

Wetland-driven shifts in suspended particulate organic matter composition of the Hudson River estuary, New York

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Abstract

Elemental carbon and nitrogen, stable isotopes, and lignin phenols were quantified for suspended particulate material exchanging between Tivoli Bays wetlands and the main stem of the freshwater–tidal Hudson River estuary (HRE) across a tidal cycle, seasonally in 2006 and monthly in 2007 during the ice-free portion of the year. Temporal shifts in organic matter (OM) composition ranged from 33.1 to 247.6 mg g⁻¹ particulate organic carbon (POC), -34.7‰ to -27.2‰ stable carbon isotopic signature of POC ($\delta^{13}\text{C}_{\text{POC}}$), -3.6‰ to 13.6‰ nitrogen isotopic signature of particulate nitrogen ($\delta^{15}\text{N}_{\text{PN}}$), and 0.8 to 25.0 mg per 100 mg OC lignin phenols. From May to August, the wetlands transferred abundant (up to 247.6 mg g⁻¹), chemically distinctive ($\delta^{13}\text{C}_{\text{POC}}$ as depleted as -34.7‰) particulate OM to the HRE, particularly Tivoli South Bay. We estimated a net export of > 60 Mg km⁻² yr⁻¹ POC from Tivoli Bays into the HRE. Mixing model iterations indicated that planktonic OM was the dominant source (50% to 86%) during summertime, while contributions from allochthonous and planktonic OM during other seasons were roughly equivalent (~ 38%). Taken together, both geochemical data and mixing modeling underscore the function and value of HRE tidal wetlands as major generators of compositionally unique and labile POC for the estuarine carbon budget. In a broader context, lateral aquatic connections with tidal wetlands at seasonal or localized scales may overshadow internal or upland influences on OM composition, production, and processing in estuaries; a latent but key consideration when deciphering temporal and longitudinal trends.

Fringing wetlands, coves, and small embayments in the tidal portion of estuaries serve important ecological functions as the link between terrestrial and aquatic systems. Rapid cycling of nutrients and high seasonal production of organic material are the principal factors in energy flow and trophic structure in tidal wetlands, largely controlling the remarkable diversity and productivity (Simpson et al. 1983). Organic matter (OM) supporting this productivity may be derived from numerous sources, including upland soils, sediments and vegetation, aquatic macrophytes, phytoplankton, and bacteria (Odum 1980; Simpson et al. 1983; Keough et al. 1996). The multitude of potential OM sources, coupled with the dynamic mixing that occurs in tidal wetlands, complicates identification of carbon and nutrient flows in these systems.

Research on OM budgets of coastal wetlands has tested whether these ecosystems generally serve as sources or sinks of carbon and nutrients (Odum 1980; Childers et al. 2000). Such studies highlighted the complexity of tidal wetlands, by both supporting and challenging their role as particulate organic matter exporters (Childers et al. 2000). In part, the differing conclusions of those works may be due to the diversity in sources of OM affecting tidal wetland biogeochemistry on both spatial and temporal scales

(Keough et al. 1996; Childers et al. 2000; Arrigoni et al. 2008). The use of stable isotopes to understand OM biogeochemistry and provenance in these lotic systems has revealed greater detail about spatio-temporal shifts and the multiple source–sink compartments for OM (Keough et al. 1996; Boschker et al. 1999; Bouchard 2007). Despite numerous studies with substantial improvement in characterization techniques, the role of tidal wetlands as a source vs. sink of particulate organic constituents often remains elusive.

Fringing wetlands of the Hudson River estuary (HRE) may serve an important and underappreciated role in OM cycling (Findlay et al. 1990; Bianchi et al. 1993; Arrigoni et al. 2008). For example, tidal wetlands comprise ~ 29 km² land area (Kiviat et al. 2006), or only about one-fourth of the tidal Hudson River surface area (Howarth et al. 1996). These ecosystems, however, are suspected to be net sources of particulate organic carbon (POC) and capable of altering carbon fluxes downstream to the HRE (Arrigoni et al. 2008). For instance, Goldammer and Findlay (1987) showed summer total suspended material (including OM) influx to Tivoli South Bay (SB) wetland supports ~ 4 times the measured annual sediment accumulation, suggesting substantial export of particles during storms or other seasons. Additional work by Benoit et al. (1999) indicated that average sediment accumulation rates in the summertime are not supported by suspended material flux, and there was no net difference in tidal suspended material concentrations. Carr et al. (2004) showed a net loss of 58% by mass of a conservative dye tracer injected in Tivoli North Bay (NB) over a tidal cycle. While these studies indicate that fringing wetlands may play an important role

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in particulate OM exchange with the HRE, they do not completely quantify the temporal variation or delineate the potential sources.

Exactly how tidal wetlands might alter particulate organic matter composition in the HRE, despite their relatively small surface area, remains unresolved. In order to address this data gap, we analyzed particulate OM pools at a high temporal resolution in Tivoli NB and South Bay (SB), located in the tidal freshwater HRE. Organic matter was characterized over a tidal cycle at seasonal (during 2006) and at least monthly (2007) timescales using several complementary indices of organic matter composition: elemental carbon and nitrogen abundances, molar organic carbon to nitrogen ratios (POC:PN), stable carbon and nitrogen isotope values ($\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{PN}}$), and lignin-derived CuO oxidation products ($\Lambda_{\text{g-POC}}$). We also analyzed suspended material at a site in the HRE downstream of Tivoli Bays during 2007. Finally, we coupled our biogeochemical approach with IsoSource, a mixing model generally used for partitioning isotopic signatures and food web structure (Phillips and Gregg 2001, 2003). Our objective was to quantify the role fringe wetlands play in influencing OM proportions and composition in the HRE.

Methods

Study site—This study was conducted at the Tivoli Bays (North and South) tidal freshwater wetland complex in the Hudson River National Estuarine Research Reserve (HRNERR) and in the HRE (Fig. 1). Tivoli Bays are located on the eastern shore of the HRE just north of the Kingston-Rhinecliff Bridge ($42^{\circ}02'15''\text{N}$, $73^{\circ}55'10''\text{W}$), Dutchess County, New York (river-km 159 north of the Battery). Tivoli NB is 1.5 km² in size, while Tivoli SB is slightly smaller at 1.15 km² (Findlay et al. 1990). Both are freshwater tidal wetlands containing emergent obligate vegetation. For example, NB is dominated by *Typha angustifolia* (narrow leaf cattail), *Nuphar advena*, and *Pontederia cordata*, while in SB the invasive floating macrophyte *Trapa natans* (water chestnut) dominates (Findlay et al. 1990; Arrigoni et al. 2008). Both wetlands have silt-clay bottom sediments and are subject to semidiurnal tides with a range of ~ 1.2 m.

Field sampling—We made all attempts during fieldwork to spread our sample collections across both the tidal regime (ebb or flood) and interannual time frame. Thus, we collected water column particulates at ~ 2 -h intervals across one tidal cycle at ~ 0.5 m depth (typically starting at ebb tide). Geochemical data are presented either as averages across the entire tidal cycle or separated into flood vs. ebb depending on direction of tidal flow at time of sample collection. All collection vessels were washed in Alconox, rinsed with tap water, and rinsed twice with the water sample prior to sample collection. Samples were collected in a 20-liter stainless steel vessel at each railroad causeway (Fig. 1) during April and November of 2006 (seasonally), and at least monthly from May to December of 2007. We also collected a single monthly grab sample of

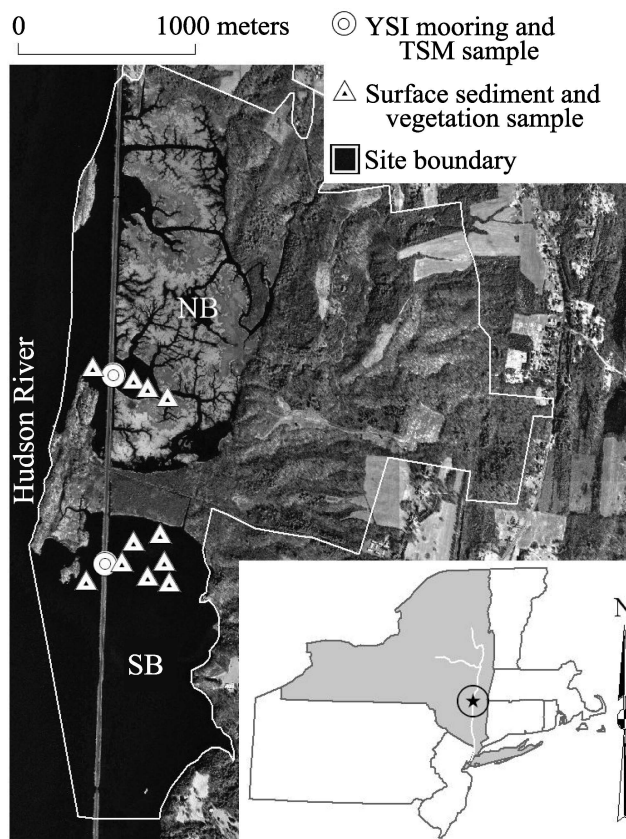


Fig. 1. Site locus and sampling map for the HRE and Tivoli NB and SB freshwater-tidal component of the HRNERR. Base map comprised of New York State Eastern Region [F8] 1994–1999, digital orthophotography derived from the National Aerial Photography Program in Universal Transverse Mercator, Zone 18, North American Datum of 1983, meter coordinates at 1-m ground resolution in single band infrared.

HRE particulates by boat during 2007, downstream at Kingston, New York (river-km 152). Each sample collection was assumed to be representative of water column conditions (Goldhammer and Findlay 1987; Findlay et al. 1991, 1998).

Particulate samples were isolated by filtering the water samples through Millipore glass fiber filters (GFF) ($0.7\text{-}\mu\text{m}$ nominal pore size) within 1 h of collection. Water samples (10 to 20 liters) were forced with compressed high-purity N_2 at ~ 0.2 kg cm^{-2} from the 20-liter stainless steel vessel through a 142-mm diameter pre-ashed GFF allowing us to concentrate ≤ 1 g of material on each GFF. Filters were then immediately frozen for subsequent geochemical analysis of vascular plant markers (lignin phenols). An additional 1-liter Nalgene bottle of whole water was collected, immediately stored on ice, and passed through precombusted and preweighed 25-mm diameter GFF (also $0.7\text{-}\mu\text{m}$ nominal pore size) within 1 h of collection. These filters were then dried at 50°C and reweighed in order to determine total suspended material (TSM) concentrations, then stored in precleaned plastic Analytslides for subsequent geochemical analyses (POC, PN, and stable isotopes). Duplicates were collected and analyzed for $\sim 20\%$ of the

samples. The average error for TSM determined by replicate analysis was $\pm 1.44 \text{ mg L}^{-1}$ (8.3%).

Bulk carbon, nitrogen, and stable isotope quantification—Bulk organic carbon (OC), nitrogen (N), and their stable isotope analyses were performed at the University of California–Davis Stable Isotope Laboratory measured on continuous flow Elemental and Isotope Ratio Mass Spectrometer (Europa Hydra 20/20). In order to remove inorganic carbon from each sample, all samples were placed in a desiccator along with a beaker containing 25 mL of concentrated HCl for 14 d, or until mass loss ceased (Harris et al. 2001). The average error determined by replicate analysis was ± 0.29 and 0.33 weight % for OC and N measurements, respectively, $\pm 0.93\text{‰}$ for $\delta^{15}\text{N}$, and $\pm 0.19\text{‰}$ for $\delta^{13}\text{C}_{\text{org}}$.

Vascular plant markers—Lignin phenols, oxidation products of macromolecular lignin, were extracted according to the method of Hedges and Ertel (1982), as modified for microwave assisted solvent extraction (MASE) (Goni and Montgomery 2000). An aliquot of particulate material concentrated on a $0.7\text{-}\mu\text{m}$ glass fiber filter (GFF) and representing 3 to 5 mg of OC (typically half of a 142 mm GFF) was oxidized with CuO under alkaline (2 mol L^{-1} NaOH) conditions in Teflon vessels sealed under a positive nitrogen atmosphere in a glove box. Although Dalzell et al. (2005) reported that monel-bomb CuO oxidation in the presence of GFF lowered lignin yields $\sim 25\%$, extractions of Tivoli Bays sediment filtered onto GFF as a slurry vs. unfiltered indicated that use of MASE may not reduce lignin yields; nonetheless we caution absolute comparisons of GFF-derived lignin yields. The gas chromatography–mass spectrometry chromatographic and spectrometric analytical conditions, as well as analytical precision, were analogous to Mitra et al. (2000). Concentrations of total lignin-derived oxidation products (i.e., Λ_8 , defined as the total of vanillyl, syringyl, and cinnamyl phenol yields) normalized to organic carbon content provide an independent estimate of the vascular plant contributions to the OM (Hedges and Ertel 1982; Goni and Montgomery 2000). The average error for Λ_8 lignin determined by replicate analysis was ± 1.74 mg per 100 mg OC.

Supporting data—Hudson River mean daily discharge (Q; not filtered for tides) data were obtained from the U.S. Geological Survey (USGS) gauge near Poughkeepsie, New York (01372058). Meteorological data were obtained from the HRNERR–National Weather Service station located at Bard College Ecological Station (middle-eastern edge of South Bay). Tidal flow velocities were recorded at the South Bay railroad causeway from June through September 2007 and combined with cross-sectional area in order to validate prior estimates of average ebb and flood water volumes exchanged between Tivoli Bays and the main stem HRE (Goldhammer and Findlay 1987; Findlay et al. 1998; Carr et al. 2004). Water depth and field water quality data (temperature, conductivity, pH, dissolved oxygen, and turbidity) were obtained from a Yellow Springs Instruments 6600 sonde deployed and monitored by HRNERR

(Fig. 1). Chlorophyll *a* (Chl *a*) data were collected monthly as part of the HRNERR long-term nutrient and water quality program.

Statistical analysis—Data were tested for normality using the Kolmogorov–Smirnov test and evaluated graphically using quantile-by-quantile plots. A Pearson's product moment correlation was used to investigate the strength and direction of relationship among the variables. Student's *t*-test ($\alpha = 0.05$) was used to test differences between stations for a particular sampling event (spatial resolution), while a one-way ANOVA ($\alpha = 0.05$) was used to test differences between sampling dates for each station (temporal differences). A least significant difference multiple comparison test was used to locate any spatial differences identified as significant by ANOVA ($\alpha = 0.05$). Statistical techniques were conducted using SPSS 15. Unless specifically noted, mention of statistical significance, difference, or lack thereof in this text refers to the 95% confidence interval ($p \leq 0.05$). Statistical significance was established on nontransformed data. Duplicates were collected and analyzed for $\sim 20\%$ of the samples, and whenever possible, error was propagated throughout all stages of sample processing and analysis.

Mixing model—We determined the relative contribution of major OM pools exchanged between Tivoli Bays and the Hudson River estuary using IsoSource, a mixing model coded using Visual Basic. Specific details of IsoSource may be found in the literature (Phillips and Gregg 2001, 2003). Error analysis is discussed and reported later in the text.

Results

Hydrographic parameters and fundamental geochemistry—Mean daily river discharge at Poughkeepsie (not filtered for tides) was typically between 155 and $905 \text{ m}^3 \text{ s}^{-1}$ (25th and 75th percentile) over the entire sampling period, with the exception of record high discharge due to major storm runoff pulses in late June through early July 2006 and spring runoff in April 2007 (Fig. 2). Concentrations of total suspended material (TSM) averaged over tidal cycles ranged from 6.9 to 53.7 mg L^{-1} and 3.9 to 115.8 mg L^{-1} , for NB and SB, respectively (Table 1), with no significant difference between sites across the entire sampling time frame (Fig. 2). Turbidity and TSM observations were strongly and positively correlated with each other ($r^2 > 0.73$) for both wetlands. Intermittent peaks in TSM and turbidity tended to coincide with increased discharge and strong wind events (Fig. 2).

Water temperature shows a typical parabolic curve representative of temperate climates with lows approaching 0°C in the winter and peaking in July and August around 28°C (Fig. 2). Dissolved oxygen (DO) exhibited a strong inverse relationship with water temperature ($r^2 = 0.72$) at both wetlands. Levels of DO were at or above saturation in the early spring, with an average greater than 93% in April and May. A rapid $\sim 30\%$ decline in DO occurred through the month of June, followed by a slow recovery toward saturation in winter. North Bay (NB) displayed

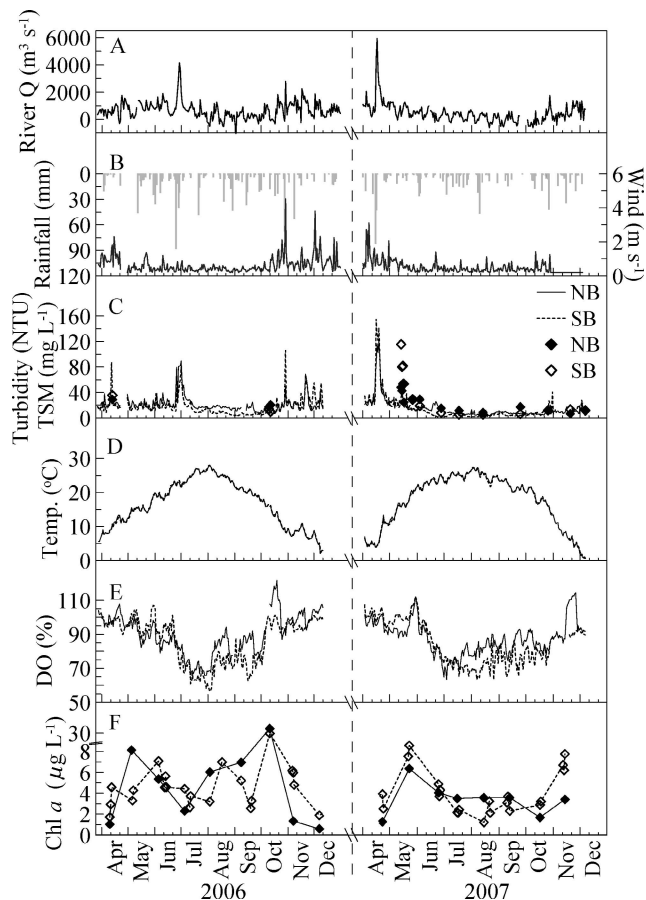


Fig. 2. Variation in mean daily (A) provisional discharge (not filtered for tides) measured at Poughkeepsie, New York (USGS 01372058), (B) rainfall and wind speed, (C) turbidity in nephelometric turbidity units (NTU) (lines) and total suspended material (TSM) (points), (D) temperature, (E) dissolved oxygen, and (F) Chl *a* measured by HRNERR at Tivoli NB and SB across the 2006–2007 sampling period.

significantly higher levels of DO than SB from July through December of 2006. Chl *a* ranged from 0.6 to 31.7 $\mu\text{g L}^{-1}$ and 1.2 to 29.9 $\mu\text{g L}^{-1}$ for NB and SB, respectively (Fig. 2). Chl *a* was significantly greater in SB than NB for November, in both sampling years.

Temporal trends in POC and PN—Particulate organic carbon in suspended matter ranged from 34.3 to 113.3 mg g^{-1} for NB and 33.1 to 247.6 mg g^{-1} for SB over the time sampled (Fig. 3; Table 1). Concentrations of POC increased in both NB and SB beginning in May, remained elevated through the summer months, and then decreased again in September. Mean POC in April, May, and from October to December was around 55 mg g^{-1} and showed no significant difference between sites. Mean POC was significantly higher in SB for June through September vs. April, May, and November through December. Alternatively, mean POC in NB was only significantly elevated during July and August. The June to September time frame also corresponds with the greatest range of POC values. This summer POC excursion is particularly evident

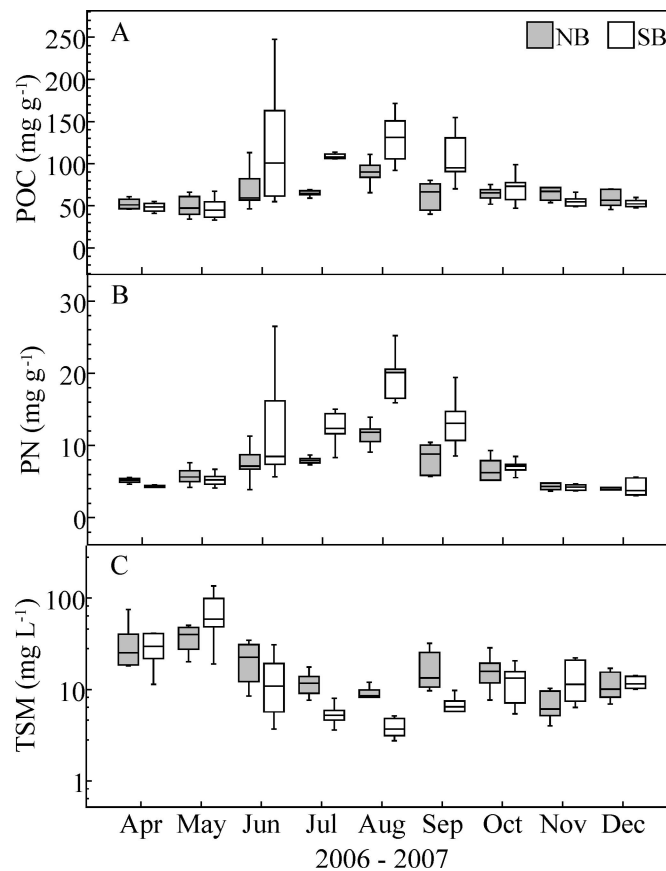


Fig. 3. Monthly box-whisker plots showing the temporal distribution of (A) particulate organic carbon (POC), (B) particulate nitrogen (PN), and (C) log total suspended material (TSM). Solid boxes show Tivoli NB, open boxes Tivoli SB. 2006 and 2007 samples are combined to highlight overall variation between years and sampling regimes. Box center, mean value; outer limits, upper and lower quartiles; inside line, median value; and whiskers, 95% confidence intervals. Outliers were removed.

for SB (Fig. 3), which shows significantly higher abundance than NB for June through September. Also, POC (mg g^{-1}) exhibited a strong negative relationship with TSM (mg L^{-1}); however, the variation in TSM was only able to explain 49% of the variation in POC at each of the sites over the sampling time frame (Fig. 3; Table 1). Generally, higher concentrations of TSM having a relatively lower proportion of POC (mg g^{-1}) were observed in spring, while summertime TSM typically dropped an order of magnitude, and the relative abundance of POC in that suspended matter increased at least twofold (Fig. 3).

The nitrogen fraction of total suspended material (PN) showed a seasonal trend similar to that of POC (Fig. 3). In fact, these two attributes of particulate matter were found to strongly correlate at $r^2 = 0.78$ for NB and 0.93 for SB. The relative abundance of PN (mg g^{-1}), like that of POC, became significantly higher for both bays from June through October when compared to early spring and winter months. The elevated PN abundance was apparent in the late summer for SB (Fig. 3), which exhibited significantly higher levels than NB for July through

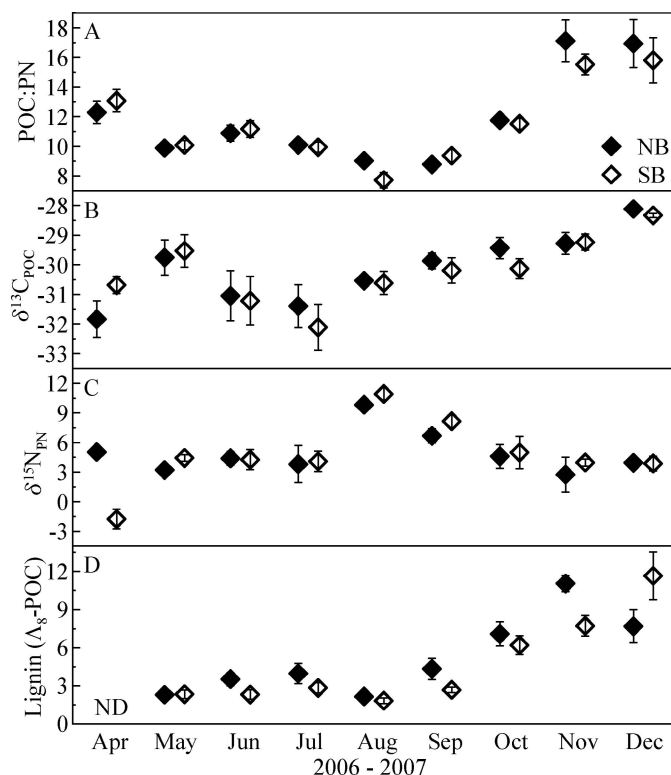


Fig. 4. Monthly variations of (A) particulate organic carbon to particulate nitrogen ratio (POC : PN), (B) stable carbon isotope signature of particulate organic carbon ($\delta^{13}\text{C}_{\text{POC}}$), (C) stable nitrogen isotope signature of particulate nitrogen ($\delta^{15}\text{N}_{\text{PN}}$), and (D) sum of lignin-derived phenols in particulate organic carbon ($\Lambda_8\text{-POC}$) at Tivoli NB and Tivoli SB. Error bars represent standard error of the mean measured across a tidal cycle. See Table 1 for detailed error estimates. ND, not determined due to insufficient sample matrix.

September. Fluctuations in POC explained 62% of the variation in PN for NB and nearly 93% of the variation at SB. High POC and PN levels were observed June through September, especially in SB (Figs. 3, 4; Table 1). The abundance of POC (mg g^{-1}) was 9.9 ± 1.2 times greater than PN for the May to September sampling time frame for both wetlands. There was a marked increase in POC : PN, with an average of 13.5 ± 2.7 from October through December, again for both wetlands (Fig. 4; Table 1).

Temporal trends in stable carbon and nitrogen isotopes, and total lignin phenols—There were two prominent seasonal shifts in the stable carbon isotope composition of particulate organic carbon ($\delta^{13}\text{C}_{\text{POC}}$) (Fig. 4). Seasonal variations of $\delta^{13}\text{C}_{\text{POC}}$ generally followed a similar trend in each wetland (Fig. 4). The $\delta^{13}\text{C}_{\text{POC}}$ showed a range of -34.7‰ to -27.2‰ for both wetlands (Fig. 4; Table 1). The most depleted $\delta^{13}\text{C}_{\text{POC}}$ values $-32.4\text{‰} \pm 1.6\text{‰}$ were observed in summer (late June–July), while more enriched values $-28.4\text{‰} \pm 0.8\text{‰}$ occurred in early May and November through December. A significantly different mean $\delta^{13}\text{C}_{\text{POC}}$ value was observed in June and July, in contrast to that observed from October through December for NB. Mean $\delta^{13}\text{C}_{\text{POC}}$ values for May and November to

December were significantly different from June and July for SB. There was an inverse but statistically significant correlation between POC and $\delta^{13}\text{C}_{\text{POC}}$ values ($r^2 = 0.41$ and 0.53) for both wetlands. Similar inverse trends and correlation between $\delta^{13}\text{C}_{\text{POC}}$ and PN were observed ($r^2 = 0.33$ and 0.41) for NB and SB, respectively. The tidal averaged $\delta^{13}\text{C}_{\text{POC}}$ values for each bay were never significantly different from one another.

Stable isotopic values of particulate nitrogen ($\delta^{15}\text{N}_{\text{PN}}$) changed markedly within Tivoli Bays throughout the seasons (Fig. 4). As noted for $\delta^{13}\text{C}_{\text{POC}}$, seasonal variation of $\delta^{15}\text{N}_{\text{PN}}$ in each wetland followed a similar trend, with most depleted values in spring, then elevated values into August, followed by a decline in the early winter (Fig. 4). The values of $\delta^{15}\text{N}_{\text{PN}}$ ranged from -3.2‰ to 10.5‰ for NB and -3.6‰ to 13.6‰ for SB (Table 1). Values of $\delta^{15}\text{N}_{\text{PN}}$ were substantially enriched in August, in contrast to values from almost all other months (except September for SB) in both wetlands. Again, as observed for $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{PN}}$ values were slightly significant and inversely correlated with POC and PN (max $r^2 = 0.47$) for both bays. Monthly averaged $\delta^{15}\text{N}_{\text{PN}}$ values for NB were significantly different from SB only during the April sampling.

Values of total lignin phenols ($\Lambda_8\text{-POC}$) averaged 4.6 ± 3.3 mg per 100 mg OC for NB, and 4.2 ± 4.0 mg per 100 mg OC for SB, throughout the sampling period with one major seasonal shift in the autumn (Fig. 4). During the October to December time frame a near twofold increase in $\Lambda_8\text{-POC}$ (mean of 8.6 ± 2.2 mg per 100 mg OC) occurred in both wetlands (Fig. 4). In fact, the elevated total lignin values for October through December in both bays were significantly different from spring and summer. Further, the November (NB) and December (SB) values were significantly different from all other times over the sampling period. A low-tide December sample in SB (25.0 mg per 100 mg OC) was significantly different from all other observations (Table 1). November was the only month in which a significantly different $\Lambda_8\text{-POC}$ value was observed between the wetlands. Total lignin phenols were directly correlated with $\delta^{13}\text{C}_{\text{POC}}$ ($r^2 = 0.63$ and 0.74 for NB and SB, respectively) but only significant for SB.

Tidal influence on OC-enriched particles and $\delta^{13}\text{C}_{\text{POC}}$ biogeochemistry—The potential for tidal influences on POC composition over our sampling time frame is represented by the relationships depicted in Fig. 5. In general, there is a relatively uniform (nearly 1 : 1) exchange of particles having comparable OC concentration (mg g^{-1}) between NB and the HRE. During June and during October through December, ebb tides flushed POC-rich suspended matter from NB into HRE. The greatest divergence from 1 : 1 for NB occurred during the month of November. In contrast, SB exchanged highly OC-enriched particles that showed departure from the 1 : 1 line during several months. The slope of the line for SB diverged substantially from 1 : 1 during the months of June and July ($\sim 2 : 1$) and notably during September (Fig. 5). During April and May, both wetlands flushed suspended particles similar in OC abundance (mg g^{-1}) into the HRE during ebb tides.

Table 1. Compositional indices for individual sample collections across a tidal cycle of total suspended material (TSM) collected at Tivoli NB and SB. POC, particulate organic carbon; PN, particulate nitrogen; ND, not determined. Error propagated standard deviation of replicates shown in parentheses.

Date	Time	TSM (mg L ⁻¹)	POC (mg L ⁻¹)	PN (mg L ⁻¹)	POC (mg g ⁻¹)	PN (mg g ⁻¹)	POC : PN	δ ¹⁵ N (‰)	δ ¹³ C _{org} (‰)	Λ ₈ Lignin (mg per 100 mg OC)
North Bay (NB)										
13 Apr 06	10:05	31.1(1.8)	1.7	0.16	55.0	5.2	12.3	4.8	-32.2	ND
	13:07	18.2(1.2)	1.1	0.09	61.0	5.1	13.9	5.0	-33.1	ND
	19:42	75(4.1)	3.4	0.35	45.9	4.6	11.6	4.9	-31.0	ND
10 Oct 06	21:54	40.2(1.8)	1.9(0.1)	0.23(0.01)	47.2(3.2)	5.6(0.4)	9.8(0.1)	5.5(1.2)	-29.9(0.04)	ND
	11:45	19.3(1.6)	1.7(0.2)	0.18(0.02)	90.2(12.3)	9.3(1.1)	11.3(0.3)	0.2(0.1)	-31.5(0.1)	ND
	19:10	19.3(2.3)	1.5(0.2)	0.15(0.02)	75.3(13.4)	8(1.4)	11(0.3)	-0.2(0.5)	-30.8(0.01)	ND
12 Oct 06	09:12	14.3(1.9)	0.9(0.1)	0.11(0.01)	65.7(12.5)	7.9(1.5)	9.7(0.3)	2.4(0.02)	-29.4(0.1)	ND
	15:14	28.5(1.1)	1.8(0.1)	0.18(0.01)	62.6(3.8)	6.3(0.4)	11.7(0.7)	2.1(1.7)	-29.7(0.1)	ND
14 May 07	17:13	50.3(3.4)	2.1	0.24	41.7	4.9	10.0	4.3	-27.5	3.3
	19:51	46(3.8)	1.6	0.22	34.3	4.7	8.5	0.0	-27.8	2.7
15 May 07	06:54	49.5(4.3)	1.8	0.25	37.1	5.1	8.5	3.0	-27.7	5.1(1.4)
	10:25	39.8(4.2)	1.6	0.19	39.1	4.7	9.7	3.9	-27.6	1.9
	19:29	50.4(3.1)	1.9(0.2)	0.27(0.02)	37.9(3.8)	5.4(0.5)	8.1(0.7)	2(0.9)	-28(0.3)	2.1(0.6)
16 May 07	20:49	31.8(2.4)	1.4	0.18	42.6	5.5	9.0	3.0	-27.8	2.7
	08:37	27.3(2.6)	1.7	0.18	62.1	6.5	11.2	4.0	-32.8	1.2
	10:27	113.1(3.8)	4.6	0.47	40.6	4.2	11.3	2.0	-31.4	0.8
17 May 07	18:26	41.2(3.1)	2.6	0.24	63.5	5.9	12.5	4.4	-32.3	1.8
	20:25	33.4(1)	1.6(0.2)	0.19(0.03)	48.6(5)	5.7(0.9)	10.1(0.6)	1.1(0.3)	-33.2(0.4)	2.4(0.7)
	09:19	27.8(1.4)	1.7	0.20	60.4	7.3	9.6	2.0	-32.1	1.7
27 May 07	11:33	22.2(1.4)	1.4	0.15	63.0	6.8	10.8	3.9	-32.6	2.2
	05:18	41.8(2.9)	2.0	0.27	47.2	6.4	8.6	5.3	-28.4	3.1
	07:06	21.3(2.1)	1.2	0.14	57.5	6.6	10.2	5.0	-29.0	2.2
04 Jun 07	11:04	20.2(1.5)	1.3	0.15	66.3	7.6	10.2	4.2	-28.0	1.4
	09:36	34.6(0.8)	1.7	0.20	49.0	5.8	9.9	3.5	-27.8	2.3
	10:52	24.7(0.7)	1.5	0.19	59.5	7.7	9.0	3.4	-28.1	5.8(0.4)
28 Jun 07	12:57	32.1(1.2)	1.7	0.22	54.6	7.0	9.1	2.9	-27.3	3.1
	15:24	22.5(0.5)	1.3	0.16	59.6	7.0	10.0	4.1	-27.5	2.0
	22:21	32.6(2.2)	1.9	0.21	59.5	6.5	10.6	4.6	-32.3	4.5
18 Jul 07	06:30	19.9(3.5)	1.5	0.18	73.6	9.3	9.2	5.2	-31.4	6.8
	08:33	11(0.8)	0.9(0.1)	0.11(0.01)	85.5(10.7)	9.9(1.2)	10.1(0.1)	5.7(0.2)	-33.4(0.2)	4.5(1.3)
	11:19	29.8(0.7)	1.4	0.12	46.2	3.9	13.9	3.1	-32.8	2.2
14 Aug 07	14:08	9.9(1.9)	0.9	0.08	94.4	8.1	13.5	9.9	-33.6	2.3
	17:28	13.4(0.1)	1.5(0.02)	0.15(0.01)	113.3(2)	11.3(0.8)	11.7(0.2)	0.5(2.8)	-32.6(0.2)	2.3(0.6)
	20:46	8.5(1)	0.7	0.06	78.7	7.2	12.8	5.3	-34.7	2.6
25 Sep 07	08:21	13.8(1.2)	1(0.1)	0.11(0.01)	69.1(9.1)	7.9(1.1)	10.3(0.2)	-3.2(4.3)	-32.7(0.4)	2.5(0.7)
	10:11	17.6(1.2)	1.2	0.14	66.9	7.9	9.8	7.1	-32.2	5.3
	12:07	13.9(0.6)	0.9	0.11	64.5	8.1	9.3	5.5	-32.9	4.2
26 Oct 07	14:34	7.7(0.5)	0.6	0.07	84.1	8.7	11.3	6.6	-33.8	1.6
	16:24	8.4(0.8)	0.5	0.05	59.3	6.3	11.0	ND	-29.6	2.4
	19:57	9.8(0.8)	0.6	0.07	62.8	7.3	10.0	3.1	-29.6	3.9
26 Oct 07	22:31	11.7(0.7)	0.7	0.10	63.5	8.3	9.0	ND	-29.1	7.9
	08:26	12(1)	0.8(0.1)	0.11(0.01)	65.7(7.9)	9.1(1.1)	8.5(0.6)	9.5(0.1)	-30(0.01)	3.5(1)
	10:26	5.3(0.6)	0.6	0.07	111.2	13.9	9.3	10.5	-30.4	1.3
26 Oct 07	12:29	8.7(0.7)	0.8	0.11	91.5	12.3	8.7	9.3	-30.4	1.5
	14:48	9.8(0.9)	0.8	0.10	83.7	10.5	9.3	9.8	-30.8	1.8
	17:26	8.3(1)	0.7	0.10	88.8	12.1	8.6	10.2	-30.9	2.2
25 Sep 07	19:35	8.2(0.6)	0.8(0.1)	0.1(0.01)	98.1(10.3)	11.6(1.3)	9.9(0.1)	9.5(0.2)	-30.7(0.3)	2.6(0.7)
	06:03	32(1.1)	1.3(0.1)	0.18(0.01)	40.1(4.6)	5.7(0.3)	8.2(0.6)	4.2(2.9)	-29(0.1)	1(0.3)
	07:50	25.4(0.7)	1.1	0.15	44.8	5.9	8.9	7.7	-29.3	2.6(2.2)
26 Oct 07	10:24	11.6(0.3)	0.8	0.12	70.1	10.0	8.1	4.7	-29.7	3.3
	12:53	10.6(0.3)	0.8(0.04)	0.1(0.01)	76.1(4)	9.7(1)	9.2(0.4)	7.6(0.02)	-30.3(0.02)	4.3(1.2)
	15:37	9.7(0.3)	0.8	0.10	80.3	10.4	9.0	7.9	-30.6	5.7
26 Oct 07	17:44	15.3(0.7)	1.0	0.12	63.3	7.9	9.3	8.1	-30.4	6.9
	06:40	14.2(0.5)	0.8	0.07	54.0	5.2	12.2	7.9	-28.8	7.9
	09:35	7.7(0.6)	0.5	0.05	69.2	7.1	11.4	8.5	-28.3	6.1
	11:59	17.4(0.6)	0.9	0.09	51.9	5.1	11.8	4.3	-28.5	3.8

Table 1. Continued.

Date	Time	TSM (mg L ⁻¹)	POC (mg L ⁻¹)	PN (mg L ⁻¹)	POC (mg g ⁻¹)	PN (mg g ⁻¹)	POC : PN	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	Λ_8 Lignin (mg per 100 mg OC)
20 Nov 07	17:16	10(0.4)	0.7(0.03)	0.06(0.01)	65.6(4.2)	5.9(0.9)	13.3(2.4)	8.2(1.3)	-29(0.2)	8.6(2.4)
	18:34	13.9(0.5)	0.8	0.07	59.6	5.2	13.5	8.1	-29.0	9.1
	02:17	4(0.1)	0.4	0.03	96.2	8.5	13.2	4.5	-27.8	10.5
	04:54	10.3(0)	0.6	0.04	54.0	4.1	15.3	5.8	-29.2	8.3
	07:15	9.6(0.4)	0.5	0.04	56.9	4.5	14.7	8.8	-29.1	12.2
	11:23	6.5(0.3)	0.4	0.02	62.8	3.9	18.9	-1.4	-29.7	12.1
07 Dec 07	13:27	5.2(0)	0.4	0.02	71.6	3.7	22.8	0.9	-29.2	12.4
	15:32	5.8(0.7)	0.4(0.1)	0.03(0.01)	71.7(17.7)	4.8(1.5)	17.9(1.5)	-2.2(2)	-30.6(1)	10.8(3.1)
	04:26	8.3(1)	0.6	0.03	69.9	4.2	19.4	4.9	-28.1	6.9
	06:43	6.9(0.8)	0.5	0.03	69.6	3.8	21.2	2.9	-27.9	8.8
	09:06	15.4(0.8)	0.8	0.06	52.4	3.9	15.6	3.9	-28.1	5.0
	11:52	17.1(0.8)	0.8	0.05	45.6	3.1	17.3	5.0	-28.2	6.6
	14:28	11.2(1.1)	0.7	0.04	61.6	3.9	18.3	5.1	-28.4	5.2
	16:46	9.1(1.4)	0.5	0.05	50.6	6.0	9.8	1.9	-28.0	13.5
South Bay (SB)										
13 Apr 06	09:35	40.9(4.9)	2.1	0.17	50.9	4.2	14.2	-0.4	-31.3	ND
	12:53	11.4(8.7)	0.6(0.5)	0.05(0.04)	55.4(60.5)	4.5(4.9)	14.3(1.6)	-3.4(0.3)	-30.5(1.4)	ND
	19:25	29.7(1.3)	1.4(0.1)	0.12(0.01)	46.3(3.1)	4.2(0.3)	12.9(0.6)	-3.6(0.3)	-31(0.2)	ND
10 Oct 06	21:44	41.6(6.3)	1.7(0.3)	0.18(0.03)	41.1(8.9)	4.4(1)	11(0.2)	0.4(0.5)	-30(0.3)	ND
	11:10	20.6(1.5)	1.5(0.1)	0.15(0.01)	73.3(7.8)	7.2(0.8)	11.9(0.1)	-1.9(0.4)	-31.8(0.02)	ND
	18:45	9.5(2.2)	0.9(0.2)	0.09(0.02)	99.1(32.3)	9.3(3)	12.5(0.6)	-0.7(1)	-31.6(0.1)	ND
12 Oct 06	08:57	5.4(3.4)	0.4(0.3)	0.05(0.03)	80.6(74.1)	8.5(7.8)	11.1(0.1)	-0.5(0.6)	-30.7(0.1)	ND
	14:56	18.3(1.5)	1.4(0.1)	0.13(0.01)	77.7(8.9)	7.4(0.9)	12.3(0.3)	3.3(0)	-29.8(0.2)	ND
14 May 07	16:46	130.7(2.9)	4.3	0.54	33.1	4.1	9.4	5.1	-27.2	3.9
	19:34	100.8(1.6)	3.7	0.45	36.7	4.5	9.6	5.0	-27.4	ND
15 May 07	06:41	71.2(4.1)	2.5(0.2)	0.35(0.02)	35(2.9)	4.9(0.4)	8.4(0)	2(0.4)	-27.7(0.01)	5.8(1.7)
	10:13	136.3(6.4)	4.6	0.58	33.4	4.3	9.1	3.4	-27.5	2.1
	19:18	57.9(4.1)	2.3	0.30	40.0	5.2	9.0	5.2	-27.4	2.3
	20:39	54.5(4.3)	2.0	0.30	36.1	5.5	7.6	1.7	-27.6	2.3
16 May 07	08:21	49.1(3.2)	2.7	0.28	55.2	5.7	11.3	5.2	-31.6	0.9
	09:48	99.2(5.4)	4.4(0.3)	0.47(0.03)	44.2(3.8)	4.7(0.4)	10.9(0.2)	4(1)	-31.4(0.04)	0.9(0.3)
	18:39	98.4(3.4)	4.4	0.45	44.8	4.5	11.5	5.1	-32.2	2.7(0.2)
17 May 07	20:13	80.7(7.7)	4.6	0.46	56.4	5.7	11.5	5.5	-31.0	1.8
	09:09	58.9(1.3)	3.0	0.31	50.3	5.2	11.2	3.7	-31.8	1.4
	11:20	48.2(6)	2.9	0.29	59.3	6.0	11.5	5.5	-31.8	1.6
27 May 07	05:03	45(2.6)	2.4(0.1)	0.26(0.02)	52.3(4.4)	5.7(0.5)	10.6(0.2)	6.3(0.4)	-32.2(0.1)	2.6(0.7)
	06:47	24.9(2)	1.4(0.1)	0.17(0.01)	54.9(6.7)	6.7(0.8)	9.5(0.1)	5(1.5)	-28.2(0.03)	2.4(0.7)
	10:46	19(1.1)	1.3(0.1)	0.15(0.01)	67.4(5.3)	7.9(0.6)	10(0.1)	3.9(0.3)	-28.1(0.1)	1.7(0.5)
04 Jun 07	09:24	17.9(1.1)	1.0	0.13	56.9	7.1	9.3	2.2	-27.7	ND
	10:41	10.9(1.6)	1.1	0.14	100.9	12.5	9.4	3.3	-28.1	2.5
	12:45	21.2(1.5)	1.3(0.1)	0.16(0.01)	61(6.1)	7.7(0.8)	9.3(0.2)	2.4(0.02)	-27.9(0.01)	3.5(1)
	15:11	15.1(0.4)	1.0	0.13	66.2	8.4	9.2	2.7	-27.7	1.5
	22:11	30.8(1.1)	1.7(0.1)	0.17(0.01)	55.2(2.7)	5.7(0.3)	11.4(0.04)	4.4(0.3)	-32.6(0.01)	3.3
28 Jun 07	06:13	4.6(0.6)	1.0	0.11	208.5	24.1	10.1	2.5	-32.4	4.7(0.3)
	08:10	4(0.6)	1.0	0.11	247.6	26.5	10.9	5.9	-32.5	1.3
	11:01	20.7(0.8)	1.3	0.12	62.4	5.7	12.8	5.0	-33.1	1.5
	13:52	8.7(1)	0.9	0.07	102.5	8.5	14.1	1.4	-34.0	1.4
	17:14	3.7(0.6)	0.8	0.07	226.7	19.9	13.3	13.6	-33.3	0.9
	20:22	7(0.8)	0.8	0.07	117.5	10.4	13.1	3.6	-34.0	2.6
18 Jul 07	08:03	3.6(0.8)	0.6	0.07	179.5	19.1	11.0	4.5	-34.3	1.8
	09:58	5.2(0.6)	0.6	0.06	106.1	12.4	10.0	5.5	-33.9	4.4
	11:51	5.4(0.3)	0.6	0.06	106.4	11.7	10.6	4.7	-33.3	3.7
	14:00	6.5(0.3)	0.7(0.03)	0.08(0.01)	107.9(6.5)	11.5(1.6)	10.9(0.2)	-1.7(3.4)	-33.2(0.4)	2.8(0.8)
	16:07	8(0.6)	0.5	0.07	64.8	8.3	9.1	6.5	-30.5	3.3
	19:41	4.2(0.5)	0.5	0.06	113.9	15.0	8.8	5.2	-30.8	2.3
14 Aug 07	22:16	5(0.9)	0.5	0.07	109.2	13.8	9.2	3.9	-28.9	1.4
	08:11	4(0.3)	0.4	0.08	91.8	20.5	5.2	12.8	-29.2	2.9
	09:40	3.1(0.8)	0.5	0.06	149.1	19.7	8.8	10.7	-30.1	1.3
	12:13	4.8(0.6)	0.5	0.08	105.9	15.9	7.8	9.8	-31.6	1.6
	14:37	5.1(0.9)	0.8(0.1)	0.11(0.02)	150.9(36.3)	20.5(4.9)	8.6(0.03)	9.5(0.6)	-31.1(0.2)	1.6(0.5)

Table 1. Continued.

Date	Time	TSM (mg L ⁻¹)	POC (mg L ⁻¹)	PN (mg L ⁻¹)	POC (mg g ⁻¹)	PN (mg g ⁻¹)	POC : PN	$\delta^{15}\text{N}$ (‰)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	Λ_8 Lignin (mg per 100 mg OC)
25 Sep 07	17:13	3.4(0.8)	0.6	0.09	171.4	25.2	7.9	10.2	-31.5	1.5
	19:19	2.8(0.9)	0.3	0.05	112.9	16.5	8.0	12.6	-30.2	2.0
	05:47	7.5(1)	0.7	0.08	93.1	10.7	10.2	9.3	-29.3	5.7(2.3)
	07:35	9.8(0.5)	0.7	0.08	70.2	8.5	9.6	7.5	-28.5	2.0
	10:08	6.2(0.6)	0.6	0.09	90.7	14.0	7.5	5.7	-30.9	2.6
	12:40	3.5(0.5)	0.5	0.07	154.8	19.4	9.3	8.8	-31.1	2.4
	15:24	5.8(0.4)	0.8	0.08	130.6	14.7	10.4	7.6	-30.9	2.5
26 Oct 07	17:32	6.8(0.2)	0.7	0.08	96.5	12.2	9.3	10.0	-30.4	3.2
	06:26	16.5(0.5)	0.8	0.09	47.0	5.5	9.9	9.8	-29.4	8.8
	09:24	15(0.1)	0.8(0.03)	0.1(0.01)	54.9(2.3)	6.6(0.7)	9.7(0)	7.9(0.2)	-29.1(0.1)	4.6(1.3)
	11:50	7.3(0.2)	0.6	0.05	76.1	7.2	12.4	10.1	-29.3	5.6
	16:59	7(0)	0.5	0.05	72.5	6.8	12.4	8.2	-30.0	5.3
20 Nov 07	18:23	14.6(0.3)	0.8	0.08	57.6	5.8	11.6	8.7	-29.4	6.8
	02:02	6.4(0)	0.4	0.03	66.3	4.5	17.0	4.2	-28.3	7.9
	04:42	14.9(0.2)	0.7(0.02)	0.07(0.01)	49.7(1.7)	4.6(0.7)	12.5(0.3)	4.4(0.5)	-29.2(0.2)	6.4(1.8)
	07:04	7.4(0.1)	0.4	0.03	58.2	4.5	15.2	4.3	-30.2	9.3
	11:08	8.6(0.2)	0.5(0.02)	0.03(0.01)	58.5(2.9)	4(1.2)	17.2(0.3)	2.3(3.1)	-29.7(0.01)	10.4(3)
07 Dec 07	13:16	22.1(0.3)	1.1	0.08	49.0	3.7	15.4	4.4	-28.8	7.3
	15:21	20.9(8.4)	1.1	0.08	51.6	3.8	15.9	4.3	-29.2	4.9
	04:13	10.3(1.1)	0.6	0.06	60.1	5.5	12.7	5.9	-28.2	12.3
	06:31	10.7(2)	0.6	0.03	52.8	3.2	19.1	1.1	-28.3	25.0
	08:52	13.9(0.9)	0.7(0.05)	0.04(0.01)	51.9(4.8)	3.1(0.7)	19.4(2)	5.2(1.5)	-28.5(0.1)	7.1(2)
	11:39	14.1(0.7)	0.7	0.04	47.4	3.1	18.1	4.2	-28.2	5.4
	14:18	12.4(1)	0.7	0.05	56.5	4.3	15.3	2.4	-28.6	5.9(0.3)
	16:36	10.1(0.6)	0.5	0.06	49.0	5.6	10.2	4.5	-28.3	14.5

Tidal regime not only affected POC abundance in Tivoli Bays (Fig. 5), but at times also profoundly influenced the variations in isotopic composition of POC. Strong evidence of altered OM composition over tidal cycles is highlighted in ebb vs. flood averaged $\delta^{13}\text{C}_{\text{POC}}$ fractionation (Fig. 6). Overall, POC with similar $\delta^{13}\text{C}$ values was exchanged between NB and the HRE during May, August to September, and November to December ($\sim 1:1$). POC depleted in $\delta^{13}\text{C}$ was exported during October and imported from the HRE into NB during April and June to July (Fig. 6). Furthermore, the ebb tide POC in NB during April was significantly enriched in $\delta^{13}\text{C}$ vs. the HRE. In contrast, POC depleted in $\delta^{13}\text{C}$ was flushed from SB from April through July and in October, while POC depleted in $\delta^{13}\text{C}$ was imported from the HRE during August, September, and November. Further, ebb tide POC for SB during the month of August was significantly enriched in $\delta^{13}\text{C}$ above the HRE. There was no statistically significant depleted export for NB; however, $\delta^{13}\text{C}_{\text{POC}}$ exports in SB during June and November were statistically unique from all other months (Fig. 6).

Discussion

In the tidal portion of the Hudson River estuary (HRE) system, wetlands are expected to only contribute $\sim 15 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Howarth et al. 1996), a relatively small percentage of the annual OC flux (Findlay et al. 1998). Substantial inputs of OC ($\sim 650 \text{ g C m}^{-2} \text{ yr}^{-1}$) from watershed-agricultural runoff appear to control the overall,

long-term carbon budget of the estuary (Howarth et al. 1996). However, earlier studies (Findlay et al. 1990, 1991; Bianchi et al. 1993) and those more recent (Arrigoni et al. 2008; del Giorgio and Pace 2008) suggest that there may be an important source of OM, especially particulate OM, to the HRE that is not subsidized by upland inputs. As such, we posed the question: how do exchanges of OM from fringing tidal wetlands affect OM cycling and composition in the HRE?

Composition of organic matter in Tivoli Bays—The composition of particulate matter in Tivoli Bays displayed monthly to seasonal scale trends. From June until September, decreasing DO and generally consistent (2006), or decreasing (2007), Chl *a* (Fig. 2) suggested the predominance of heterotrophic respiration in Tivoli Bays. Furthermore, the elevated abundance of POC (mg g^{-1}) during these months (115.5 ± 34.0 , SB) in contrast to average values of POC during April and October to December (54.7 ± 5.5 , SB) (Fig. 3; Table 1) coincide with proportions of POC greater than that predicted by the regression line with TSM, during these warmer summer months. We posit that the abundant POC proportions observed during June through September (particularly in SB), above those recorded in the HRE (Fig. 7), are fueled by autochthonous productivity within Tivoli Bays. Both autochthonous productivity and heterotrophic respiration of fresh OM appear to be working in concert during the summer months, which may suggest that the bays were synthesizing compositionally unique suspended OM during this time frame.

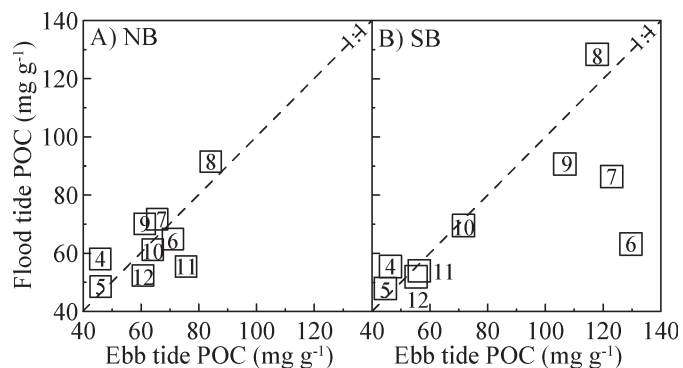


Fig. 5. Monthly mean particulate organic carbon (POC) depicting the differences between flood and ebb tidal regimes at (A) Tivoli NB and (B) Tivoli SB. Dashed line depicts a 1:1 relationship between flood and ebb tides. Datapoints above the 1:1 line indicate flood tide import (below 1:1, ebb tide export) of POC across a tidal cycle. Numbers indicate month of collection. See Table 1 for detailed error estimates.

The proportions of carbon and nitrogen in particulate matter (mg g^{-1}) in NB were fairly consistent or slightly lower than in the HRE (sampled just downstream of Tivoli Bays), except for June and November (Fig. 7). In contrast, the proportions of carbon and nitrogen were variable in SB over time, and significantly higher than in the HRE as depicted for SB in Fig. 7. This suggests a strong compositional difference between the OM pool in Tivoli Bays and HRE. This is particularly evident in SB, which has the potential to remarkably affect OM composition in the adjacent HRE. Indeed, our data suggest that net tidal exchanges favor flushing of carbon-enriched suspended matter from both wetlands into the river, with largest gradients for SB (Figs. 5–7). These interpretations are corroborated by a recent short-term study modeling organic matter abundance and dynamics in Tivoli Bays (Arrigoni et al. 2008).

In Tivoli Bays, the POC:PN ratio averaged 11.4 ± 3.0 (Fig. 4; Table 1) with a significant regression for PN vs. POC (Fig. 3; NB, $r^2 = 0.62$; SB, $r^2 = 0.92$) and statistically similar slope of ~ 0.16 , indicating broad-scale similarity in OM pools across both bays. Nitrogen-rich organic matter did increase in Tivoli Bay particulates throughout the warmest months of July to September (Figs. 3, 7), as indicated by the lower mean POC:PN of 9.1 ± 0.9 . This ratio closely approximated the 8.8 value noted by Goldman et al. (1987) and falls within the range of bacterioplankton; thus it may reflect the contribution of bacterial carbon (Findlay et al. 1992). However, studies throughout the HRE indicate that the contribution of bacterial carbon to the overall OM pool is typically small relative to external sources of POC (Findlay et al. 1992, 1998). Use of POC:PN ratios alone did not allow us to discern between the planktonic, terrestrial, and vascular plant OM pool.

Studies on OM in the freshwater HRE highlighting the use of isotopes and molecular markers on a tidal to interannual scale add to our ability to separate sources (McCallister et al. 2004). The $\delta^{13}\text{C}_{\text{POC}}$ values for both wetlands were usually more depleted than would be

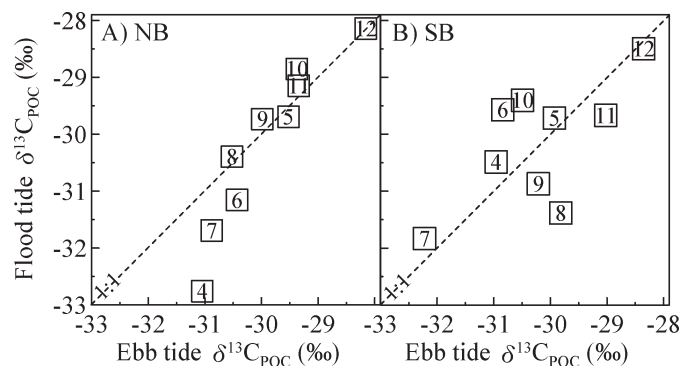


Fig. 6. Monthly mean carbon isotopic signature of particulate organic carbon ($\delta^{13}\text{C}_{\text{POC}}$) highlighting the differences between flood and ebb tidal regimes at (A) Tivoli NB and (B) Tivoli SB. Dashed line depicts a 1:1 relationship between flood and ebb tides. Data points above the 1:1 line indicate flood tide import of enriched (below 1:1, ebb tide export of enriched) $\delta^{13}\text{C}_{\text{POC}}$ across a tidal cycle. Numbers indicate month of collection. See Table 1 for detailed error estimates.

expected for a system dominated by terrestrial or allochthonous inputs (Tables 1, 2). We did observe isotopically heavier $\delta^{13}\text{C}_{\text{POC}}$ values (Table 1; Fig. 4) during portions of the year expected to be controlled by high inputs of watershed–agricultural runoff, such as April and May (Howarth et al. 1996). But, at smaller timescales (i.e., tidal to monthly) other mechanisms, such as in situ productivity, may help to explain the $\delta^{13}\text{C}_{\text{POC}}$ values we observe (Keough et al. 1996; Boschker et al. 1999; Raymond et al. 2004). Additionally, we documented monthly $\delta^{15}\text{N}_{\text{PN}}$ variations across tidal conditions (Tables 1, 2). The enriched $\delta^{15}\text{N}_{\text{PN}}$ values probably result from anaerobic decomposition driven by elevated temperatures coupled with peak growth of macrophytes (Caraco et al. 1998). Such $\delta^{15}\text{N}_{\text{PN}}$ values associated with microbial assimilated nitrogen during organic decomposition have been explained in detail by Caraco et al. (1998).

There are striking compositional excursions in POC pools in suspended material within Tivoli Bays, suggested by the abundant (up to 247.6 mg g^{-1}) and ^{13}C depleted POC (as depleted as -34.7‰) that was present in SB and to some degree NB. This OM was ebbbed to the HRE and contributed to spring and summer variations in POC composition of the adjacent estuary (Figs. 4–7). Overall, we surmise that the combination of enriched POC ($106.2 \pm 46.6 \text{ mg g}^{-1}$), moderate POC:PN (9.1 ± 0.9), and depleted $\delta^{13}\text{C}_{\text{POC}}$ ($-31.8\text{‰} \pm 1.6\text{‰}$), along with elevated $\delta^{15}\text{N}_{\text{PN}}$ ($6.5\text{‰} \pm 3.9\text{‰}$) during the warmer summer time frame of late June through August reflects a planktonic source with composition influenced by: (1) communities using depleted $\delta^{13}\text{C}$ carbon sources, (2) active respiration by heterotrophic bacteria, (3) depleted and recycled fossil carbon from natural or anthropogenic inputs, or (4) macrophyte productivity.

Although macrophyte productivity and decaying plant detritus can provide substantial contributions to the OM budget in HRE tidal wetlands (Findlay et al. 1990), our present work indicates that macrophyte OM is not responsible for spring or summertime exports from Tivoli Bays. Other studies have suggested that the food webs of

tidal wetlands are primarily plankton based, rather than supported by living macrophyte biomass (Keough et al. 1996; Boschker et al. 1999). The summertime $\delta^{13}\text{C}_{\text{POC}}$ values for both wetlands were more depleted ($-31.8\text{‰} \pm 1.6\text{‰}$; Table 1) than would be expected for organic matter that was substantially derived from macrophytes ($\delta^{13}\text{C}_{\text{org}}$ of $-26.1\text{‰} \pm 1.4\text{‰}$; Table 2). In addition, the OC:N ratios typical of Tivoli Bays macrophytes, 12.4 ± 1.2 (not including *Typha* at 37; Table 2), was above the overall spring to summer average 9.1 ± 0.9 OC:N of particulates and well above several individual sample collections (≥ 5.2 ; Table 1). In addition to isotopic signatures and elemental ratios, we supported our reasoning with an independent estimate of the vascular plant contributions by characterizing lignin phenols, which revealed fairly distinct levels of Λ_8 in particulate, sedimentary, and direct vascular plant OM pools (Tables 1, 2; Fig. 4). The elevated levels of Λ_8 -POC (8.6 ± 2.2 mg per 100 mg OC) during the October to December time frame indicated that localized macrophyte detritus may contribute substantially to suspended matter composition during fall senescence (Fig. 4), but not during spring and summer ($\geq 50\%$ lower Λ_8 -POC). Furthermore, the lower relative river discharge and no appreciable change in precipitation events during autumn vs. spring (Fig. 2), coupled with the observed Λ_8 -POC values during October to December, contradicts upland runoff as a dominant control on lignin yields in autumn. This is particularly true during November and December, when several observations of Λ_8 -POC exceeded 10 mg per 100 mg OC (Table 1). Such elevated concentrations are within the range of fresh to decaying vascular plant material, but do not exceed other particulate lignin phenol observations (Table 2 and references therein).

Aged terrestrial OM stored in soils or fossil carbon of high percentage organic matter stored in sedimentary rocks (Petsch 2000; Longworth et al. 2007) may be a source of $\delta^{13}\text{C}$ depleted OM to downstream Tivoli Bays productivity (Petsch 2000; McCallister et al. 2004; Longworth et al. 2007). However, the $\delta^{13}\text{C}_{\text{POC}}$ values for both wetlands were more depleted ($-31.8\text{‰} \pm 1.6\text{‰}$; Table 1) than typical for sedimentary rocks ($-29.3\text{‰} \pm 0.6\text{‰}$, Petsch 2000; Table 2), as well as soils and surface sediments ($-28.8\text{‰} \pm 0.7\text{‰}$; Table 2, Longworth et al. 2007) that might be supplied from the upper HRE. Moreover, the $\delta^{13}\text{C}_{\text{POC}}$ was even more depleted than that of bed sediments within the wetlands ($-27.0\text{‰} \pm 1.5\text{‰}$; Table 2). Additionally, if the observed $\delta^{13}\text{C}_{\text{POC}}$ values resulted from bacterioplankton, then $\delta^{13}\text{C}_{\text{POC}}$ would be expected to be more enriched based on the $\delta^{13}\text{C}$ specific to bacterial nucleic acids (-26.6 ± 1.2 , McCallister et al. 2004). Therefore, we largely discounted upland soils, sedimentary rocks, wetland surface sediments, and bacterioplankton as major contributors to the OM pools of these wetlands. This suggests that planktonic communities in each wetland use a depleted carbon source (Fry and Sherr 1984; Keough et al. 1996; Deegan and Garritt 1997), particularly during summer months when $\delta^{13}\text{C}_{\text{POC}}$ values were most depleted (Figs. 4, 6).

Mixing model—Recent studies have shown that IsoSource can be successfully applied to understand the OM

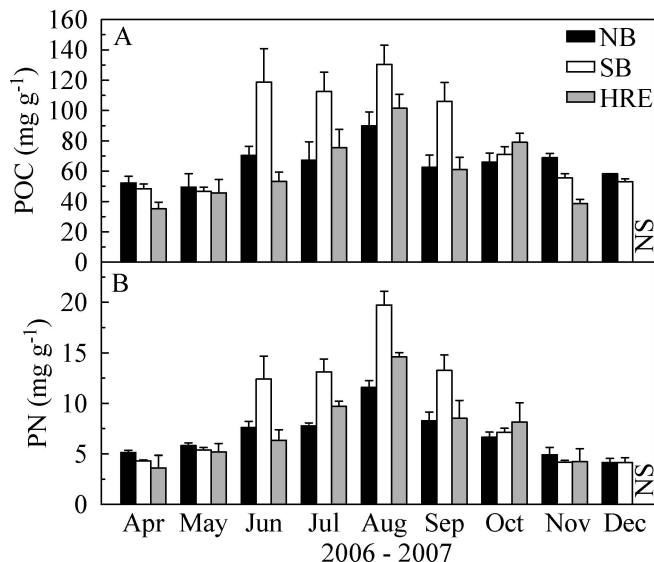


Fig. 7. Monthly bar charts of (A) particulate organic carbon (POC) and (B) particulate nitrogen (PN) depicting the difference between Tivoli Bays and the Hudson River estuary just downstream at Kingston. Riverine values for PN from April to July were estimated based on regression relationship ($\text{PN}_{\text{HRE}} = 0.151 \times \text{POC}_{\text{HRE}} - 1.696$; $R^2 = 0.886$) for the months August to November. NS = not sampled. Error bars represent standard error of the mean measured across a tidal cycle. See Table 1 for detailed error estimates.

contributions of headwater watersheds to the HRE (Longworth et al. 2007). We used IsoSource to obtain an independent estimate of OM provenance for Tivoli Bay wetlands. We limited our end member pools to allochthonous material (ALLOC), assumed to be watershed-derived POC transported to the vicinity of Tivoli Bays by the Hudson River; wetland fine sediments (BAYSED); vegetation growing in the wetland (BAYVEG); and freshwater planktonic sources (FWPLNK), produced either within or in the vicinity of the wetlands. Each OM pool classification, ALLOC, BAYSED, BAYVEG, and FWPLNK, respectively, in IsoSource, is based on the following potential OM sources using $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{PN}}$, N:OC, and total lignin phenols (Λ_8 -POC), as noted in Table 2. In order to test sensitivity and estimate error, IsoSource calculations were completed across the 95% confidence interval of potential end member OM values (Table 2), as long as reasonable values of tolerance (≤ 1) satisfactorily produced an iterative solution (Phillips and Gregg 2001, 2003).

The relative variation of these sources contributing to the mixed OM pool for SB on a mass and volumetric basis is depicted in Fig. 8, with the potential variation and error shown in Table 3. We chose only to highlight the composition of OM pools for SB based on earlier text and depictions that indicated this wetland underscored maximum variation in OM composition (Figs. 3–7). The relative contribution as a percentage ranged from ALLOC (1% to 72%), BAYSED (2% to 41%), BAYVEG (1% to 42%), and FWPLNK (4% to 86%), respectively (Table 3). Our results indicated high temporal variability in OM sources in the Tivoli Bays system, from $\sim 70\%$ river-borne

Table 2. Compositional indices of potential organic matter sources to Tivoli Bays and those used in the mixing model. Sources include material exchanged in the Hudson River estuary, as well as end members noted in other relevant studies.

OM source(s)	OC : N	$\delta^{13}\text{C}_{\text{org}}$ (‰)	$\delta^{15}\text{N}$ (‰)	Λ_8 lignin (mg per 100 mg OC)	Reference(s)
Background literature:					
Vascular plants—terrestrial	18.8 to 39.9	-24.6 to -30.0	-2.0 to 12.0		Fry and Sherr 1984; Deegan and Garritt 1997; Cloern et al. 2002
Vascular plants—submerged, emergent, floating	6.9 to 46.2	-21.3 to -28.8	5.4 to 14.4		Fry and Sherr 1984; Deegan and Garritt 1997; Cloern et al. 2002
Sediments—riverine to coastal	11.8 to 32.1	-22.7 to -26.1		0.4 to 5.2	Hedges et al. 1984
Sediments—estuarine (0–5 cm)	12.8 to 25.6			1.3 to 4.2	Louchouart et al. 1997
Sediments—freshwater to mesohaline bay (0–5 cm)	4.0 to 28.0	-22.7 to -28.5		1.2 to 14.0	Goni et al. 2003
Sediments—field, floodplain, stream channel		-25.4 to -27.5		1.3 to 5.0	Dalzell et al. 2005
POM—freshwater	6.9 to 9.0	-25.9 to -30.0	6.4 to 7.9		Raymond and Bauer 2001; McCallister et al. 2004, 2006
POM—riverine and tributaries	6.8 to 29.6	-26.1 to -32.4		1.0 to 22.5	Hedges et al. 1986
POM—riverine	6.9 to 16.6	-18.5 to -26.4		0.5 to 26.9	Hopkinson et al. 1998; Onstad et al. 2000
POM—riverine baseflow to flood conditions		-26.9 to -32.0		0.2 to 1.8	Dalzell et al. 2005
POM—riverine and tributaries	7.2 to 13.6	-19.7 to -26.9	4.5 to 11.6	0.8 to 3.2	Gordon and Goni 2003; Bianchi et al. 2007
POM—freshwater to brackish	6.0 to 32.7	-21.9 to -30.4	2.4 to 14.7		Hoffman and Bronk 2006
Phytoplankton—freshwater	5.2 to 8.0	-27.3 to -30.0	2.4 to 7.5		Cloern et al. 2002
Phytoplankton—freshwater wetland		-30.3 to -32.6	2.3 to 3.8		Keough et al. 1996; Keough et al. 1998
Specific to the Hudson River estuary:					
Vascular plants—submerged, floating, emergent		-21.5 to -27.8	5.1 to 11		Caraco et al. 1998; McCallister et al. 2004
Vascular plants—rooted standing <i>T. angustifolia</i>	36.8 to 37.2	-27.5 to -27.6	8.6 to 8.8	50.3 to 56.7	This study
Vascular plants—rooted floating <i>T. natans</i>	12.5 to 13.1	-26.1 to -26.4	7.5 to 7.7	4.7 to 4.9	This study
Vascular plants—emergent <i>N. advena</i>	12.9 to 13.6	-25.9 to -26.1	5.6 to 6.0	8.8 to 12.5	This study
Vascular plants—submerged <i>Vallisneria americana</i>	9.9 to 12.3	-23.9 to -24.0	8.2 to 8.6	0.6 to 0.9	This study
Allochthonous—sediments, maple/oak leaves		-23.8 to -28.8	-3.6 to 6.1		Caraco et al. 1998
Rock—sedimentary	1.0 to 18.0	-25.2 to -32.2			Petsch 2000; Longworth et al. 2007
Soils/sediments—surface/forest litter, streambeds	7.0 to 26.0	-18.0 to -29.7*			Longworth et al. 2007
Sediments—Tivoli Bays (0–3 cm)	6.8 to 17.8	-24.0 to -29.9	4.2 to 5.8	4.8 to 21.6	This study
POM—tidal, upper Hudson, and tributaries	1.5 to 19.6	-26.1 to -33.3	2.8 to 6.0		Raymond and Bauer 2001; McCallister et al. 2004; Raymond et al. 2004; Longworth et al. 2007
POM—river-km 146, monthly August to November	8.1 to 11.3	-29.7 to -31.1	1.8 to 11.5	2.6 to 13.4	This study
POM—Tivoli Bays; details noted in Table 1	5.2 to 22.8	-27.2 to -34.7	-3.6 to 13.6	0.8 to 25	This study
Phytoplankton		-24.2 to -31.1	6.2 to 10.8		Caraco et al. 1998; McCallister et al. 2004
ALLOC:†	8.1 to 19.9‡	-26.8 to -29.7	-1.7 to 4.2	0.98 to 3.7	This study
BAYSED:†	9.2 to 11.1‡	-25.9 to -27.7	4.7 to 5.1	3.4 to 9.6	This study
BAYVEG:†	7.8 to 10.4‡	-24.2 to -27.0	6.1 to 8.8	9.4 to 15.8	This study
FWPLNK:†	5.4 to 7.5‡	-29.2 to -36.6	6.8 to 9.6	0.0	This study

* Extreme outlier (-46.7‰) removed.

† 95% confidence interval for IsoSource end member.

‡ Used reciprocal (N : OC) in mixing model.

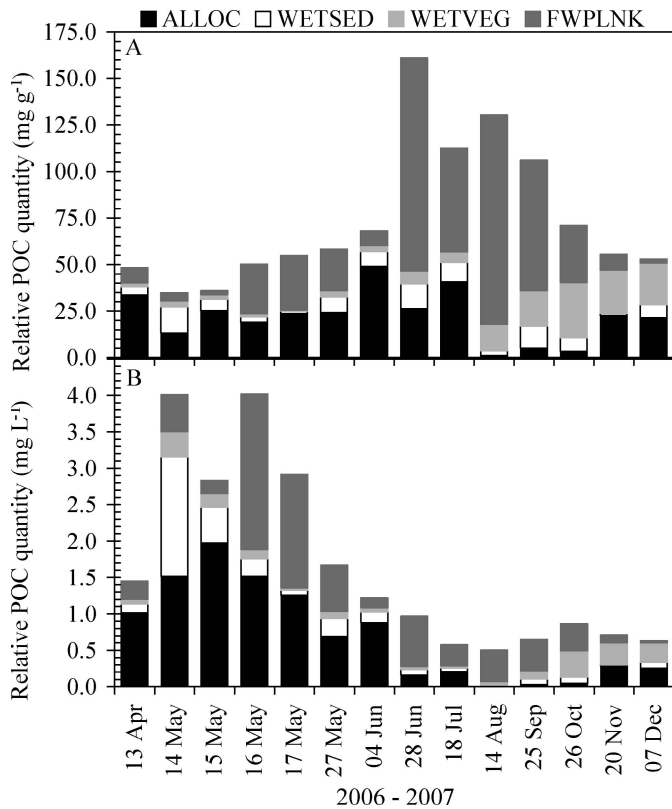


Fig. 8. Seasonal shifts in organic matter pool contribution shown (A) on a mass basis in units of mg g^{-1} and (B) on a volumetric basis in units of mg L^{-1} at Tivoli SB. Relative quantities based on percentage contributions derived from IsoSource using $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, N:OC, and the sum of lignin phenols (A_8 -POC). ALLOC, allochthonous material; BAYSED, sediments within SB; BAYVEG, vegetation within SB; FWPLNK, freshwater plankton. SB highlights the greatest deviation and shifts in organic matter (Figs. 3–7); therefore for clarity we do not show NB contributions. See Table 1 for sampling details, Table 3 for error estimates.

allochthonous OM to 86% freshwater planktonic and microbial OM. Clearly, the importance of terrestrial OM inputs from the upper watershed are highlighted in April and May (Fig. 8), as accentuated in Howarth et al. (1996) and further corroborated by McCallister et al. (2004). In addition, our mixing model showed that autochthonous productivity dominated over allochthonous productivity on both a mass and volumetric basis from late May until October (Fig. 8). This observed dominance of autochthonous OM, coupled with the strong shifts in OM composition that occur during this time frame (Figs. 5–7), suggest that SB, and to a lesser degree NB, are highly productive generators of OM, predominately of planktonic or microbial origin. Overall, the annual trends might be divided into two main stages based on allochthonous inputs (spring) and autochthonous productivity (summer) with strong episodic pulses of OM in response to mixing events (Fig. 8).

Individual hydrometeorological events appear capable of causing dramatic shifts in OM composition. Our data sets included strong winds on 14 May and 15 May 2007 and

Table 3. Estimated relative contribution of major OM pool exchanges between Tivoli South Bay and the freshwater tidal portion of the Hudson River estuary. ALLOC, allochthonous material; BAYSED, sediments within SB; BAYVEG, vegetation within SB; and FWPLNK, freshwater plankton. Error propagated standard deviation shown in parentheses. See Table 1 for sample details.

Date	Relative percentage contribution				Relative POC quantity (mg g^{-1})				Relative POC quantity (mg L^{-1})			
	ALLOC	BAYSED	BAYVEG	FWPLNK	ALLOC	BAYSED	BAYVEG	FWPLNK	ALLOC	BAYSED	BAYVEG	FWPLNK
13 Apr	69.7(6.9)	8.8(6.5)	4.6(3.5)	16.8(3.5)	33.8(5.4)	4.3(3.2)	2.2(1.7)	8.1(2)	1.01(0.44)	0.13(0.11)	0.07(0.06)	0.24(0.12)
14 May	37.7(11.8)	41(18)	8.7(7.5)	12.6(3.9)	13.1(4.2)	14.3(6.4)	3(2.6)	4.4(1.4)	1.51(0.5)	1.64(0.74)	0.35(0.3)	0.51(0.17)
15 May	69.5(11.4)	17.5(11.6)	6.7(4.9)	6.3(4)	25.1(4.6)	6.3(4.2)	2.4(1.8)	2.3(1.5)	1.97(0.87)	0.5(0.39)	0.19(0.16)	0.18(0.14)
16 May	37.7(5.6)	6.1(5)	3.1(2.8)	53.2(3.3)	18.9(3.7)	3.1(2.5)	1.6(1.4)	26.7(3.9)	1.51(0.4)	0.24(0.21)	0.12(0.12)	2.14(0.48)
17 May	43.1(2.5)	2.4(2.2)	1.1(1.2)	53.5(1.4)	23.6(3.1)	1.3(1.2)	0.6(0.7)	29.3(3.5)	1.25(0.08)	0.07(0.06)	0.03(0.03)	1.56(0.06)
27 May	41.4(11.7)	14.8(10.3)	5.8(4.4)	38(7.6)	24.1(7.6)	8.6(6.1)	3.4(2.6)	22.1(5.4)	0.69(0.31)	0.25(0.19)	0.1(0.08)	0.63(0.26)
04 Jun	71.9(9.6)	11.8(9.1)	4.8(3.9)	11.5(6.8)	48.9(15)	8(6.6)	3.3(2.8)	7.8(5.1)	0.88(0.24)	0.14(0.12)	0.06(0.05)	0.14(0.09)
28 Jun	16.3(7.5)	8.3(6.7)	4.4(3.7)	71.1(4.5)	26.2(17.3)	13.4(12.5)	7.1(6.8)	114.4(54.7)	0.16(0.08)	0.08(0.07)	0.04(0.04)	0.69(0.13)
18 Jul	36.2(8.5)	9.4(7.7)	4.9(4.2)	49.5(5)	40.7(15.5)	10.6(9.2)	5.5(5)	55.7(17.7)	0.21(0.06)	0.05(0.04)	0.03(0.02)	0.28(0.05)
14 Aug	0.9(1)	2(1.9)	10.8(8.7)	86.3(7.9)	1.2(1.3)	2.6(2.6)	14.1(11.8)	112.5(28.8)	0(0.01)	0.01(0.01)	0.05(0.05)	0.43(0.15)
25 Sep	4.7(3.6)	11.4(7.6)	18(5.3)	66(3.1)	5(4.1)	12.1(8.8)	19.1(7.9)	69.9(20.6)	0.03(0.02)	0.07(0.05)	0.12(0.04)	0.43(0.06)
26 Oct	4.8(3.8)	10.4(7.7)	41.7(10.2)	43.1(9.1)	3.4(2.8)	7.4(5.7)	29.6(9.8)	30.6(9.4)	0.04(0.04)	0.09(0.08)	0.36(0.18)	0.37(0.18)
20 Nov	40.5(1.3)	2.2(2.2)	42.3(1)	15(1)	22.5(2.8)	1.2(1.2)	23.5(2.9)	8.3(1.1)	0.29(0.13)	0.02(0.02)	0.3(0.13)	0.11(0.05)
07 Dec	40.5(6.5)	13.4(10.6)	42.2(5)	3.9(1.7)	21.4(3.9)	7.1(5.6)	22.3(3.3)	2.1(0.9)	0.25(0.05)	0.08(0.07)	0.26(0.05)	0.02(0.01)

rainfall just prior to 04 June 2007 (Fig. 2). The OM relative contributions during the wind event of 14 May to 15 May suggest that resuspended ALLOC (estuarine) and BAYSED (internal sediments) probably resupply the water column with POC and other nutrients. This appeared to trigger substantial changes in composition, as shown in the 16 May and 17 May FWPLNK levels (Fig. 8). This same “trigger” occurred during the rainfall event just prior to 04 June, with subsequent OM pool response as indicated during 28 June (Fig. 8). Additionally, the importance of macrophyte detritus export from SB is depicted in elevated total lignin levels (Fig. 4) and OM relative contributions ($\sim 42\%$) from October to December (Fig. 8). Overall, these OM pool estimates clearly indicated that fringing wetlands may contribute compositionally distinct OM for incorporation into food webs and biogeochemical cycles of the HRE.

The results of this mixing model quantified the role of tidal wetlands in the HRE OM budget, offering a refined estimate of mid-HRE OM pools (McCallister et al. 2004). We do note that our sampling did not include periods of peak watershed runoff, such as those occurring during early spring in the HRE (i.e., major terrestrial, or “ALLOC” inputs). During our “ice-free” sample time periods, allochthonous and planktonic contributions to the exchanges between Tivoli Bays and the HRE are nearly equal, with a mean of 37% and 38%, respectively. However, allochthonous OM throughout the HRE watershed and its transport downstream through the drainage basin likely dominates the overall mass flux of carbon during the spring snow melt.

Radiocarbon dating of Hudson River OM has shown the relative age of particulate OM decreases while proceeding downstream (Cole and Caraco 2001; Raymond and Bauer 2001). Our work lends support to the notion that younger carbon generated in wetlands fringing the HRE could dilute the old fractions, resulting in the observed age decline. The major fate of this “fresh” organic matter has been suggested to be bacterial degradation (Findlay et al. 1992, 1998; Del Giorgio and Pace 2008). If so, our results underscore the significance of fringe wetlands in influencing OM proportions and altering OM composition in the HRE, substantiating that these ecosystems may play a major role in HRE biogeochemical cycles.

Potential flux from Tivoli Bays and fringe wetlands in the HRE—The Tivoli Bays represent two of the larger fringing wetlands along the HRE (Arrigoni et al. 2008). Dye release studies on NB have shown that water exchanges as a “plug” into and out of the innermost reaches of the wetlands within the bay (Carr et al. 2004; Arrigoni et al. 2008). In this work, we showed that suspended matter within this plug undergoes striking alteration while in residence in Tivoli Bays, returning OC-rich ($\leq 247.6 \text{ mg g}^{-1}$), ^{13}C depleted POC (≥ -34.7) back to the HRE (Figs. 5–7; Table 1). Our results established that fringe wetlands of the HRE do generate substantial quantities of compositionally unique POC and appear to flush this material during ebb tides. On a tidally averaged volumetric basis, our results suggest that Tivoli Bays may exchange $1.1 \pm 0.8 \text{ mg L}^{-1} \text{ tide}^{-1}$ POC with the HRE (Table 1), resulting in an average net export of $\sim 0.2 \text{ mg L}^{-1} \text{ tide}^{-1}$ POC (Figs. 5, 7). We used the average

ebb vs. flood POC levels observed each month multiplied by the tidal exchange values from Findlay et al. (1998) (NB = $5 \times 10^8 \text{ L tide}^{-1}$, SB = $1 \times 10^9 \text{ L tide}^{-1}$), as validated by our velocity observations, to estimate the POC flux for the Tivoli Bays ecosystem. Overall, we estimated that NB and SB yielded a net export of 110 Mg yr^{-1} and 56 Mg yr^{-1} POC, respectively, or $63 \text{ Mg km}^{-2} \text{ yr}^{-1}$ POC combined (area = 2.65 km^{-2}). Taken in the context of total tidal freshwater wetland area in the HRE (29 km², Kiviat et al. 2006), we estimate a net export of $\sim 1800 \text{ Mg yr}^{-1}$ POC from these ecosystems into the HRE, which is roughly equivalent to the estimated carbon flux by Howarth et al. (1996) arrived at via an independent approach. Although this work highlighted the complex interactions between wetlands and main stem estuary within the HRE, in a broader context, our results underscore the effects that riparian zones may have on the particulate biogeochemistry of aquatic ecosystems.

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