (December-March) and greatest in the summer months (May-October) (Figure 7a), largely because the difference between the inlet and outlet DOC concentrations was smallest in the winter and greatest in the summer (Figure 4a). Net THM-precursor loads followed the same seasonal pattern as the DOC loads (Figure 7). Net POC loads were lowest during the winter and mid-summer peaks in TSS (Figures 7, 4g) because the pond was an efficient trap for suspended sediment from the inlet water, and greatest in the late summer months when algal growth in the pond was greatest (R. Miller, U.S. Geological Survey, written comm. 2005).

In contrast, net loads from the agricultural fields were primarily a function of water management on the fields. Mobile organic carbon in the agricultural fields is largely produced by microbial activity in the soils during the summer, but requires addition of water to move it from the soils to the drains. On Twitchell Island, fields are flooded much of the winter, which provides water to move the soluble organic carbon. Water is also applied to the fields during the summer irrigation season, but the flow of water is insufficient to move a large load of organic carbon from the soils. As a result, net loads of DOC, THM-precursor, and POC from the agricultural fields are all higher in the winter months than in the summer months (Figure 7) (Deverel et al. 2007).

#### Changes in Loads Through Time

Construction of a permanently flooded wetland on a former agricultural site changed the oxidation state of the shallow soil layer from aerobic to anaerobic and therefore changed the biogeochemical processes controlling the release of DOC from the soils. However, such a change in oxidation conditions does not occur instantaneously. In addition, the change in hydrologic flow paths in the soil altered the exchange of DOC between soil and water thus affecting the flushing of DOC present in the shallow soil layer. The data for East Pond suggest that the shallow soil layer did not completely attain a steady-state condition during the time period encompassed by this study (from initial flooding of the site in October 1997 to March 2003). DOC concentration at H-SP (Figure 6a) and $SUVA_{254}$ and STHMFP in H-SP, J-SP, and K-SP (Figure 6b, c) were still changing at the end of the study period. Therefore, the measured net loads of DOC and THM-precursors in 2002 may not be representative of the long-term net loads from constructed wetlands of this type.

Projected annual net loads of DOC from East Pond suggest that the measured net load will be equivalent to the no-seepage net load approximately 15 years after the establishment of the pond (Figure 8). Annual net loads were calculated assuming that the annual water budget and surface water DOC concentrations measured in 2002 (Figures 3 and 4) were representative for all years. The decrease in DOC concentrations with time in H-SP (Figure 6a) was fit with an exponential decay function to provide estimated DOC concentrations of the seepage flow in each year. Net daily DOC loads then were calculated using equation 1, and summed from January 1 to December 31 to give annual net loads. The annual net DOC load measured for 2002, 1000 kg $Ha^{-1}$, was approximately three times the no-seepage load of 300 kg $Ha^{-1}$, but only one-third of the load in 1998, the first full year of the pond's existence (Figure 8).

This estimate of 15 years to flush out the mobile DOC in the shallow peat soil under East Pond based on the decrease in DOC concentration in H-SP is consistent with an estimate made using the results of the laboratory experiments with Twitchell peat soil cores. The

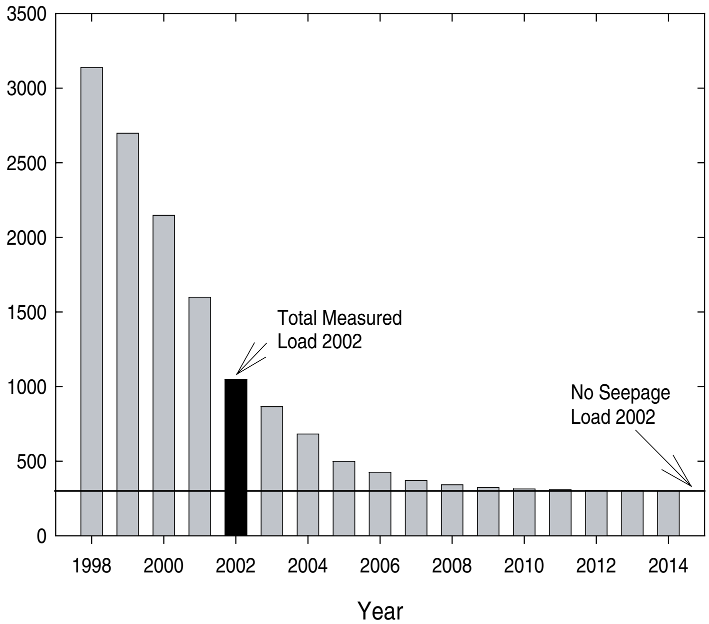


**Figure 8.** Annual DOC load calculated with declining DOC concentration in seepage compared to No-Seepage load in 2002.

experiments showed that approximately 100 pore volumes of inlet water continuously flowing through the soil core were required to flush out the mobile DOC (T. Mathany, U.S. Geological Survey, unpub. data). Assuming a mean seepage rate of 200 m3 day$^{-1}$ (Figure 3) and a porosity of 80% (Gamble et al. 2003), it would take 16 years for 100 pore volumes of water to seep through the 1.5 m thick shallow soil layer between the center of the pond and the north bank (50 m width) along the entire north side of the pond (200 m length) (see Figure 2 for pond geometry).

Measured net DOC and THM-precursor loads from sites under agricultural management also have a large contribution from the shallow soil layer (Deverel et al. 2007). However, under current agricultural management practices, export of DOC and THM-precursors from the shallow soil layer will not decrease with time. The agricultural fields flood for approximately three months every winter, long enough to leach salts and DOC from the shallow soil layer and temporarily depress soil respiration rates, but not long enough to significantly change oxidation conditions in the soil. Upon drainage, the shallow soil layer returns to aerobic conditions, soil respiration rates increase, and the soil organic matter undergoes aerobic decomposition. The pool of leachable DOC is therefore renewed every year.

#### Uncertainties in Load Calculations

Measurements of surface water flux and concentrations were highly accurate, direct measurements taken at high temporal resolution over a relatively long time-scale, giving confidence to the surface load calculations. However, subsurface loads, a significant contribution to the total loads, were largely based on assumptions about flows and concentrations rather than direct measurements, making total loads difficult to quantify. Subsurface flow was calculated as the imbalance in the water budget, which is a reasonable approach but has a greater error than a direct measurement because it contains the propagated errors from all the other measurements from which it was derived. The assumptions about the direction and location of subsurface flows are more speculative. The development of our conceptual flow model for East Pond addresses many of the concerns regarding flow uncertainties; however, the calculations are limited by a scarcity of data insufficient to address the uncertainty due to spatial variability in pore-water concentration. The failure of the monitoring well at Pier I was largely responsible for this limitation. Because of the disturbance caused by the formation of the boil and materials used to fix it, Pier I pore-water data were considered unrepresentative of normal wetland development. As a result, only Pier H data was used to calculate loads. Although Pier I data could not be used, initial trends at both Pier I and Pier H were similar prior to the Pier I boil formation (data not shown), suggesting that spatial variability on the north side of the pond was less than the variability between the north and south side of the pond.

We can attempt to address the uncertainties in subsurface flows and concentrations by running other realistic scenarios for the 2002 period. If we still assume that the flow is in the shallow layer and average the pore-water concentrations for all four piers and surface water to account for all water potentially passing through the soil, we can obtain a pond-wide averaged estimate for the load. For this scenario, the average concentration of shallow pore-waters is 52 mg L$^{-1}$, a concentration twice that in H-SP, and similar to the mean of H-SP and J-SP alone. If we assume that pier K is as isolated as the data suggest and remove it from the average, the mean concentration of all shallow pore-waters in 2002 is 32 mg $L^{-1}$. If these concentrations are applied to the water flux for 2002, the calculated load for East Pond is roughly 25 to 100% greater than that calculated for H-SP alone. This level of uncertainty is common in wetland subsurface load models. Scenarios using K-SP or J-SP concentrations alone for the load calculations are substantially higher but are not realistic.

The calculation of the change in loads over time also contains significant uncertainty. Changes in water management may cause differences in the contribution of DOC to the surface waters from the soil. Longer residence times would likely increase diffusion of DOC from soils to water column and increase DOC concentrations in the outlets; however, recent data in rice fields show that increase in concentration is compensated by lower water flux resulting in a similar load (P.M. Bachand, Bachand and Associates, written comm., 2006). The future model also assumes that the pore-waters will reach pond water concentrations as DOC is flushed out, assuming no internal generation. Shallow pore-waters may equilibrate at a higher minimum DOC concentration under current flow conditions, and changing flow conditions may affect that equilibrium state. More research is necessary to determine what equilibrium state of different flow conditions are and what managements most affect loads.

## MANAGEMENT IMPLICATIONS

Under current agricultural management in the Delta, as oxidative loss of peat soils continues, the threat to the stability of levees around the subsided peat islands will only increase (Mount and Twiss 2005). Mitigating or reversing subsidence, and thus reducing stress on the levees, requires halting oxidation of the peat soils on the islands. Permanent flooding of the soils can result in conditions that suppress oxidation. However, unmanaged flooding of these islands may result in formation of environments with little desired ecosystem value, minimal subsidence reversal potential, and unpredicted, deleterious effects on water quality for downstream users, particularly drinking water utilities. It has been demonstrated that permanently shallowly flooded wetlands supporting emergent vegetation (tules and cattails) successfully halt oxidation of the peat soil and result in subsidence reversal through accumulation of biomass.

The results of this study indicate that the net loads of DOC, POC, and THM-precursors from a permanently flooded wetland supporting dense emergent vegetation can be similar in magnitude to the net loads produced by agricultural management of similar areas with peat soils (Figure 7). However, because the altered, oxidized shallow peat soil layer of drained peat islands contains a large reservoir of mobile DOC, minimizing net loads of DOC, POC, and THM-precursors from a wetland constructed in a similar manner as East Pond requires minimizing water flow through the shallow soil layer beneath the wetland. Our results suggest seepage flow from the wetland would eventually flush the mobile DOC out of the shallow soils, but large net loads of DOC will be produced during the intervening 15 (approximately) years (Figure 8). Seepage flow through the shallow soil layer can be minimized by reducing the hydraulic gradient between the constructed wetland and the surrounding areas, although this may be difficult to achieve on islands where agricultural operations requiring drained soils continue nearby. Whole-island flooding would likely produce the least subsurface drainage, but large-scale flooding of peat islands must be carefully planned so that optimal water depths and surface water flows required for sustainable emergent vegetation wetlands can be maintained.

Conversion of agricultural land on Delta peat islands to wetlands may also provide an opportunity to control the timing of DOC exports from the peat islands to Delta channels. Estimated net loads from the East Pond wetland under no-seepage conditions were similar in magnitude to net loads from agricultural fields, but had the opposite seasonal variation (Figure 7). From May through November, wetland net loads were greater than agricultural net loads. Exports from the Delta have been greatest from July through October (Figure 9a), the period when agricultural loads to the Delta are low. An increase in the contribution of DOC to Delta waterways in summer and fall from non-tidal wetland construction on deeply subsided islands could exacerbate the drinking water problem by contributing

DOC to the system when flows and concentrations are low and even small contributions can have large effects (Figures 9b,c). Water treatment facilities use an action limit of DOC concentration of 3.0 mg $L^{-1}$ (running average) to determine the need for costly enhanced treatment techniques, and currently, Delta channel DOC concentrations are below the action limit only during low flow conditions. An increase in DOC concentrations in the summer months would greatly increase treatment costs.

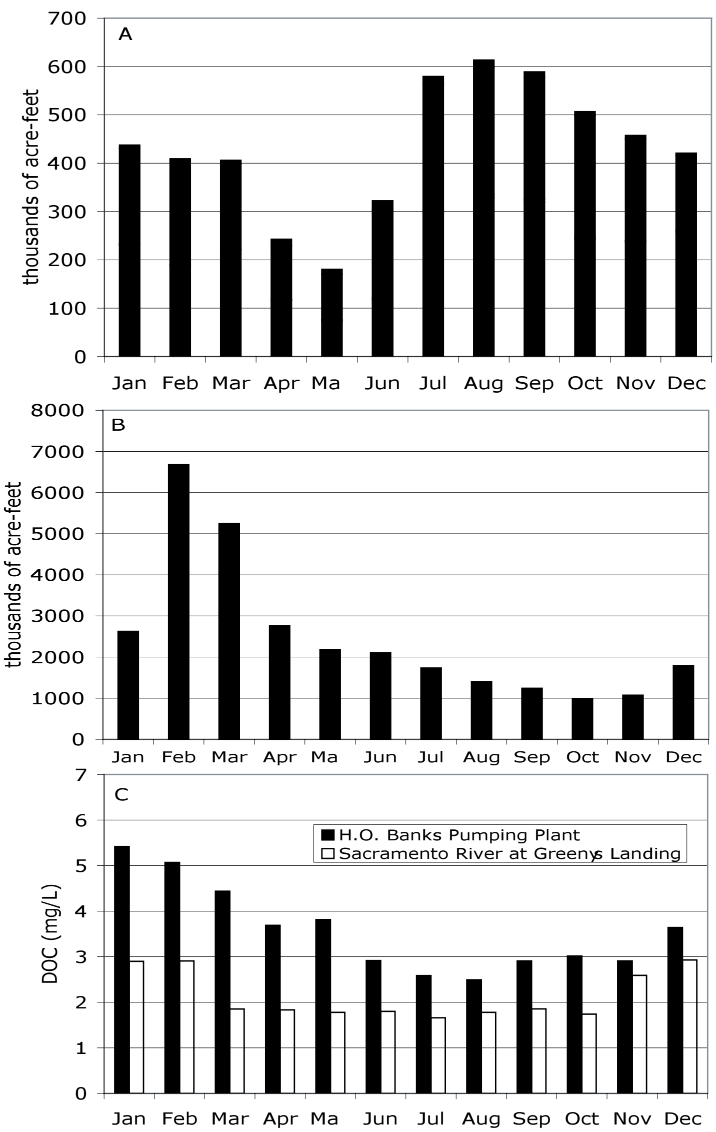


**Figure 9.** Mean monthly trends for A) Delta export pumping, B) Delta inflow, and C) DOC concentrations in Sacramento River north of the Delta and at H.O. Banks Pumping Plant.

Alternatively, a significant portion of the DOC in Delta channel waters in winter and spring is contributed from agricultural loading within the Delta. The Sacramento River, just north of the Delta, which supplies 80% of the Delta inflow has mean monthly DOC concentrations below the action limit throughout the year (Figure 9c). Conversion of agricultural land in the Delta to well-planned, constructed wetlands may reduce the load of DOC and THM-precursors added to these large winter/early spring flows as they pass through the Delta, thereby improving the quality of this water as a source of drinking water and reducing treatment costs in these high flow months. Furthermore, low Delta flows during late summer and fall limit future increases in exports, already at half the total Delta inflow during this period. Therefore, as demands on water from the Delta rise, the large freshwater flows in the winter and early spring will increasingly be captured to replenish reservoirs and recharge aquifers. The change in the timing of DOC loads brought on by conversion of row crops to wetlands may lower DOC enough in the higher flow months to allow exports to occur at a time when current exports are limited by high DOC concentrations.

In spite of these considerations, it is important to acknowledge that there are still a number of unknowns that could affect management decisions. The organic carbon in wetland surface water appears to be derived from fresher sources of organic matter, and thus may be more likely to undergo further processing and decomposition in Delta channels than the recalcitrant carbon derived from the peat soils that dominates the agricultural organic carbon loads. More research is needed to determine the fate of wetland-derived DOC in Delta channels. Wetland net loads of POC are dominated by algal material, which is an essential component of the aquatic food web in the Delta channels and downstream in the Estuary. The effect of the change in particle type on water treatment facilities is unknown and also requires further research.

## CONCLUSIONS

The construction of the non-tidal wetland on Twitchell Island resulted in higher loads of DOC and THM precursors to Delta waterways. The increase in DOC loads can be attributed to increasing water flow through the shallow soil layer of the island where oxidative subsidence from the site's agricultural history has concentrated a large reservoir of easily mobilized DOC in the soil matrix. It appears that this load was greater after initial flooding of the wetland and is decreasing with time as the DOC in the shallow soil layer is flushed out by seepage from the wetland. The load of THM precursors was more elevated than DOC because of an increase in the propensity of the DOC to form THMs under wetland flooding. The increase in loads may be controlled through proper wetland design and water management that would reduce the water flow through the shallow soil layer. If the loads from the shallow soil layer can be eliminated through management, the loads from the wetland surface water outlets are comparable to agricultural operations. Finally, the timing of the loads from the wetland is different from agricultural operations. Further research is recommended to identify the consequences of the change in the timing of the loads.

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