

Interannual variation in stable carbon and nitrogen isotope biogeochemistry of the Mattaponi River, Virginia

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Abstract

Seasonal and interannual variation of the stable carbon (C) and nitrogen (N) isotope composition of suspended particulate organic matter (POM) was measured in the brackish and tidal freshwater regions of the Mattaponi River, a tributary of the York River, Virginia, and a pristine end member on a continuum of anthropogenic modification within Chesapeake Bay. A principal components analysis indicated that seasonal variation was related to physical mixing and river discharge. Freshwater POM had high C:N (>12), depleted particulate organic carbon isotopic composition ($\delta^{13}\text{C}_{\text{POC}}$, -26‰ to -30‰), and depleted particulate nitrogen isotopic composition ($\delta^{15}\text{N}_{\text{PN}}$, 2‰ – 10‰) compared to brackish water POM, which had lower C:N and enriched $\delta^{13}\text{C}_{\text{POC}}$ (-24‰ to -27‰) and $\delta^{15}\text{N}_{\text{PN}}$ (7‰ – 15‰). During high discharge events, the $\delta^{13}\text{C}_{\text{POC}}$ was enriched, the $\delta^{15}\text{N}_{\text{PN}}$ depleted, and the C:N high relative to low discharge periods, indicating a large contribution from terrestrial-derived material. Within tidal freshwater, POM was comprised of humic-rich sediment, vascular plant matter, and phytoplankton produced in situ. Nonconservative mixing behavior was observed. Endogenously produced phytoplankton increased POC concentrations in tidal freshwater and oligohaline portions during base flows. Where estuarine and riverine POM mixed, the isotopic composition of the POM was homogenized, blurring source-specific characters observed upriver and thereby emphasizing the need to characterize the freshwater end member of estuaries carefully in order to identify POM sources.

In estuaries, identifying the origin of particulate organic matter (POM) is difficult because POM is received from multiple sources, including riparian vegetation, adjacent marsh vegetation, submerged and emergent aquatic vegetation and associated epiphytes, and phytoplankton produced in situ. Early research using the stable isotope composition of estuarine POM to identify its dominant origins and fates led investigators to conclude that estuarine phytoplankton and terrestrial material were the major contributors to estuarine organic matter (OM; dissolved and particulate fractions) and that these sources

fueled the heterotrophic food webs within estuaries (Parker 1964; Haines 1976). Since that time, research has revealed that many processes may contribute to the stable isotope composition of POM in aquatic ecosystems, potentially complicating the interpretation of stable isotope data. For example, the isotopic composition of the POM pool can be altered by the decomposition of vegetation due to the preferential removal of select compounds (Benner et al. 1987) or by short-term changes in the concentration and isotopic composition of nutrient pools, which can affect phytoplankton fractionation (Cifuentes et al. 1988). In complex ecosystems, such as estuarine–riverine complexes, overlapping stable isotope compositions and seasonal variability will further hinder identification of sources (e.g., Cloern et al. 2002). Despite these difficulties, it has been possible to infer major biogeochemical processes and sources of OM using stable isotopes, particularly when these processes are tracked through an entire season (e.g., Cifuentes et al. 1988; Hellings et al. 1999) or watershed (e.g., Cai et al. 1988).

At the watershed scale, differences exist between the stable carbon isotope composition ($\delta^{13}\text{C}$) of upland vegetation and marine phytoplankton because these plants utilize different carbon (C) pools that have distinct isotopic compositions (Mook and Tan 1991). The $\delta^{13}\text{C}$ of total dissolved CO_2 (DIC) in the ocean is about 0‰ (Mook et al. 1974) because of the equilibrium fractionation of atmospheric CO_2 ($\delta^{13}\text{C} = -7\text{‰}$; Deines 1980) across the atmosphere–ocean boundary. The isotope fractionation by C_3 plants is about -21‰ , which results in a marine phytoplankton $\delta^{13}\text{C}$ of about -21‰ (Tan and Strain 1983), though fractionation can vary as a result of DIC concentration, phytoplankton growth rate, and nutrient availability (O’Leary 1981; Farquhar et al. 1982; Rau et al. 1982). In contrast, riparian plants that utilize the C_3 pathway have a $\delta^{13}\text{C}$ of about -28‰ (Smith and Epstein

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1971). In freshwater systems where the DIC $\delta^{13}\text{C}$ is highly depleted ($< -10\text{‰}$), phytoplankton may also be distinguished from riparian vegetation.

Variability in the stable nitrogen isotope composition ($\delta^{15}\text{N}$) of POM has been attributed to both the POM sources and a number of biogeochemical processes that influence the $\delta^{15}\text{N}$ of phytoplankton. Terrestrial woody matter and soils have a $\delta^{15}\text{N}$ of 0–6‰, which may be similar to freshwater phytoplankton (3–7‰) but less than estuarine and marine phytoplankton (7–9‰; Deegan and Garritt 1997). This may allow discrimination between these sources. The $\delta^{15}\text{N}$ of POM, however, can be altered indirectly by changes in the isotope value of nitrogen (N) substrates due to preferential uptake of isotopically light N by phytoplankton (Wada and Hattori 1978; Cifuentes et al. 1988), nitrification, and denitrification (Mariotti et al. 1981) or altered directly by microbially mediated degradation (Miyake and Wada 1971; Altabet 1988).

We quantified the C and N stable isotope composition of suspended POM in the tidal freshwater and oligohaline portions of the Mattaponi River, a secondary tributary to Chesapeake Bay, Virginia, from spring through fall over 2 yr (2003 and 2004). This region of estuaries merits attention because the interactions between POM sources (e.g., riparian vegetation, in situ production, and estuarine OM) and physical forces (freshwater outflow, physical mixing) result in spatially and temporally dynamic sources of POM. In contrast to the lower estuary, which has been the subject of much research, the causes of variability in the isotopic composition of POM within the tidal freshwater region are relatively unknown. The Mattaponi River is a valuable study site because this coastal plain tributary has a small anthropogenic influence in its watershed, indicated by the absence of a dam or other flow-regulating structure and its intact wetlands and riparian forests. A multiyear study was used to characterize POM variability at both the seasonal and the interannual scales, particularly with respect to variable hydrography. The objectives of this study were (1) to quantify spatial and temporal variability of the C and N stable isotope composition of suspended POM and (2) to identify the origins of suspended POM based on the stable isotope composition and other chemical characteristics.

Methods

Study site—The Mattaponi River is one of two major tributaries to the York River, Virginia, a brackish, partially mixed, coastal plain tributary located in the southern end of the Chesapeake Bay (Fig. 1). The York River estuary is net heterotrophic; its metabolism is supported, in part, by OM received from its two tributaries, the Mattaponi and Pamunkey rivers (Raymond et al. 2000; Neubauer and Anderson 2003). The Mattaponi River is almost entirely fresh and is approximately 85 km long, flowing from the foothills of Virginia's Piedmont region (2,274-km² watershed); about 61% of the watershed lies in the coastal plain. The watershed is predominantly rural; 67% of the watershed is forest, 15% is cropland, 7% is grassland, 8% is wetland, and only 1% is urban (Bilkovic et al. 2002).

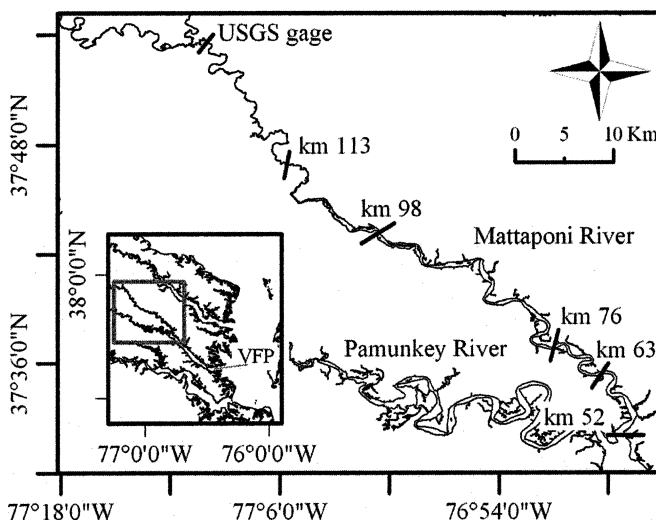


Fig. 1. The Mattaponi and Pamunkey rivers, Virginia. Bars indicate sampling areas. Insert shows location of these rivers in relation to the York River and Chesapeake Bay. Marker indicates location of the VIMS's ferry pier (VFP), near the mouth of the York River. The mouth of the York River is at km 0, and the head of tide is at about Mattaponi River km 115.

During spring, Mattaponi River discharge is high ($> 35 \text{ m}^3 \text{ s}^{-1}$), and the residence and turnover times are short (44.8 and 13.5 d, respectively), whereas during mean discharge ($14.4 \text{ m}^3 \text{ s}^{-1}$), residence and turnover times are long (88.4 and 28.5 d, respectively), indicative of the strong influence discharge exerts on the residence time (Shen and Haas 2004). Although the Mattaponi River is generally fresh above km 60 to 75, incursion of brackish water can extend above km 85 during extended periods of low discharge, whereas freshwater can extend below km 54, into the York River, during high discharge. The head of tide is located at about river km 115; within the Mattaponi River, the mean tide range varies from 0.9 m at km 52 (river mouth) to 1.2 m at km 98. The location of the salt wedge shifts 4–5 km on an ebb cycle; this distance is related to the tidal excursion, which varies in relation to discharge (Bilkovic et al. 2002).

Field sampling—During 2003, surface water from five stations in the tidal freshwater portion of the Mattaponi River was sampled biweekly from May to October (Fig. 1). Initially, sampling occurred at three stations between river km 76 and 113; however, the sampling area and number of stations increased after 06 June (four stations, from river km 52 to 113) because the salt wedge was located further downriver as a result of high discharge. In 2004, four stations were sampled between river km 52 and 113 as well as a single station located at the Virginia Institute of Marine Science (VIMS) ferry pier near the mouth of the York River (km 7). Stations were chosen in relation to the geomorphology and salinity of the Mattaponi River (Table 1). In order to avoid sampling the same water mass twice during a tidal cycle, the distance between stations was always greater than the tidal excursion (Table 1; Bilkovic et al. 2002).

Table 1. Description of stations in the Mattaponi River. The tidal excursion, the distance a particle is estimated to travel during a tidal cycle, is from Bilkovic et al. (2002), estimated for average May discharge (1942–2000). York River mouth is located at river km 0.

Station	Location (km)	Channel (width×depth)	Characteristics	Tidal excursion (km)
Mattaponi River mouth	52	~1,000 m×11 m	Extensive salt marshes	4.0
Lower tidal freshwater	63, 76	300–500 m×11 m	Location of the salt wedge	5.5, 5.0
Central tidal freshwater	98	200–400 m×3 m	Vegetated islands begin to disappear	3.5
Upper tidal freshwater	115	50–100 m×2 m	River rapidly narrows	4.5

The stations were sampled in the center of the river channel from a vessel or immediately adjacent to the channel from a pier. To the best of our ability, stations were sampled on a similar tidal cycle on a given date. Surface water was collected using a 5-L Niskin bottle deployed to 1-m depth. Replicate surface water samples were analyzed for POM (mg L⁻¹, $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{PN}}$, atomic C:N), chlorophyll *a* (Chl *a*: $\mu\text{g L}^{-1}$), and dissolved inorganic carbon (DIC: $\delta^{13}\text{C}_{\text{DIC}}$). Temperature and salinity profiles were measured with a YSI model 600 QS sonde. Freshwater stations (salinity <1) were always well mixed.

For POM and Chl *a* analysis, surface river water was prefiltered with a 125- μm sieve and filtered onto a pre-combusted Whatman GF/F filter (25-mm diameter; 500°C for 2 h). The POM filters were rinsed with 10% HCl to remove carbonates, rinsed with deionized water, placed in a sterile test tube, and then stored on ice during transport to the laboratory for drying. This method results in similar particulate organic carbon (POC) and particulate nitrogen (PN) mass, similar $\delta^{15}\text{N}_{\text{PN}}$, but slightly more enriched $\delta^{13}\text{C}_{\text{POC}}$ (+0.3‰) compared to vapor-phase acidification (Lorrain et al. 2003). The Chl *a* filters were placed in a sterile test tube, wrapped in aluminum foil, and frozen at -20°C for subsequent analysis.

We used a gas evolution technique for DIC (ΣCO_2) analysis (Atekwana and Krishnamurthy 1998). Samples of river water were injected through a sterile 0.2-micron Supor filter into a sterile vacuum tube (either 25-mL Vacutainer septum tubes [Becton Dickinson and Company] or 10-mL Exetainer septum tubes [Labco Limited]) that contained 0.5 mL 85% phosphoric acid. Samples were placed on ice while in the field and refrigerated prior to analysis.

Laboratory analysis—The POM samples were dried at 45°C for 24 h within 8 h of collection and stored in a desiccator prior to shipping. All stable isotope samples were analyzed with a Europa Hydra 20-20 continuous flow isotope ratio mass spectrometer (University of California–Davis Stable Isotope Facility). Before isotope analysis, the DIC samples were concentrated with an ANCA TGII trace gas concentration unit, and the POM samples were combusted with an ANCA GSL gas purification module and elemental analyzer. Stable isotope ratios were calculated as $\delta\text{X}: \delta\text{X} = (R_{\text{sample}}/R_{\text{standard}} - 1) \times 10^3$, where X is the stable isotope of C or N, *R* is the ratio of heavy:light stable isotopes, and Pee Dee Belmrite and air were the standards for $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$, respectively. The analytical error, measured using replicate reference material, was $\pm 0.13\text{‰}$ for DIC and $< \pm 0.1\text{‰}$ for POC and PN.

In 2003, the filters collected for pigment analysis were sonicated, extracted in 90% acetone, and then analyzed on a Shimadzu UV-1601 model spectrophotometer for Chl *a* and pheophytin *a* according to Standard Methods (1989). Data for 2003 are unavailable because the acetone failed to extract the pigment effectively. In 2004, filters were extracted for 24 h in 8 mL dimethyl sulfoxide and acetone extractant and then analyzed on a Turner Designs Flourimeter according to the U.S. Environmental Protection Agency (1997).

External data—River discharge (Q) data were obtained from the U.S. Geological Survey (USGS) gauge on the Mattaponi River near Beulahville, Virginia (#01674500). The gauge is located approximately 20 river km above the head of tide (Fig. 1); we used the data to represent discharge variation because no major tributaries enter the Mattaponi River between the gauge and the river mouth. Water quality data (temperature, specific conductivity, salinity, dissolved oxygen [DO], pH, turbidity, and Chl *a*) were obtained from two YSI 6600 EDS sondes in the Mattaponi River stationed at km 60 and 98 (Virginia Department of Environmental Quality [VADEQ] unpubl. data). The sonde data, obtained every 15 min, were averaged from 00:00 to 23:59 h to obtain a daily average. Additionally, Chl *a* (extracted; same methods as in this study), NO_3^- , NO_2^- , and NH_4^+ concentrations along the river axis (km 52–101) were obtained from monthly cruises (May–October), during which surface water was sampled every 5–6 km (VADEQ unpubl. data). All VADEQ metadata are located at <http://www.chesapeakebay.net/wqual.htm>.

Conservative mixing model—Samples were obtained from the estuarine end member in 2004 (VIMS ferry pier), and thus it was possible to apply a conservative mixing model to suspended POC data (2004 data only) to identify nonconservative dynamics (Cai et al. 1988).

$$\delta^{13}\text{C}_{\text{conservative}} = (K_1S - K_2)/(K_3S - K_4) \quad (1)$$

$$K_1 = C_a\delta^{13}\text{C}_a - C_b\delta^{13}\text{C}_b \quad (2)$$

$$K_2 = S_bC_a\delta^{13}\text{C}_a - S_aC_b\delta^{13}\text{C}_b \quad (3)$$

$$K_3 = C_a - C_b \quad (4)$$

$$K_4 = S_bC_a - S_aC_b \quad (5)$$

In the model, *a* and *b* denote the respective fresh and marine end members, *C* is the POC concentration, $\delta^{13}\text{C}$ is the measured $\delta^{13}\text{C}_{\text{POC}}$, and *S* is the salinity, measured in the marine end member from the VIMS ferry pier (YSI 6600 EDS sonde). Samples from the marine end member were unavailable for May and June 2004. We used the average values at the VIMS ferry pier (km 7) in July to represent May and June ($\delta^{13}\text{C}_{\text{POC}} = -22.2\text{‰}$, $[\text{POC}] = 1.5 \text{ mg L}^{-1}$) because the salinity at the VIMS ferry pier was similar between May–June and July and the $\delta^{13}\text{C}_{\text{POC}}$ at the Mattaponi River mouth was similar between May–June and July. Mixing curves were developed for three temporal periods, May–June, July, and August–October, because there was a distinct shift in the $\delta^{13}\text{C}_{\text{POC}}$ of the freshwater end member between June and July and a distinct climate shift between July and August–October. We used the average of all cruises during the time block to represent the respective end members in the model.

Statistical analysis—We performed a principal components analysis (PCA) on the 2004 data from the Mattaponi River (km 52–113) using the correlation matrix of the seven primary variables: $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{PN}}$, $\delta^{13}\text{C}_{\text{DIC}}$, $\text{C}:\text{N}_{\text{POM}}$, Chl *a*, salinity, and river discharge. We performed a similar analysis on data from 2003, though Chl *a* could not be included. Discharge was estimated by averaging the recent daily discharge over the same time period that a water mass would travel about 2 km, or a river reach (Shen and Haas 2004); for samples obtained at low discharge (ca. $4 \text{ m}^3 \text{ s}^{-1}$), the daily average discharge was averaged for the previous 10 d; for samples obtained at medium discharge (ca. $14 \text{ m}^3 \text{ s}^{-1}$), we averaged the previous 5 d; and for samples obtained at high discharge (ca. $38 \text{ m}^3 \text{ s}^{-1}$ or higher), we averaged the previous 2 d. Discharge data were obtained from the USGS gauge, and discharge was the same for all stations on a sampling date.

Results

Water chemistry—In 2003, river discharge was unusually high from April through June (discharge was $\geq 95\%$ of historical values throughout June and early July), eventually returning to base flow by late August (Fig. 2). From April to September, DO was undersaturated (ca. 50–80%), and the average daily pH ranged between 6 and 7. On 19 September, tropical storm Isabel entered Chesapeake Bay. Discharge subsequently increased to $106 \text{ m}^3 \text{ s}^{-1}$ on 25 September, followed by a steep decline in DO and pH (Fig. 2). Chl *a* concentrations were low in mid-June, during high discharge, and peaked at about $20 \mu\text{g L}^{-1}$ in July and August (Fig. 3). Chl *a* concentrations were highest toward the river mouth, with additional peaks within tidal freshwater. The NH_4^+ concentration was about $1 \mu\text{mol L}^{-1}$ during high discharge and declined during the bloom period. Generally, the concentration of NO_3^- was higher than that of NH_4^+ and decreased from upriver to downriver, though during July NH_4^+ was elevated at the river mouth, suggesting high denitrification rates (Fig. 3C).

In 2004, a spring freshet was followed by high summer base flow, though less than in 2003 (Fig. 2). The average

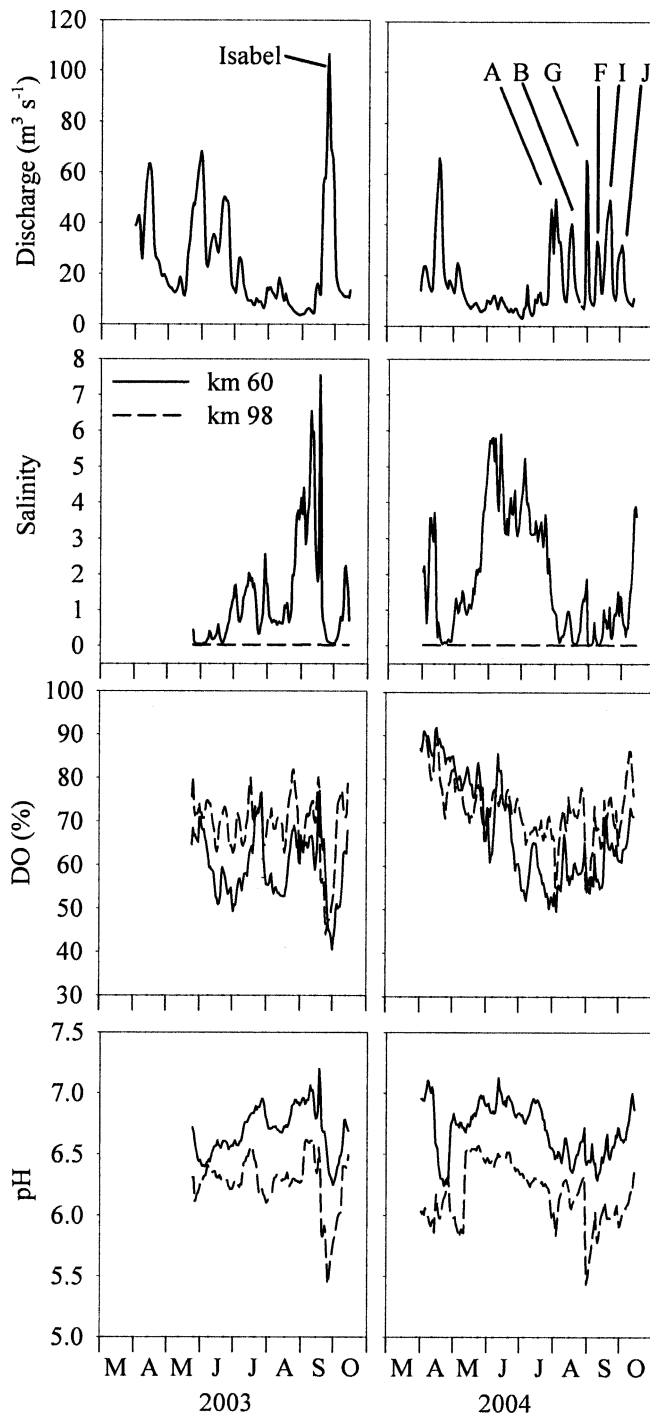


Fig. 2. Seasonal variation in average daily discharge, salinity, dissolved oxygen (DO), and pH for the Mattaponi River in 2003 and 2004. Water quality data were obtained at river km 60 and 98. Labels indicate discharge events associated with the remnants of tropical hurricanes (A, Alex; B, Bonnie; F, Frances; G, Gaston; I, Ivan; J, Jeanne; remnants from Hurricane Gaston arrived before those from Hurricane Floyd).

daily salinity, DO, and pH were all slightly higher in 2004 compared to the spring and summer of 2003. Declines in DO and pH were observed after peak discharge associated with Hurricanes Alex ($50.1 \text{ m}^3 \text{ s}^{-1}$) and Gaston

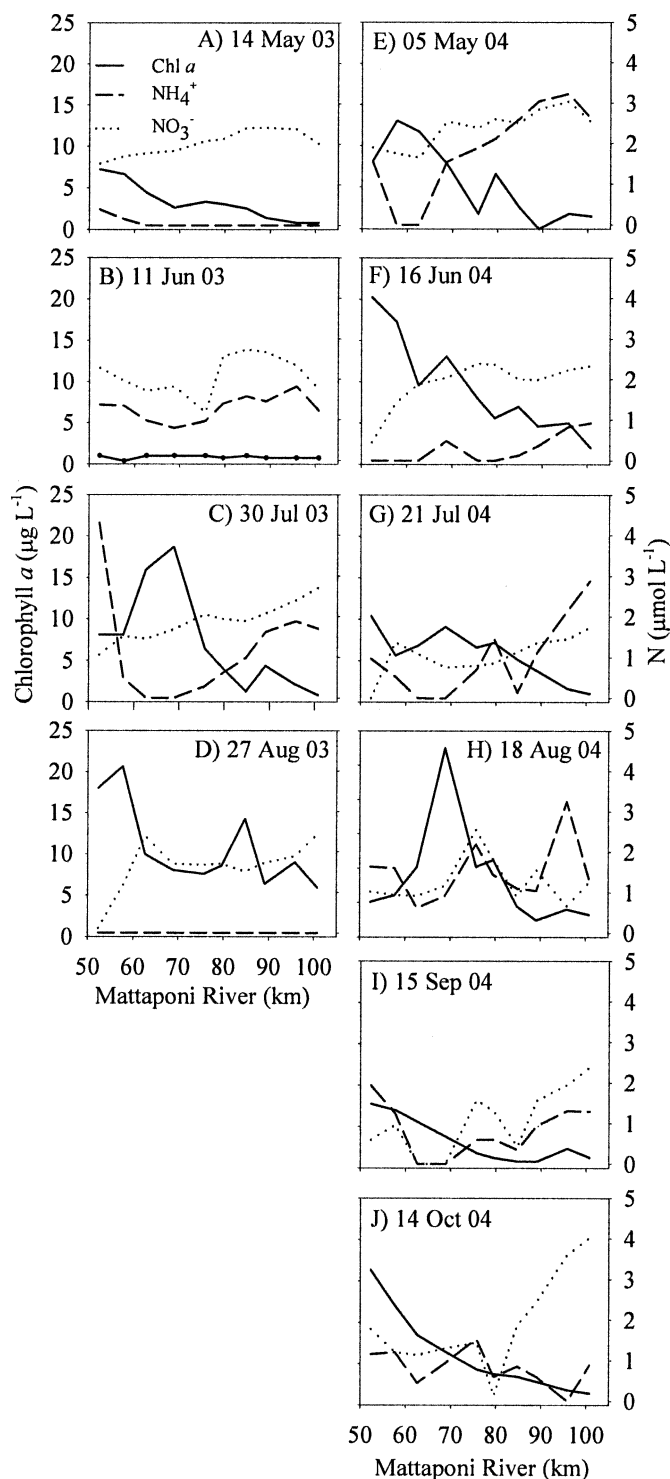


Fig. 3. Seasonal variation in Chl *a*, NO_3^- , and NH_4^+ concentrations along the Mattaponi River on (A) 14 May 2003, (B) 11 June 2003, (C) 30 July 2003, (D) 27 August 2003, (E) 05 May 2004, (F) 16 June 2004, (G) 21 July 2004, (H) 18 August 2004, (I) 15 September 2004, and (J) 14 October 2004.

($65.4 \text{ m}^3 \text{ s}^{-1}$). Chl *a* concentrations were lowest during the most intense storm period in mid-September. Similar to 2003, Chl *a* increased toward the river mouth, and multiple modes were observed in tidal freshwater

(Fig. 3). Nitrogen concentrations were generally lowest in regions of Chl *a* peaks and highest during high discharge, particularly in May and October (Fig. 3E,J).

Carbon biogeochemistry—The $\delta^{13}\text{C}_{\text{POC}}$ was depleted in the tidal freshwater (-24.9% to -30.1%), enriched at the salt wedge (-24.1% to -26.6%), and most enriched at the York River mouth (Tables 2, 3; Fig. 4). The $\delta^{13}\text{C}_{\text{POC}}$ in upper tidal freshwater (km 113) was enriched during May–June 2004 compared to 2003 (average \pm SD, 2004: -26.0% \pm 0.4; 2003: -28.5% \pm 0.2). Within tidal freshwater, the location of the most depleted $\delta^{13}\text{C}_{\text{POC}}$ shifted upriver as the season progressed (Tables 2, 3). Seasonal variation in $\delta^{13}\text{C}_{\text{POC}}$ km 54 was low compared to km 98 (Fig. 4B,E).

The $\delta^{13}\text{C}_{\text{DIC}}$ was depleted in tidal freshwater and enriched toward the river mouth (Fig. 4). The $\delta^{13}\text{C}_{\text{DIC}}$ was often lighter and the DIC concentration higher at km 98 than at km 113, particularly during June and July 2004 (June and July average; km 98: $\delta^{13}\text{C}_{\text{DIC}}$ -13.3% , DIC $460 \mu\text{mol L}^{-1}$; km 113: $\delta^{13}\text{C}_{\text{DIC}}$ -11.2% , DIC $288 \mu\text{mol L}^{-1}$). Seasonal variation in $\delta^{13}\text{C}_{\text{DIC}}$ was low in tidal freshwater (Fig. 4A,E). Interannual variability was significant; in 2003, the $\delta^{13}\text{C}_{\text{DIC}}$ was depleted (-4% to -6%) and the DIC concentration lower throughout the tidal freshwater compared to 2004 (average \pm SD; 2003: $244 \pm 65 \mu\text{mol L}^{-1}$, 2004: $464 \pm 176 \mu\text{mol L}^{-1}$).

Nitrogen biogeochemistry—The $\delta^{15}\text{N}_{\text{PN}}$ was increasingly enriched along the river from km 113 to km 52 (Tables 2, 3; Fig. 4) and most enriched at km 7 (average $\delta^{15}\text{N}_{\text{PN}} \pm$ SD: $9.9 \pm 1.3\%$). Seasonal variation was higher in 2004 than in 2003 (Fig. 4C,F). Within tidal freshwater, maximum enrichment occurred at km 52, km 113, or both. The $\delta^{15}\text{N}_{\text{PN}}$ was depleted during high discharge, with the exception of 25 June 2003, indicated by a negative correlation to the recent average daily discharge ($r = -0.45$, $p < 0.005$). At km 52 and 98, the $\delta^{15}\text{N}_{\text{PN}}$ enrichment preceded the summer Chl *a* peak (Fig. 5).

C:N of POM—The C:N_{POM} declined along the river axis (Tables 2, 3). Elevated C:N_{POM} were observed during high discharge, although the C:N_{POM} during early May to early June in 2004 was much lower than in 2003 (average 11.6 and 32.5, respectively), implying a different POM source. In 2003, elevated C:N_{POM} (>30) at km 98 and 113 was associated with $\delta^{13}\text{C}_{\text{POC}}$ of about -28.5% and $\delta^{15}\text{N}_{\text{PN}}$ of 6.0 to 8.7‰ (Table 2), whereas in 2004, elevated C:N_{POM} (>13) in the upper river was associated with $\delta^{13}\text{C}_{\text{POC}}$ of -26.0 to -29.3% and $\delta^{15}\text{N}_{\text{PN}}$ of 3.6 to 5.2‰ (Table 3). C:N_{POM} was generally 10–15 at tidal freshwater stations and only approximated Redfield ratios near km 52 (6.3–10.0) and, in 2004, km 7 (6.6–9.7).

Physical mixing—POC, PN, and Chl *a* concentrations generally were highest at km 52 when the station was located in the region of the York River estuary turbidity maximum (salinity ca. 5; Tables 2, 3). The $\delta^{13}\text{C}_{\text{POC}}$ was similar to the conservative mixing curve in July but not in May–June and August–October 2004 (Fig. 6). On 07 May, the $\delta^{13}\text{C}_{\text{POC}}$ at km 52 and 76 was slightly more enriched

Table 2. Average $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{PN}}$, C:N_{POM} (atomic ratio), POC (mg L⁻¹), and salinity for the Mattaponi River during 2003 (km, river kilometer [0 is at the mouth of the York River]; SD, standard deviation of replicate samples; —, data not available).

Date	km	$\delta^{13}\text{C}_{\text{DIC}}$ (SD)	$\delta^{13}\text{C}_{\text{POC}}$ (SD)	$\delta^{15}\text{N}_{\text{PN}}$ (SD)	C:N _{POM}	POC	Salinity
07 May 03	76	-16.8 (0.4)	-27.2 (0.1)	5.5 (1.3)	17.6	1.01	0.03
	98	-17.9 (—)	-28.4 (0.1)	5.8 (0.4)	23.5	0.96	0.02
	113	-16.9 (—)	-28.7 (0.2)	8.7 (0.9)	32.4	1.45	0.02
06 Jun 03	52	-16.5 (0.5)	-26.0 (0.1)	6.6 (3.5)	20.6	1.56	0.04
	98	-18.2 (0.0)	-28.2 (0.1)	—	—	0.60	0.02
	113	-17.6 (0.3)	-28.5 (0.1)	6.0 (0.2)	32.7	1.44	0.02
25 Jun 03	52	-10.0 (0.2)	-26.6 (0.1)	8.8 (0.7)	15.1	0.86	2.32
	63	-16.8 (0.3)	-28.7 (1.2)	7.9 (2.3)	13.9	1.03	0.04
	98	-18.8 (0.1)	-29.3 (0.0)	7.0 (1.2)	16.2	0.72	0.02
	113	-19.0 (0.5)	-28.3 (—)	8.4 (—)	18.6	1.22	0.02
10 Jul 03	52	-9.9 (0.1)	-25.2 (0.0)	8.4 (0.2)	10.8	2.42	2.32
	63	-13.1 (0.3)	-27.2 (1.0)	9.4 (0.3)	14.2	1.83	0.04
	98	-18.7 (0.2)	-29.2 (0.2)	5.8 (0.5)	14.5	0.51	0.02
	113	-17.9 (0.4)	-29.2 (0.1)	5.5 (0.7)	16.8	1.23	0.02
24 Jul 03	52	-11.3 (0.2)	-25.7 (0.1)	7.5 (0.3)	10.0	1.45	2.33
	63	-13.9 (0.1)	-26.8 (0.0)	9.0 (0.7)	12.8	1.38	0.13
	98	-17.9 (0.5)	-28.8 (0.0)	5.6 (0.1)	14.2	0.65	0.03
	113	-18.2 (0.1)	-29.1 (0.0)	6.9 (0.2)	18.7	1.56	0.02
12 Aug 03	52	-13.4 (—)	-26.1 (0.1)	10.1 (0.2)	12.6	1.93	4.22
	63	-15.8 (0.2)	-27.1 (0.0)	10.2 (1.1)	13.2	1.19	0.06
	98	-17.7 (0.0)	-29.4 (0.0)	7.8 (1.1)	17.9	0.73	0.03
	113	-17.8 (0.7)	-29.3 (0.1)	10.1 (0.3)	25.3	1.50	0.02
2 Sep 03	52	—	-25.6 (0.1)	9.6 (0.4)	8.7	1.23	5.73
	63	—	-26.6 (0.0)	7.7 (0.1)	10.3	1.47	2.23
	98	—	-30.4 (0.1)	7.7 (0.6)	12.9	0.58	0.03
	113	—	-30.1 (0.1)	9.8 (4.6)	16.0	0.57	0.03
5 Oct 03	52	-12.1 (3.0)	—	—	—	—	1.55
	63	-10.3 (0.6)	—	—	—	—	0.03
	98	-12.9 (1.4)	—	—	—	—	0.02
	113	-9.7 (0.4)	—	—	—	—	0.02

than expected (+1.2‰) and again from August through October (average enrichment +1.1‰). In contrast, from late May through June, the $\delta^{13}\text{C}_{\text{POC}}$ from km 52 to 98 was more depleted than expected (average depletion -1.6‰). The results were similar if we assumed greater freshwater influence ($\delta^{13}\text{C}_{\text{POC}} = -24\text{‰}$) at the marine end member. In both May–June and July, the tidal freshwater was most often a net source of POC (Fig. 6), whereas POC was highly variable during August–October, with elevated POC concentrations at km 113 and 54 (Fig. 6F). The $\delta^{13}\text{C}_{\text{POC}}$ throughout the Mattaponi River should have been similar in August–October because nearly the whole river was fresh. A shift in isotopic composition below km 113 was not observed until km 54 (Fig. 6C), suggesting that POM removal (i.e., deposition and consumption) was most important during August–October.

Principal components analysis—Variability in the isotopic composition of the POM was related to physical mixing along the river axis and river discharge (Fig. 7). The first two principal components account for 68% of the variance for 2003 data (PC 1 = 51.0%, PC 2 = 17.3%) and for about 78% of the variance for 2004 data (PC 1 = 61.2%, PC 2 = 16.8%). The first principal component was

composed of the variation along the river axis, dividing the tidal freshwater stations with low Chl *a*, high C:N_{POM}, and depleted $\delta^{15}\text{N}_{\text{PN}}$, $\delta^{13}\text{C}_{\text{DIC}}$, and $\delta^{13}\text{C}_{\text{POC}}$ from the brackish stations with high Chl *a*, low C:N_{POM}, and enriched $\delta^{15}\text{N}_{\text{PN}}$, $\delta^{13}\text{C}_{\text{DIC}}$, and $\delta^{13}\text{C}_{\text{POC}}$. For 2003, the loadings on PC 1 were highest and similar for $\delta^{13}\text{C}_{\text{DIC}}$ (-0.53), $\delta^{13}\text{C}_{\text{POC}}$ (-0.50), and salinity (-0.49). For 2004, the loadings were similar on Chl *a* (-0.46), salinity (-0.43), C:N_{POM} (+0.42), $\delta^{15}\text{N}_{\text{PN}}$ (-0.41), $\delta^{13}\text{C}_{\text{DIC}}$ (-0.35), and $\delta^{13}\text{C}_{\text{POC}}$ (-0.26).

The second principal component corresponds to seasonal variability in discharge, dividing the stations sampled during high and base flows. For 2003, PC 2 was derived almost entirely of river discharge (-0.95). For 2004, the loadings on PC 2 were highest on discharge (-0.68), $\delta^{13}\text{C}_{\text{DIC}}$ (-0.54), C:N_{POM} (-0.37), and salinity (-0.27). The PCA indicates a broad change in composition. During high discharge, the $\delta^{13}\text{C}_{\text{DIC}}$ was depleted, the C:N_{POM} and POC concentration elevated, the Chl *a* concentration low, the spatial variation in $\delta^{13}\text{C}_{\text{POC}}$ small, and the $\delta^{13}\text{C}_{\text{POC}}$ similar to riparian vegetation ($\delta^{13}\text{C} = -28\text{‰}$) and humic soils ($\delta^{13}\text{C} = -26\text{‰}$). During base flows, the $\delta^{13}\text{C}_{\text{DIC}}$ became enriched, the C:N_{POM} and POC concentration was lower, the Chl *a* concentration was elevated, and the $\delta^{13}\text{C}_{\text{POC}}$ became increasingly depleted.

Table 3. Average $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{15}\text{N}_{\text{PN}}$, C : N_{POM} (atomic ratio), POC (mg L⁻¹), Chl *a* ($\mu\text{g L}^{-1}$), and salinity for the Mattaponi and York rivers during 2004 (km, river kilometer [0 is at the mouth of the York River]; SD, standard deviation of replicate samples; —, data not available).

Date	km	$\delta^{13}\text{C}_{\text{DIC}}$ (SD)	$\delta^{13}\text{C}_{\text{POC}}$ (SD)	$\delta^{15}\text{N}_{\text{PN}}$ (SD)	C : N _{POM}	POC	Chl <i>a</i>	Salinity
07 May 04	52	-9.1 (0.0)	-24.1 (0.1)	7.0 (1.4)	10.4	1.83	8.1	1.14
	76	-13.2 (0.3)	-24.9 (0.0)	5.3 (1.8)	12.2	1.13	1.8	0.03
	98	-13.5 (0.5)	-26.0 (0.2)	3.6 (2.7)	13.3	0.81	1.8	0.02
	113	-12.0 (0.7)	-26.4 (0.2)	4.2 (1.5)	11.8	0.80	0.4	0.02
24 May 04	52	-6.0 (0.1)	-25.3 (0.3)	10.9 (2.3)	7.5	1.44	16.6	5.41
	76	-11.6 (0.3)	-26.3 (0.4)	5.4 (2.0)	9.8	1.01	9.4	0.04
	98	-13.2 (0.0)	-27.8 (0.2)	6.1 (2.7)	9.9	0.77	6.0	0.03
	113	-13.5 (0.2)	-25.4 (0.5)	2.4 (2.1)	12.0	0.43	0.4	0.02
03 Jun 04	52	-5.6 (0.1)	-26.6 (0.2)	14.7 (5.7)	6.3	1.34	25.0	6.92
	76	-14.2 (0.1)	-27.7 (1.0)	10.7 (1.3)	8.6	0.80	5.0	0.04
	98	-13.6 (—)	-27.6 (1.5)	9.4 (0.4)	8.6	0.89	5.2	0.03
	113	-12.1 (0.0)	-26.2 (0.9)	4.2 (1.6)	11.0	0.44	0.4	0.02
22 Jun 04	52	-6.0 (0.1)	-24.4 (0.2)	8.7 (0.3)	7.4	1.41	20.2	6.64
	76	-13.5 (0.2)	-27.1 (0.2)	7.6 (2.4)	8.6	0.71	8.1	0.05
	98	-13.9 (0.1)	-28.4 (0.2)	6.2 (0.7)	8.9	0.60	7.0	0.03
	113	-12.4 (0.3)	-26.2 (0.5)	8.6 (2.5)	10.4	0.37	0.6	0.02
9 Jul 04	7	-2.1 (0.4)	-22.5 (0.0)	10.5 (2.8)	6.6	1.46	15.0	16.79
	52	-7.2 (0.2)	-26.1 (0.2)	—	—	2.86	17.2	6.62
	76	-13.0 (0.6)	-28.2 (—)	—	—	1.07	3.8	0.12
	98	-13.0 (0.7)	-29.4 (1.8)	—	—	1.26	4.0	0.03
22 Jul 04	113	-9.8 (0.9)	-29.0 (0.1)	—	—	1.39	2.4	0.02
	7	-0.8 (0.3)	-21.9 (0.1)	9.3 (0.1)	9.7	1.53	7.9	18.48
	52	-8.1 (0.1)	-26.4 (0.3)	8.1 (0.6)	8.2	1.96	15.3	6.54
	76	-12.4 (1.2)	-29.4 (0.0)	5.9 (1.3)	10.2	0.89	3.0	0.04
16 Aug 04	98	-12.8 (0.1)	-30.0 (0.0)	4.2 (2.0)	12.6	0.67	2.8	0.02
	113	-10.6 (0.4)	-29.2 (0.1)	5.2 (2.5)	15.2	0.65	1.1	0.02
	7	-3.4 (0.2)	-24.5 (0.2)	8.6 (1.0)	9.3	0.70	6.6	16.31
	52	-8.6 (2.8)	-26.8 (0.0)	7.5 (3.1)	11.8	2.35	5.2	0.52
3 Sep 04	76	-12.4 (3.3)	-28.3 (0.1)	4.6 (1.3)	12.5	0.82	2.1	0.03
	98	-11.4 (0.4)	-28.2 (0.0)	3.4 (2.0)	14.9	1.54	2.1	0.02
	113	-9.7 (1.1)	-28.4 (0.1)	3.8 (1.4)	16.0	2.52	1.3	0.02
	7	-3.7 (0.0)	-24.6 (0.1)	9.4 (0.8)	7.6	1.23	18.6	12.64
5 Oct 04	52	-12.0 (0.8)	-26.8 (0.0)	7.0 (1.2)	12.1	1.83	6.5	0.04
	76	-14.8 (0.7)	-27.4 (0.0)	2.7 (0.4)	15.4	2.98	2.3	0.02
	98	-15.2 (0.4)	-28.1 (0.1)	4.0 (1.4)	13.5	1.36	1.2	0.02
	113	-16.0 (0.8)	-28.1 (0.0)	3.9 (2.2)	13.1	2.21	1.9	0.02
5 Oct 04	7	-2.0 (1.5)	-23.8 (0.0)	11.9 (0.1)	7.7	1.43	17.9	14.11
	52	-8.6 (0.7)	-26.8 (0.1)	7.6 (0.2)	10.4	1.33	6.2	1.15
	76	-13.8 (0.4)	-28.3 (0.1)	6.0 (1.6)	12.7	0.66	1.7	0.03
	98	-9.5 (4.4)	-29.3 (0.1)	4.2 (0.0)	14.4	0.45	1.4	0.02
	113	-11.5 (1.3)	-29.1 (0.1)	5.1 (1.6)	15.4	1.04	0.5	0.02

Discussion

Here, we focus on (1) POM source identification using distinct characteristics of autochthonous and allochthonous POM, (2) the influence of physical mixing and river discharge on POM variability, (3) additional variability associated with $\delta^{15}\text{N}_{\text{PN}}$, and (4) POM export to the lower estuary.

Source identification—Linear regression of POC and PN concentrations (mmol L⁻¹) can be used to assess homogeneity within the OM pool (Hedges et al. 1986; Ruttenberg and Goñi 1997). We obtained a significant regression for data from river km 98 and 113 (2003 and 2004 data combined; $\text{POC} = 0.03 + 9.75 \text{ PN}$, $r^2 = 0.14$, $p < 0.05$). The

positive intercept at a POC of 0 implies an N-poor source to the OM pool, consistent with a terrestrial-derived OM source. The low correlation indicates that multiple OM sources with different elemental ratios varied in their contribution over the study period, implying that multiple measures of POM character are needed for POM identification. For example, the large C : N_{POM} differences between May 2003 and May 2004 imply that different sources were contributed from upstream to the tidal freshwater.

We identified potential POM sources using $\delta^{13}\text{C}_{\text{POC}}$, C : N_{POM}, and Chl *a* : POC data. Terrestrial-derived humic-rich sediment has a $\delta^{13}\text{C}$ value of -26‰ and a C : N of 10–12, whereas vascular plant matter has a $\delta^{13}\text{C}$ value of -28‰ (C₃ plants) or -13‰ (C₄ plants, including *Spartina*

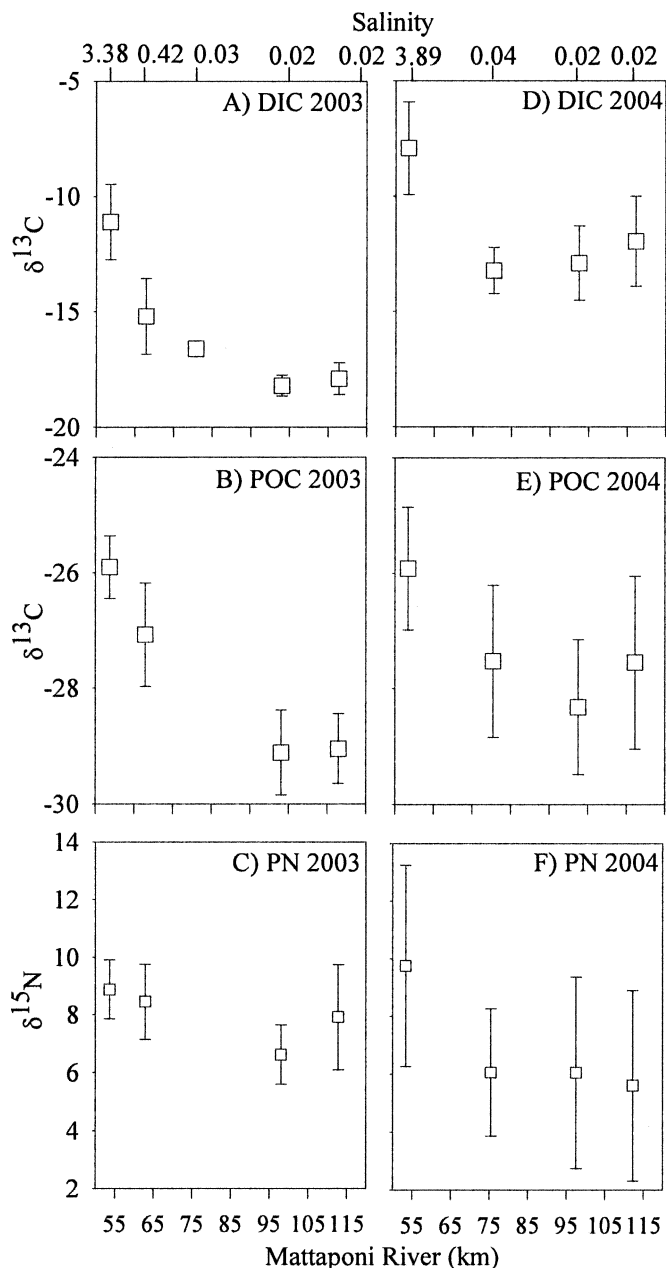


Fig. 4. Average stable isotope composition (± 1 SD) of $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{13}\text{C}_{\text{POC}}$, and $\delta^{15}\text{N}_{\text{PN}}$ from May through October during (A–C) 2003 and (D–F) 2004.

and upland grasses) and a C:N >25 (Hedges et al. 1986; Mook and Tan 1991). These terrestrial-derived OM sources have low Chl *a*:POC. Further, we expected that autochthonously produced phytoplankton would be isotopically light relative to allochthonous sources, with a $\delta^{13}\text{C}$ value of $< -30\text{‰}$, assuming that the uptake of C occurred under a constant fractionation of 21‰ (i.e., $\delta^{13}\text{C}_{\text{POC-phyto}} = \delta^{13}\text{C}_{\text{DIC}} - 21\text{‰}$; Mook and Tan 1991), with a C:N similar to the Redfield ratio (ca. 7). Estuary OM was defined by samples from km 7 ($\delta^{13}\text{C}_{\text{POC}}$ ca. -22‰ , C:N_{POM} = 7–10, Chl *a*:POC > 5). Using this definition, we heuristically defined phytoplankton-dominated POM samples as those with a Chl *a*:POC > 5. We attempted to use this

classification to associate specific $\delta^{15}\text{N}$ values with POM sources; however, this method failed because the $\delta^{15}\text{N}$ was not distinct between sources at any station.

The POM at km 113 generally was derived from a mix of vascular plant OM and humic sediments and was dominated by a different source in 2003 (vascular plant) versus 2004 (humic-rich sediment; Fig. 8). Factors that may have influenced the POM sources are numerous; however, the PCA analysis indicates that C:N_{POM} is correlated with discharge (Fig. 7). Further, for 2004, the third-highest principal component accounts for 9.5% of the variance and is composed primarily of $\delta^{13}\text{C}_{\text{POC}}$ (positively associated with discharge), indicating that enriched $\delta^{13}\text{C}_{\text{POC}}$, associated with terrestrial-derived POM, during high discharge is a small but identifiable source of variability. Thus, surface flow or rapid delivery of OM from the nontidal river or both could be important processes delivering high C:N, terrestrial-derived, vegetative POM to the tidal freshwater. POM resuspension during high-discharge events may also be important; preferential association of vascular plant OM with lower water column depths has been observed (Goñi et al. 2005). Specific vegetation sources, such as riparian plants or upland trees, were not identified in our research. Conservatively, the vascular plant signal that is identifiable represents any C₃ vegetation, including OM derived from vegetation in the upper watershed, OM from the immediate riparian zone delivered to the channel during high discharge, as well as OM from tidally inundated freshwater marshes.

In both years, the POM samples had an isotopically light $\delta^{13}\text{C}$ composition relative to terrestrial sources during June through August, implying a contribution from isotopically light phytoplankton (Fig. 8). At km 98, a similar mix of OM was inferred; however, there was a greater contribution of phytoplankton to the POM, indicated by the isotopically lighter POM and higher Chl *a*:POM than at km 113. As at km 113, a difference between OM sources during May 2003 and May 2004 was observed at km 98; however, the signal was less distinct, presumably because of mixing with additional OM sources in the lower river.

Mixing with estuarine POM lead to reduced variation in $\delta^{13}\text{C}_{\text{POC}}$, C:N_{POM}, and Chl *a*:POC at km 63–76 and at km 54 (Fig. 8); samples had a $\delta^{13}\text{C}$ and C:N similar to humic sediments but were likely derived from a mix of humic sediments, vascular plant, freshwater phytoplankton, and estuarine OM. Phytoplankton produced in situ and estuarine OM likely were important during June and July, but humic sediments and vascular plant OM, along with estuarine OM, were important in May and during high-discharge conditions. From these data, we conclude that sampling upper tidal freshwater portions of estuaries is important for POM source identification. Indeed, recent research in the York River in which a single station was located in the lower tidal freshwater portion led to unequivocal source identification (McCallister et al. 2004).

Influence of physical mixing—The PCA provides evidence that the largest source of temporal and spatial variation in the stable isotope composition of POM within the Mattaponi River was related to the transition from

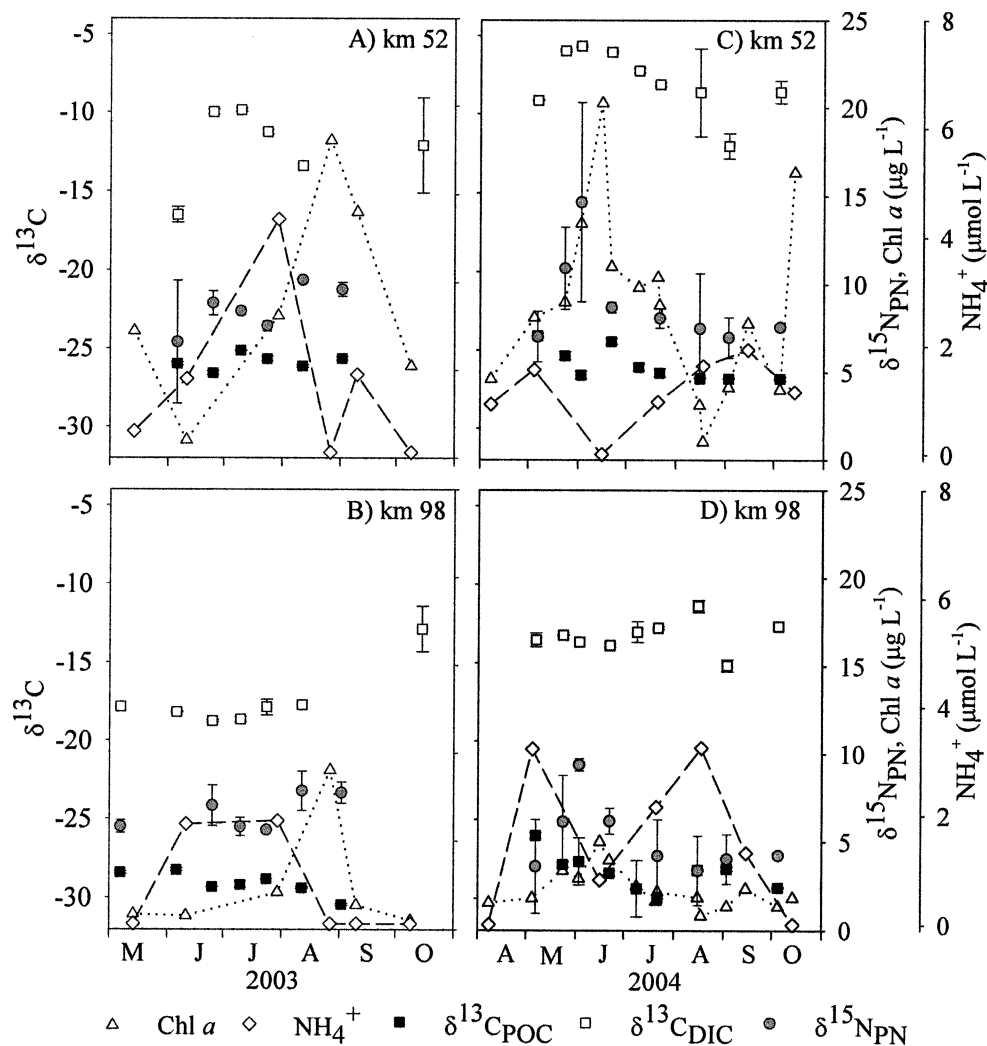


Fig. 5. Seasonal variation in $\delta^{13}\text{C}_{\text{POC}}$, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{15}\text{N}_{\text{PN}}$, and Chl *a* and NH_4^+ concentrations at (A, C) the river mouth and (B, D) central tidal freshwater. Error bar represents ± 1 SD from replicate samples.

fresh to estuarine waters. The most parsimonious hypothesis to explain the stable isotope variability along the river axis (depleted POM and DIC upriver and enriched POM and DIC downriver) is that the distribution is explained by physical mixing with the lower estuary. York River POM influence was observed at km 54 and 63–76 (Figs. 6, 8); however, nonconservative dynamics were pronounced during high discharge, and the freshwater stations did not conform well to the conservative mixing model (Fig. 7).

The depletion relative to the POM conservative mixing curve in tidal freshwater during May and June 2004 (Fig. 6), resulting in $\delta^{13}\text{C}_{\text{POC}} = -25$ to -28‰ , is consistent with an increased contribution of in situ-produced, isotopically light phytoplankton or a localized contribution from riparian sources because freshwater marsh $\delta^{13}\text{C}_{\text{DOC}}$ ranges from -22.3‰ to -26.3‰ (Raymond and Bauer 2001) and emergent vascular freshwater marsh plants have an average $\delta^{13}\text{C}$ from -26‰ to -28‰ (Cloern et al. 2002). The latter hypothesis is supported by several observations. First, a phytoplankton bloom occurred in tidal freshwater

coincident with the depleted POM (Fig. 5D). Second, the Chl *a*:POC of these samples was elevated, and the C:N_{POM} was lower than expected if vascular plants were the source (C:N_{POM} < 15; Fig. 8). Third, the $\delta^{15}\text{N}_{\text{PN}}$ in tidal freshwater ranged from 2.4‰ to 6.1‰ during May, whereas the $\delta^{15}\text{N}$ of emergent and submerged vascular plants is 7–10‰ (Cloern et al. 2002).

The enrichment relative to conservative mixing that was observed at km 54 on 07 May 2004 ($\delta^{13}\text{C}_{\text{POC}} = -24.1\text{‰}$) and during August through October 2004 ($\delta^{13}\text{C}_{\text{POC}} = -26.8\text{‰}$) occurred under high discharge and low salinity. Potential causes include reduced phytoplankton fractionation (i.e., fast growth rate [Laws et al. 1995] or C limitation [Rau et al. 1996]) or a local contribution of enriched $\delta^{13}\text{C}_{\text{POC}}$. The former hypothesis is unlikely because algal biomass was low and high turbidity (Sin et al. 1999) and CO_2 supersaturation (Raymond et al. 2000) are characteristic of the system. Alternatively, at least two sources of $\delta^{13}\text{C}_{\text{POC}}$ are available because of the proximity to the estuary turbidity maximum: fringing salt marsh

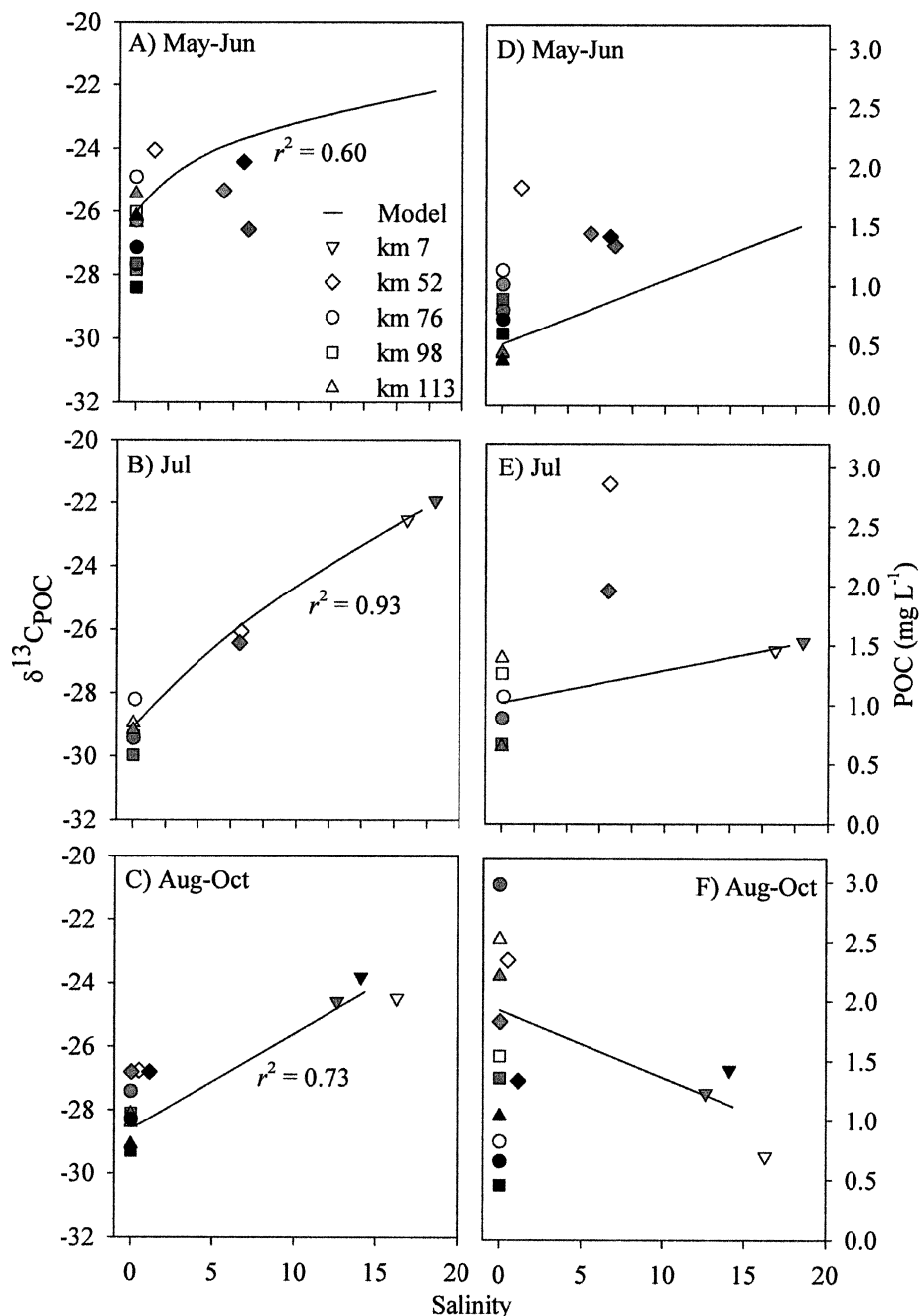


Fig. 6. Conservative mixing curve for Mattaponi River POM in 2004. The $\delta^{13}\text{C}_{\text{POC}}$ conservative mixing curve and $\delta^{13}\text{C}_{\text{POC}}$ are shown for (A) May–June, (B) July, and (C) August–October. The POC conservative mixing line and POC concentrations are also shown for (D) May–June, (E) July, and (F) August–October. Symbols indicate the location of sample, including York River km 7 and Mattaponi River km 52, 76, 98, and 113. Shading indicates sample date: (A, D) white, 07 May; gray, 24 May and 03 June; black, 22 June; (B, E) white, 09 July; gray, 22 July; (C, F) white, 16 August; gray, 03 September; black, 05 October.

plants ($\delta^{13}\text{C} = -13\text{‰}$, $\delta^{15}\text{N} = 4\text{‰}$; Peterson et al. 1985) and estuarine sediments ($\delta^{13}\text{C} = -23\text{‰}$; Arzayus and Canuel 2004). In tidal freshwater, at km 98, the POM during August through October was a mix of vascular plant OM, humic sediments, and freshwater phytoplankton, characterized by a $\delta^{15}\text{N}_{\text{PN}}$ of ca. 4‰ and a $\text{C}:\text{N}_{\text{POM}}$ of 14–15 (Fig. 8). Downriver, the POM at km 54 had a $\delta^{15}\text{N}_{\text{PN}}$

of ca. 7‰ and a $\text{C}:\text{N}_{\text{POM}}$ of 10–12, implying that the $\delta^{15}\text{N}_{\text{PN}}$ had increased and the $\text{C}:\text{N}_{\text{POM}}$ declined compared to upriver. This shift is most consistent with an increased fraction of estuarine-derived sediments in the POM pool, as we would expect a decrease in $\delta^{15}\text{N}_{\text{PN}}$ and increase in $\text{C}:\text{N}_{\text{POM}}$ if salt marsh vegetation were the additional POM source.

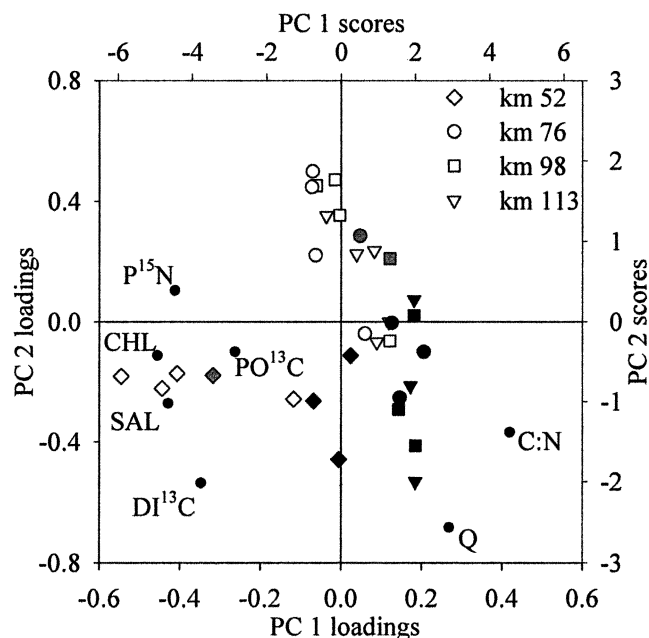


Fig. 7. Biplot of the loadings on principal components 1 and 2 (PC 1, PC 2) from the PCA of $\delta^{13}\text{C}_{\text{POC}}$ (PO^{13}C), $\delta^{13}\text{C}_{\text{DIC}}$ (DI^{13}C), $\delta^{15}\text{N}_{\text{PN}}$ (P^{15}N), $\text{C}:\text{N}_{\text{POM}}$ ($\text{C}:\text{N}$), $\text{Chl } a$ (CHL), salinity (SAL), and discharge (Q) data from the Mattaponi River, 2004. Symbols indicate the location of sample, including Mattaponi River km 52, 76, 98, and 113. Shading indicates sample date: white, May and June; gray, July; black, August through October.

Conservative DIC behavior was apparent during early May 2004 (Fig. 9). Thereafter, the behavior was non-conservative; the DIC added was isotopically light, likely respired from fluvial OM because there is little fractionation during respiration. This biogenic DIC likely was respired from phytoplankton; the isotopically depleted DIC, the greater lability of phytoplankton, and the simultaneous phytoplankton bloom and shift in POM composition are consistent with this hypothesis. Respired DIC from allochthonous OM sources may also have contributed; bacteria can preferentially respire terrestrial-derived OM in tidal freshwaters (Boschker et al. 2005; Marangar et al. 2005). The DIC behavior in the brackish estuary was similar to that reported by Raymond et al. (2000).

Influence of river discharge—The second major source of POM variability is related to discharge (Fig. 7). The data support the hypothesis that during high discharge, terrestrial-derived POM is transported into the river channel and primary production is suppressed, presumably because of high turbidity and rapid flushing rates, resulting in small isotopic variation along the river axis and dominance by terrestrial-derived POM (Fig. 8). Support for this hypothesis was evaluated by testing relationships between POM and the recent average daily discharge. The variation in the $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$ among the tidal freshwater stations (km 63 or 76–km 113), represented by the standard deviation of the average $\delta^{13}\text{C}_{\text{POC}}$ and $\delta^{15}\text{N}_{\text{PN}}$ of the three stations, was negatively linearly correlated to recent

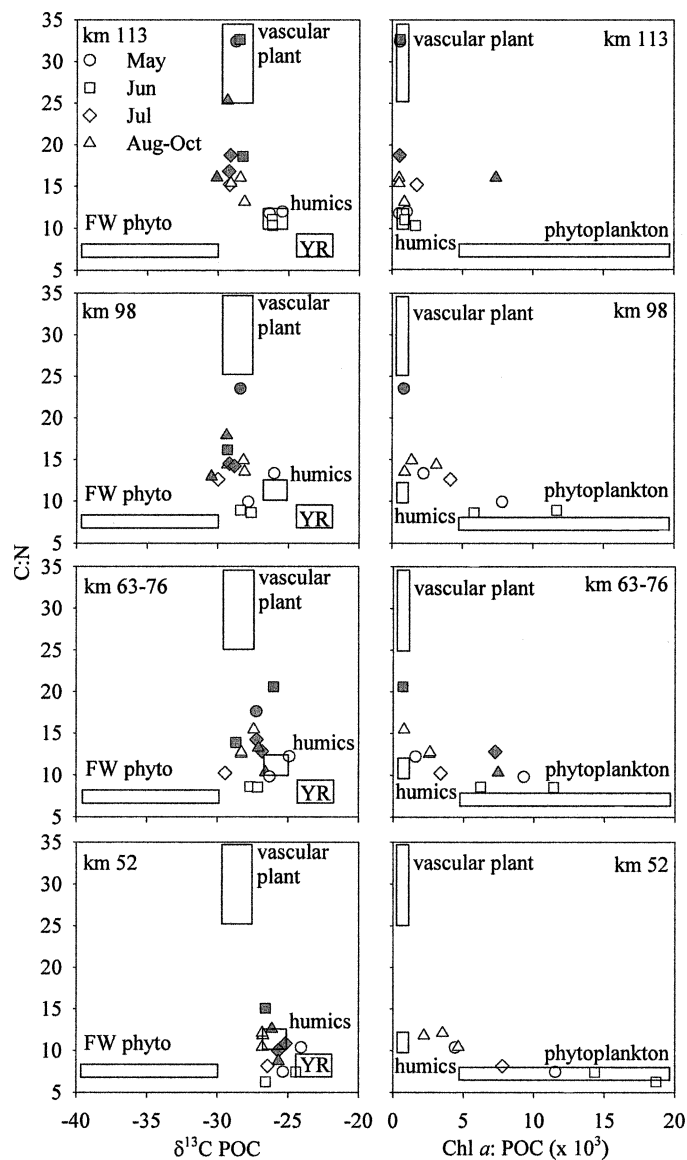


Fig. 8. POM sources in the Mattaponi River during 2003 and 2004. Boxes represent typical values of POM sources, including vascular plant tissue (vascular plant), humic-rich sediment (humics), freshwater phytoplankton (FW phyto), and York River estuary OM (YR). See text for details on source values. Shading indicates year: gray, 2003; white, 2004. $\text{Chl } a$ data for a few 2003 samples were available from VADEQ surveys on similar dates (unpubl. data).

discharge ($r = -0.51$, $p = 0.04$ and $r = -0.48$, $p = 0.07$, respectively), as was the average $\text{Chl } a$ among the three stations ($r = -0.78$, $p = 0.02$). Notably, there was no relationship between POC or PN concentrations and discharge, reflecting the influence of multiple fates and sources of POM, as well as the high POC concentration variability, during variable flow conditions (Fig. 6F).

Interannual variation was much larger than seasonal variation in $\delta^{13}\text{C}_{\text{DIC}}$ and DIC concentrations at tidal freshwater stations. Variation in $\delta^{13}\text{C}_{\text{DIC}}$ is a result of the balance between the inflow of light $\delta^{13}\text{C}_{\text{DIC}}$, invasion of

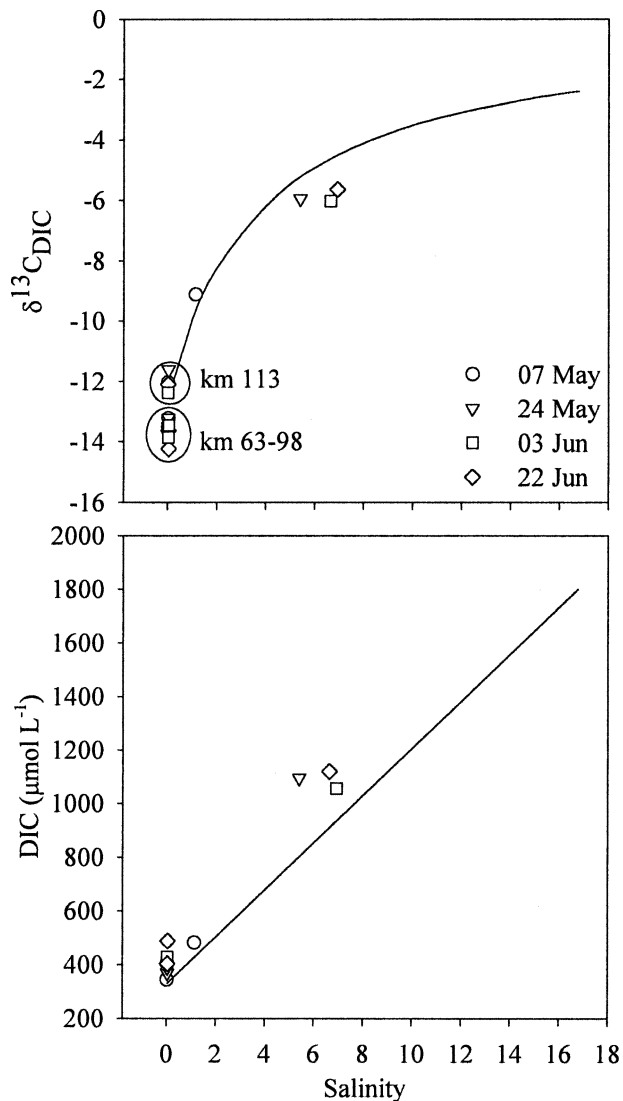


Fig. 9. $\delta^{13}\text{C}_{\text{DIC}}$ conservative mixing curve and samples from May and June 2004. Mixing curve estimated using equations from Mook et al. (1991). The marine end member was represented using the average salinity at km 7 among the sampling dates (16.79), the average $\delta^{13}\text{C}_{\text{DIC}}$ measured at km 7 in 2004 (-2.4‰), and $[\text{DIC}] = 1,800 \mu\text{mol L}^{-1}$, which was the $[\text{DIC}]$ measured at km 7 in early July. The freshwater end member was represented by the average values measured at km 113 in May and June (salinity 0.03, $\delta^{13}\text{C}_{\text{DIC}} = -12.5\text{‰}$, $[\text{DIC}] = 330 \mu\text{mol L}^{-1}$).

atmospheric CO_2 , as well both the respiration and decomposition of sediment and phytoplankton produced in situ, versus outflow, atmospheric evasion, and the preferential uptake of light $\delta^{13}\text{C}_{\text{DIC}}$ during in situ phytoplankton production (Quay et al. 1986; Mook and Tan 1991). In the York River, the $\delta^{13}\text{C}_{\text{DIC}}$ reflects the DIC sources: respiration of terrestrial-derived OM ($\delta^{13}\text{C}_{\text{DIC}} -25\text{‰}$) and atmospheric CO_2 ($\delta^{13}\text{C} -7\text{‰}$; Raymond et al. 2004). In 2003, depleted $\delta^{13}\text{C}_{\text{DIC}}$ in the freshwater stations was associated with lower DIC concentrations than in 2004. This change likely was related to higher discharge, during which biogenic DIC made up a larger portion of the DIC

pool and DIC concentrations were reduced by DIC-poor runoff and increased CO_2 evasion from increased turbulence (Finlay 2003).

Stable nitrogen isotope biogeochemistry—Depleted $\delta^{15}\text{N}_{\text{PN}}$ in the upper Mattaponi River reflects the dominance of terrestrial-derived POM. Similarly, increased contribution of terrigenous POM combined with suppressed production of phytoplankton in the river channel during high discharge from August through October 2004 likely caused the shift toward lighter $\delta^{15}\text{N}_{\text{PN}}$. In part, enriched $\delta^{15}\text{N}_{\text{PN}}$ in the lower Mattaponi River can be attributed to mixing with isotopically heavy, estuarine POM. Additional processes may also contribute to the observed enrichment.

Fast rates of OM recycling, microbial decomposition of POM (e.g., Altabet 1988), nitrification (Mariotti et al. 1981), and utilization of inorganic substrates favor the enriched $\delta^{15}\text{N}_{\text{PN}}$ in the lower Mattaponi River. High rates of bacterial production are characteristic of the low-salinity reaches of the York River (Schultz et al. 2003), as is net heterotrophy (Raymond et al. 2000), which are consistent with the low saturation of DO measured in the lower river. Enriched $\delta^{15}\text{N}$ may be characteristic of the mesohaline estuary; York River bacteria collected at 10 salinity have enriched $\delta^{15}\text{N}$ (12.6–17.3‰; McCallister et al. 2004), and we observed $\delta^{15}\text{N}_{\text{PN}}$ ranging from 8.1‰ to 14.7‰ at salinities of 4–7. In contrast, the enriched $\delta^{15}\text{N}_{\text{PN}}$ observed throughout the river during the summer is likely due to a prolonged period of phytoplankton production, in which discrimination against heavy NH_4^+ resulted in a small, enriched nutrient pool (Cifuentes et al. 1988). In both years, the most enriched $\delta^{15}\text{N}_{\text{PN}}$ at a station was observed within 2 weeks of the Chl *a* maximum and was coincident with lower NH_4^+ concentrations.

Either one or all of these processes may account for the $\delta^{15}\text{N}_{\text{PN}}$ enrichment at km 113 relative to km 98. Alternatively, the presence of lighter $\delta^{15}\text{N}_{\text{PN}}$ at km 98 under varying discharge may be due to reduced nutrient limitation or denitrification; elevated NH_4^+ concentrations in this region lend support to this hypothesis. The combined evidence suggests that enriched PN may arise from different processes, and we therefore concur with Lehmann et al. (2004) that $\delta^{15}\text{N}_{\text{PN}}$ must be interpreted cautiously as an indicator of individual biogeochemical processes.

POM export—The POM exported to the York River estuary is a mix of terrestrial-derived OM, including humic soils and vascular plant matter, as well as freshwater phytoplankton (Fig. 8). During high discharge, when transit time is short and the POC concentration is high, the POM in the tidal freshwater was made up largely of terrestrial-derived POM. During base flows, when transit time is long, the contribution of phytoplankton to the POM increased. Long residence times favor the accumulation of living and detrital phytoplankton in the POM pool; the steady $\delta^{13}\text{C}_{\text{POC}}$ depletion over the summer months during both years is evidence for this accumulation, as are the nonconservative dynamics resulting from phytoplankton

production. Export of riverine POM to the York River mouth was not observed during the study period, indicated by the relatively marine $\delta^{13}\text{C}_{\text{POC}}$ (ca. -24‰), which, assuming an uptake fractionation of 21‰ , is the expected $\delta^{13}\text{C}$ of York River phytoplankton given the observed $\delta^{13}\text{C}_{\text{DIC}}$ (ca. -2.4‰).

These findings build on recent research in the York River estuary. Raymond and Bauer (2001) and Neubauer et al. (2001) identify terrestrial-derived DOC ($\delta^{13}\text{C} = -28\text{‰}$ to -29‰) and freshwater marsh-derived DOC (5–6 cm below surface, $\delta^{13}\text{C} = -26\text{‰}$) as important OM sources in the oligohaline reaches of the Pamunkey River. Variable mixing dynamics, however, favor misclassification of tidal freshwater OM; for example, at km 98 in June 2004, POM samples were likely a mix of freshwater phytoplankton ($\delta^{13}\text{C} < -30\text{‰}$) and humic-rich sediment ($\delta^{13}\text{C} -26\text{‰}$), resulting in a $\delta^{13}\text{C}_{\text{POC}}$ of -28‰ , similar to that from vascular plants. Phytoplankton was an important POM source at km 76 during 2004 (Fig. 8), and summer phytoplankton production increased POC concentrations (Fig. 6), indicating that POM derived from in situ-produced phytoplankton could be exported into the York River estuary under the right hydrographic conditions. In this study, those conditions were a prolonged period of stable base flow, allowing for the production and accumulation of phytoplankton-derived POM in the tidal freshwater.

In conclusion, variability in the isotopic composition of POM is related to three major biological processes. First, variation along the river is attributed to the greater influence of allochthonous OM in the tidal freshwater, indicated by the prevalence of isotopically light POM. Terrestrial-derived OM sources varied as well, increasing POM variability. Second, intra-annual variation is attributed to seasonal production cycles, including phytoplankton production within tidal freshwater. Third, $\delta^{15}\text{N}_{\text{PN}}$ enrichment is attributed to processes affecting the availability and stable isotope composition of N substrates as well as bacterial decomposition.

River discharge and physical mixing are important forces that account for much of the variation. During high discharge, terrestrial-derived POM is delivered to the river channel and primary production suppressed, resulting in small isotopic variation along the river axis. During low discharge, the temporal and spatial variation increase because of the contribution of in situ production in tidal freshwater and the greater estuarine influence in the lower river from incursion of brackish water. In the lower Mattaponi River, mixing of estuarine and riverine POM homogenizes the distinct character of freshwater POM sources, potentially resulting in misclassification and emphasizing the need to characterize the freshwater end member of estuaries carefully.

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