Estuaries and Coasts (2008) 31:898–911
DOI 10.1007/s12237-008-9073-4

Organic Matter Sources Supporting Lower Food Web Production in the Tidal Freshwater Portion of the York River Estuary, Virginia

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Received: 27 November 2007 / Revised: 9 July 2008 / Accepted: 10 July 2008 / Published online: 1 August 2008

Abstract The Mattaponi River is part of the York River estuary in Chesapeake Bay. Our objective was to identify the organic matter (OM) sources fueling the lower food web in the tidal freshwater and oligohaline portions of the Mattaponi using the stable isotopes of carbon (C) and nitrogen (N). Over 3 years (2002–2004), we measured zooplankton densities and C and N stable isotope ratios during the spring zooplankton bloom. The river was characterized by a May–June zooplankton bloom numerically dominated by the calanoid copepod *Eurytemora affinis* and cladocera *Bosmina freyi*. Cluster analysis of the stable isotope data identified four distinct signatures within the lower food web: freshwater riverine, brackish water, benthic, and terrestrial. The stable isotope signatures of pelagic zooplankton, including *E. affinis* and *B. freyi*, were consistent with reliance on a mix of autochthonous and allochthonous OM, including OM derived from vascular plants and humic-rich sediments, whereas macroinvertebrates consistently utilized allochthonous OM. Based on a dual-isotope mixing model, reliance on autochthonous OM by pelagic zooplankton ranged from 20% to 95% of production, declining exponentially with increasing river discharge. The results imply that discharge plays an important role in regulating the energy sources utilized by pelagic zooplankton in the upper estuary. We hypothesize that this is so because during high discharge, particulate organic C loading to the upper estuary increased and phytoplankton biomass decreased, thereby decreasing phytoplankton availability to the food web.

Keywords Allochthonous · Zooplankton · *Eurytemora* · *Bosmina* · Chesapeake Bay

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Introduction

River–estuary complexes are highly heterogeneous systems characterized by variable salinity, residence time, light attenuation, and tidal energy; diverse riparian and upland plant communities; and temporally and spatially variable zooplankton and fish assemblages. This heterogeneity presents formidable challenges for developing generalities about their food webs. Both autochthonous carbon (C), from local photosynthetic autotrophic production, and allochthonous C, from riparian and upland vegetation, may be utilized by aquatic metazoan grazers such as zooplankton and benthic macroinvertebrates. Terrestrial C subsidies can fuel aquatic ecosystem metabolism (Cole and Caraco 2001), increase production of upper trophic levels (Carpenter et al. 2005), and stabilize predator–prey interactions (Huxel et al. 2002). In higher-order streams and lakes, invertebrate consumers utilize allochthonous organic matter (OM) transported from terrestrial and riparian ecosystems, thereby enhancing ecosystem productivity (Jones 1992; Wallace et al. 1997). The current consensus for river–estuary complexes, however, is that their metazoan food webs are endogenously fueled by photosynthetic autotrophs (phytoplankton) even though phytoplankton generally comprise <10% of the particulate OM (POM)

available to consumers (Deegan and Garritt 1997; Hughes et al. 2000; Chanton and Lewis 2002; Sobczak et al. 2005). This is because allochthonous matter has lower nutritional value than phytoplankton, thus bioavailability of POM to upper trophic levels is largely determined by its phytoplankton content.

The factors that influence the relative importance of autochthonous and allochthonous C to aquatic food webs in river–estuary complexes are poorly understood. Vannote et al. (1980) hypothesize that a phytoplankton-based food web could arise in large rivers due to their semi-lentic nature, consistent with findings that river–estuary food webs are endogenously fueled. Along the southeastern coast of North America, coastal tributaries generally have extensive tidal freshwater regions—many of these tributaries have high concentrations of terrestrially derived chromophoric dissolved OM (CDOM), resulting in characteristic tea to black colors. The metabolism of coastal plain, blackwater tributaries, however, has increased reliance on allochthonous C with increasing size (Meyer and Edwards 1990). Further, CDOM can account for a large portion of light attenuation in estuaries (Branco and Kremer 2005), resulting in reduced productivity. It, therefore, seems plausible that allochthonous C could be important to the lower food web in blackwater, turbid estuaries. These contrasting perspectives are particularly applicable to those tidal blackwater systems characterized by both rapid light attenuation and long water residence times.

We used the C and nitrogen (N) stable isotope ratios of potential OM sources, zooplankton, and macroinvertebrates to identify those sources utilized by the lower food web. The C and N stable isotope ratios ($\delta^{13}C$, $\delta^{15}N$) among upland plants, marsh vegetation, freshwater phytoplankton, and estuarine phytoplankton differ with respect to C or N source and method of C fixation (Table 1). Consumers reflect these differences in their diet, demonstrating an average trophic discrimination (i.e., the difference between the consumer and its diet) of +0.4‰ $\delta^{13}C$ and +3.4‰ $\delta^{15}N$ per trophic level (Vander Zanden and Rasmussen 2001). The stable C isotope composition ($\delta^{13}C$) of upland vs. aquatic vegetation differs because these plants utilize different C pools with distinct isotopic ratios. Riparian plants utilizing the C_3 pathway have a $\delta^{13}C$ of about −28‰ because there is an uptake fractionation of about −21‰ over atmospheric CO_2 ($\delta^{13}C$ −7‰). In contrast, *Spartina* spp. are enriched ($\delta^{13}C$ −13‰) owing to reduced discrimination associated with the C_4 pathway (Mook and Tan 1991). Freshwater and estuarine phytoplankton can be separated where they utilize isotopically distinct pools of dissolved inorganic carbon (DIC); their ^{13}C discrimination, though generally −21‰, can vary with DIC concentration, phytoplankton growth rate, and nutrient availability (Mook and Tan 1991). In general, periphytons are more enriched than phytoplankton due to boundary layer effects that reduce isotopic discrimination (France 1995). The N stable isotope composition ($\delta^{15}N$) can help separate terrestrial sources (depleted) from aquatic (enriched; Table 1). Particulate $\delta^{15}N$ source values should be interpreted cautiously, however, because they can be altered indirectly (e.g., preferential uptake of isotopically light N by phytoplankton; Cifuentes et al. 1988) and directly (e.g., microbial activity; Altabet 1988).

Our objective was to characterize the contribution of autochthonous phytoplankton and allochthonous OM, both

Table 1 Stable isotope ratios of organic matter sources to the York River estuary based on published data from other estuaries (References) and the York River (typical ranges or means±1 standard deviation)

Organic matter source	References		York river estuary	
	$\delta^{13}C$	$\delta^{15}N$	$\delta^{13}C$	$\delta^{15}N$
Woody vegetation (C_3)[a,b,c]	−26 to −30	−4 to 4		
Emergent vascular plants (C_3)[c,d]	−28 to −30	6 to 10	−28.7 (±1.3)	8.4 (±1.3)
Humic-rich soils[b,d]	−26	0 to 4	−25.9 (±0.6)	4.2 (±1.1)
Benthic diatoms (salinity <5)[c,e,f]	−18 to −22	6 to 7		
Tidal freshwater marsh sediment[c,g]	−26	4 to 7	−26.4 (±0.1)	
Freshwater phytoplankton[b,c,d]	Variable	0 to 8	−32.1 to −38.3	4.7 (±0.5)
Estuarine phytoplankton[c,d,h]	−18 to −26	5 to 10	−23.5 (±1.2)	9.9 (±1.3)
Spartina spp. (C_4)[h]	−10 to −14	2 to 6		

[a] Peterson and Fry 1987
[b] Fry 1991
[c] Cloern et al. 2002
[d] Hoffman and Bronk 2006
[e] Deegan and Garritt 1997
[f] Hughes et al. 2000
[g] Raymond and Bauer 2001
[h] Fry and Sherr 1984

terrestrial (i.e., humic-rich soils) and riparian-derived (i.e., vascular plants), to zooplankton and macroinvertebrate production in the Mattaponi River, Virginia—a large, tea-colored tributary in the York River estuary. Specifically, we examined whether phytoplankton were the primary C source fueling the lower food web under naturally varying discharge rates. We contrasted spring (May–June) conditions among years (2002–2004) and spring and summer (July–September) conditions in 2003. Concurrently, we characterized the concentration, stable isotope ratios, and sources of DIC (ΣCO_2) and particulate organic C (POC) and N (Hoffman and Bronk 2006), as well as stable isotope ratios of the dominant pelagic fish, young American shad (*Alosa sapidissima*; Hoffman et al. 2007a).

Materials and Methods

Study Site The Mattaponi River is one of two major tributaries to the York River, a brackish, coastal plain tributary located in the southern end of Chesapeake Bay. The Mattaponi River is approximately 85 km long and almost entirely fresh (mouth at 76°47′12″ W, 37°31′40″ N). The river has one of the few largely forested watersheds left in Chesapeake Bay (upper river watershed 73.6% forest, 0.2% developed; Bilkovic et al. 2002). The head of tide is near river km 115 (km 0 is the York River mouth, km 52 the Mattaponi River mouth), the salt wedge is typically between km 67–76 (during the study, it ranged from km 52 at extreme low discharge to km 85 at extreme high discharge), and the tide range is approximately 1 m. Spring discharge is generally >35 m^3 s^{-1} and the turnover and residence times are short (14 and 45 days, respectively), whereas average discharge is 14.4 m^3 s^{-1} and turnover and residence times are long (29 and 88 days, respectively; Shen and Haas 2004).

Environmental Data Temperature and salinity profiles were measured at each zooplankton station with a YSI model 600 QS sonde. Freshwater stations were always well mixed. River discharge data were obtained from the U.S. Geological Survey gage located near Beaulahville, Virginia (#01674500), approximately 20 river km above the head of tide. No major tributaries enter the Mattaponi River between the gage and the river mouth so we treated the data as representative of the whole river.

Chlorophyll α and POC data were obtained from river-wide cruise data (Hoffman and Bronk 2006), though neither data were available for 2002. We estimated May–June POC loading to the upper estuary by multiplying each average daily discharge (1 May to 30 June) by the seasonal average POC concentration measured biweekly at the head of tide (km 115; n=4) and summing the daily values. Because POC data were not available for 2002, a potential range was estimated using 2003 and 2004 data. We report here monthly, river-wide Chl α means, which are the average of samples taken along the river axis (taken every 5–6 km from km 52 to 101). Finally, we estimated the portion of POC that was from phytoplankton using a C to Chl α conversion of 35:1, calculated from the regression published by Cloern et al. 1995 (Eq. 2; variables are temperature, irradiance, and phytoplankton growth rate). We used published light attenuation coefficient and phytoplankton growth rates from the upper York River estuary (Sin et al. 1999) and irradiance data from a buoy at the York River mouth (Virginia Institute of Marine Science unpublished data [P.O. Box 1346, Gloucester Point, Virginia 23062. Metadata and data are located at http://www.vims.edu/resources/databases.html#pier]).

Zooplankton Samples We sampled zooplankton and macroinvertebrates biweekly with a neuston net equipped with a flow meter (diurnally; 1.0×0.5 m net, 180 μm mesh). The timing and duration of samples varied in accordance with the timing and duration of peak discharge. We sampled from April through July 2002 (only monthly nonvolumetric samples), May through September 2003 (biweekly samples through August), and May through June 2004. Samples were taken along the river axis from km 115 to the limit of salt intrusion, randomly choosing a station from each of five (2002, 2004) or six (2003) 9.3 km strata (in 2003, six strata were used due to the higher discharge, resulting in a larger freshwater region). We towed the net near the surface over the deepest portion of the river channel (2–11 m depth). For 2003 and 2004, at each station, a short tow (approximately 1 min; preserved in 2% formaldehyde for archival purposes) was used for abundance estimation and a long tow (approximately 3 min; preserved in 95% ethanol) was used to collect invertebrates for stable isotope analysis. Ethanol was used for preservation because the effect on stable isotope ratios is small (Feuchtmayer and Grey 2003).

We estimated zooplankton and macroinvertebrate abundance by counting consecutive aliquots until at least 100 members of each taxon had been counted or 25% of a sample searched and then corrected for subsample and tow volume. Organisms were identified to the highest taxonomic resolution feasible (minimum of order). Adult copepods were tallied separate from earlier instars and nauplii. All cladoceran instars were tallied together. To characterize the spatial and temporal patterns in plankton abundance, we used a canonical correspondence analysis (CCA) on the $\log_{10}$-transformed density estimates (i.e., $\log(N+1)$) for the 22 most numerically abundant plankton. The environmental variables were salinity ($\log_{10}$-transformed), river kilometer, surface water temperature, and day of year. Data for 2003 and 2004 were analyzed together.

Stable Isotope Analysis Zooplankton and macroinvertebrates were picked from the sample, cleaned of detritus, and sorted by taxa. Additionally, a sample of mysids (*Neomysis americana*), which we did not sample by neuston net, was obtained in August 2003 (km 54; density estimate not available). We analyzed composite samples of small zooplankton. Large zooplankton and macroinvertebrates were analyzed whole or ground and subsampled. No isotopic analysis was performed if the biomass was insufficient. Samples were rinsed in deionized (DI) water and dried at 45°C for 24 h before analysis. When possible, we took replicate samples.

All stable isotope samples were combusted with an ANCA GSL gas purification module and elemental analyzer and analyzed with a Europa Hydra 20–20 continuous flow isotope ratio mass spectrometer (University of California—Davis Stable Isotope Facility, Davis, CA). Stable isotope ratios were calculated as $\delta X : \delta X = \left(R_{\text{sample}}/R_{\text{standard}} - 1\right) \times 10^3$, where X is the stable C or N isotope, R is the ratio of heavy to light stable isotopes, and Pee Dee Belmnite and air were the standards for δ^{13}C and δ^{15}N, respectively. The standard deviation (SD) between replicate reference samples was <±0.1‰ for C and N. The SD between replicate zooplankton samples was ±0.2‰ for C and ±0.3‰ for N. We corrected isotope ratios for mass (standardized to 100 μg N and 500 μg C based on linear standard curve) and ethanol preservation (+0.4‰ δ^{13}C, +0.6‰ δ^{15}N; Feuchtmayer and Grey 2003).

Food Web Characterization We identified trophic similarities related to feeding mode (taxa), region (sampling location), or both using an unweighted pair group method with arithmetic mean cluster analysis (UPGMA; Euclidean distance) using the δ^{13}C and δ^{15}N data (pooling all sampling dates). Data from 2003 and 2004 were analyzed separately. The analysis only included organisms sampled on at least three dates. Macroinvertebrate data from multiple strata occasionally were pooled in order to obtain at least three samples.

We examined differences in the springtime food web among years by estimating the proportional contribution (F) of each OM source to the most common pelagic zooplankton and macroinvertabrate (i.e., *Eurytemora affinis*, *Bosmina freyi*, cyclopoid copepods, and chironomid larvae) using a dual-isotope, three-source mixing model that incorporates OM source error (Phillips and Gregg 2001). In the freshwater portion of the Mattaponi River, the isotopic ratios of the major sources contributing to the POM pool (particulates <125 μm)—humic-rich terrestrial soils, vascular plant-derived matter, and endogenously produced phytoplankton—are sufficiently unique to discriminate among sources (Table 1). The mixing model mathematically states that the isotopic ratio of the tissue represents the proportional contribution from each source (F_{phyto}, F_{plant}, and $F_{\text{terrestrial}}$, respectively). For each date and freshwater region sampled, the model was applied to the zooplankton (z) δ^{13}C and δ^{15}N, adjusted for trophic discrimination (Δ_l, where Δ represents the average discrimination per trophic level and l the trophic level).

$$\delta^{13}\mathrm{C}_z - \Delta_l = \delta^{13}\mathrm{C}_{\text{plant}} \times F_{\text{plant}} + \delta^{13}\mathrm{C}_{\text{terrestrial}} \times F_{\text{terrestrial}} + \delta^{13}\mathrm{C}_{\text{phyto}} \times F_{\text{phyto}} \quad (1)$$

$$\delta^{15}\mathrm{N}_z - \Delta_l = \delta^{15}\mathrm{N}_{\text{plant}} \times F_{\text{plant}} + \delta^{15}\mathrm{N}_{\text{terrestrial}} \times F_{\text{terrestrial}} + \delta^{15}\mathrm{N}_{\text{phyto}} \times F_{\text{phyto}} \quad (2)$$

$$1 = F_{\text{plant}} + F_{\text{terrestrial}} + F_{\text{phyto}} \quad (3)$$

We used an average trophic discrimination of +0.4‰ δ^{13}C and estimated the δ^{15}N discrimination and the trophic level (methods below). The SD of the F estimates arising from both OM source and consumer isotopic variation was, on average, 0.08 for F_{phyto} (95% of all SD <0.15), 0.10 for $F_{\text{terrestrial}}$ (95% of all SD <0.14), and 0.13 for F_{plant} (95% of all SD <0.19).

Stable isotope ratios for the OM sources were estimated from Mattaponi River POM samples that resembled a pure source (Hoffman and Bronk 2006), similar to our previous application of the model to American shad data (Hoffman et al. 2007a; Table 1). The stable isotope ratios of OM sources were constants except for phytoplankton δ^{13}C ($\delta^{13}\mathrm{C}_{\text{phyto}}$). The $\delta^{13}\mathrm{C}_{\text{phyto}}$ varied by date and was estimated from the DIC δ^{13}C ($\delta^{13}\mathrm{C}_{\text{DIC}}$) using a typical −21‰ uptake discrimination (i.e., $\delta^{13}\mathrm{C}_{\text{phyto}}=\delta^{13}\mathrm{C}_{\text{DIC}}$ −21‰). This approach was corroborated by zooplankton data, which indicated utilization of a C source of about −35‰ when the $\delta^{13}\mathrm{C}_{\text{DIC}}$ was −13‰, and appeared reasonable because the temperature, pH, and nutrient and DIC concentrations were similar among years (Hoffman and Bronk 2006).

Source δ^{15}N ratios can be difficult to determine from field data. The $\delta^{15}\mathrm{N}_{\text{phyto}}$ (4.7‰) was estimated from a limited number of samples (n=5) but is consistent with dissolved inorganic N (DIN) ratios from unpolluted rivers (approximately 2–8‰; McClelland et al. 1997; Deegan and Garritt 1997), assuming little uptake discrimination. The $\delta^{15}\mathrm{N}_{\text{terrestrial}}$ (0±1.0‰ SD) in the food web model represents a fresh terrestrial signal because the cladoceran *B. freyi* often had δ^{15}N <4‰. Mattaponi River humic-rich soil OM, however, has enriched δ^{15}N compared to terrestrial soils (0–2‰; Martinelli et al. 1999), implying some microbial processing had occurred (Table 1). The C to N ratios of these POM samples were 10:12, which is typical of rivers and likely from soils of similar C to N (Hedges et al. 1986). Vascular plant-derived OM has many potential

sources in the watershed. The signature in the Mattaponi River, with enriched $\delta^{15}N$ (8.3‰) and high C to N (19–33), suggests it originates from littoral emergent vegetation (Cloern et al. 2002).

We treated trophic level as a variable in the model to account for potential bacteria consumption or omnivory. The model was fit to the data with respect to taxa and variable trophic level (l) with respect to region. We used a constant $\delta^{13}C$ trophic discrimination (+0.4‰) and estimated the $\delta^{15}N$ discrimination ($\Delta\delta^{15}N$) for each species by letting l=1.0 (grazer) and then maximizing $\Delta\delta^{15}N$ (up to +3.4‰) such that $F \geq 0$ for each source. Then the upper and lower l for each species were iteratively estimated by river stratum (each year analyzed separately), constrained by the result that for each OM source $F \geq 0$ (if such a solution was not possible, the sum of all negative F values was minimized, yielding only one trophic level estimate), and the mid-points used for the model output. We estimated river-wide means by sampling date, averaging among strata (two to four per date, depending on estuarine distribution).

We then tested whether utilization of autochthonous OM varies with river discharge using the output from the mixing model. We fit an exponential model using nonlinear, least-squares regression (three parameters; SigmaPlot 9.0) to the average F_{phyto} by sampling date for *E. affinis* and *B. freyi* and the average recent daily discharge, a 5-day running average, for each sampling date. The analysis included May–June results, 2002–2004. Similarly, we tested whether there is a relationship between the difference in $\delta^{13}C$ between either zooplankton (*Eurytemora* or *Bosmina*; $\delta^{13}C_z$) and the bulk POM pool ($\delta^{13}C_{POC}$) and river discharge using a nonlinear, least-squares regression. We used an exponential model with the difference $\delta^{13}C_z - \delta^{13}C_{POC}$ (again estimated for each sampling location and averaged by sampling date) as the dependent variable, which was used to test for a grazing response with regards to river discharge. A small $\delta^{13}C$ difference (approximately 1‰) between zooplankton and the bulk particulate pool implies nonselective grazing, whereas an increasingly depleted zooplankton signature compared to the bulk pool implies increasingly strong selection (or preferential assimilation) for an isotopically depleted source (i.e., phytoplankton).

Finally, the tidal freshwater food web for spring (May–June; 2002–2004) and the oligohaline tidal freshwater food webs for summer (July–September; 2003 only) were

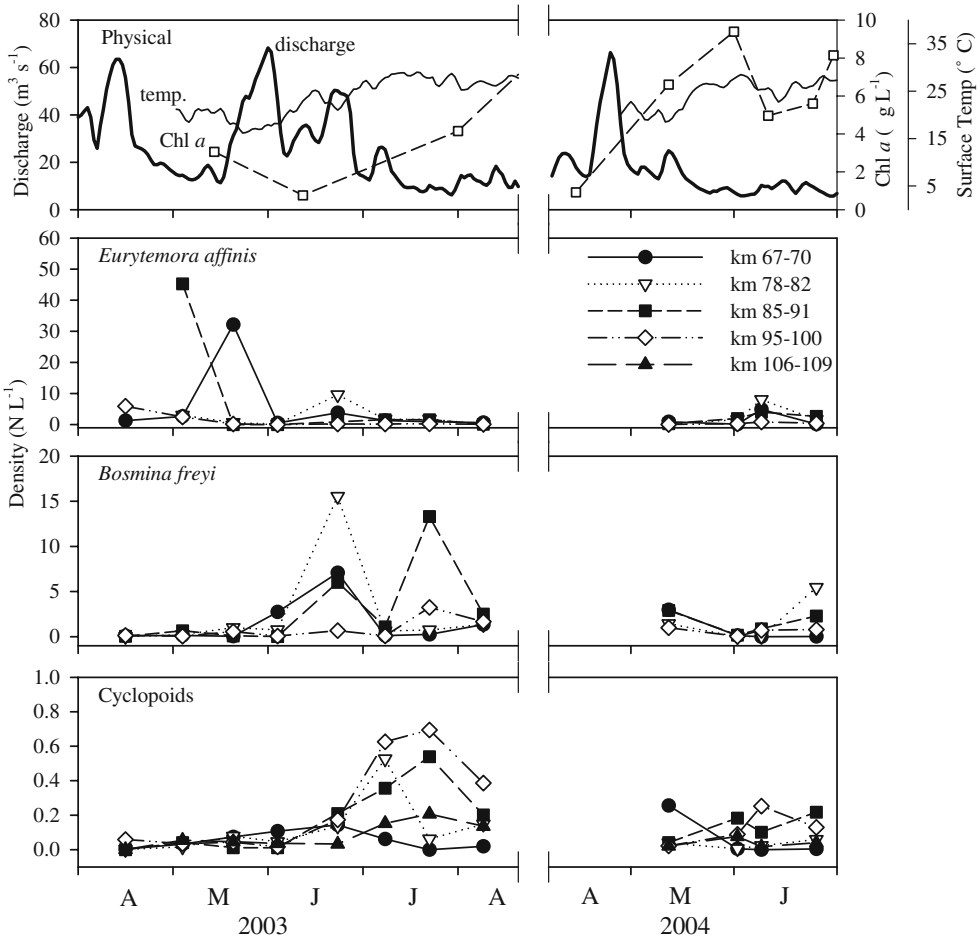


Fig. 1 Discharge, average chlorophyll α (*Chl* α), average daily surface temperature (measured at km 98), and *E. affinis*, *B. freyi*, and cyclopoid copepod (includes *Eucyclops* sp., *Paracyclops* sp., and *A. vernalis*) densities for the Mattaponi River, 2003 and 2004

qualitatively analyzed using stable isotope biplots to compare the stable isotope ratios of the consumers with potential sources. The mean $\delta^{13}C$ and $\delta^{15}N$ for a particular taxon within a season was estimated by averaging among sampling dates (freshwater stations pooled by date).

Results

Physical Environment In 2002, discharge was at or near historical lows owing to a regional draught, though a small spring freshet was observed in early May (15.3 m^3 s^{-1}). In 2003, a spring freshet in late March (90.9 m^3 s^{-1}) preceded unusually high discharge that was ≥95% of historical values throughout June and early July, returning to base flow by late-August (Fig. 1). In 2004, a spring freshet in mid-April (65.7 m^3 s^{-1}) was followed by typical springtime discharge, around 10 m^3 s^{-1}, and a return to base flow during summer.

Low flows during May–June of 2002 decreased springtime POC loading to the upper estuary by an order of magnitude compared to 2004, whereas high flows during 2003 increased allochthonous C loadings by an order of magnitude (Table 2). Compared to 2004, both the peak and mean Chl α concentrations were reduced in 2003, as was the proportion of POC comprised of phytoplankton (Table 2).

Zooplankton Abundance In general, the species-specific densities of zooplankton were low, less than 10 L^{-1}. The densities of aquatic macroinvertebrates were even lower, less than 1 L^{-1}. *E. affinis* and *B. freyi* were the most common of the 43 taxonomic groups identified (Table 3). The average density (±SD) of *E. affinis* during May and June 2003 was higher than May and June 2004 −5.1 (4.8) compared to 1.4 (1.5) L^{-1}, respectively. A similar result was obtained for *B. freyi* density −1.5 (0.2) compared to 1.0 (0.9) L^{-1}, respectively. In both years, the *B. freyi* peak followed the *E. affinis* peak (Fig. 1). The peak density of *E. affinis* and *B. freyi* was higher in 2003 than in 2004 (45 vs. 8 L^{-1} and 16 vs. 5 L^{-1}, respectively). In both years, cyclopoid copepod (including *Paracyclops* spp., *Eucyclops* spp., and *Acanthocyclops vernalis*) densities were low, less than 1 L^{-1}, peaking in July.

The assemblage was organized along the estuary (Fig. 2), indicated by the first CCA axis (28% of the variability). Cladocerans, cyclopoid copepods, and the calanoid copepod *Diaptomus* sp. were most abundant towards the head of tide, whereas gammarid amphipods, mud and fiddler crab zoea (*Uca* spp.), and the calanoid copepod *Acartia* spp. were located near the oligohaline river mouth. The second CCA axis is related to seasonality (10% of the variability): *Acartia* spp., amphipods, harpacticoid copepods, *Chydorus* sp., and *Diaptomus* sp. were most abundant during the spring when the river was cool. The two most ubiquitous zooplankton, *E. affinis* and *B. freyi*, were located in the center of the CCA triplot; their peak abundance occurred during mid- to late-spring in the lower and central portions of the tidal freshwater.

Food Web Characterization The results from the UPGMA cluster analysis indicate that organisms from different habitats relied on different OM sources (Fig. 3). The UPGMA analysis clusters organisms by various habitats, including terrestrial (i.e., flying ants (Formicidae)); brackish estuary (*Acartia* spp., *Halicyclops* sp., mysids); benthic (i.e., harpacticoid copepods, gammarid amphipods, *Uca* spp. zoea); and riverine (e.g., *E. affinis*, *B. freyi*, cyclopoids). Among this latter group, they cluster into those with relatively depleted $\delta^{15}N$ (*B. freyi*, chironomid larvae) and those with higher $\delta^{15}N$ (*E. affinis*, cyclopoids), owing to either differences in trophic level or diet (i.e., those with depleted $\delta^{15}N$ are more reliant on terrestrial-derived fine POM) or both. Results for 2004 were similar, though the isotopic ratios of benthic invertebrates and zooplankton were closer to one another, resulting in a slightly different clustering hierarchy than in 2003.

The dual-stable isotope mixing model indicates that zooplankton utilization of the different OM sources varied by year, taxonomic group, and season (Fig. 4). The largest difference among years was the marked shift in reliance on

Table 2 Characterization of the tidal freshwater portion of the Mattaponi River, Virginia during May and June, 2002 through 2004

Year	Q (m^3 s^{-1})	POC (mg L^{-1})	Loading (mt C)	Chl α (μg L^{-1})		Proportion phytoplankton
	Range	Mean (SD)		Mean (SD)	Max	% POC (SD)
2002	0.0–0.4	0.5–1.4	0.2–0.6	n/a	n/a	n/a
2003	11.4–68.2	1.4 (0.1)	234	1.6 (1.1)	1.0, 4.4	13 (7)
2004	4.6–24.9	0.5 (0.2)	26	3.9 (2.1)	6.6, 8.0	4 (2)

See "Materials and Methods" for data sources and calculations. Discharge (Q) ranges refer to daily values, 1 May to 30 June. For Chl α, both the mean and SD among monthly samples and monthly peak (max) values are shown for May and June, respectively
n/a Data not available

Table 3 Taxa identified from the Mattaponi River, Virginia, including the location (river kilometer, km 52 is the Mattaponi River mouth) and day of peak density (max), as well as the number of stations where they were captured during 2003 and 2004 (stations; 71 total stations)

Group	Taxon	Max (N m^{-3})	Location (km)	Day	Stations (*n*)	Code
Calanoida	*E. affinis*	45,289.3	87	4-May	69	EU
	Acartia spp.	5,024.7	57	21-Jul	13	AT
	Diaptomus sp.	22.2	108	5-May	12	DI
Cyclopoida	*Halicyclops* sp.	1,824.2	67	5-May	19	HL
	Eucyclops sp.	1,293.4	91	2-Sep	64	EC
	Paracyclops sp.	50.6	67	5-May	33	PC
	A. vernalis	371.5	91	2-Sep	40	AC
	Cyclops spp.	1,664.9	91	2-Sep	64	CY
	Copepodites	1,167.1	91	25-May	32	
	Nauplii	25.1	54	22-Jun	35	
Poecilostomatoida	*Ergasilus* sp.	14.5	57	21-Jul	11	PS
Harpacticoida	Harpacticoids	429.0	56	3-Jun	44	HR
Cladocera	*B. freyi*	15,516.4	78	22-Jun	71	BO
	Chydorus sp.	548.8	108	4-May	38	CS
	Chydoridae	46.7	108	5-May	54	CD
	Ceriodaphnia sp.	323.7	109	3-Jun	45	CR
	Scapholeberis mucronata	300.0	91	2-Sep	48	SC
	Diaphanosoma brachyurum	469.8	78	22-Jun	47	DA
	Daphnia sp.	47.9	108	5-May	15	
	Leptodora kindti	4.0	98	2-Sep	1	
	Cladocera (unknown)	3.5	108	5-May	1	
Malacostraca	*Uca* spp.	586.7	70	17-Jun	22	UC
	Gammaridae	74.5	56	3-Jun	12	GM
	Decapoda: Astacoidea	0.2	106	1-Jun	1	
Ostrocoda	Ostracoda	53.8	67	4-May	49	OS
Achari	Araneae	4.7	89	17-Jun	11	AR
	Acarina	14.6	108	25-May	50	AR
Gastropoda	Gastropoda	281.3	70	21-Jul	33	GS
Insecta (larvae)	Chironomidae	17.8	106	21-Jul	32	CM
	Chaoboridae	3.4	106	2-Sep	1	
	Trichoptera	4.6	108	7-Jul	8	TR
	Plecoptera	8.3	108	4-May	2	
	Ephemeroptera	23.6	106	2-Sep	34	EP
Insecta (pupae)	Diptera	2.3	109	3-Jun	5	PD
Insecta (adults)	Formicidae	1.2	108	5-May	3	FR
	Thysanoptera	12.9	108	5-May	9	
	Hemiptera	1.2	108	5-May	1	
	Diptera	11.7	108	5-May	23	AD
	Insecta (unknown)	6.5	106	21-Jul	17	
Other	Tardigrada	0.8	95	4-May	2	
	Oligochaete	1.9	106	21-Jul	3	
	Collembola	31.6	108	5-May	26	

Cyclops spp. is *Eucyclops* sp., *Paracyclops* sp., and *A. vernalis* combined

autochthonous phytoplankton by the pelagic zooplankton *E. affinis*, *B. freyi*, and cyclopoids in 2002 and 2004 to reliance on allochthonous sources in 2003. In May–June 2002 and 2004, pelagic zooplankton production generally was fueled by phytoplankton (F_{phyto} 0.61–0.93), whereas terrestrial and vascular plant-derived matter fueled the majority of production in May–June 2003 (F_{phyto} 0.14–0.32; Table 4).

In contrast, isotopic ratios of benthic (e.g., amphipods) and terrestrial (e.g., flying ants) organisms were similar among years, as were *Diaptomus* sp. and the ephemeropteran and chironomid larvae (Fig. 4). Notably, whereas chironomid pupae and adults had similar $\delta^{13}C$, we sampled both life stages with either enriched (approximately 8–10‰) or depleted (approximately 2–3‰) $\delta^{15}N$, implying a trophic difference, likely owing to both ontogenetic and species

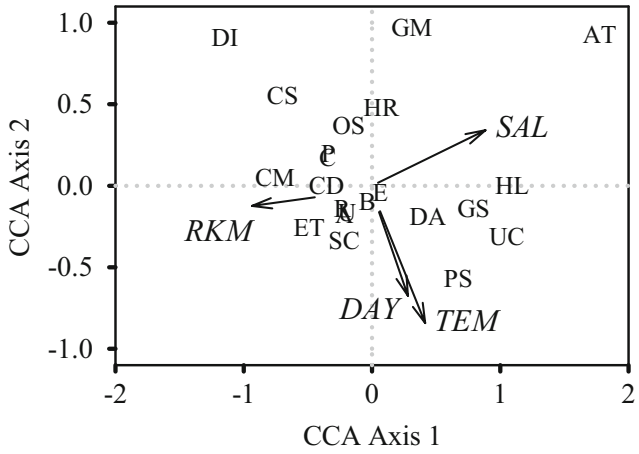


Fig. 2 Canonical correlation analysis (*CCA*) of the 22 most abundant zooplankton in the Mattaponi River, Virginia; species codes generally follow Table 3, except *E. affinis* (*E*), *B. freyi* (*B*), *Paracyclops* sp. (*P*), *A. vernalis* (*A*), *Ceriodaphnia* sp. (*C*), Achari (spiders and mites combined; *R*), and pooled ephemeroptera and trichoptera larvae (*ET*). Environmental variables are salinity (*SAL*), river kilometer (*RKM*), day of year (*DAY*), and surface temperature (*TEM*)

Fig. 4 Stable isotope ratios of common Mattaponi River tidal freshwater zooplankton for May–June 2002–2004. *Symbols* indicate average ±1 SD. The average (±SD) isotopic compositions of freshwater phytoplankton (*phytoplankton*), humic-rich sediments (*terrestrial*), and vascular plant-derived matter (*plant*) are shown by the boxes (see "Materials and Methods" for details). The *dotted line* indicates the expected stable isotope ratios of consumers utilizing phytoplankton, assuming typical trophic discrimination (+0.4‰ $\delta^{13}C$, +3.4‰ $\delta^{15}N$ per trophic level). Tidal freshwater included stations above km 76. Zooplankton symbols were assigned based on the cluster analysis (*circle*—fine particulate organic matter grazer; *triangle*—phytoplankton/omnivorous grazer; *square*—benthic; *upside-down triangle*—terrestrial). Species codes are listed in Table 3; larvae (*CM*), pupae (*CM**), and adult (CM^+) life stages of chironomids are indicated

differences. Still, the majority of chironomid larvae production was fueled by allochthonous OM in 2003 and 2004 (Table 4). Trophic dissimilarities among the groups identified in the cluster analysis were apparent. Gammarid amphipods, harpacticoid copepods, and *Uca* spp. had enriched $\delta^{13}C$, consistent with a benthic OM source. Flying ants had an isotopic composition similar to soils and humic-rich sediments. *Diaptomus* sp., ephemeropteran larvae, and chironomids utilized a mix of autochthonous and allochthonous OM.

The nonlinear regression of F_{phyto} for *E. affinis* and *B. freyi* and discharge was significant (Fig. 5). Reliance on phytoplankton by *E. affinis* and *B. freyi* significantly declines as river discharge increases. The relationship spans the 3-year time series and predicts the fraction of zooplankton production supported by phytoplankton (r^2= 0.72). This relationship is likely due to the decreased phytoplankton availability during high discharge (Table 2), reducing the zooplankton's ability to preferentially assimilate or selectively graze phytoplankton, indicated by increasingly depleted zooplankton $\delta^{13}C$ compared to POC (e.g., $\delta^{13}C_{Bosmina}$–$\delta^{13}C_{POC}$) as river discharge decreases (Fig. 5).

The stable isotope biplots from summer sampling revealed additional seasonal and spatial differences in the food web. There was evidence for increased utilization of autochthonous phytoplankton by the pelagic zooplankton in

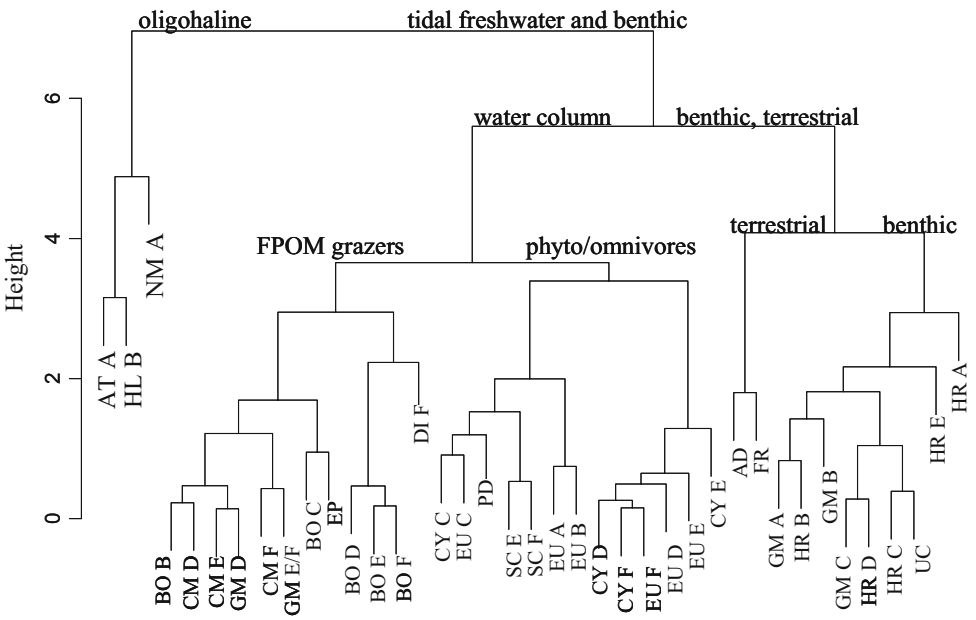
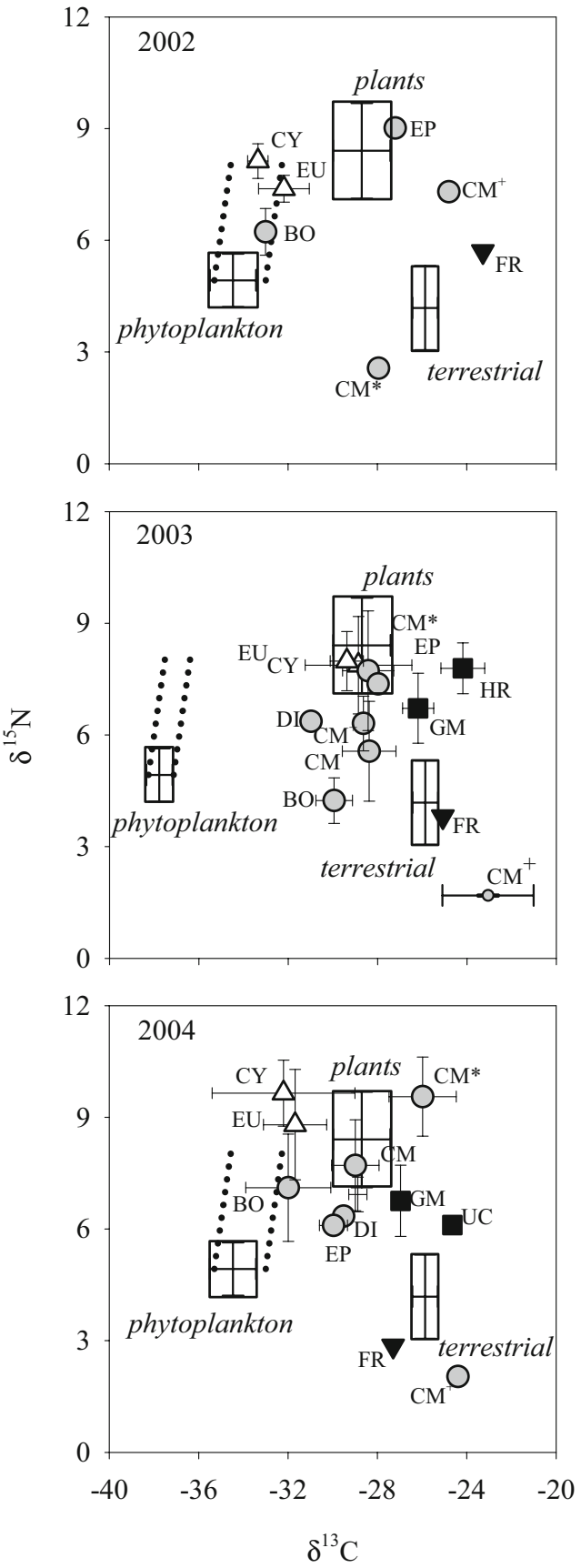


Fig. 3 Dendogram from the cluster analysis (unweighted pair group with arithmetic mean method) of zooplankton $\delta^{13}C$ and $\delta^{15}N$ data from 2003. The *first two letters* are the species codes, listed in Table 3; *NM N. americana*. The *next letter* denotes the region of the river, which is defined as follows: *A*—km 52–65; *B*—km 67–74; *C*—km 76–83; *D*—km 85–93; *E*—km 95–102; *F*—km 104–111. If no region code is given, the value is a river-wide average. The descriptions at the branches are interpretative, based on the biology of the various organisms (e.g., fine particulate organic matter (*FPOM*) grazer)



summer compared to spring 2003 (Fig. 5), indicated by a shift toward more depleted $\delta^{13}C$ (Fig. 6). Benthic and terrestrial organisms did not demonstrate a similar seasonal shift. In the oligohaline portion of the river (Fig. 6), *E. affinis*, *B. freyi*, and the amphipods were isotopically enriched compared to tidal freshwater, with isotopic signatures more similar to the brackish water zooplankton, such as *N. americana*. This implies increased reliance on lower estuary sources, possibly phytoplankton-derived OM (delivered to the region via estuarine circulation), salt marsh grasses, or both.

Discussion

The data imply that estuarine pelagic zooplankton production is not necessarily limited by aquatic primary productivity because the lower food web can utilize terrestrial C, switching from an endogenous, phytoplankton-based food web to an exogenous, terrestrial- and riparian vegetation-based food web. The tidal freshwater food web relies on allochthonous OM during high discharge periods. Pelagic zooplankton switch to reliance on autochthonous production once base flow conditions resume and phytoplankton availability increases. In contrast, benthic and terrestrial organisms rely on C sources specific to their respective habitats, even though they occupy the water column. Organic matter produced in the lower estuary is utilized in the oligohaline region by some zooplankton and macroinvertebrates during base flow. Thus, the reliance on cross-ecosystem subsides relies on watershed-scale physical forces (i.e., discharge), the OM sources available, and the feeding habit of the organism.

Our interpretation hinges on whether we can correctly constrain the major OM sources to those used in the food web model. There is evidence to support our approach. The three sources were chosen because suspended POM in the freshwater portion of the Mattaponi River was dominated by vascular plant-derived matter and humic-rich sediments during spring; phytoplankton contribution increased during summer (Hoffman and Bronk 2006). Three upper-estuarine OM sources were not included in the model: benthic algae or periphyton, salt marsh grasses (*Spartina* spp., a C_4 plant), and freshwater marsh sediments. Periphyton and salt marsh grasses were not included because they are more $\delta^{13}C$ enriched than is consistent with the consumer data (Table 1). Further, periphyton biomass is likely negligible in the river channel, relative to other OM sources, owing to periphyton's resistance to flushing and export to the channel. Marsh sediment was not included because it is isotopically similar to terrestrial sediments (Table 1); however, in all isotope research in the York River estuary, the enriched $\delta^{13}C$ signal (−26‰ to −28‰) is found to

Table 4 Fraction (*F*) contributed by autochthonous phytoplankton (phyto) and allochthonous humic-rich sediments (terrestrial) and vascular plant-derived organic matter (plant) to production of *E. affinis*, *B. freyi*, *Cyclops* spp. (includes *Eucyclops* sp., *Paracyclops* sp., and *A. vernalis*), and chironomid larvae in the Mattaponi River, May and June 2002–2004

Species	Year	F_{phyto} (±SD)	$F_{terrestrial}$ (±SD)	F_{plant} (±SD)
Eurytemora	2002	0.82 (0.17)	0.13 (0.13)	0.05 (0.03)
	2003	0.25 (0.03)	0.40 (0.08)	0.35 (0.08)
	2004	0.61 (0.13)	0.18 (0.21)	0.21 (0.10)
Bosmina	2002	0.92 (0.02)	0.09 (0.14)	−0.01 (0.15)
	2003	0.32 (0.09)	0.52 (0.11)	0.16 (0.03)
	2004	0.74 (0.16)	0.17 (0.14)	0.09 (0.05)
Cyclops spp.	2002	0.93 (0.00)	0.06 (0.03)	0.01 (0.03)
	2003	0.14 (0.06)	0.49 (0.27)	0.37 (0.31)
	2004	0.74 (0.28)	0.09 (0.09)	0.16 (0.20)
Chironomidae	2002	n/a	n/a	n/a
	2003	0.16 (0.05)	0.55 (0.17)	0.30 (0.22)
	2004	0.28 (0.26)	0.53 (0.16)	0.19 (0.16)

Fractions from the dual-isotope, three-source mixing model are means among dates sampled (±SD, two to four dates per year depending on estuarine distribution) and, therefore, may not sum to 1.0 exactly
n/a Data not available

originate from terrestrial-derived C (Raymond and Bauer 2001; McCallister et al. 2004; Hoffman and Bronk 2006).

Feeding Behaviors Different grazing strategies among *E. affinis* and *B. freyi* were indicated by their different $\delta^{15}N$ ratios. *E. affinis*, a cosmopolitan, euryhaline calanoid copepod, consumes microzooplankton, diatoms, detritus, and particle-attached bacteria (Hughes et al. 2000; Tackx et al. 2004; Kerner et al. 2004; Reaugh et al. 2007), consistent with the opportunistic feeding behavior indicated by their isotopic shift. Microzooplankton consumption by the omnivorous *E. affinis* is consistent with its enriched $\delta^{15}N$ composition, generally about +3‰, or a trophic level, relative to *B. freyi*. The enriched $\delta^{15}N$ was likely the combined result of greater consumption of vascular plant-derived OM that is $\delta^{15}N$ enriched compared to humic-rich sediments (Table 4), greater trophic discrimination due to increased omnivory, and feeding at an elevated trophic level (Table 5). *B. freyi* is a small, cosmopolitan, filter-feeding cladoceran that feeds on detritus, unicellular algae, and bacteria (Kerner et al. 2004). The $\delta^{15}N$ ratio of *B. freyi* was generally equal to or less than the $\delta^{15}N_{PN}$, implying either assimilation of a particulate fraction with similar $\delta^{13}C$ to the bulk pool but with depleted $\delta^{15}N$ or else low trophic fractionation (Table 5), likely due to the high C to N of POM (e.g., Adams and Sterner 2000).

Cyclopoids were less numerous than calanoids, though increasingly important towards the head of tide. The stable isotope ratios of *Cyclops* spp. and *E. affinis* were similar in all regions of the river, implying reliance on a similar OM source; however, the data are difficult to interpret because there are multiple taxa in this group, including *Paracyclops* sp., *Eucyclops* sp., and *A. vernalis*. We separated these taxa for analysis but their isotopic ratios were similar. *Paracyclops* sp. and *Eucyclops* sp. consume POM and microzooplankton (Williamson 1983; Brandl 2005), whereas *A. vernalis* consumes microzooplankton (Brandl 2005). Our finding could be due to either similar feeding behavior or contamination of the sample resulting from misidentification of early instars. The enriched $\delta^{15}N$ of *Halicyclops* sp. (Fig. 6), a benthic, oligohaline cyclopoid, is consistent with preferential grazing on bacteria (e.g., Carman and Thistle 1985).

Chironomid larvae were the most common macroinvertebrate sampled and are an important prey for young fishes. Their isotopic signature indicated reliance on allochthonous OM, likely a mix of terrestrial-derived fine particulates and amorphous detritus (Hall and Meyer 1998). Similarly, ephemeropteran larvae consumed a mix of allochthonous and autochthonous OM (Fig. 4).

Those organisms identified by a benthic signature (enriched $\delta^{13}C$, −24‰ to −26‰, and depleted $\delta^{15}N$, 2‰ to 5‰), including harpacticoid copepods, gammarid amphipods, and *Uca* zoea (Fig. 3), were likely consuming allochthonous detritus, either degraded terrestrial matter or freshwater marsh sediments (Table 1). The stable isotope ratios are equivocal owing to the isotopic similarity of these last two OM sources. The mouthparts of these detrivores are adapted for tearing, raking, and scraping, not filtration (Smith 2001), which likely explains the lack of a seasonal shift toward utilization of autochthonous OM, despite their apparent ability to occupy water column habitat.

Influence of River Discharge The results suggest that river discharge influences energy source and trophic level. Both physical mixing and river discharge are important physical processes that influence Mattaponi River POM composition

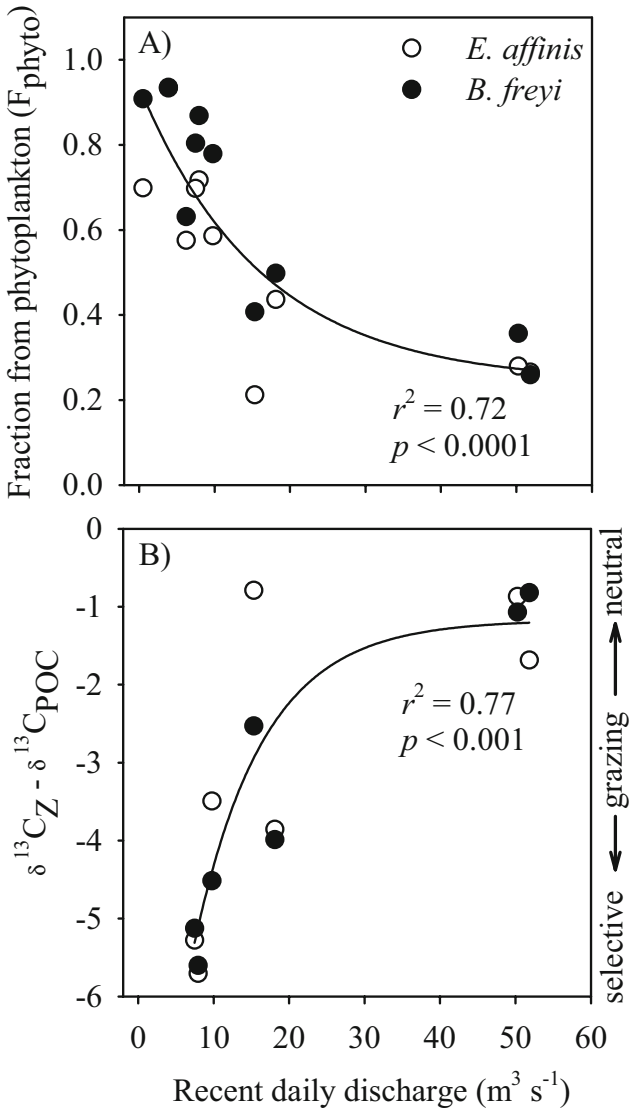


Fig. 5 Fraction (*F*) of the diet obtained from endogenous phytoplankton (**a**) and the isotopic difference between the available particulate organic carbon (*POC*) and either the calanoid copepod *E. affinis* or the cladoceran *B. freyi* ($\delta^{13}C_z - \delta^{13}C_{POC}$; **b**) in response to river discharge. *Points* represent river-wide means for a sampling date (generally three stations). The *lines* show the best-fit exponential model

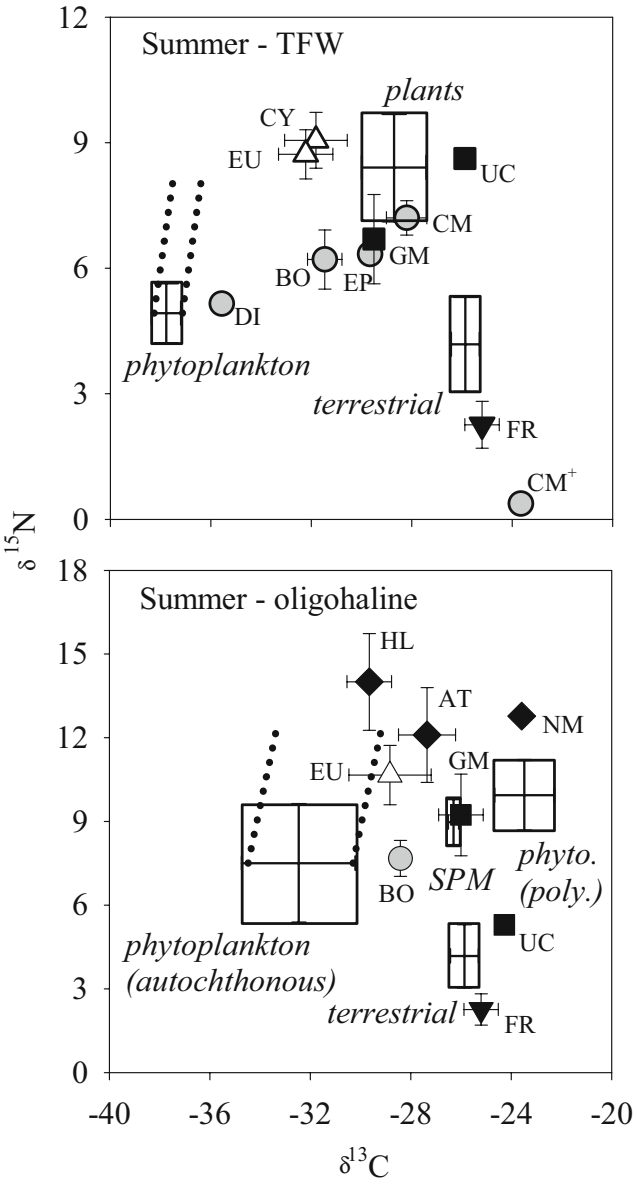


Fig. 6 Stable isotope biplot of common Mattaponi River zooplankton during 2003 for oligohaline (km 52–74) and tidal freshwater (km 76–111) regions. *Symbols* indicate July–September average (±1 SD). The *dotted line* and the potential sources for tidal freshwater (*TFW*) follow Fig. 3. Additional sources for the oligohaline portion include autochthonous phytoplankton ($\delta^{13}C_{phytoplankton}$ estimated from $\delta^{13}C_{DIC}$—see "Materials and Methods" for details; $\delta^{15}N_{phytoplankton}$ from literature (Table 1)), phytoplankton from the polyhaline York River estuary ("*phyto.* (*poly.*)"; Table 1), and suspended particulate organic matter (*SPM*) measured from this region (interpreted to be a mix of all available sources, including vascular plant-derived matter; Hoffman and Bronk 2006). *Symbols* were assigned as in Fig. 4, including oligohaline zooplankton (*diamond*). Species codes are listed in Table 3; *NM N. americana*

(Hoffman and Bronk 2006). During high discharge, quick residence time and low transparency flush and suppress phytoplankton production (Sin et al. 1999), and suspended POC concentrations increase, dramatically increasing allochthonous C loadings to the upper estuary (Table 3). In May–June 2003, Chl α concentration was low (<1 μg L^{-1}), C to N_{POM} high (>20; Hoffman and Bronk 2006), and phytoplankton comprised less than 5% of the bulk POM pool, supporting only 14–25% of pelagic zooplankton production. In contrast, during May–June 2004, phytoplankton comprised >10% of the bulk POM pool and supported 61–74% of pelagic zooplankton production. Allochthonous OM, therefore, is utilized by zooplankton during high discharge when phytoplankton are scarce, but endogenously produced phytoplankton is disproportionately utilized once available.

Table 5 The ^{15}N trophic fractionation ($\Delta\delta^{15}N$) and average trophic level (l) estimated when fitting the three-source mixing model to zooplankton data from May–June in 2002–2004 (see "Materials and Methods" for details)

Plankton	$\Delta\delta^{15}N$			Trophic level, l (±SD)		
	2002	2003	2004	2002	2003	2004
E. affinis	3.0	2.1	3.4	1.0 (0.0)	1.7 (0.8)	1.2 (0.2)
B. freyi	1.4	0.7	1.7	1.0 (0.0)	2.0 (0.5)	1.2 (0.2)
Cyclops spp.	3.1	3.4	3.4	1.1 (0.1)	1.3 (0.3)	1.2 (0.2)
Chironomidae	n/a	2.4	3.0	n/a	1.1 (0.2)	1.6 (0.5)

The average trophic level is the mean among stations and dates of the fitted trophic level midpoints. A single outlier was identified and excluded from the average trophic level: *Bosmina*, km 78 on 22 June 2004 (2.7)
n/a Data not available

This finding is corroborated by the observation that pelagic zooplankton were increasingly isotopically depleted with respect to POC as discharge decreased (Fig. 5). This analysis presumes that isotopic turnover is sufficiently rapid to respond to environmental conditions. At typical May–June temperatures, the instantaneous weight-specific growth rate of *E. affinis* would range from 0.03 to 0.08 $days^{-1}$ (Escaravage and Soetaert 1995) and of *B. freyi* from 0.2 to 0.6 $days^{-1}$ (Acharya et al. 2006). At these rates, we expect the zooplankton to reach isotopic equilibrium within 10–30 days (Hoffman et al. 2007b), which is likely a conservative estimate because it does not take into account individual metabolism or population growth.

Allochthonous Energy Transfer The question arises as to whether the data support the hypothesis that allochthonous particles or bacteria were consumed. The results suggest that bacteria are important, but likely not directly consumed. The model trophic level of zooplankton was >1 (Table 5), implying consumption of bacteria (whether free-living or particle attached), microzooplankton, or both. A study within Chesapeake Bay performed over the same years found that *E. affinis* consumes more microzooplankton in high discharge years (Reaugh et al. 2007). Consistently, the trophic fractionation was lower and trophic level was higher during 2003 (high discharge year) for *E. affinis* and *B. freyi*. Microzooplankton consumption is implied by the elevated trophic levels in this study (l >1.5), though the same effect could be achieved if zooplankton consumed detritus enriched by microbial colonization because assimilation of DIN by microbes can significantly enrich $\delta^{15}N$ (Caraco et al. 1998). Deegan and Garritt (1997) concluded that microzooplankton were likely not an important diet source for estuarine zooplankton. Their argument was that microbes would be utilizing water column NH_4^+ ($\delta^{15}N$ 5‰); thus, bacteria would have enriched $\delta^{15}N$ (6‰), resulting in enriched $\delta^{15}N$ of microzooplankton (9‰) and mesozooplankton (12‰). The maximum *E. affinis* $\delta^{15}N$ was approximately 11‰, however, so it is possible that microzooplankton, including rotifers, which are bacteriovores that can dominate the upper estuary zooplankton community in Chesapeake Bay (Park and Marshall 2000), completed the trophic link between bacteria and *E. affinis*.

In lakes, POC is the major allochthonous OM fraction supporting zooplankton production; bacteria support only a small fraction (Cole et al. 2006). A mix of detritus and bacteria can yield high trophic transfer to invertebrates (Caraco et al. 1998; Hall and Meyer 1998). The OM source may be relevant. In May–June 2003, the POM was largely derived from vascular plants, whereas humic-rich sediments were the major source in May–June 2004 (Hoffman and Bronk 2006). If fresh, the vascular plant OM is more labile than humics, which are largely refractory (Mann 1998), particularly by supplying bioavailable dissolved leachates to consumers (Sun et al. 1997). Further, dissolved organic C can form microparticles, potentially bypassing the microbial food web and increasing uptake efficiency into higher trophic levels (Kerner et al. 2003).

Cross-ecosystem Subsidies *E. affinis* biomass in the mainstem of Chesapeake Bay increases during high discharge years (Kimmel et al. 2006; Reaugh et al. 2007). We found a similar result in the York River estuary. In the Chesapeake Bay mainstem, where the *Eurytemora* peak biomass is located in brackish water, it is hypothesized that it is due to greater phytoplankton productivity owing to higher nutrient loading (Reaugh et al. 2007). In the York River estuary, where the *E. affinis* peak biomass is located in tidal freshwater, reliance on allochthonous OM apparently supports the larger biomass. High allochthonous C loadings might offset the presumably low lability of this energy source, potentially increasing secondary production; however, this hypothesis remains a frontier for research. Reduced predation on mesozooplankton is not a likely explanation because juvenile American shad (*A. sapidissima*) density, the dominant zooplankton consumer in this river, was higher in 2003 than in 2004 (Hoffman et al. 2007a). This study elucidates an important role for

allochthonous OM in the estuarine food web. The Chesapeake Bay watershed has been and continues to be dramatically transformed by urbanization (Jantz et al. 2005). Disconnecting the estuary from its floodplain through the construction of dams and the filling of wetlands could profoundly impact the food web.

Acknowledgements We thank Deborah Steinberg, Michael Sierszen, John Morrice, and two anonymous reviewers for helpful comments on the manuscript; Brian Watkins, Patricia Crewe, Kristen Delano, Ashleigh Rhea, and Demetria Christo for field assistance; and Demetria Christo, Melanie Chattin, and David Harris for preparation and analysis of stable isotope samples. This work was supported by a National Science Foundation Graduate Research Fellowship to J. C. Hoffman and sponsored in part by NOAA Office of Sea Grant, US Department of Commerce, under Grant NA03OAR4170084 to the Virginia Graduate Marine Science Consortium and Virginia Sea Grant College Program, with additional support from the Wallop–Breaux program of the US Fish and Wildlife Service through the Marine Recreational Fishing Advisory Board of the Virginia Marine Resources Commission (Grants F-116-R-6 and 7). This is contribution of the Virginia Institute of Marine Science, The College of William and Mary.

References

Acharya, K., P.A. Bukaveckas, J.D. Jack, M. Kyle, and J.J. Elser. 2006. Consumer growth linked to diet and RNA-P stoichiometry: response of *Bosmina* to variation in riverine food resources. *Limnology and Oceanography* 51: 1859–1869.

Adams, T.S., and R.W. Sterner. 2000. The effect of dietary nitrogen content on trophic level ^{15}N enrichment. *Limnology and Oceanography* 45: 601–607.

Altabet, M.A. 1988. Variations in nitrogen isotopic composition between sinking and suspended particles: implications for nitrogen cycling and particle transformation in the open ocean. *Deep Sea Research* 35: 535–554.

Bilkovic, D.M., C.H. Hershner, and J.E. Olney. 2002. Macroscale assessment of American shad spawning and nursery habitats in the Mattaponi and Pamunkey rivers. *North American Journal of Fisheries Management* 22: 1176–1192.

Branco, A.B., and J.N. Kremer. 2005. The relative importance of chlorophyll and colored dissolved organic matter (CDOM) to the prediction of the diffuse attenuation coefficient in shallow estuaries. *Estuaries* 28: 643–652.

Brandl, Z. 2005. Copepods and rotifers: predators and their prey. *Hydrobiologia* 546: 475–489.

Caraco, N.F., G. Lampman, J.J. Cole, K.E. Limburg, M.L. Pace, and D. Fischer. 1998. Microbial assimilation of DIN in a nitrogen rich estuary: implications for food quality and isotope studies. *Marine Ecology Progress Series* 167: 59–71.

Carman, K.R., and D. Thistle. 1985. Microbial food partitioning by three species of benthic copepods. *Marine Biology* 88: 143–148.

Carpenter, S.R., J.J. Cole, M.L. Pace, M. Van de Bogert, D.L. Bade, D. Bastviken, C.M. Gille, J.R. Hodgson, J.F. Kitchell, and E.S. Kritzberg. 2005. Ecosystem subsidies: terrestrial support of aquatic food web from ^{13}C addition to contrasting lakes. *Ecology* 86: 2737–2750.

Chanton, J., and F.G. Lewis. 2002. Examination of coupling between primary and secondary production in a river-dominated estuary: Apalachicola Bay, Florida, USA. *Limnology and Oceanography* 47: 683–697.

Cifuentes, L.A., J.H. Sharp, and M.L. Fogel. 1988. Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. *Limnology and Oceanography* 33: 1102–1115.

Cloern, J.E., C. Grenz, and L. Vidergar-Lucas. 1995. An empirical model of the phytoplankton chlorophyll:carbon ratio—the conversion factor between productivity and growth rate. *Limnology and Oceanography* 40: 1313–1321.

Cloern, J.E., E.A. Canuel, and D. Harris. 2002. Stable carbon and nitrogen isotope composition of aquatic and terrestrial plants of the San Francisco Bay estuarine system. *Limnology and Oceanography* 47: 713–729.

Cole, J.J., and N.F. Caraco. 2001. Carbon in catchments: connecting terrestrial carbon losses with aquatic metabolism. *Marine and Freshwater Research* 52: 101–110.

Cole, J.J., S.R. Carpenter, M.L. Pace, M.C. Van de Bogert, J.L. Kitchell, and J.R. Hodgson. 2006. Differential support of lake food webs by three types of terrestrial organic carbon. *Ecology Letters* 9: 558–568.

Deegan, L.A., and R.H. Garritt. 1997. Evidence for spatial variability in estuarine food webs. *Marine Ecology Progress Series* 147: 31–47.

Escaravage, V., and K. Soetaert. 1995. Secondary production of the brackish copepod communities and their contribution to carbon fluxes in the Westerschelde estuary (The Netherlands). *Hydrobiologia* 311: 103–114.

Feuchtmayer, H., and J. Grey. 2003. Effect of preparation and preservation procedures on carbon and nitrogen stable isotope determinations from zooplankton. *Rapid Communications in Mass Spectrometry* 17: 2605–2610.

France, R.L. 1995. Differentiation between littoral and pelagic food webs in lakes using stable carbon isotopes. *Limnology and Oceanography* 40: 1310–1313.

Fry, B. 1991. Stable isotope diagrams of freshwater food webs. *Ecology* 72: 2293–2297.

Fry, B., and E. Sherr. 1984. $d^{13}C$ measurements as indicators of carbon flow in marine and freshwater ecosystems. *Contributions in Marine Science* 27: 13–47.

Hall, R.O., and J.L. Meyer. 1998. The trophic significance of bacteria in a detritus-based stream food web. *Ecology* 79: 1995–2012.

Hedges, J.I., W.A. Clark, P.D. Quay, J.E. Richey, A.H. Devol, U. de, and M. Santos. 1986. Compositions and fluxes of particulate organic material in the Amazon River. *Limnology and Oceanography* 31: 717–738.

Hoffman, J.C., and D.A. Bronk. 2006. Inter-annual variation in stable carbon and nitrogen isotope biogeochemistry of the Mattaponi River, Virginia. *Limnology and Oceanography* 51: 2319–2332.

Hoffman, J.C., D.A. Bronk, and J.E. Olney. 2007a. Contribution of allochthonous carbon to American shad production in the Mattaponi River, Virginia using stable isotopes. *Estuaries and Coasts* 30: 1034–1048.

Hoffman, J.C., D.A. Bronk, and J.E. Olney. 2007b. Tracking nursery habitat use by young American shad in the York River estuary, Virginia using stable isotopes. *Transactions of the American Fisheries Society* 136: 1285–1297.

Hughes, J.E., L.A. Deegan, B.J. Peterson, R.M. Holmes, and B. Fry. 2000. Nitrogen flow through the food web in the oligohaline zone of a New England estuary. *Ecology* 81: 433–452.

Huxel, G.R., K. McCann, and G.A. Polis. 2002. Effects of partitioning allochthonous and autochthonous resources on food web stability. *Ecological Research* 17: 419–432.

Jantz, P., S. Goetz, and C. Jantz. 2005. Urbanization and the loss of resource lands in the Chesapeake Bay watershed. *Environmental Management* 36: 808–825.

Jones, R.I. 1992. The influence of humic substances on lacustrine planktonic food chains. *Hydrobiologia* 229: 73–91.

Kerner, M., H. Hohenberg, S. Ertl, M. Reckermann, and A. Spitzy. 2003. Self-organization of dissolved organic matter to micelle-like microparticles in river water. *Nature* 422: 150–154.

Kerner, M., S. Ertl, and A. Spitzy. 2004. Trophic diversity within the planktonic food web of the Elbe Estuary determined on isolated individual species by ^{13}C analysis. *Journal of Plankton Research* 26: 1039–1048.

Kimmel, D.G., W.D. Miller, and M.R. Roman. 2006. Regional scale climate forcing of mesozooplankton dynamics in Chesapeake Bay. *Estuaries and Coasts* 29: 375–387.

Mann, K.H. 1998. Production and use of detritus in various freshwater, estuarine, and coastal marine ecosystems. *Limnology and Oceanography* 33: 910–930.

Martinelli, L.A., M.C. Piccolo, A.R. Townsend, P.M. Vitousek, E. Cuevas, W. McDowell, G.P. Robertson, O.C. Santos, and K. Treseder. 1999. Nitrogen stable isotopic composition of leaves and soil: tropical versus temperate forests. *Biogeochemistry* 46: 45–65.

McCallister, L.S., J.E. Bauer, J.E. Cherrier, and H.W. Ducklow. 2004. Assessing sources and ages of organic matter supporting river and estuarine bacterial production: a multiple isotope ($D^{14}C$, $d^{13}C$, and $d^{15}N$) approach. *Limnology and Oceanography* 49: 1687–1702.

McClelland, J.W., I. Valiela, and R.H. Michener. 1997. Nitrogen-stable isotope signatures in estuarine food webs: a record of increasing urbanization in coastal watersheds. *Limnology and Oceanography* 42: 930–937.

Meyer, J.L., and R.T. Edwards. 1990. Ecosystem metabolism and turnover of organic carbon along a blackwater river continuum. *Ecology* 71: 668–677.

Mook, W.G., and F.C. Tan. 1991. Stable carbon isotopes in rivers and estuaries. In *Biogeochemistry of major world rivers*, eds. E.T. Degens, S. Kempe, and J.E. Richy, 245–264. New York: Wiley.

Park, G.S., and H.G. Marshall. 2000. The trophic contributions of rotifers in tidal freshwater and estuarine habitats. *Estuarine, Coastal and Shelf Science* 51: 729–742.

Peterson, B.J., and B. Fry. 1987. Stable isotopes in ecosystem studies. *Annual Review of Ecology and Systematics* 18: 293–320.

Phillips, D.L., and J.W. Gregg. 2001. Uncertainty in source partitioning using stable isotopes. *Oecologia* 127: 171–179.

Raymond, P.A., and J.E. Bauer. 2001. DOC cycling in a temperature estuary: a mass balance approach using natural ^{14}C and ^{13}C isotopes. *Limnology and Oceanography* 46: 655–667.

Reaugh, M.L., M.R. Roman, and D.K. Stoecker. 2007. Changes in plankton community structure and function in response to variable freshwater flow in two tributaries of the Chesapeake Bay. *Estuaries and Coasts* 30: 403–417.

Shen, J., and L. Haas. 2004. Calculating age and residence time in the tidal York River using three-dimensional model experiments. *Estuarine, Coastal and Shelf Science* 61: 449–461.

Sin, Y., R.L. Wetzel, and I.C. Anderson. 1999. Spatial and temporal characteristics of nutrient and phytoplankton dynamics in the York River estuary, Virginia: analyses of long-term data. *Estuaries* 22: 260–275.

Smith, D.G. 2001. Pennak's freshwater invertebrates of the United States: Porifera to Crustacea. 4New York: Wiley.

Sobczak, W.V., J.E. Cloern, A.D. Jassby, B.E. Cole, T.S. Schraga, and A. Arnsberg. 2005. Detritus fuels ecosystem metabolism but not metazoan food webs in San Francisco Estuary's freshwater delta. *Estuaries* 28: 124–137.

Sun, L., E.M. Perdue, J.L. Meyer, and J. Weis. 1997. Use of elemental composition to predict bioavailability of dissolved organic matter in a Georgia river. *Limnology and Oceanography* 42: 714–721.

Tackx, M.L.M., N. de Pauw, R. Van Miegham, F. Azémar, A. Hannouti, S. Van Damme, F. Fiers, N. Daro, and P. Meire. 2004. Zooplankton in the Schelde estuary, Belgium and The Netherlands. Spatial and temporal patterns. *Journal of Plankton Research* 26: 133–141.

Vander Zanden, M.J., and J.B. Rasmussen. 2001. Variation in $d^{15}N$ and $d^{13}C$ trophic fractionation: Implications for aquatic food web studies. *Limnology and Oceanography* 46: 2061–2066.

Vannote, R.L., G.W. Minshall, K.W. Cummins, J.R. Sedell, and C.E. Cushing. 1980. The river continuum concept. *Canadian Journal of Fisheries and Aquatic Sciences* 37: 130–137.

Wallace, J.B., S.L. Eggert, J.L. Meyer, and J.R. Webster. 1997. Multiple trophic levels of a forest stream linked to terrestrial litter inputs. *Science* 277: 102–104.

Williamson, C.E. 1983. Invertebrate predation on planktonic rotifers. *Hydrobiologia* 104: 385–39.