

Primary consumers and particulate organic matter: Isotopic evidence of strong selectivity in the estuarine transition zone

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Abstract

The freshwater–saltwater transition zones of upper estuaries often contain high concentrations of particulate organic matter (POM) that could potentially support their productive food webs. Our objectives were to define the carbon and nitrogen isotopic characteristics of POM across the estuarine transition zone (ETZ) of the St. Lawrence River, Canada, and to determine the availability of this material to primary consumers. The $\delta^{13}\text{C}$ of seston from upstream freshwater samples ($-26.3 \pm 0.9\text{‰}$) indicated a large contribution of terrestrially derived organic material, whereas downstream sites had higher values ($-24.8 \pm 0.5\text{‰}$) attributable to dilution with marine phytoplankton. The ETZ turbidity maximum had more negative values ($-27.0 \pm 1.6\text{‰}$), especially the $<5\text{-}\mu\text{m}$ fraction ($-30.0 \pm 1.3\text{‰}$) that contributed 56–86% of the POM. The $\delta^{13}\text{C}$ of the dominant consumer species in the ETZ (*Bosmina longirostris*, *Keratella* sp., *Eurytemora affinis*, and adult *Dreissena polymorpha*) averaged $-21.0 \pm 0.9\text{‰}$, well above the seston values. The $\delta^{15}\text{N}$ of the three animals of lowest trophic position averaged $7.3 \pm 0.8\text{‰}$, less than 2‰ above the seston $\delta^{15}\text{N}$ ($5.7 \pm 0.2\text{‰}$ for all sites). Our results imply that the bulk POM is largely detrital and unavailable to the ETZ food web and that the primary consumers feed selectively on phytoplankton despite its low contribution ($<10\%$) to total POM. A cross-system comparison of isotopic data shows that the large enrichment of ^{13}C in consumers relative to POM is unusual, underscoring the distinctive character of turbid, upper estuarine ecosystems.

The freshwater-saltwater transition zone of estuaries is an ecotonal region of sharp gradients, high concentrations of particulate organic matter (POM), and a productive food web. The exact source of organic carbon for primary consumers in such regions, and estuaries in general, has been a subject of much discussion. Some studies have identified the importance of phytoplankton and benthic microalgae in estuarine food webs (Mallin and Paerl 1994) while others have drawn attention to POM derived from salt marshes (Deegan et al. 1990). Conversely, some authors have argued that salt marsh particles and terrestrial inputs would not play a major role in estuarine trophic processes because of the complex

detrital processing cycle that would largely dissipate the carbon and energy (Peterson et al. 1994). These organic-rich heterotrophic ecosystems typically contain abundant populations of bacteria and protist grazers (Frenette et al. 1995) that also might play a role in fueling higher trophic levels.

The estuarine transition zone (ETZ) is critically important for upstream as well as downstream ecological processes, for example, as a larval fish nursery and in contaminant processing (Vincent and Dodson 1999), yet the biogeochemical and food web relationships of such transition zones have been little explored. In the present study we applied a stable isotope approach to determine the sources and fate of particulate organic matter in the St. Lawrence estuary and to evaluate the relationship between consumers and bulk POM across the ETZ. Stable carbon and nitrogen isotopes have been considered valuable tracers because POM from different sources often have distinctive isotopic compositions (e.g., Thornton and McManus 1994; Kendall et al. 2001), although recent studies have drawn attention to the great variability in these signatures in estuarine ecosystems (Cloern et al. 2002). From our analysis of field samples and a cross-system comparison with marine and freshwater environments elsewhere, we conclude that the ETZ represents an unusual ecosystem type in which the bulk POM is largely unavailable to the food web and that highly selective feeding on a continuous supply of autochthonous carbon supports the biological productivity of this frontal system.

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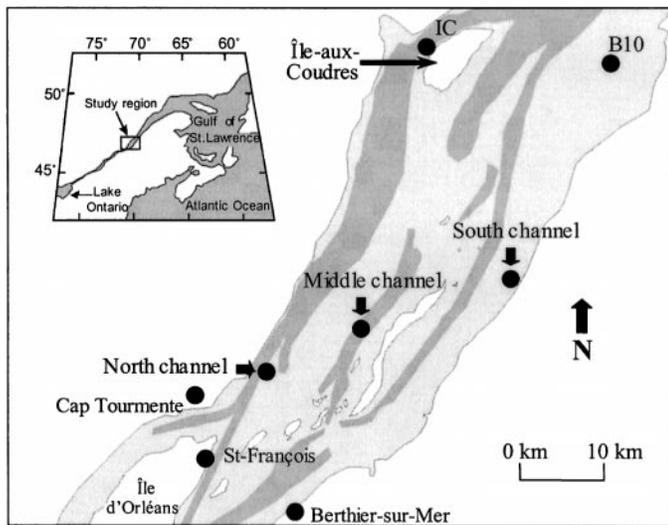


Fig. 1. Location of sampling sites in the St. Lawrence River estuarine transition zone. Additional sampling was in the freshwater reach at Québec City, 40 km upstream of Berthier-sur-Mer. The darker shading indicates >10-m depth.

Materials and methods

Study area—The turbid upper estuary of the St. Lawrence River is characterized by high rates of phytoplankton and bacterial production (Vincent et al. 1996) and large standing stocks of mysids and other zooplankton (Winkler et al. 2003). It is a productive fish nursery, specifically for Atlantic tomcod (*Microgadus tomcod*) and Rainbow smelt (*Osmerus mordax*) (Dodson et al. 1989). The ETZ has a complex topography and is divided into three main channels: north, middle, and south. The maximum depth of the South Channel in the salinity range of 1–2 is 8 m, in comparison to 25 m (salinity ~ 5) in the North Channel. There are semidiurnal variations in salinity and related properties at all sites in the ETZ as water masses are advected up and down the estuary by tens of kilometers over each tidal cycle (Barnard et al. 2003; Winkler et al. 2003). Marshes in this upper estuarine region are dominated by three plant species (all are C3 plants): *Scirpus americana*, *Sagittaria latifolia*, and *Zizania aquatica*.

Sampling—Three sampling cruises were undertaken in summer 2001 (10 and 20 July, 1 August) across the ETZ to obtain samples in each of the three main channels (Fig. 1): North and Middle Channel where surface water salinities averaged 1.3, and the South Channel where salinities averaged 3.6. In addition, two upstream, freshwater stations were visited (in front of Québec City; salinity = 0.1) every week, and two stations well downstream of the ETZ (salinity = 11–14) were sampled, on 20 July in the North Channel and on 8 August in the South Channel. One of the downstream stations was located 10-m offshore Île-aux-Coudres (north shore) and the second was in the South Channel opposite the township of La Pocatière (Sta. B10). Temperature and salinity were measured by profiling with a Sea Bird CTD

probe model Sealogger SBE-19 and the turbidity of discrete samples was measured with a shipboard nephelometer (HF Scientific, model DRT-15CE).

Four liters of surface water were collected at each sampling site on the river and estuary for seston analysis. Sub-samples of water for isotopic and chlorophyll *a* (Chl *a*) fractionation were prefiltered through 250 μm (total seston) or 250 μm then 5 μm (<5 μm seston), and then through pre-combusted (500°C, 1 h) Whatman GF/F filters that were stored frozen until analysis. For POM estimation (ash-free dry weight), 300–500 ml of the prescreened water were filtered through preweighed, precombusted GF/F filters that were then dried (overnight at 60°C), reweighed, combusted at 500°C for 1 h and weighed again.

Zooplankton samples were obtained by horizontal trawls in the ETZ (North, Middle, and South Channels) using a 64- μm net. The samples were preserved on ice until laboratory processing, and the dominant species were then sorted by hand, washed with deionized water, freeze-dried, and kept in a desiccator until subsequent analysis. Five samples of *Bosmina longirostris*, 14 samples of *Eurytemora affinis*, and four samples of *Keratella* sp. (South Channel only) were analyzed from the ETZ, each a composite of >10 individuals. Six samples of 5–10 adult zebra mussels (*Dreissena polymorpha*) were collected by hand at low tide at St. François and Berthier-sur-Mer on exposed rocky substrata near the shore, and the tissue removed from the shells. All animal samples were washed, freeze-dried, and then ground using an agate mortar and pestle.

Plant and sediment sampling was carried out twice during summer at the Cap Tourmente Nature Reserve. This site is situated adjacent to the region of maximum turbidity and is considered a source of sediments into the estuary (Lucotte and d'Anglejan 1986). The hand-picked plants were carefully washed with deionized water before freeze-drying and ground with an agate mortar and pestle. Duplicate sediment samples were taken at each of the two stations at Cap Tourmente with a 10-ml syringe. These were acidified with 10% HCl followed by three consecutive rinses with deionized water (Schubert and Nielsen 2000).

Sample analysis—Samples for Chl *a* analysis were extracted in ethanol (95%) and measured by fluorometry (Sequoia-Turner, Model 450) following Nusch (1980) with calculations from Jeffrey and Welschmeyer (1997). Samples for isotopic analysis were acidified with fuming 36% HCl (Yamamoto and Kayanne 1995; Kendall et al. 2001). This method was selected because it showed no loss of organic C or N during inorganic carbon removal. Isotopic analyses were carried out by the Commission Géologique du Canada using an Isotope Ratio Mass Spectrometer (Fisons Instruments, model VG Prism Isotech) coupled with an Elemental Analyzer (NA 2500 series). Stable isotope ratios were expressed in δ notation as parts per thousand (‰) according to the equation

$$\delta X = [(R_{\text{sample}}/R_{\text{standard}}) - 1] \times 1000$$

where *X* is ^{13}C or ^{15}N and *R* is the corresponding ratio $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$. The standards for ^{13}C and ^{15}N were PeeDee Belemnite (PDB) and atmospheric N_2 , respectively. Repli-

Table 1. Characteristics of the surface waters, total seston, and $<5 \mu\text{m}$ fraction across the freshwater–saltwater transition zone of the Saint Lawrence River. Each seston value is the mean of 18 samples collected July–August 2001 (\pm SD). Values are in milligrams per cubic meter (Chl *a*), grams per cubic meter (POM), or parts per thousand (isotopic abundance).

	Estuarine transition zone				
	Upstream	South channel	Middle channel	North channel	Downstream
Temperature ($^{\circ}\text{C}$)	21.68	22.37	21.03	21.04	14.80
Salinity	0.10	3.60	0.90	2.54	12.65
Turbidity (NTU)	6.73	38.33	26.93	81.97	37.00
Seston					
Chl <i>a</i> , total	1.3 \pm 0.4	7.3 \pm 3.5	3.5 \pm 1.7	7.0 \pm 9.6	1.8 \pm 2.6
< 5 μm	0.9 \pm 0.3	1.1 \pm 0.5	1.3 \pm 0.6	1.4 \pm 0.5	0.6 \pm 0.7
POM, total	2.4 \pm 0.8	7.7 \pm 2.6	4.9 \pm 0.9	11.7 \pm 8.3	10.0 \pm 2.5
< 5 μm	1.9 \pm 0.5	6.6 \pm 4.2	4.0 \pm 1.2	6.5 \pm 2.1	8.0 \pm 3.5
$\delta^{13}\text{C}$, total	-26.0 \pm 0.9	-25.7 \pm 1.7	-28.2 \pm 1.0	-27.2 \pm 1.3	-24.8 \pm 0.5
< 5 μm	-26.9 \pm 1.2	-29.8 \pm 1.8	-29.9 \pm 1.5	-30.6 \pm 0.8	-26.2 \pm 0.2
$\delta^{15}\text{N}$, total	5.9 \pm 0.7	6.1 \pm 0.3	5.9 \pm 0.6	5.8 \pm 0.5	5.0 \pm 2.1
< 5 μm	5.4 \pm 1.3	6.1 \pm 0.2	5.8 \pm 0.5	5.5 \pm 0.5	6.6 \pm 0.4

cate analyses of standards gave analytical errors (SD) of $\pm 0.23\text{‰}$ for carbon and $\pm 0.28\text{‰}$ for nitrogen.

Results and discussion

Temperature, salinity, and seston—The ETZ sites had similar surface temperatures to the riverine freshwater site, but were up to 7°C warmer than the downstream marine stations (Table 1). Salinity of the ETZ sites was highly variable, ranging from 0.5–5 depending on the tidal state. Throughout the period of sampling, the ETZ contained markedly higher concentrations of seston (turbidity and POM; Table 1) relative to the upstream and downstream sites, consistent with earlier studies on this frontal region (Winkler et al. 2003). Chlorophyll *a* concentrations were also higher in this region (Table 1) but less than values reported in the early 1990s prior to the invasion of zebra mussels throughout the St. Lawrence River system (Vincent et al. 1996). The $<5\text{-}\mu\text{m}$ fraction contributed the majority of Chl *a* in the freshwater section of the river (on average 68%, Table 1), but in the ETZ this fell to 15–40%, consistent with the entrapment of larger cells by estuarine recirculation (Frenette et al. 1995) and aggregation of picoplankton and nanoplankton into heterogeneous flocs (Barnard et al. 2003). Fine material dominated the seston at all sites, with the $<5\text{-}\mu\text{m}$ fraction contributing 56–86% of the total POM. Previous studies on the sedimentology of the St. Lawrence estuary identified 4 μm as the median particle size within the ETZ (Kranck 1979).

Isotopic variation in the seston—The ^{13}C characteristics of the seston (Table 1) varied as a function of size fraction, site, and date of sampling. There were highly significant differences between fractions, with $\delta^{13}\text{C}$ values always much more negative in the $<5\text{-}\mu\text{m}$ relative to the total fraction (for all stations and dates, $t = 612$, $n = 35$, $\text{df} = 34$; $p < 0.0001$). In the ETZ, $\delta^{13}\text{C}$ values of both fractions varied significantly among sampling dates (three-way analysis of

variance [ANOVA] for three dates, three stations, and two fractions; $F_{2,17} = 14.42$, $n = 2$; $p < 0.0001$). In the freshwater region, however, there was no significant temporal variation (two-way ANOVA for eight dates and two fractions; $F_{7,18} = 1.46$, $n = 4$; $p = 0.24$). $\delta^{13}\text{C}$ values differed significantly among stations (two-way ANOVA for all six stations and fractions; $F_{5,50} = 16.90$; $n = 2$; $p < 0.0001$) and even within the ETZ (three-way ANOVA; $F_{2,17} = 5.11$; $n = 2$; $p < 0.0001$), with highest values in the Middle Channel where salinities were lowest. The $\delta^{15}\text{N}$ values were uncorrelated with $\delta^{13}\text{C}$ ($r = -0.153$; $n = 60$, $\text{df} = 58$; $p = 0.24$) and showed much less variation, with no significant differences between fractions for all sites, nor among sampling dates either in the ETZ (three-way ANOVA; $F_{2,17} = 1.95$, $n = 2$; $p = 0.16$) or at the upstream site (two-way ANOVA; $F_{7,18} = 1.45$; $n = 4$, $p = 0.25$). Differences among stations were at the limit of significance (two-way ANOVA for all six stations and fractions; $F_{5,50} = 2.44$, $n = 2$; $p = 0.05$).

The isotopic analyses showed ^{13}C -depleted POM in all channels of the ETZ on all sampling dates, with an overall mean of $-27.0 \pm 1.6\text{‰}$ (total) and more negative values in the $<5\text{-}\mu\text{m}$ fraction ($-30.0 \pm 1.3\text{‰}$). These results are consistent with a study by Tan and Strain (1983) that also measured highly negative values in the maximum turbidity zone ($\sim -28\text{‰}$). Our results are also similar to the trends observed in carbon isotopic ratios among upstream, ETZ, and downstream stations by Gearing and Pocklington (1990). However, our data showed a negative offset of approximately 2‰ relative to the latter study, probably due to the removal of inorganic carbon in our samples by acidification. Increasing $\delta^{13}\text{C}$ enrichment of the seston along saltwater gradients has been observed in estuaries elsewhere and has been attributed to the shift in particles originating from terrigenous versus marine sources (Riera and Richard 1997).

Isotopic characteristics of the primary consumers—The $\delta^{13}\text{C}$ values for the four consumer species in the ETZ ranged from -22.5 to -20.5‰ , with a mean overall value of -21.0

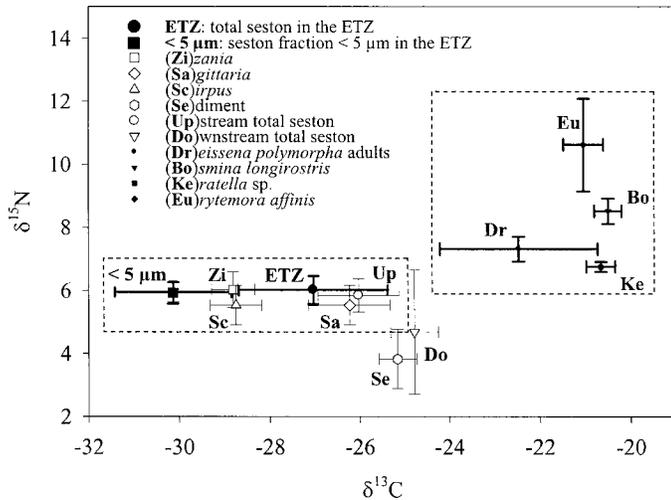


Fig. 2. Dual isotope plot for seston, plants, sediments, and primary consumers in the St. Lawrence estuary, July–August 2001. The boxes demarcate the values within the estuarine transition zone for total and $<5\text{-}\mu\text{m}$ seston (left) and for the animal populations (right). Each value is the mean \pm SD for all samples.

$\pm 0.9\text{‰}$. There were no significant differences between the four species; however, the *Dreissena* populations showed a much greater variance in their isotopic signal than the others (Fig. 2). The mean value for the four species lies strikingly above the $\delta^{13}\text{C}$ signatures for the ETZ seston: 6‰ above the total fraction and 9‰ above the $<5\text{-}\mu\text{m}$ fraction that dominates the POM of this region. These differences greatly exceed the typical trophic enrichment of $\leq 1\text{‰}$ between organisms and their food sources (Cabana and Rasmussen 1996). The $\delta^{15}\text{N}$ values averaged 8.5‰ (± 1.9) for the four animals, with significantly higher values for *Eurytemora*, reflecting its higher trophic position and its known feeding on prey items in addition to phytoplankton including bacteria, aggregates, and even individuals of its own species (Heerkloss et al. 1993; Zimmermann-Timm 2002). The difference between the mean value for the three animal populations of lowest trophic rank and the ETZ seston was 1.4‰ , well below the usual trophic enrichment of $3\text{--}5\text{‰}$ (Cabana and Rasmussen 1996), although ^{15}N enrichment can be highly variable depending on the exact diet (McCutchan et al. 2003). These results imply that most of the organic seston in the ETZ is not used by primary consumers and that the animals are highly selective, using a component that amounts to only a small, isotopically distinct fraction of the total POM pool. This strong selectivity among food sources could take place during filtration and particle capture by the animals or by selective digestion, assimilation, and egestion of this material.

Sources of POM for the primary consumers—POM enters the St. Lawrence upper estuary from at least eight different sources: (1) terrestrial-derived plant and soil materials from upstream; (2) plant material and sediments from the adjacent salt marshes; (3) benthic macroalgae and periphyton; (4) bacterioplankton and protist grazers arriving by advection

and produced by in situ growth; (5) organic matter derived from municipal wastes; (6) freshwater phytoplankton advecting in from upstream; (7) phytoplankton produced in situ; and (8) marine phytoplankton entering from downstream. The isotopic and associated data allow an initial triage to determine which of these sources predominate in the ETZ and which might potentially fuel the estuarine food web.

The ETZ and upstream freshwater seston had a strongly negative $\delta^{13}\text{C}$ signal, suggesting that terrestrial materials (source 1) are likely to be the dominant contribution to POM within this system, as in upper estuaries elsewhere (Riera and Richard 1997). Our measurements are within the range reported by Barth et al. (1998) for POM samples several hundred km further upstream in the upper St. Lawrence River. The latter authors suggested that the upstream ratios were mostly the result of phytoplankton photosynthesis in the Great Lakes at the head of the St. Lawrence; however, the ETZ values also lie close to the signature for terrestrial C3-plants (-27‰ ; Cai et al. 1988; Kendall et al. 2001) and within the range compiled by Finlay (2001) for riverine POM, riparian vegetation, and dissolved organic carbon (-26 to -30‰). A strong terrestrial influence on isotopic signatures in the St. Lawrence estuary is consistent with stoichiometric analyses by Barnard et al. (2003), who found that seston from the same ETZ sites as those sampled in the present study had an average C:N ratio of 9.7 (by weight). This value lies well above the Redfield ratio for plankton (5.6 by weight), indicating a major contribution of carbon-rich terrestrial detritus to the total POM pool. The disparity between the $\delta^{13}\text{C}$ of the consumers and seston implies that little of this terrestrial C passes into the estuarine food web.

To evaluate source 2 we analyzed three plant species and the organic-rich sediments of Cap Tourmente (Fig. 1). These samples had $\delta^{13}\text{C}$ signatures that fell within 2‰ of the POM values and could thus also be a contributing source for the sestonic pool. The ^{15}N signatures of the three plant species were similar to each other and to the POM pool; however, Cap Tourmente sediments had relatively light $\delta^{15}\text{N}$, implying little contribution. These sediments, as well as the plants, lie well away from the consumers in terms of ^{13}C and are unlikely to be an important food source. The highly turbid waters of the ETZ allow very little light penetration to the bottom (1% irradiance at less than 1-m depth; Vincent et al. 1996) and therefore the benthic mechanism, source 3, would also seem unlikely to play a significant role in this ecosystem.

Given that the dominant source of dissolved organic carbon and POM is likely to be terrigenous, it seems that bacterioplankton would have a signal approximating that of terrestrial material and therefore well below that of the consumers. Elsewhere, the carbon isotopic signature of bacteria has been found to be negative relative to phytoplankton (Kelley et al. 1998), reflecting the isotopic ratio of the bulk dissolved organic carbon (Coffin et al. 1989), which in rivers reflects that of terrestrial POM (Finlay 2001). The bacterial contribution of total carbon flux to the invertebrates (mechanism 4) therefore seems unlikely to be large, but this will require direct testing.

Significant quantities of sewage-derived C and N enter the

St. Lawrence from discharge at Montreal, Quebec City, and other municipalities. Analyses by Debruyne and Rasmussen (2002) showed that sewage POM discharged from the Montreal urban community had relatively enriched $\delta^{13}\text{C}$ values, around -20.48% . This could potentially contribute to an increment in $\delta^{13}\text{C}$ for any consumers that fed on this material. However, the signature of sewage particulate organic nitrogen was -3.35% , well below that of the consumers ($+7.3$) and implying little feeding on POM from this source. This leaves phytoplankton advected in and produced by in situ growth (mechanisms 6–8) as the most likely candidates for the transfer of carbon to the primary consumers.

A first-order estimate of the phytoplankton contribution to the total POM pool can be made by converting the Chl *a* values in Table 1 to carbon. Using a conversion factor of 50:1 (Vincent et al. 1996) gives estimates of phytoplankton-C within the ETZ of 175–363 mg m^{-3} . This amounts to only 6–9% of the carbon in the total POM pool, insufficient to affect the overall POM isotopic signature. However, this quantity is still large in absolute terms. For example, Winkler et al. (2003) estimate the average population density of *Eurytemora* in this region as 25,000 individuals m^{-3} with an average body biomass of 4 $\mu\text{g C}$. This gives a total estimated biomass for this dominant zooplankton species of about 100 mg C m^{-3} , well below our estimate of the standing stock of phytoplankton. The latter are also likely to have much faster replacement rates via growth and advection than the copepods.

If phytoplankton were a major food component for the ETZ consumers, then the algal $\delta^{13}\text{C}$ signature should lie well above that of the seston, which is highly likely. Direct measurements were not possible in this environment because of the overlap in size range between algal and detrital particles, and the overwhelming dominance of all size fractions by the latter. Marine phytoplankton have $\delta^{13}\text{C}$ values around -21% (Fry 1996), well above the St. Lawrence ETZ seston and similar to the ETZ consumers. Freshwater algal $\delta^{13}\text{C}$ is variable within and among systems (Kendall et al. 2001), but an estimate can be made from $\delta^{13}\text{C}$ in the dissolved inorganic carbon (DIC) pool (as in Riera and Richard 1997). Summer $\delta^{13}\text{C}$ values for DIC in the freshwater inflow to the St. Lawrence ETZ are around -2% (Hélie et al. 2002). A fractionation value for phytoplankton relative to DIC of -15.6% (mean summer value for the Delaware estuary; Fogel et al. 1992) would give algal $\delta^{13}\text{C}$ in the ETZ around -18% , also well above the $\delta^{13}\text{C}$ values for ETZ bulk seston and consistent with a strong preference by the consumers for phytoplankton relative to terrigenous organic matter.

Intersystem comparison—To place the St. Lawrence ETZ data in a broader context we compiled data from a wide range of studies that have measured $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ of POM and primary consumers (Table 2). In almost all of these studies, including the St. Lawrence, the consumers had $\delta^{15}\text{N}$ values that were enriched relative to the seston; the St. Lawrence ETZ values fall at the lower end of this enrichment range, however. The ^{13}C data show a more striking distinction. In 11 of the 24 sites or data sets, the herbivore $\delta^{13}\text{C}$ values were within 2‰ of the bulk seston, while in six of the studies, their $\delta^{13}\text{C}$ signatures were more negative. In con-

trast, the three lowermost herbivores in the St. Lawrence ETZ were on average 6‰ (total POM) to 9‰ ($<5\text{-}\mu\text{m}$ fraction) more enriched relative to the seston (Table 2). For individual taxa and the $<5\text{-}\mu\text{m}$ seston that dominates the estuarine POM, this offset ranged from 8‰ (*Dreissena*) to 10‰ (*Bosmina*). Four other data sets with large positive offsets were obtained from benthic mollusk populations in estuaries. These included oysters in the turbid Marennes Oléron Bay that fed preferentially on resuspended benthic diatoms, even at times of year when the bulk POM was dominated by terrestrial materials; this resulted in $\delta^{13}\text{C}$ enrichment of up to 5.7‰ (Riera and Richard 1997). Similarly, a freshwater benthic invertebrate study showed that filter-feeding black fly larvae (Simuliidae) fed preferentially on suspended filamentous algae derived from upstream periphyton, resulting in a $\delta^{13}\text{C}$ signature that was enriched by 5.5‰ relative to the terrestrial-dominated, suspended POM (Finlay et al. 2002).

Several studies have drawn attention to the heterotrophic nature of estuaries and their inflowing rivers. These ecosystems are typically supersaturated in CO_2 (Frankignoulle et al. 1998), implying an excess of respiration over photosynthesis and, thus, negative net ecosystem productivity. This has led to the conclusion that the food webs in such environments could be largely fueled by terrigenous carbon sources (Howarth et al. 1996). However, the results presented here from the St. Lawrence ETZ show that the large populations of primary consumers have an isotopic signal that differs substantially from terrigenous carbon and that autochthonous carbon is likely to be much more important. These results are consistent with previous studies on the ETZ that identified zooplankton grazing as the mechanism causing substantial loss of phytoplankton from the inflowing river water and from stocks produced in situ (Winkler et al. 2003). Our observations also support the view that although microbial processes dominate the overall biogeochemical fluxes in heterotrophic ecosystems, these systems may contain sufficient high-quality autotrophic biomass to fuel the metazoan food web (Vincent et al. 1996; Thorp et al. 1998; Thorp and Delong 2002). Consistent with the revised riverine productivity model for large river ecosystems (Thorp and Delong 2002), the ETZ consumer food web would seem to be only loosely linked to decomposer pathways. From his compilation of river isotopic data, Finlay (2001) concluded that the consumer community in rivers switches from a reliance on terrestrial sources to algae once the watershed exceeds 10 km^2 . Our results indicate that this autotrophic dominance of consumer food webs extends all the way downstream into the region where large rivers first meet the sea.

Our cross-system analysis of isotopic data underscores the distinctive character of the estuarine transition zone. The St. Lawrence ETZ contains high concentrations of POM, but this pool is dominated by small particles that differ by 8–10‰ in $\delta^{13}\text{C}$ from the grazing zooplankton and benthos. This magnitude of difference between consumers and POM is unusual relative to most other marine or freshwater environments, although it finds parallel in some benthic communities that preferentially feed on suspended algae despite the much greater abundance of terrigenous POM. In the St.

Table 2. Intersystem comparison of the isotopic characteristics of seston (POM) and primary consumers.*

Site	Environment	$\delta^{13}\text{C}$ (‰)		$\delta^{15}\text{N}$ (‰)		$\pm \delta^{13}\text{C}$	Reference
		POM	Primary consumers	POM	Primary consumers		
Lake Baikal	Lake	-29.5 to -27.0	-29.9 to -22.8	4.2	5.6 to 7.5	++	Yoshii et al. (1999)
United Kingdom	Lakes (24)	-24.7	-29.2	NA	NA	--	Grey et al. (2000)
Arctic lakes	Lakes (8)	-28.5	-31.3	2.31	5.98	--	Kling et al. (1992)
Smith Lake	Eutrophic lake	-33.3	-34.5	1.7	-1.2 to 8.5	-	Gu et al. (1994, $\delta^{13}\text{C}$; 1997, $\delta^{15}\text{N}$)
Lake Suwa	Eutrophic lake	-25.0 to -15.0	-20.0	3.0 to 10.0	6.0 to 12.0		Yoshioka et al. (1994)
Oneida Lake	Eutrophic lake	-29.8 to -30.7	-33.6	6.0 to 7.5	8.3 to 8.8	--	Mitchell et al. (1996)
Loch Ness	Oligotrophic lake	-25.5	-28.0	3.8 to 12.0	7.5 to 17.5	--	Grey et al. (2001)
South Fork Eel River	River (midsummer)	-27.0 (epi)	-23.5 to -20.0	NA	0.0 to 3.0	+++	Finlay et al. (2002)
Ohio River	River	-29.0 to -27.0	-29.5 to -29.0	1.5 to 3.5	7.5 to 12.0	-	Thorp et al. (1998)
Charente River	River	-36.7	-24.7 to -19.7	NA	NA	+++	Riera and Richard (1997)
Avon-Heathcote	Estuary	-24.4	-20.0	NA	NA	++	Stephenson and Lyon (1982)
Tijuana Estuary	Estuary	-20.8	-21.8	10.9	14.1	-	Kwak and Zedler (1997)
Plum Island Sound	Upper estuary	-27.9	-26.5	6.7	7.6	+	Deegan and Garritt (1997)
Plum Island Sound	Middle estuary	-21.6	-24.3	5.6	7.7	--	Deegan and Garritt (1997)
Plum Island Sound	Lower estuary	-21.9	-22.4	6.7	7.6	-	Deegan and Garritt (1997)
Marenness-Oléron Bay	Estuary plume	-23.5	-20.3	NA	NA	++	Riera and Richard (1997)
Ria de Arosa	Estuary	-24.2	-14.5	7.0	9.8	+++	Page and Lastra (2003)
Georges Bank	Ocean	-21.3	-20.8	5.1	7.0	+	Fry (1988)
Seto Island	Ocean	-22.1	-20.8	9.43	8.5	+	Takai et al. (2002)
Australian Coast	Ocean	-21.5	-21.3	6.1	7.7	+	Davenport and Bax (2002)
North Water Polynya	Ocean (Arctic)	-22.3	-21.1 to -20.6	6.8	7.9 to 9.1	+	Hobson et al. (2002)
Les Baleines	Ocean (Atlantic)	-20.6	-21.5	NA	NA	-	Riera and Richard (1997)
Prince Edward Islands	Ocean (Antarctic)	-24.8	-27.0 to -25.0	NA	-1.0	-	Kaehler et al. (2000)
St. Lawrence River ETZ	Transition zone						This study
	total POM	-27.0	-21.0	5.9	7.3	+++	
	<5 μm POM	-30.0	-21.0	5.8	7.3	+++	

* epi – epilithic algae; NA – data not available; -/+ less than 2‰ difference in $\delta^{13}\text{C}$; --/+ 2-5 ‰ difference in $\delta^{13}\text{C}$; +++ >5‰ ^{13}C -enriched. The St. Lawrence ETZ consumer data are means for the three species of lowest $\delta^{15}\text{N}$ trophic rank (*Dreissena polymorpha*, *Bosmina longirostris*, and *Keratella* sp.). Full references for the data sources are given in Web Appendix 1 at http://www.aslo.org/lo/toc/vol_49/issue_5/1679al.pdf.

Lawrence ecosystem, and probably upper estuaries elsewhere, there is weak coupling between overall POM and the metazoan food web. Our results imply that the primary consumers selectively feed on phytoplankton POM and that this minor fraction of the bulk seston carbon pool ultimately supports the productive ETZ as a larval fish nursery.

References

- BARNARD, C., J.-J. FRENETTE, AND W. F. VINCENT. 2003. Planktonic invaders of the St. Lawrence estuarine transition zone: Environmental factors controlling the distribution of zebra mussel veligers. *Can. J. Fish. Aquat. Sci.* **60**: 1245–1257.
- BARTH, J. A. C., J. VEIZER, AND B. MAYER. 1998. Origin of particulate organic carbon in the upper St. Lawrence: Isotopic constraints. *Earth Planet. Sci. Lett.* **162**: 111–121.
- CABANA, G., AND J. RASMUSSEN. 1996. Comparison of aquatic food chains using nitrogen isotopes. *Proc. Natl. Acad. Sci. U. S. A.* **93**: 10844–10847.
- CAI, D.-L., F. C. TAN, AND M. EDMOND. 1988. Source and transport of particulate organic carbon in the Amazon River and Estuary. *Estuar. Coast. Shelf Sci.* **26**: 1–14.
- 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. *Limnol. Oceanogr.* **47**: 713–729.
- COFFIN, R. B., B. FRY, B. J. PETERSON, AND R. T. WRIGHT. 1989. Carbon isotopic compositions of estuarine bacteria. *Limnol. Oceanogr.* **34**: 1305–1310.
- DEBRUYN, A. M. H., AND J. B. RASMUSSEN. 2002. Quantifying assimilation of sewage-derived organic matter by riverine benthos. *Ecol. Appl.* **12**: 511–520.
- DEEGAN, L. A., B. J. PETERSON, AND R. PORTIER. 1990. Stable isotopes and cellulase activity as evidence for detritus as a food source for juvenile Gulf menhaden. *Estuaries* **13**: 14–19.
- DODSON, J. J., J.-C. DAUVIN, G. R. INGRAM, AND B. D'ANGLEJAN. 1989. Abundance of larval rainbow smelt (*Osmerus mordax*) in relation to the maximum turbidity zone and associated macroplanktonic fauna of the Middle St. Lawrence Estuary. *Estuaries* **12**: 66–81.
- FINLAY, J. C. 2001. Stable-carbon-isotope ratios of river biota: Implications for energy flow in lotic food webs. *Ecology* **82**: 1052–1064.
- , S. KHANDWALA, AND M. E. POWER. 2002. Spatial scales of carbon flow in a river food web. *Ecology* **83**: 1845–1859.
- FOGEL, M. L., L. A. CIFUENTES, D. J. VELINSKI, AND J. H. SHARP. 1992. Relationship of carbon availability in estuarine phytoplankton to isotopic composition. *Mar. Ecol. Prog. Ser.* **82**: 291–300.
- FRANKIGNOULLE, M., G. ABRIL, A. BORGES, I. BOURGE, C. CANON, B. DELILLE, E. LIBERT, AND J.-M. THÉATE. 1998. Carbon dioxide emissions from European estuaries. *Science* **282**: 434–436.
- FRENETTE, J.-J., W. F. VINCENT, J. J. DODSON, AND C. LOVEJOY. 1995. Size-dependent variations in phytoplankton and protozoan community structure across the St. Lawrence River transition region. *Mar. Ecol. Prog. Ser.* **120**: 1–3.
- FRY, B. 1996. $^{13}\text{C}/^{12}\text{C}$ fractionation by marine diatoms. *Mar. Ecol. Prog. Ser.* **134**: 1–3.
- GEARING, J. N., AND R. POCKLINGTON. 1990. Organic geochemical studies in the St. Lawrence estuary. In M. J. El-Sabh and N. Silverberg [eds.], *Oceanography of a large-scale estuarine system: The St. Lawrence*. Springer-Verlag.
- HEERKLOSS, R., U. SCHIEWER, N. WASMUND, AND E. KUEHNER. 1993. A long-term study of zooplankton succession in enclosures with special reference to *Eurytemora affinis* (Poppe) calanoid copepods. *Rostocker Meeresbiol. Beitr.* **1**: 25–35.
- HÉLIE, J.-F., C. HILLAIRE-MARCEL, AND B. RONDEAU. 2002. Seasonal changes in the sources and fluxes of dissolved inorganic carbon through the St. Lawrence River— isotopic and chemical constraints. *Chem. Geol.* **186**: 117–138.
- HOWARTH, R. W., R. SCHNEIDER, AND D. SWANEY. 1996. Metabolism and organic carbon fluxes in the tidal freshwater Hudson River. *Estuaries* **19**: 848–865.
- JEFFREY, S. W., AND N. A. WELSCHEMEYER. 1997. Spectrophotometric and fluorometric equations in common use in oceanography, p. 597–615. In S. W. Jeffrey, R. F. C. Mantoura, and S. W. Wright [eds.], *Phytoplankton pigments in oceanography*. UNESCO.
- KELLEY, C. A., R. B. COFFIN, AND L. A. CIFUENTES. 1998. Stable isotope evidence for alternative bacterial carbon sources in the Gulf of Mexico. *Limnol. Oceanogr.* **43**: 1962–1969.
- KENDALL, C., S. R. SILVA, AND V. J. KELLY. 2001. Carbon and nitrogen isotopic compositions of particulate organic matter in four large river systems across the United States. *Hydrol. Process.* **15**: 1301–1346.
- KRANCK, K. 1979. Dynamics and distribution of suspended particulate matter in the St. Lawrence Estuary. *Nat. Can.* **106**: 163–173.
- LUCOTTE, M., AND B. D'ANGLEJAN. 1986. Seasonal control of the St. Lawrence maximum turbidity zone by tidal-flat sedimentation. *Estuaries* **9**: 84–95.
- MALLIN, M., AND H. W. PAERL. 1994. Planktonic trophic transfer in an estuary: Seasonal diet and community effects. *Ecology* **75**: 2168–2184.
- MCCUTCHAN, J. H., JR., W. M. LEWIS, C. KENDALL, AND C. C. MCGRATH. 2003. Variation in trophic shift for stable isotope ratios of carbon, nitrogen, and sulfur. *Oikos* **102**: 378–390.
- NUSCH, E. A. 1980. Comparison of different methods for chlorophyll and phaeopigment determination. *Arch. Hydrobiol. Beih.* **14**: 14–36.
- PETERSON, B. J., B. FRY, M. HULLAR, S. SAUPE, AND R. WRIGHT. 1994. The distribution and stable carbon isotopic composition of dissolved organic carbon in estuaries. *Estuaries* **17**: 111–121.
- RIERA, P., AND P. RICHARD. 1997. Temporal variation of $\delta^{13}\text{C}$ in particulate organic matter and oyster *Crassostrea gigas* in Marennes-Oléron Bay (France): Effect of freshwater inflow. *Mar. Ecol. Prog. Ser.* **147**: 105–115.
- SCHUBERT, J. C., AND B. NIELSEN. 2000. Effects of decarbonation treatments on $\delta^{13}\text{C}$ values in marine sediments. *Mar. Chem.* **72**: 55–59.
- TAN, F. C., AND P. M. STRAIN. 1983. Sources, sinks and distribution of organic carbon in the St. Lawrence estuary, Canada. *Geochim. Cosmochim. Acta* **47**: 125–132.
- THORNTON, S. F., AND J. MCMANUS. 1994. Application of organic carbon and nitrogen stable isotope and C/N ratios as source indicators of organic matter provenance in estuarine systems: Evidence from the Tay Estuary, Scotland. *Estuar. Coast. Shelf Sci.* **38**: 219–233.
- THORP, J. H., AND M. D. DELONG. 2002. Dominance of autochthonous autotrophic carbon in food webs of heterotrophic rivers. *Oikos* **96**: 543–550.
- , ———, K. GREENWOOD, AND A. CASPER. 1998. Isotopic analysis of three food web theories in constricted and floodplain regions of a large river. *Oecologia* **117**: 551–563.
- VINCENT, W. F., AND J. J. DODSON. 1999. The St. Lawrence River, Canada-USA: The need for an ecosystem-level understanding of large rivers. *Jpn. J. Limnol.* **60**: 29–50.
- , ———, N. BERTRAND, AND J.-J. FRENETTE. 1996. Photosynthetic and bacterial production gradients in a larval fish

- nursery: The St. Lawrence River transition zone. *Mar. Ecol. Prog. Ser.* **139**: 227–238.
- WINKLER, G., J. J. DODSON, N. BERTRAND, D. THIVIERGE, AND W. F. VINCENT. 2003. Trophic coupling across the St. Lawrence River estuarine transition zone. *Mar. Ecol. Prog. Ser.* **251**: 59–73.
- YAMAMURO, M., AND H. KAYANNE. 1995. Rapid direct determination of organic carbon and nitrogen in carbonate-bearing sediment with a Yanaco MT-5 CHN analyser. *Limnol. Oceanogr.* **40**: 1001–1005.
- ZIMMERMANN-TIMM, H. 2002. Characteristics, dynamics and importance of aggregates in rivers—an invited review. *Int. Rev. Hydrobiol.* **87**: 197–240.

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