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The freshwater tidal wetland Liberty Island, CA was both a source and sink of inorganic and organic material to the San Francisco Estuary

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Abstract It is hypothesized that perennial freshwater tidal wetland habitat exports inorganic and organic material needed to support the estuarine food web and to create favorable habitat for aquatic organisms in San Francisco Estuary. It is also hypothesized that most of the material flux in this river-dominated region is controlled by river flow. The production and export of material by Liberty Island were measured and compared using discrete monthly and continuous (15 min) measurements of a suite of inorganic and organic materials and flow between 2004 and 2005. Seasonal material flux was estimated from monthly discrete data for inorganic nutrients, suspended solids and salts, organic carbon and nitrogen and phytoplankton and zooplankton group carbon and chlorophyll *a* and pheophytin pigment. Estimates of material flux from monthly values were compared with measured daily material flux values for chlorophyll *a* concentration, salt and suspended solids obtained from continuous

measurements (15 min) using YSI water quality sondes. Phytoplankton carbon produced within the wetland was estimated by in situ primary productivity. Most inorganic and organic materials were exported from the wetland on an annual basis, but the magnitude and direction varied seasonally. Dissolved inorganic nutrients such as nitrate, soluble phosphorus, total phosphorus and silica as well as total suspended solids were exported in the summer while total and dissolved organic carbon were exported in the winter. Salts like chloride and bromide were exported in the fall. Chlorophyll *a* and pheophytin were exported in the fall and associated with diatom and cyanobacteria carbon. Mesozooplankton carbon was dominated by calanoid copepods and exported most of the year except summer. Continuous sampling revealed high hourly and daily variation in chlorophyll *a*, salt and total suspended solids flux due to high frequency changes in concentration and tidal flow. In fact, tidal flow rather than river discharge was responsible for 90% or more of the material flux of the wetland. These studies indicate that freshwater tidal wetlands can be a source of inorganic and organic material but the export of material is highly variable spatially and temporally, varies most closely with tidal flow and requires high frequency measurements of both tidal flow and material concentration for accurate estimates.

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Introduction

The outwelling hypothesis suggests salt marshes and estuaries are sources of inorganic and organic material needed for food web production in adjacent marine or coastal aquatic habitats (Odum and de la Cruz 1967). This concept also applies to freshwater wetlands where floodplains and shallow water wetlands are thought to enhance riverine production through the export of inorganic and organic material (Junk et al. 1989). Nutrients are often released within wetlands through decomposition processes. Silica needed for phytoplankton growth in the Schelede River estuary was released from organic matter decomposition in adjacent wetlands (Struyf et al. 2005). Similarly, phosphorus needed for wetland vegetation was released by decomposition of leaf litter in Australian wetlands (Qui et al. 2002). Dissolved organic carbon and nitrogen export is also high in freshwater wetlands where processes such as denitrification occur (Bouchard 2007; Arrigoni et al. 2008). In fact, organic carbon is an important product of wetlands. In the mangrove wetlands of the Everglades, dissolved organic carbon can comprise over 80% of the carbon exported (Romigh et al. 2006) and in the Rhone River organic matter export was 5–6 times greater than the amount imported (Chauvelon 1998). Other processes in wetlands release nutrients stored in sediments such as the translocation of phosphorus from the sediments into the water column by plant uptake (Noe and Childers 2007).

Wetlands can also be a sink for nutrients such as nitrogen and phosphorus due to sedimentation, absorption, decomposition and vegetation uptake (Saunders and Kalff 2001). Only 6% of the nitrogen and 4% of the phosphorus imported into the drainage area was exported to Vaccares lagoon on the Rhone River (Chauvelon 1998). Inorganic salts such as chloride and sulfate are often stored in wetlands (Kang et al. 1998). Particulate carbon is stored in wetlands within the aquatic organisms such as phytoplankton and zooplankton. Phytoplankton carbon storage in freshwater tidal wetlands is usually due to enhanced primary productivity associated with a high euphotic zone to mixed depth ratio (Heip et al. 1995) and accumulation of phytoplankton cells due to high residence time (Hein et al. 1999).

Because of their impact on inorganic and organic material, wetlands are commonly used to improve

water quality of point and non-point source pollutants (Mitsch et al. 2000). Plant uptake, sediment absorption and decomposition processes remove high levels of nutrients such as nitrogen and phosphorus from receiving water (Kang et al. 1998). By passing the water through the Mai Po Marshes, it was possible to remove 83% of the ammonium nitrogen and 45% of the soluble phosphorus from sewage waste water before it entered the Shenzhen River in Hong Kong (Lau and Chu 2000). In the Everglades, passing the water through freshwater marshes also decreased the ionic concentration and removed sodium and chloride salts (Flora and Rosendahl 1982). Dissolved organic matter in wetlands also affected the bioavailability of heavy metals such as copper (Brooks et al. 2007). Some of the improvement of water quality due to wetlands is simply due to storage. In the Patuxent River Estuary, nutrient loss in tidal marshes was attributed to storage in the sediment, water column and biota (Boynton et al. 2008). Wetland vegetation further facilitates nutrient removal by enhancing the sedimentation (Morse et al. 2004).

Research in salt marsh and estuarine habitats demonstrated that material flux is highly variable and varies with climate, geomorphology, hydrology, biochemistry, wind, tide, material concentration and biological material cycling (Childers et al. 2000). Long-term material exchange for 10 wetlands along the Hudson River varied in both direction and magnitude and was generally not related to any specific variable (Arrigoni et al. 2008). In contrast, intertidal emergent vegetation was a key factor controlling the variation of material flux in the Cooper River estuary, NC (McKellar et al. 2007). Tidal range was also an important factor affecting the variability of material flux in the Everglades (Romigh et al. 2006). This variability can operate at very small scales as in San Francisco Estuary (SFE) where chlorophyll *a* flux was influenced by the coincident timing of daylight hours and ebb tide (Lucas et al. 2006).

Modeling studies suggest freshwater tidal wetlands are sources of inorganic and organic material in SFE (Jassby and Cloern 2000). Modeling results were supported by field research in the Yolo Bypass floodplain where approximately 14–37% of the total, diatom and green algal carbon and wide diameter cells were exported to the estuary downstream (Lehman et al. 2008). Sequential peaks of chlorophyll *a* concentration in the Yolo Bypass floodplain and the

adjacent Sacramento River further supported the transfer of carbon from the floodplain to the river (Schemel et al. 2004). Flux measurements at Mildred Island, a flooded island in the SFE delta region, confirmed the export of chlorophyll *a* and sediment from freshwater tidal wetland habitat to adjacent river channels during the spring and summer (Lopez et al. 2006). No information is available on the annual flux of inorganic and organic material from perennial freshwater tidal wetlands in SFE. It is hypothesized that these wetlands could enhance the export of nutrients and organic matter needed for food web production in SFE (Brown 2003). The export of organic carbon from wetlands may be critical for riverine food webs that use this organic matter to support secondary production (Deegan et al. 2000; Keckeis et al. 2003).

The purpose of this study is to address the hypothesis that Liberty Island is a source of inorganic and organic matter to the lower Sacramento River and that the flux in the wetland is primarily due to river flow. This information will provide valuable insight into the potential contribution of freshwater perennial tidal wetlands to estuarine fishery production and environmental factors that control this contribution. Such information is needed for fishery management in SFE where a long-term decline in production at all trophic levels since the 1970s coupled with a recent decline in of zooplankton and threatened and endangered fish species since 2000 has caused concerns about the health of the estuary (Kimmerer 2004; Sommer et al. 2007).

Methods

Study area

Liberty Island wetland is a 21 km² freshwater perennial tidal wetland that was created by a levee failure in 1998. A system of levees separates this wetland from surrounding mixed use farmland, seasonal and perennial wetlands, the Sacramento River on the south, Shag Slough on the west and the Yolo Bypass toe drain on the east (Fig. 1). The upper third of the wetland consists of two shallow ponds (Upper and Lower Beaver Pond) that contain emergent vegetation and are hydraulically connected to Main Pond, a large open water pond which drains into the Sacramento River. Main Pond remains wet all year and is <1 m at low tide

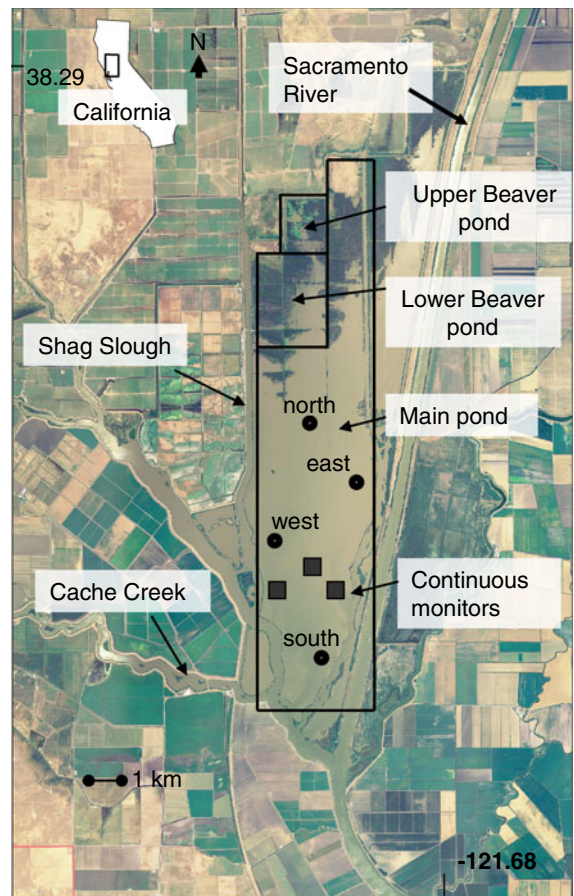


Fig. 1 Aerial photograph of Liberty Island indicating the location of discrete (*dot*) and continuous (*square*) sampling stations

at the northern end and gradually increases in depth toward the southern end where it is 20 m deep. The depth of Main Pond also decreases west to east from 1.5–3 to 0.3–2 m.

The flow of water in Liberty Island is controlled by exchange with the adjacent river channels at numerous breaks in the levees and a semi-diurnal tide. Average daily discharge in the Sacramento River was variable over the study period and ranged from -64 to $257 \text{ m}^3 \text{ s}^{-1}$, but the average net daily discharge was small at $0.5 \text{ m}^3 \text{ s}^{-1}$.

Field sampling

Inorganic and organic material concentration among seasons were measured from discrete water samples

collected monthly at four stations located in the north, south, east and west of Main Pond between February 2004 and June 2005 for a total of 16 sampling days (Fig. 1). Water samples were collected from just below the surface using a van Dorn water sampler. Replicate water samples for measurement of chlorophyll *a* and pheophytin concentration were filtered through a Millipore APFF glass fiber filter, treated with 1 ml of saturated magnesium carbonate solution as a preservative, and the filter was frozen until spectrophotometric analysis (APHA 1998). A pre-combusted Millipore APFF glass fiber filter was also used to filter water for dissolved organic carbon analysis (APHA 1998). Water for measurement of dissolved inorganic materials including soluble reactive phosphorus, nitrate, ammonium, silica, chloride and bromide was filtered through a HA nucleopore filter, and the filtrate was either frozen or kept at 4°C until analysis (US EPA 1983; USGS 1985). Unfiltered water for total suspended solids, volatile suspended solids, total organic carbon, total nitrogen (Kjeldahl) and total phosphorus was kept at 4°C until analysis (APHA 1998).

Water for phytoplankton identification and enumeration was placed in a 50 ml amber glass bottle and preserved with 1 ml of Lugol's solution. Phytoplankton cells of at least 6 µm in diameter were identified, sized and enumerated at 700× using the inverted microscope technique (Utermöhl 1958). The biomass of these cells was computed from cell volumes based on cell dimensions applied to simple geometric shapes (Menden-Deuer and Lessard 2000). The internal carbon production and respiration in the lower pond were measured by the dissolved oxygen light and dark bottle technique from bottles incubated for 24 h near the surface in Main Pond (Lehman 2007).

Mesozooplankton were collected at each station by 3 min horizontal tows of a 0.5 m diameter plankton net fitted with 150 µm mesh netting. Animals were immediately dyed and preserved in 10% buffered formalin with Rose Bengal Dye. Species identification and enumeration were conducted using a dissecting scope. Mesozooplankton were collected for a total of six sampling days over the study.

Chlorophyll *a* fluorescence, specific conductance, turbidity as NTU, pH, water temperature and dissolved oxygen were also measured at 15-min intervals with three Yellow Springs Instrument (YSI)

6600 water quality sondes between June 2004 and August 2006. The sondes were placed horizontally across the center of Main Pond at fixed stations separated by 1.57 and 0.89 km between the western and central, and eastern and central sondes, respectively (Fig. 1).

Hydrodynamic measurements

Main Pond is virtually a lake with small openings due to breaks in the surrounding levee. Because there was no practical way to calculate the flow at each opening, the total flow from the pond was calculated from the change in water volume estimated by from total area and depth. Because the flow computation only required the relative change in water level, not absolute values, the average change in depth was determined from two pressure transducers within YSI 6600 water quality sondes that were located in the southern portion of the Main Pond. It was assumed that 90% of the land was flooded during high tide, and 85% of the land was flooded during low tide. A three-point moving average was applied to the calculated flow to reduce the short-term fluctuation. Hourly flow data was available between June 2004 and June 2005.

Estimates of flow using this method are not reliable during periods of very high flow when water levels over top the levees, causing sheet flow across the wetland that prevents an accurate estimate of water depth. During these conditions, flow across Liberty Island was influenced by overland flow from Yolo Bypass upstream. Such conditions occurred over an 11-day period between January 3 and 13, 2005.

Analysis

Seasonal flux of inorganic and organic material was estimated from the sum of monthly flux values calculated from hourly flow data multiplied times the single material concentration measured for each month. Estimates of seasonal flux from continuous measurements of chlorophyll *a*, total suspended solids and salt concentration were calculated from the sum of the tidally averaged advective and dispersive flux computed from hourly flow and material concentration. Advective flow is the average

flow over a tidal day (25 h) while dispersive flow characterizes the deviation of the hourly flow from the tidal day average. Advective and dispersive flux for each variable were computed as

$$<Q(t)> <C(t)> \text{ and } <Q'(t)C'(t)>$$

where $Q(t)$ is flow at a given time and $C(t)$ is concentration at a given time, ' denotes variation from the tidal average and $<>$ denotes tidal average values computed with a GODIN tidal filter. Application of a GODIN tidal filter to hourly data computes the net tidal day flow and was computed for this study by successively averaging hourly flux values over 24 h (twice) and then 25 h (Walters and Heston 1982; Lopez et al. 2006). Seasonal flux was computed for winter (December–February), spring (March–May), summer (June–August) and fall (September–November) by summing daily flux values.

Continuous measurements of chlorophyll *a* fluorescence, specific conductance and turbidity from the YSI 6600 sondes were converted to chlorophyll *a* concentration, salinity and total suspended solids concentration before flux calculations. Chlorophyll *a* and total suspended solids concentrations were estimated by regression equations developed from concurrent discrete and continuous measurements ($r_s = 0.58$ and $r_s = 0.66$ for chlorophyll *a* and total suspended solids, respectively). Specific conductance was first converted to chloride using location-specific equations developed by the CA Department of Water Resources (iep.water.ca.gov/Suisun/facts/salin/index.html). Chloride values were then converted to salinity using the standard equation: salinity (g l^{-1}) = $1.80655 \times \text{chloride} (\text{g l}^{-1})$; APHA 1998).

Significant differences among data values were computed using non-parametric statistical techniques because of the non-normality of the data. Statistical analyses were computed using non-parametric statistical analyses from Statistical Analysis Software (SAS) or PRIMER-e version 6 (PRIMER) software (SAS Institute, Inc. 2004; Clarke and Gorley 2006). Differences among data were determined using single or multiple comparison tests (Wilcoxon and Kruskal–Wallis tests in SAS or ANOSIM test in PRIMER). Correlations among data were computed by Spearman rank correlation, r_s . Analyses were considered significant or highly significant at the 0.05 and 0.01 significance levels, respectively.

Results

Monthly sampling

Hydrodynamics

Water flow in Liberty Island was highly variable between June 2004 and July 2005. Daily average flow ranged between -254 and $785 \text{ m}^3 \text{ s}^{-1}$, with hourly flows ranging from -707 to $991 \text{ m}^3 \text{ s}^{-1}$. The average net tidal day flow (GODIN filter) was at least an order of magnitude lower and ranged between -20 and $26 \text{ m}^3 \text{ s}^{-1}$. Average and net tidal day flow varied among seasons by a factor of 3 (average flow of 0.32, 0.98, 0.37 and $-0.40 \text{ m}^3 \text{ s}^{-1}$ and net flow of 0.10, -0.08 , -0.38 and $-0.42 \text{ m}^3 \text{ s}^{-1}$ for winter, spring, summer and fall, respectively) and were not significantly different among seasons.

The concentration of most inorganic and organic material was also highly variable. Concentrations of each inorganic or organic material did not differ significantly among the four stations in Main Pond, but concentrations in the winter differed from the spring, summer and fall while those in the fall differed from the spring for all materials ($P < 0.05$; ANOSIM). Among materials, the concentrations of total suspended solids, chloride and silica were orders of magnitude greater ($P < 0.05$) than that of the dissolved inorganic nutrients ammonium, soluble reactive phosphorus, nitrate, total nitrogen and total phosphorus (Fig. 2). Concentrations of total and dissolved organic carbon and nitrogen were greater ($P < 0.05$) than dissolved inorganic nutrients. Total organic carbon concentration was also greater ($P < 0.05$) than chlorophyll *a* concentration (54% of the total organic carbon was in the dissolved fraction). Dissolved organic nitrogen was the largest ($P < 0.05$) source of nitrogen in the wetland and exceeded dissolved inorganic nitrogen (dissolved inorganic nitrate plus ammonium) by up to 18 times. Although both nitrate (average $0.38 \pm 0.20 \text{ mg l}^{-1}$) and ammonium (average $0.08 \pm 0.06 \text{ mg l}^{-1}$) concentrations were relatively high, total dissolved inorganic nitrogen to soluble phosphorus ratios (molar) of 13.4 ± 4.4 were below the Redfield value of 16.

Most inorganic and organic materials were exported on an annual basis, but the direction and magnitude of the flux differed among seasons for

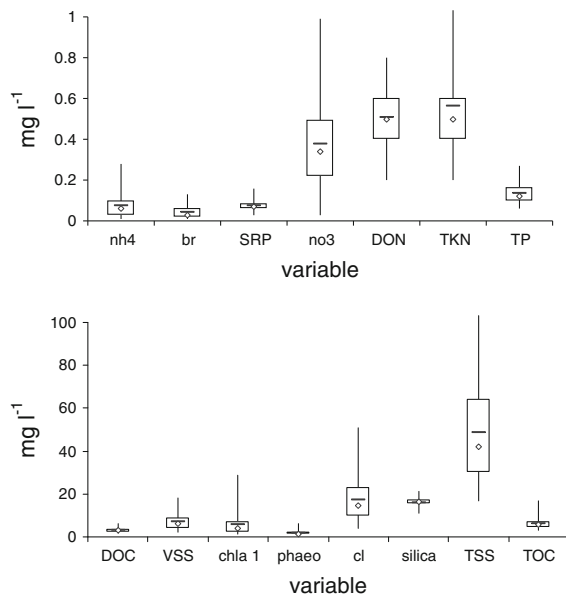


Fig. 2 Monthly average (horizontal line), median (diamond), 75 and 25% percentiles (box) and range (lines) for the concentration of organic and inorganic materials measured for four stations in Main Pond between February 2004 and June 2005; $n = 64$

each material. Among inorganic materials, total phosphorus, soluble phosphorus, silica, total nitrogen and total suspended solids were exported annually while nitrate, ammonium, chloride and bromide salts were stored (Table 1). Among seasons, inorganic material flux during the winter usually differed from other seasons, but the direction of the flux varied among materials. More total phosphorus was exported in the summer and fall than the winter and contrasted with soluble phosphorus which was exported in the winter. Both nitrate and ammonium were exported in the summer and stored in the winter and fall. This contrasted with total nitrogen which was exported in the winter. Silica was exported in all seasons, but more was exported in the summer and fall. Total suspended solids were exported in the summer and fall while salts like chloride and bromide were only exported in the fall.

Organic material was exported on an annual basis with most of the export in the winter, summer and fall (Table 1). Among organic materials, chlorophyll *a* and pheophytin were exported in the fall and stored in the spring. Chlorophyll *a* and pheophytin did not vary

Table 1 Average and standard deviation of inorganic and organic material flux (season)⁻¹ for Liberty Island between June 2004 and July 2005, $n = 44$

	Winter (1)	Spring (2)	Summer (3)	Fall (4)	Annual	Sign.
Chlorophyll <i>a</i>	-1 ± 3	18 ± 3	-0.5 ± 4	-20 ± 7	-3 ± 16	4 & 1,2,3
Pheophytin	-3 ± 1	0.4 ± 2	-2 ± 3	-9 ± 2	-1 ± 4	4 & 2,3
Total P	-3 ± 181	-69 ± 159	-124 ± 155	-56 ± 73	-251 ± 50	1 & 3,4
Soluble P	-56 ± 34	-11 ± 52	-119 ± 88	-61 ± 21	-247 ± 44	1 & 2,3,4
Bromide	69 ± 9	166 ± 13	31 ± 36	-57 ± 7	209 ± 93	1 & 2,3,4; 2 & 4
Nitrate	83 ± 201	-18 ± 132	-120 ± 415	476 ± 122	420 ± 261	3 & 1,2,4; 4 & 1
Ammonium	151 ± 123	20 ± 90	-369 ± 154	223 ± 65	24 ± 264	1 & 2,3,4; 3 & 4
Dissolved organic nitrogen	288 ± 291	65 ± 222	-2,287 ± 259	71 ± 293	-1,863 ± 1,218	1 & 2,3,4; 4 & 2,3
Total Kjeldahl nitrogen	-1,778 ± 604	771 ± 298	-711 ± 310	-375 ± 334	-2,094 ± 1,050	1 & 2,3
Dissolved organic carbon × 10 ²	-74 ± 10	192 ± 19	-29 ± 16	-8 ± 7	-91 ± 39	1 & 2,3,4; 2 & 3
Chloride × 10 ²	92 ± 65	523 ± 102	66 ± 75	-87 ± 11	595 ± 262	1 & 2,3,4; 2 & 4
Volatile solids × 10 ²	-133 ± 53	143 ± 108	-200 ± 192	-181 ± 55	-372 ± 160	2 & 3,4
Silica × 10 ²	-211 ± 34	-4 ± 16	-489 ± 84	-320 ± 10	-1,023 ± 203	1 & 3,4
Total organic carbon × 10 ²	-223 ± 82	-16 ± 78	-13 ± 33	-24 ± 26	-275 ± 103	1 & 2,3; 2 & 3
Suspended solids × 10 ²	-482 ± 207	672 ± 482	-1,645 ± 807	-1,838 ± 1,412	-3,294 ± 1,163	2 & 3,4

Positive values indicate material storage while negative values indicate material export. Significant differences between seasons at the 0.05 level or higher are separated by a & sign

with total organic carbon which was exported in all seasons, primarily the winter. Dissolved organic carbon was also exported in most seasons, except the spring. Unlike dissolved organic carbon, dissolved organic nitrogen was exported in the summer, but both were stored in the spring.

Inorganic and organic material export during the winter may be underestimated due to the absence of reliable flow values between January 3 and 13 when water flowed overland from Yolo Bypass upstream. Similar material concentrations in January for Liberty Island and Yolo Bypass suggest that the material flux was probably influenced more by advective flow than material concentration for chlorophyll *a*, ammonium, nitrate, soluble P, silica, total suspended solids or total organic carbon ($2.55 \pm 0.85 \mu\text{g l}^{-1}$, $0.07 \pm 0.03 \text{ mg l}^{-1}$, $0.42 \pm 0.04 \text{ mg l}^{-1}$, $0.10 \pm 0.00 \text{ mg l}^{-1}$, $16.65 \pm 0.75 \text{ mg l}^{-1}$, $33.50 \pm 7.94 \text{ mg l}^{-1}$ and $11 \pm 4.26 \text{ mg l}^{-1}$ for Liberty Island, respectively and $2.78 \pm 0.26 \mu\text{g l}^{-1}$, $0.04 \pm 0.01 \text{ mg l}^{-1}$, $0.34 \pm 0.01 \text{ mg l}^{-1}$, $0.09 \pm 0.00 \text{ mg l}^{-1}$, $15.20 \pm 0.00 \text{ mg l}^{-1}$, $36.5 \pm 10.61 \text{ mg l}^{-1}$, $6.90 \pm 0.00 \text{ mg l}^{-1}$ for Yolo Bypass, respectively).

The phytoplankton carbon in Main Pond was primarily composed of diatoms, green algae and chrysophytes (Fig. 3). The amount of carbon in these three phytoplankton groups was similar among stations except that there were more ($P < 0.05$) diatoms at station 4 than station 3 and more ($P < 0.05$) miscellaneous flagellates at station 3 than

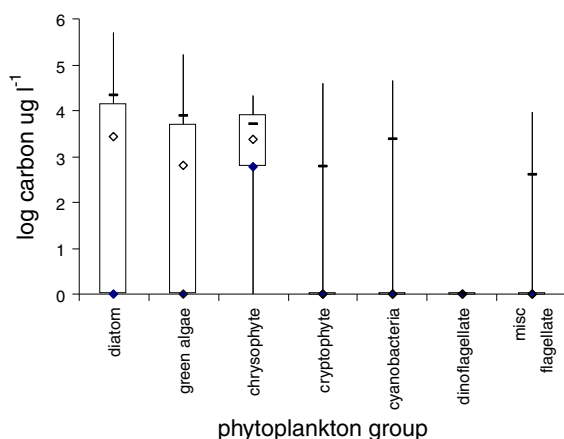


Fig. 3 Monthly average (horizontal line), median (diamond), 75 and 25% percentiles (box) and range (lines) for carbon among phytoplankton groups from four stations in Main Pond between February 2004 and June 2005, $n = 64$

1 or 2. The amount of carbon in these three phytoplankton groups combined was also greater ($P < 0.01$) than cryptophyte, cyanobacteria, dinoflagellate and miscellaneous flagellate carbon. Among seasons, there was more total phytoplankton carbon in the spring than the winter, diatoms in the summer and fall ($P < 0.01$), green algae in the summer and fall ($P < 0.01$) and chrysophytes in the summer ($P < 0.05$).

Average flux values suggest total phytoplankton carbon was exported in winter and spring and stored in the summer and fall. However, because the monthly variation was large, the flux was not significantly different among seasons (mean and standard deviation of $-7,185 \pm 55,523$, $-8,193 \pm 22,169$, $6,175 \pm 31,640$ and $10,016 \pm 45,026 \text{ g carbon (season)}^{-1}$ for winter, spring, summer and fall, respectively). Among phytoplankton groups, diatoms, green algae and chrysophytes comprised a greater percentage ($P < 0.01$) of the daily total carbon flux than cyanobacteria, miscellaneous flagellates, cryptophytes and dinoflagellates for all seasons (Fig. 4). At optimum growth rates, in situ phytoplankton growth could contribute an additional $3,487 \text{ kg C day}^{-1}$ (range $334 \text{ kg C day}^{-1}$ to $13,433 \text{ kg C day}^{-1}$) to the carbon flux in Main Pond; equivalent to $293 \mu\text{g l}^{-1} \text{ day}^{-1}$. Carbon production was associated with an average maximum growth potential of $50 \pm 34 \text{ mg C (mg chlorophyll } a)^{-1} \text{ day}^{-1}$.

Most of the mesozooplankton carbon in Main Pond was composed of calanoid copepods (Fig. 5).

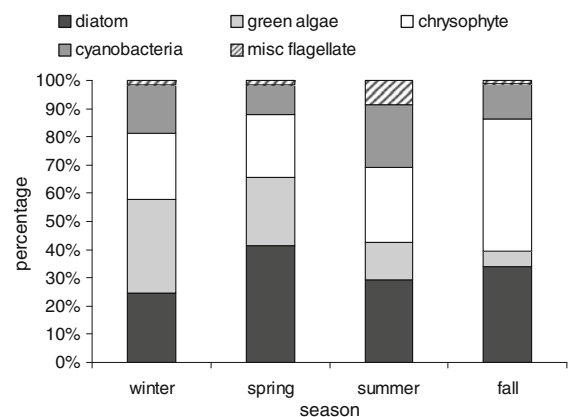


Fig. 4 Percentage contribution of phytoplankton groups to the carbon flux for Main Pond between July 2004 and June 2005, $n = 44$

Calanoid copepod carbon was an order of magnitude greater ($P < 0.01$) than cladocera or cyclopoid copepod carbon and two orders of magnitude greater than rotifer or harpacticoid carbon. Neither mesozooplankton carbon nor the associated carbon flux was significantly different among the four stations in Main Pond. Total mesozooplankton carbon export was the greatest ($P < 0.05$) in the fall (-8 ± 2 , -31 ± 13 , 29 ± 11 and -83 ± 34 kg C (season) $^{-1}$ for winter, spring, summer and fall, respectively). For most mesozooplankton groups, carbon was exported in the winter, spring and fall ($P < 0.01$; Fig. 6); only rotifer carbon was exported in the summer. Calanoid copepod carbon comprised 90% or more of the mesozooplankton carbon flux except in winter when cladocera and cyclopoid carbon were high (93%). Calanoid carbon flux was the greatest ($P < 0.01$) in the fall and differed somewhat from cladocera carbon



Fig. 5 Monthly average (horizontal line), median (diamond), 75 and 25% percentiles (box) and range (lines) carbon among mesozooplankton groups measured at four stations in Main Pond between February 2004 and June 2005, $n = 64$

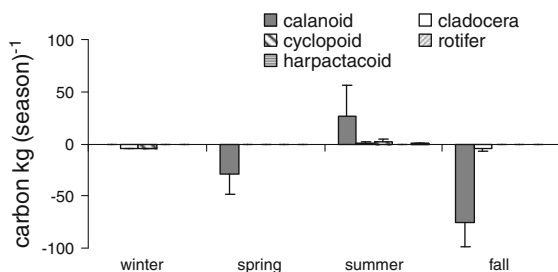


Fig. 6 Monthly average and 75 and 25% percentiles for zooplankton carbon flux among zooplankton groups for four stations in Main Pond between July 2004 and June 2005, $n = 24$. Positive flux values indicate storage and negative flux values indicate export

flux which was the greatest ($P < 0.01$) in the fall and winter and cyclopoid copepod carbon flux which was the greatest ($P < 0.01$) in the winter. Rotifer and harpacticoid carbon flux varied little over the seasons with similarly high ($P < 0.01$) rotifer carbon flux in

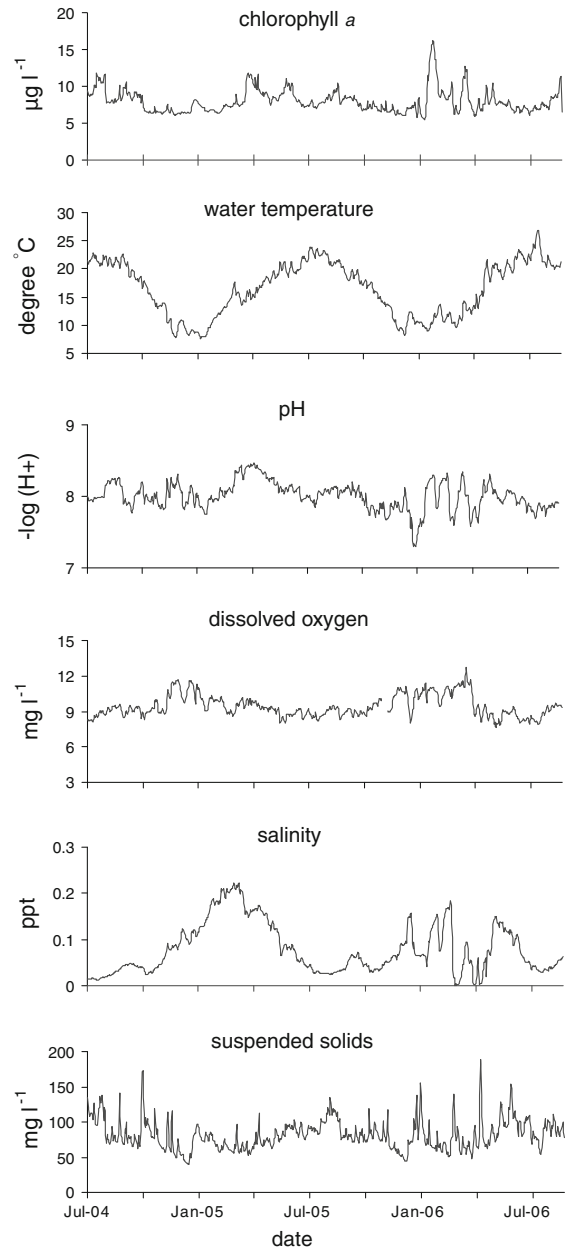


Fig. 7 Daily average chlorophyll *a* concentration, salinity, water temperature, pH, dissolved oxygen concentration and total suspended solids concentration measured at 15-min intervals for three stations across Main Pond between July 2004 and August 2006, $n = 2,337$

the winter, summer and fall. Harpacticoid carbon flux was similar in all seasons.

Continuous sampling

High variability in the daily average water temperature, salinity, pH and dissolved oxygen, chlorophyll *a* and total suspended solids concentration suggested that both environmental conditions and the concentration of inorganic and organic material changed rapidly on a daily basis in Main Pond (Fig. 7). Over the year, water temperature, dissolved oxygen concentration, pH, salinity, total suspended solids and chlorophyll *a* concentration varied by a factor of

3–33 with coefficients of variation that ranged from 2 to 69.

The daily flux of chlorophyll *a*, salt and total suspended solids computed from hourly material concentration and flow was also highly variable. Over the year, daily values varied by a factor of 2–3 with the direction of flux dominated by negative values (Fig. 8). For 59–68% of the days, chlorophyll *a*, salt and total suspended solids flux were negative. Among seasons, continuous data indicated total suspended solids were exported in the spring, summer and fall ($P < 0.01$, ANOSIM) while salt was exported in the spring ($P < 0.01$, ANOSIM). The flux of these materials contrasted with the chlorophyll *a* concentration which was stored in all seasons, with greater ($P < 0.01$, ANOSIM) storage in the spring and summer than the fall or winter.

Over 90% of the total material flux of chlorophyll *a*, total suspended solids and salt were due to tidal dispersion (Table 2). Because dispersive flux comprised such a large percentage of the total flux, it varied in the same fashion as total flux over the seasons. In contrast, the direction and magnitude of the advective flux often differed from that of either the total or dispersive flux. Advective flux was greatest ($P < 0.01$, ANOSIM) in the spring or summer than the fall and winter for chlorophyll *a* concentration, the summer for total suspended solids and the winter and spring for salt.

Differences in the direction and magnitude of material flux estimates between continuous and discrete monthly monitoring programs were due to the strong contribution of dispersive flux to the total flux. However, the similar direction and magnitude of material flux computed from a single monthly concentration and hourly flow compared with material flux computed from hourly concentration and hourly advective flow suggest the estimates of material flux from monthly values and hourly flow were good estimates of advective flux.

High frequency data also suggested material flux varied at small spatial scales. Chlorophyll *a*, salinity and total suspended solids flux differed ($P < 0.01$; ANOSIM) among the three continuous stations and was 3 to 5 times greater at the western than the center or eastern station (3.1×10^3 , 1.2×10^3 and -1.6×10^3 kg year⁻¹ for chlorophyll *a*; 4.3×10^7 , -0.8×10^7 and -0.5×10^7 kg year⁻¹ for salinity and -4.8×10^7 , 3.6×10^7 and -1.3×10^7 kg year⁻¹ for total

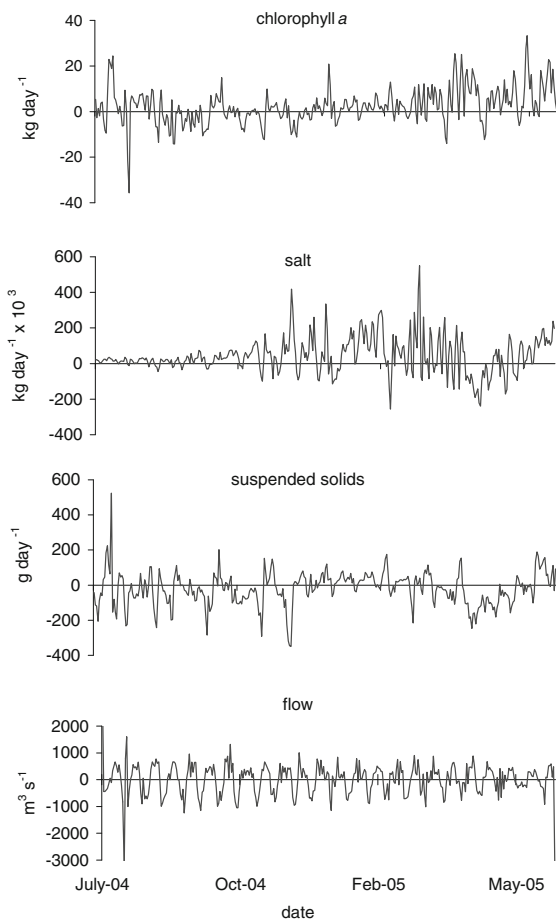


Fig. 8 Daily average total flux of chlorophyll *a* concentration, salinity and suspended sediments computed from 15-min measurements of water quality conditions and flow at three stations across Main Pond between July 2004 and June 2005, $n = 1,041$

Table 2 Average daily total, advective and dispersive flux of chlorophyll *a*, suspended sediments and salt by season calculated from 15-min data collected at three continuous monitors positioned across Main Pond between July 2004 and June 2005, $n = 1,041$

	Chlorophyll <i>a</i> (kg)	Suspended sediments (kg $\times 10^4$)	Salt (kg $\times 10^4$)
Total			
Winter	137 $\pm$ 104	19 $\pm$ 435	625 $\pm$ 271
Spring	391 $\pm$ 1,907	−439 $\pm$ 1,053	−94 $\pm$ 1,843
Summer	506 $\pm$ 1,054	−67 $\pm$ 1,311	297 $\pm$ 455
Fall	322 $\pm$ 1,006	−358 $\pm$ 1,548	155 $\pm$ 341
Advective			
Winter	−1 $\pm$ 4	14 $\pm$ 15	−18 $\pm$ 4
Spring	−17 $\pm$ 5	−8 $\pm$ 16	14 $\pm$ 15
Summer	−16 $\pm$ 26	−33 $\pm$ 22	−2 $\pm$ 5
Fall	−11 $\pm$ 41	−28 $\pm$ 15	−11 $\pm$ 8
Dispersive			
Winter	137 $\pm$ 101	5 $\pm$ 430	643 $\pm$ 269
Spring	408 $\pm$ 1,909	−431 $\pm$ 1,042	−108 $\pm$ 1,850
Summer	523 $\pm$ 1,027	−34 $\pm$ 1,314	299 $\pm$ 460
Fall	335 $\pm$ 967	−330 $\pm$ 1,552	165 $\pm$ 349

Positive values indicate storage and negative values indicate export

suspended solids at western, center and eastern stations, respectively). Differences in material flux may have been affected by depth which was greater at the western station (3 m) than the center or eastern stations (1 m).

Discussion

Material flux

Liberty Island was both a source and a sink of inorganic and organic material to SFE. Most inorganic and organic materials were exported from the wetland over the year. This supports the hypothesis that freshwater tidal wetlands are sources of inorganic and organic material to estuaries (Junk et al. 1989). However, high daily and seasonal variation in the direction and magnitude of material flux suggest there was no overriding pattern in the flux among materials in Liberty Island on short-term time scales. The absence of an overriding pattern in the flux among materials was also measured for 10 wetlands along the Hudson River (Arrigoni et al. 2008). Such unpredictable variation was probably due to the importance of tidal dispersion to material flux in SFE. Tidal dispersion in Liberty Island varied on an hourly

basis and was sensitive to small changes in flow and material concentration.

Liberty Island was a potentially large source of dissolved organic carbon that could support primary productivity. Dissolved organic carbon is commonly high in SFE and averaged 42–90% of the total organic carbon in Liberty Island during 2004 and 2005. The dissolved organic carbon flux was similarly greater than the particulate organic carbon flux in Lake Erie wetlands (Bouchard 2007). Although dissolved organic carbon can support bacterial primary productivity in some estuaries, it may not be important in SFE. Biochemical oxygen demand studies suggested particulate carbon associated with chlorophyll *a*, and not dissolved organic carbon, was the most biologically available form of carbon in SFE (Sobczak et al. 2002). This finding was supported by in situ studies which indicated that bacterial primary productivity was small compared with phytoplankton primary productivity in SFE (Murrell and Hollibaugh 1998).

Dissolved organic nitrogen was many times greater than dissolved inorganic nitrogen in Liberty Island, but the biological availability and the use of dissolved organic nitrogen for primary productivity in SFE is unknown. Inorganic nitrogen is usually high and considered to be non-limiting in SFE (Jassby

2008). Yet, dissolved organic nitrogen is a major source of nitrogen in unimproved wetlands and can account for up to one-third of the nitrogen in all watersheds (Pellerin et al. 2004). Research suggests this dissolved organic nitrogen is biologically available and stimulates growth of bacteria and phytoplankton, particularly diatoms and dinoflagellates (Seitzinger and Sanders 1999). The long-term loss of phytoplankton carbon and shift toward phytoplankton and zooplankton species with small biovolume in the estuary may have increased the potential for use of dissolved organic carbon and nitrogen by the food web through the microbial loop in SFE (Lehman 2000b; 2004; Bouley and Kimmerer 2006). In fact, recent research suggests bacterial production can periodically be a greater percentage of the primary productivity than phytoplankton in northern SFE (A. Parker, personal communication).

Variability

Material flux was highly variable due to the influence of tidal dispersion on material flux. The importance of tidal dispersion was unexpected because Liberty Island is adjacent to the Sacramento River, the largest river that flows into SFE. Advection from the discharge of such a large river was expected to have the greatest impact on material flux. Yet, the high material export in fall when river discharge was low strongly supported the finding that river discharge was not the primary driver of material flux in SFE. Tide was also important for material flux in Mildred Island, a flooded island in the central delta region of SFE, where the amplitude of chlorophyll *a* and suspended sediment flux in the summer and fall was sensitive to tidal asymmetry (Ganju et al. 2006). The tidal range was similarly important to material flux in the Everglades (Romigh et al. 2006). In contrast, the export of organic and inorganic material is commonly attributed to hydrology because material flux increases with water depth and discharge (Moustafa 1999). River discharge was the primary source of variation in nitrogen, phosphorus and carbon flux for wetlands in Florida Bay and dissolved organic carbon and total suspended solids flux in the Shark River, Florida (Sutula et al. 2003; Romigh et al. 2006). In SFE, river discharge was probably the main cause of material flux throughout the region for 11 days in winter when flooding caused overland flow, but most

of this flow was probably controlled by upstream sources.

High frequency spatial and temporal variability characterized material flux at Liberty Island. High variability might be expected in tidal wetlands that are comprised of varying habitat types and exposed to a large number of internal and external physical, chemical and biological factors including discharge, climate, geomorphology, biochemistry, biological cycling and tide (Childers et al. 2000). In Yolo Bypass, just upstream from Liberty Island, primary production and phytoplankton species composition were sensitive to small changes in residence time (Lehman et al. 2008). Short-term studies of material flux in the SFE delta similarly suggested carbon flux was sensitive to small changes in the timing of daylight hours on ebb tide (Lucas et al. 2006). Such small changes in material concentration would be particularly important for Liberty Island where net flow is small. Further, the factor of 3 to 5 difference in material concentrations measured within a distance of 2 km by continuous monitors may describe only a small portion of the spatial variation in material flux for Liberty Island. Chlorophyll *a* concentrations varied by up to 17-fold over a mere 0.3 km² in the Cosumnes River wetland in northern California (Ahearn et al. 2006).

Food web

Organic material flux from tidal dispersion may be a key factor affecting the contribution of Liberty Island to food web production in SFE. Juvenile fish often occur in river channels adjacent to wetlands (Sommer et al. 2004). Inorganic and organic material can move many kilometers into the estuary each day with tidal excursion, exposing aquatic organisms to a wealth of nutrient and food resources from the wetland. Yet, because the net flow is small, these resources are retained in the wetland, making them available on a daily basis. In addition, the diatom, green algae and chrysophyte phytoplankton carbon that grow in Liberty Island are particularly good food resources for local mesozooplankton because they are within the optimum feeding size range of the calanoid copepods *Eurytemora affinis* and *Pseudodiaptomus forbesii*, important mesozooplankton food for juvenile fish (Lehman 2000a; Kimmerer 2004). New phytoplankton carbon produced by primary

productivity in the wetland during spring could further enhance the phytoplankton food available for mesozooplankton growth. Similarly, high net phytoplankton growth rate and abundant diatom and green algae carbon in the spring characterized the Yolo Bypass floodplain immediately upstream of Liberty Island where the abundance of juvenile native fish in the spring is attributed to the presence of abundant phytoplankton and zooplankton food resources (Sommer et al. 2004; Lehman et al. 2008).

Management implications

Understanding the storage, export and tidal dispersion of inorganic and organic materials at Liberty Island may be important for development of habitat needed to enhance the fishery production in SFE. The export of total suspended solids and salt from Liberty Island in the winter and spring may provide salts and sediment needed for optimum fish habitat. Juvenile fish occur in freshwater tidal wetlands in late winter and early spring before they move downstream into the estuary (Sommer et al. 2004). Some fish, including the endangered delta smelt, occur in the lower Sacramento River near Liberty Island where salinity and turbidity are thought to be more favorable for growth and survival (Nobriga et al. 2008).

Management of the retention and export of organic carbon sources that includes consideration of both tide and river discharge may increase the food resources available in the wetland to support the aquatic food web. Wetland management needs to achieve a balance between the daily dispersion of material from the wetland into the estuary with the tide, sufficient residence time to allow accumulation and growth of organisms at the base of the food web and material recycling and flow needed to export inorganic and organic material into the estuary at critical times for the fishery.

High intra-annual variability suggests that a full understanding of this material flux requires measurement over long interannual time scales. The material flux in Liberty Island during 2004 and 2005 represents a small fraction of the potential variability in material flux of the wetland over time. The Sacramento River discharge alone varies by at least a factor of 5 over two decades due to climatic change in California which is characterized by periods of wet and dry conditions. These conditions affect physical, chemical

and biological factors in the estuary and are expected to become more extreme with climate change (Lehman 2000b; California Department of Water Resources 2006). Organic material flux, including phytoplankton, zooplankton and benthic species may also vary over time due to climate change and the exotic species invasions which characterize SFE (Lopez et al. 2006; Cohen and Carlton 1995).

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