Millennial-aged organic carbon subsidies to a modern river food web

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Abstract. Recent studies indicate that highly aged material is a major component of organic matter transported by most rivers. However, few studies have used natural ^{14}C to trace the potential entry of this aged material into modern river food webs. Here we use natural abundance ^{14}C, ^{13}C, and deuterium (^{2}H) to trace the contribution of aged and contemporary organic matter to an important group of consumers, crustacean zooplankton, in a large temperate river (the Hudson River, New York, USA). Zooplankton were highly ^{14}C depleted (mean Δ^{14}C = −240‰) compared to modern primary production in the river or its watershed (Δ^{14}C = −60‰ to +50‰). In order to account for the observed ^{14}C depletion, zooplankton must be subsidized by highly aged particulate organic carbon. IsoSource modeling suggests that the range of the aged dietary subsidy is between ~57%, if the aged organic matter source was produced 3400 years ago, and ~21%, if the organic carbon used is ≥50 000 years in age, including fossil material that is millions of years in age. The magnitude of this aged carbon subsidy to river zooplankton suggests that modern river food webs may in some cases be buffered from the limitations set by present-day primary production.

Key words: *allochthonous and autochthonous food sources; ancient carbon; ^{14}C depletion; deuterium; food-web subsidies; Hudson River, USA; IsoSource modeling; natural abundance isotopes; river food webs; zooplankton.*

INTRODUCTION

The growth of fish and invertebrate consumers in aquatic systems is supported by both primary production from within the system (autochthonous sources) and organic carbon subsidies imported from the surrounding watershed and upstream water bodies (allochthonous sources; Peterson et al. 1986). The allochthonous component is a diverse mix of dissolved and particulate organic materials that may have been produced from recent photosynthesis or stored in soils and floodplain sediments for thousands of years or more (Raymond et al. 2004, Denzek et al. 2009). While it is clear that allochthonous inputs exceed riverine primary production in a majority of rivers (Peterson et al. 1986, Cole and Caraco 2001), the importance of allochthonous material to aquatic consumers is still debated (Thorp and Delong 2002, Sobczak et al. 2005, Doucett et al. 2007, Zeug and Winemiller 2008, Van den Meersche et al. 2009). The most prevalent current view is that allochthonous sources of modern origin largely fuel microbial respiration (Mayorga et al. 2005), while modern autochthonous sources are the dominant food source of animal consumers (Thorp and Delong 2002,

Martineau et al. 2004, Sobczak et al. 2005). However, there is some evidence that highly aged allochthonous material can be an important carbon subsidy to both microbes (McCallister et al. 2004) and animal consumers (Schell 1983).

The continued debate on the importance of allochthonous subsidies persists in part because of the difficulties inherent in studying organic matter transfers under natural conditions, particularly in large open systems such as rivers. While natural abundance stable isotopes may successfully distinguish autochthonous from allochthonous food sources in certain rivers (Thorp and Delong 2002), in others isotopic overlap of carbon sources as well as spatiotemporal variability of isotope signatures (Caraco et al. 1998, Cloern et al. 2002) make this task difficult. Additionally, purposeful additions of tracer-level stable isotopes are not feasible in large rivers and cannot distinguish aged detrital material from modern allochthonous subsidies (Cole et al. 2006).

Natural abundance radiocarbon (^{14}C) represents a potentially useful tool both for tracing the flow of carbon through aquatic food webs and for identifying consumer use of noncontemporary (i.e., aged) organic matter sources (McCallister et al. 2004; Appendix A). Highly aged (i.e., ^{14}C-depleted) organic matter has been found in arctic (Guo et al. 2007), tropical (Mayorga et al. 2005), and temperate rivers (Denzek et al. 2009), including the Hudson River, New York, USA

(McCallister et al. 2004, Raymond et al. 2004). However, the possibility that this material may be an important subsidy to modern food webs has not been adequately assessed due to the very limited data on the ^{14}C content of consumers in rivers (Broecker and Walton 1959, Schell 1983). Here we use natural abundance ^{14}C (as Δ^{14}C; Appendix A), in conjunction with stable carbon (δ^{13}C) and hydrogen (δ^2H) isotopes, to examine whether aged organic matter inputs from the watershed of the Hudson River can subsidize the nutritional and energetic requirements of an important group of planktonic consumers in this river. Specifically, we distinguished between two possibilities: (1) that the isotopic signatures of riverine crustacean zooplankton can be explained by assimilation of contemporary, autochthonous production; or (2) that subsidies of allochthonous organic matter, possibly aged within the watershed for extended periods of time (e.g., millennia or more), are required to explain the isotopic signatures of zooplankton consumers.

MATERIALS AND METHODS

Study site

The tidal Hudson River is located in eastern New York (USA) and extends for 250 km (Fig. 1). The present study was conducted in a 150-km stretch that is both tidal and entirely fresh water. Three tributaries contribute 90% of the 350 m^3/s flow to this section of the river (Fig. 1). The land use of the entire watershed is 65% forested, 30% agricultural, and 5% developed. Of the three major tributaries the Upper Hudson (U) is the most forested (90%), while the Mohawk (M) and the Wallkill (W) are approximately 55% forested (Fig. 1; Phillips and Hanchar 1996).

The water column of the freshwater tidal Hudson is relatively deep (7 m average) and vertically well-mixed, and primary production is light limited (Cole and Caraco 2006). Gross primary production (GPP) in the Hudson River averages ~200 g C·m^{-2}·yr^{-1} and is dominated by phytoplankton (~100 g C·m^{-2}·yr^{-1}) and two species of aquatic plants (*Vallisneria americana*, a submersed species [SAV], and *Trapa natans*, a plant with floating aquatic vegetation [FlAV]; Cole and Caraco 2006).

Allochthonous organic carbon inputs to the tidal freshwater Hudson average ~700 g C·m^{-2}·yr^{-1} (Cole and Caraco 2006). Much of the allochthonous input is of terrestrial origin with agricultural land use contributing a disproportionately large fraction of the total carbon input (Swaney et al. 1996). Organic matter sources from sewage inputs to the tidal freshwater Hudson are at present relatively small and originate primarily from the Albany area (Fig. 1; Hetling et al. 2003).

Compared to inputs of organic matter from autochthonous and allochthonous sources, respiration by crustacean zooplankton in the Hudson River is low (<10 g C·m^{-2}·yr^{-1}; Strayer et al. 1996); however, these

organisms are important to both resident and anadromous fishes. Cladocera (dominantly *Bosmina freyi*) and copepods (*Diacyclops bicuspidatus thomasi*, *Halicyclops* sp., and *Eurytemora affinis*) can contribute >90% of the diet of larval fish in the Hudson River (Pace et al. 1992, Limburg et al. 1997). Unfortunately, the food sources supporting crustacean zooplankton in the freshwater Hudson are not distinguished well using natural abundance ^{15}N and ^{13}C (Caraco et al. 1998). Recent natural abundance ^{14}C analysis of suspended particulate organic carbon (POC) and bacteria in the Hudson River (McCallister et al. 2004, Raymond et al. 2004) suggest that this isotope may be useful for distinguishing between food sources.

Sampling and analyses

Water samples were collected at monthly to bimonthly intervals in 2004–2005 by kayak from ~0.2 m below the surface in mid channel at three stations in the freshwater tidal section of the Hudson River and in three of its tributaries (Fig. 1). Particulate organic carbon (POC), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC), pH, and temperature were measured at each sampling site and time (Cole and Caraco 2006). Dissolved and particulate samples for Δ^{14}C and δ^{13}C samples were separated by filtration with Whatman QMA quartz fiber filters (0.8 μm nominal pore size; Whatman, Clifton, New Jersey, USA). Prior to processing, DOC samples were frozen, POC samples were air dried, and DIC samples were preserved with HgCl$_2$ (see Appendix A for details). On two occasions in summer 2006, a 20-L sample of water was collected from site G (Fig. 1) and serially fractionated into three size categories (<10, 10–35, and >35 μm) using Nitex nylon netting. The Nitex-harvested particles were rinsed with deionized water onto QMA filters and dried prior to sample processing and analysis.

Samples of the two dominant aquatic plants (submersed *Vallisneria* and floating *Trapa*) were hand collected at five locations between stations N and G (Fig. 1). Samples were rinsed to remove detritus, dried, and homogenized by grinding before analysis. Phytoplankton δ^{13}C and Δ^{14}C signatures were determined for the growing season (June–September) from both dilution regrowth incubations (Appendix A) and plankton net samples that happened to be comprised entirely of phytoplankton, based on microscopic examination (Appendix A). Between the months of June and September in both 2004 and 2005, crustacean zooplankton were collected using 170-μm mesh plankton netting at stations G and N (Fig. 1). The zooplankton samples were held at 15–25°C temperatures for 3–5 h in order for the animals to void their guts (Irigoien 1998), then hand-sorted onto QMA filters, and dried prior to analysis. All aspects of sample collection and processing were carried out using natural abundance ^{14}C-clean techniques and laboratory facilities (details in Appendix A).

During 2007, samples were collected for the measurement of δ^2H. Methods for sampling of aquatic plants, zooplankton, DOC and POC, and phytoplankton were similar to those for carbon isotopes (Doucette et al. 2007), with the exception that 47-mm, 1.2 μm pore size Metricel filters (Pall Corporation, Port Washington, New York, USA) were used to collect POC. The particles were backwashed from these filters into glass Petri dishes and dried at 60°C. Samples were collected from the Hudson for the δ^2H content of water during the growing season between May and October. Finally, terrestrial samples consisting of leaves and needles of major plant species in the watershed (oak, maple, beach, pine, and hemlock) and surface soil organic materials were collected during October 2007 for δ^2H content.

Carbon inputs

Total tributary input of POC and DOC was calculated from USGS-measured discharge and POC and DOC concentrations measured in this study (see *Sampling and analyses*). Thus, daily POC input from each tributary is

$$\sum 0.5(POC_t + POC_{t+1}) \times discharge/(day_{t+1} - day_t).$$
(1)

The highly aged or fossil carbon component of POC and DOC was calculated from IsoSource modeling (Phillips and Gregg 2003, *available online*)[6] using the C load-corrected mean $\delta^{13}C$ and $\Delta^{14}C$ isotope input values. Discharge is the cumulative discharge between time t and time $t+1$. For example, the C load-corrected $\Delta^{14}C$ value of POC is calculated as

$$\sum 0.5(POC_t + POC_{t+1})$$
$$\times discharge\ 0.5(\Delta^{14}C_{POC_t} + \Delta^{14}C_{POC_{t+1}})$$
$$\div \sum (discharge \times POC).$$
(2)

Areal autochthonous inputs to the tidal Hudson are based on a recent review that estimated production of phytoplankton, submersed aquatic species (SAV), and floating aquatic vegetation (FlAV; Cole and Caraco 2006). Sewage inputs were calculated from year 2000 estimates of water flow from sewage plants to the freshwater tidal Hudson (Hetling et al. 2003) and average organic carbon content of sewage in treatment plants of the lower Hudson River estuary (Griffith et al. 2009). The fossil carbon content of this sewage was estimated as 20% of total carbon input based on ^{14}C measurements of sewage carbon (Griffith et al. 2009). Zooplankton carbon demand is based on an estimate of zooplankton respiration in years following the zebra mussel invasion in the Hudson River (Strayer et al. 1996). The subsidy by aged or fossil carbon is based on IsoSource modeling of the fractional contribution of

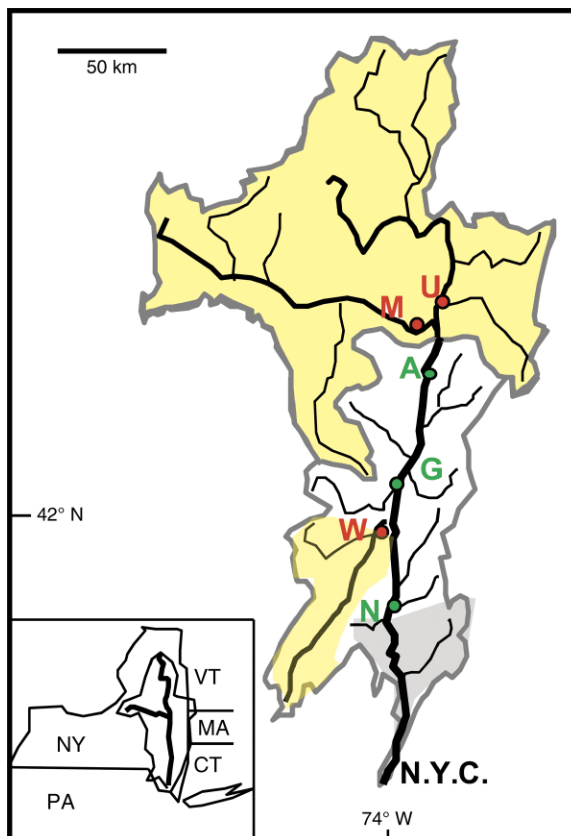[6] ⟨http://www.epa.gov/wed/pages/models/stableIsotopes/isosource/isosource.htm⟩

FIG. 1.   Map of the Hudson River and watershed showing sampling locations in the tidal freshwater Hudson River (green) and its tributaries (red), and their locations in relation to the northeastern United States (inset). River stations A, G, and N refer to the cities/towns nearest to the sampling sites (Albany, Germantown, and Newburgh, respectively). Tributary stations M, U, and W refer to the tributary names (Mohawk, Upper Hudson, and the Wallkill River, respectively). The watersheds of these tributaries are shown in yellow; the gray area is the watershed to the brackish section of the tidal Hudson River.

these carbon sources to the biomass of zooplankton and the total carbon demand of zooplankton.

Isotopic models

The modeling program IsoSource (Phillips and Gregg 2003) was used to calculate feasible food source combinations that could explain the isotopic ($\Delta^{14}C$, $\delta^{13}C$, and δ^2H) signatures of zooplankton. In addition to the potential for the subsidization of zooplankton by aged or fossil carbon in the Hudson River, there are three potential modern autochthonous sources as well as a contemporary allochthonous input based on recent primary production in the watershed (Table 1). The isotopic values of the three autochthonous sources (phytoplankton, SAV, and FlAV) and those of the zooplankton were based on average values from this study. Carbon isotopic values of modern allochthonous sources are based on literature values of C_3 terrestrial plant production in the Hudson watershed (Table 1),

TABLE 1. The $\delta^{13}C$, $\Delta^{14}C$, and δ^2H values of zooplankton and their potential food sources from the Hudson River or its watershed.

Sources	$\Delta^{14}C$		$\delta^{13}C$		δ^2H	
	Mean	SD	Mean	SD	Mean	SD
Zooplankton	−236	25	−26.2	0.4	−170	4
Phytoplankton	−51	6	−32.0	0.2	−235	12
Submersed aquatic vegetation (SAV)	−65	7	−22.2	1.0	−132	3
Floating aquatic vegetation (FlAV)	46	2	−25.2	0.5	−122	7
Modern terrestrial	50†		−26.5‡		−117	5
Aged terrestrial (S1)	−350§		−25.0¶		−101††	
Fossil organic (S2)	−1000#		−29.0‖		...	

Notes: Values are in ‰ deviation from Pee Dee Belemnite (PDB), oxalic acid II (OX-II), and standard mean ocean water (SMOW) standards. Carbon isotope and δ^2H values are expressed as the mean and standard deviation of measured values for 2004–2005 and 2007, respectively.

† Based on atmospheric values in the northeastern United States (Hsueh et al. 2007).
‡ Based on direct measurements of oak leaves from the Hudson watershed (Caraco et al. 1998).
§ Based on the lowest measured $\Delta^{14}C$ value for zooplankton.
¶ Enriched by 1.5‰ relative to present-day values; i.e., the "Suess Effect" (Francey et al. 1999).
# The $\Delta^{14}C$ of fossil carbon in shales in the Hudson watershed (Longworth et al. 2007).
‖ The ^{13}C value of both petroleum and shale in the Hudson watershed (Longworth et al. 2007, Griffith et al. 2009).
†† From a single soil organic matter measurement in the Hudson watershed.

while the δ^2H value is the average of leaf material collected from the Hudson watershed.

Because the exact ^{14}C signatures and sources of one or more potential highly aged sources are uncertain, we modeled two extreme scenarios that bracket the possible outcomes. In Scenario 1 (S1), we use the least ^{14}C-depleted value possible that still can explain the ages of all zooplankton samples; this constrains the maximum possible amount of aged organic material assimilated by zooplankton. In Scenario 2 (S2), we assume that the oldest assimilated organic matter is fossil carbon; this constrains the minimum possible amount of aged source used by zooplankton. For S1, the $\Delta^{14}C$ of the most ^{14}C-depleted zooplankton (−350‰) represents material that is 3400 years in equivalent age. This value is also similar to the measured $\Delta^{14}C$ content of small size fraction POC in the Hudson River (see *Results*). S1 highly aged material is assumed to originate from terrestrial material that has aged in soils before being delivered to the Hudson, and the $\delta^{13}C$ and δ^2H values are representative of these soil values (Table 1). S2 assumes that the ^{14}C-depleted end member is ^{14}C "dead" ($\Delta^{14}C = −1000‰$). While organic matter having $\Delta^{14}C = −1000‰$ is equivalent to at least 50 000 years in age, it also does not preclude the existence of material up to millions of years old. Such material could originate, for example, from abundant shale deposits present in the Hudson watershed (Longworth et al. 2007) as well as from petroleum pollution (Griffith et al. 2009). For both of these sources, $\delta^{13}C$ values are approximately −29‰ (Longworth et al. 2007, Griffith et al. 2009). Literature values of δ^2H content of shales and fossil fuels are highly variable (Lis et al. 2006). As we do not have site specific measurements of δ^2H for shale and petroleum, S2 modeling used only carbon isotopes for the aged source (Table 2).

In both S1 and S2 model scenarios, $\delta^{13}C$ and δ^2H values were corrected for trophic enrichment and dietary

water, respectively (Phillips and Gregg 2003). For $\delta^{13}C$, we used a trophic enrichment factor of 0.4‰ per trophic level (Post 2002). The reported dietary water contribution to sample δ^2H values varies between studies and consumer groups (Solomon et al. 2009). For the consumers measured in this study, we used a 10% dietary water contribution for baseline modeling but tested the sensitivity of the model to dietary water contributions of 0% and 20%. Sample $\Delta^{14}C$ values were corrected for fractionation by their respective $\delta^{13}C$ values, and therefore no further adjustment to these values was needed (Appendix A).

The IsoSource model was also used to calculate source contributions to the POC and DOC pools of tributary inputs. Methods were identical to zooplankton source modeling using S1 and S2, except models were run using only $\Delta^{14}C$ and $\delta^{13}C$ as we do not have δ^2H values for POC and DOC in the Hudson River tributaries. The $\Delta^{14}C$ and $\delta^{13}C$ values of the allochthonous organic material were carbon load-weighted values (Eq. 2).

RESULTS

The $\delta^{13}C$ values for autochthonous riverine organic matter sources ranged between −32.2‰ and −23.3‰, with phytoplankton and submersed species (SAV) having the lowest and highest values, respectively (Table 1, Fig. 2). Zooplankton, as well as the particulate organic carbon (POC) and dissolved organic carbon (DOC) in the Hudson River and its tributaries, had $\delta^{13}C$ values intermediate between these autochthonous end members and were generally similar to terrestrial C_3 plants (Table 2, Fig. 2). The δ^2H values of various living and nonliving organic materials had a range of over 100‰ (Table 1, Fig. 2). Phytoplankton had the lowest δ^2H values (mean value −230‰). δ^2H values of the other organic matter sources were all substantially higher and fell within a relatively narrow range (from −130‰ to

TABLE 2. Measured $\Delta^{14}C$ and $\delta^{13}C$ values of organic (POC and DOC) and inorganic (DIC) carbon at three stations in the Hudson River and its tributaries (see Fig. 1).

| River sites | $\Delta^{14}C_{POC}$ | | $\delta^{13}C_{POC}$ | | $\Delta^{14}C_{DOC}$ | | $\delta^{13}C_{DOC}$ | | $\Delta^{14}C_{DIC}$ | | $\delta^{13}C_{DIC}$ | |
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Hudson River												
A	−166	43	−27.3	1.3	36	24	−26.6	0.6	−74	19	−10.2	1.3
G	−115	50	−27.0	0.6	51	12	−26.4	0.8	−50	14	−10.1	1.2
N	−154	23	−26.8	0.8	34	25	−26.6	0.9	−48	15	−10.0	0.5
Tributaries of Hudson River												
M	−66	39	−27.4	1.3	28	30	−26.9	0.6	−68	19	−10.2	0.7
U	−68	37	−27.4	1.5	77	17	−26.7	0.5	−25	18	−10.5	1.2
W	−131	50	−27.2	2.5	−47	44	−27.1	0.7	−38	20	−9.7	1.3

Notes: $\Delta^{14}C$ and $\delta^{13}C$ are expressed as the deviation in parts per thousand (‰) from known standards (Appendix A). Values are means and standard deviations of replicate analyses. POC is particulate organic carbon; DOC is dissolved organic carbon; DIC is dissolved inorganic carbon.

−100‰). POC and DOC were also elevated in δ^2H (mean δ^2H = −121‰ and −119‰, respectively) compared to phytoplankton. Average zooplankton δ^2H values (−170‰) were intermediate between those of phytoplankton and other organic matter source values. Taken together, both the $\delta^{13}C$ and δ^2H values suggest that zooplankton contain a significant nonphytoplankton component, but it is unclear from the stable isotope data alone if this source is modern terrestrial material, SAV, floating aquatic vegetation (FlAV), very old soil, or fossil organic matter.

$\Delta^{14}C$ values of organic materials reflect the $\Delta^{14}C$ inorganic carbon source at the time of photosynthesis (Broecker and Walton 1959) and in the present study varied by nearly 100‰ (Tables 1 and 2). FlAV had $\Delta^{14}C$ values averaging +45‰, consistent with fixation of contemporary atmospheric CO_2. In contrast, both SAV and phytoplankton $\Delta^{14}C$ values (−64‰ and −51‰, respectively) were consistent with the fixation of moderately ^{14}C-depleted dissolved inorganic carbon (DIC) in the Hudson River.

DOC in the Hudson River and its tributaries was generally elevated in $\Delta^{14}C$ compared to phytoplankton or SAV (Tables 1 and 2; Appendix B). In contrast, POC was typically ^{14}C depleted in comparison to these autochthonous sources or present-day atmospheric
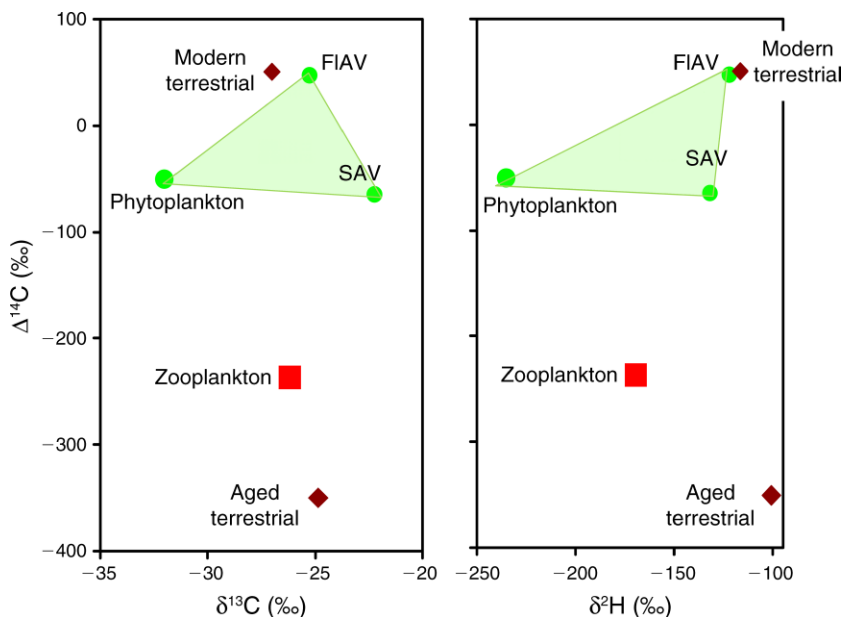

FIG. 2. Isotope bi-plots of $\Delta^{14}C$ vs. $\delta^{13}C$ (left side) and $\Delta^{14}C$ vs. δ^2H (right side). Zooplankton (red squares) and autochthonous sources (green circles) are based on average measured values in the Hudson River. SAV and FlAV are submersed and floating aquatic vegetation, respectively. Modern and aged terrestrial values (brown diamonds) represent values of modern C-3 plants in the watershed and C-3 plants for 3400 years BP, respectively. These values are the same as S1 values shown in Table 1, which also displays S2 values for modeling. Note that the measured carbon isotopes are from 2004 and 2005, while δ^2H values are from 2007 samplings (see *Materials and methods: Sampling and analyses*).
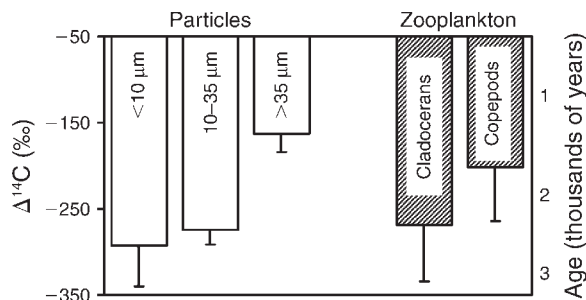
Fig. 3. $\Delta^{14}C$ values and equivalent ages of three size fractions of particulate organic carbon (POC) and two types of crustacean zooplankton (cladocerans and copepods; shaded bars). The bars are mean values, and the error bars are standard deviations of the mean.

$\Delta^{14}C$ values, even during summer months (Table 2; Appendix B). Carbon load-weighted average $\Delta^{14}C$ values (Eq. 2) of allochthonous DOC and POC sources were +25‰ and −120‰, respectively. Hudson River $\Delta^{14}C$ values of DOC and POC were similar to these average loading values (Table 2). There was also substantial variation in the $\Delta^{14}C$ values of different size classes of particles (Fig. 3). Small (<10 μm) and intermediate (10–35 μm) size classes of POC were significantly more ^{14}C depleted than large particles (>35 μm) that are likely unavailable to zooplankton (Fig. 3).

Zooplankton were more ^{14}C depleted than any of the potential autochthonous organic carbon sources or contemporary terrestrial production. The average $\Delta^{14}C$ of zooplankton (−240‰) was nearly 200‰ lower than the average phytoplankton $\Delta^{14}C$, and nearly 300‰ lower than modern terrestrial plant biomass. Furthermore, both groups of zooplankton were even more ^{14}C depleted than "average" POC in the Hudson River or its tributaries (Tables 1 and 2), but had comparable $\Delta^{14}C$ values to the smaller size classes of POC in the river (Fig. 3). The cladoceran, Bosmina, which generally favors smaller particles than do copepods (Cottingham 1999), was on average 65‰ lower in $\Delta^{14}C$ than copepods (Fig. 3).

Food source modeling using IsoSource suggests that highly aged (at least thousands of years old) or even fossil (≥50 000 years) material is an important subsidy to zooplankton in the Hudson River. If the material is highly aged soil material (S1), the old end member accounts for ~57% of zooplankton biomass (Fig. 4A). If the old end member is entirely fossil material (S2), it would contribute a smaller but still substantial part of zooplankton biomass (~21%; Fig. 4A). Variations in dietary water did not substantially change the outcome for the two models based on all three isotopes. For example, for S1 a dietary water content of 0% and 20% yielded modeled contributions of ancient terrestrial material to the diet of zooplankton of 59% and 48%, respectively. The S1 and S2 modeling results, combined with the total organic carbon demand by zooplankton
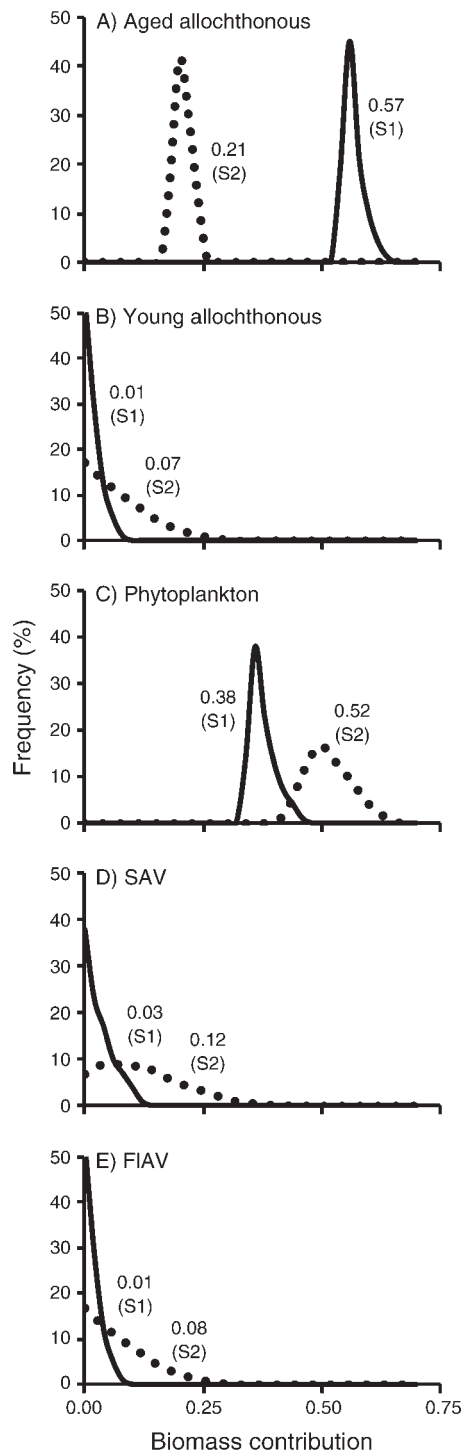

Fig. 4. IsoSource modeled probability distribution of (A, B) allochthonous and (C–E) autochthonous organic matter sources for zooplankton based on two scenarios: highly aged soil material (S1, solid line) and fossil material (S2, dotted line) of the aged carbon end member (see Table 1). In addition to the probability frequencies, the mean modeled values for S1 and S2 are labeled (in fraction of diet). Organic matter sources besides phytoplankton are submerged aquatic vegetation (SAV) and floating aquatic vegetation (FlAV). The IsoSource models are available at ⟨http://www.epa.gov/wed/pages/models/stableIsotopes/isosource/isosource.htm⟩.

(10 g C·m^{-2}·yr^{-1}), suggest that zooplankton assimilation of aged material in the Hudson River system is between 2 g and 5 g C·m^{-2}·yr^{-1}. In both scenarios, phytoplankton is modeled to be an important modern carbon source, contributing from 38% to 52% of the biomass of zooplankton (Fig. 4C). SAV, FlAV, as well as modern terrestrial production all likely contribute relatively small amounts of organic matter to zooplankton biomass in the Hudson River (Fig. 4B, D, E).

IsoSource modeling suggests that allochthonous sources of POC to the Hudson, like zooplankton, have a significant contribution from highly aged (S1 = ~40%) or fossil (S2 = ~15%) organic matter. By comparison, phytoplankton only accounts for ~15% of the POC pool for S1. On the other hand, DOC was modeled to contain only 2% and 0.5% aged material for S1 and S2, respectively, and under both scenarios terrestrial material of recent origin is likely the major contributor to tributary organic carbon inputs to the river. The calculated tributary input of organic carbon to the Hudson is 155 g C·m^{-2}·yr^{-1} for POC and 610 g C·m^{-2}·yr^{-1} for DOC (Eq. 1). Thus, the input of old organic material to the Hudson is between 25 g and 70 g C·m^{-2}·yr^{-1} for S2 and S1, respectively. In addition to this tributary input, an additional 2 g C·m^{-2}·yr^{-1} of fossil carbon is calculated to enter the tidal freshwater Hudson as petroleum-based pollution in sewage. Thus, the input of highly aged (S1) or fossil (S2) organic carbon is more than 10-fold greater than the zooplankton carbon demand under both scenarios, but is far smaller than the input of modern organic carbon to the river (~200 g C·m^{-2}·yr^{-1} autochthonous inputs and >600 g C·m^{-2}·yr^{-1} allochthonous inputs).

DISCUSSION

In the Hudson River, crustacean zooplankton are far more ^{14}C depleted than autochthonous carbon sources or present-day terrestrial production (Fig. 2, Table 1). This depletion could be explained by a large (~57%) contribution of the diet by material that is several thousands of years old (i.e., highly aged for S1), or a moderate (~21%) contribution of fossil material that is at least 50 000 years old and potentially up to millions of years old (i.e., fossil aged for S2; Fig. 4A). By comparison, the modeled contribution of phytoplankton and modern terrestrial production are 38–52% and 10%, respectively. A significant contribution of phytoplankton to zooplankton biomass and secondary production is not surprising as this material is generally thought to be a significant food source to this group of consumers (Martineau et al. 2004, Cole et al. 2006). However, the relatively small dietary contribution of young allochthonous material and the major contribution from highly aged material is unexpected.

Organic material that has withstood decomposition for thousands of years would generally be predicted to be a poor food source compared to recently produced material. The Hudson River findings suggest that this is not always necessarily the case, as zooplankton in this system assimilate highly aged particulate organic carbon (POC) to a greater extent than young terrestrial material. We know of no previous studies showing this extent of use of highly aged material, and to our knowledge only one previous study has demonstrated significant use of highly aged riverine material (Schell 1983). In this study of an arctic river, ancient peat dominated organic matter inputs to the river (Schell 1983). The present study demonstrates that organic matter greater than several millennia in age can be an important subsidy to zooplankton, even when this aged material accounts for a relatively low proportion of the total organic matter input to the river.

The importance of aged terrestrial organic materials to the diets of two different zooplankton groups in the Hudson River further corresponds to its comparatively high abundance in the two smallest classes of particles (Fig. 3). These small particles can be directly consumed by both cladocerans such as *Bosmina* and by small copepods (Cottingham 1999). Larger particles (>35 μm) are less ^{14}C depleted due to a higher proportion of young organic matter such as large phytoplankton (primarily colonial cyanobacteria or large diatoms in the Hudson River; Caraco et al. 2006) and relatively young detrital carbon of benthic and terrestrial origin. Young dissolved organic carbon (DOC) of contemporary age, which dominates both the allochthonous inputs and standing stocks of organic carbon in the Hudson River (Findlay 2005), can potentially be converted to small edible particles (i.e., as microbial biomass). However, in the Hudson River and perhaps in other rivers (Van den Meersche et al. 2009), the transfer of such material to higher trophic levels is apparently low.

Possible reasons for a low transfer of young river DOC to the grazing food web include low bacterial growth efficiency (del Giorgio et al. 2006) and high transfer losses due to protozoan grazers (Vaque et al. 1992). Although the transfer of the large pool of young DOC to zooplankton is low in the Hudson River, there is some evidence that the small fraction of DOC that is old (<2%) is transferred with higher efficiency into microbes (McCallister et al. 2004) and possibly certain zooplankton groups. We hypothesize that this microbial transfer of aged DOC, in addition to the direct grazing of aged detrital POC, both account for the use of highly aged material by zooplankton.

Numerous anthropogenic activities may have increased the relative importance of aged organic matter as a food subsidy in the Hudson River, and these also likely influence a large number of other rivers. For example, declines in DOC quality due to soil acidification may be occurring throughout much of Europe and North America as well as in the Hudson River (Findlay 2005). In addition, sewage inputs of fossil carbon (Griffith et al. 2009) and increased inputs of highly aged soil organic matter resulting from erosion in

agricultural lands (Swaney et al. 1996) occur throughout populated regions of the world. Lastly, introductions of exotic grazers that can both decrease phytoplankton biomass and increase the proportion of inedible phytoplankton species have occurred in a large number of lakes, estuaries, and rivers globally (Caraco et al. 2006, Maguire and Grey 2006).

Previous studies have shown that a large number of rivers transport significant amounts of ^{14}C-depleted POC (Raymond et al. 2004). Expanded use of natural abundance ^{14}C in food web studies is needed to determine if highly aged river organic matter is an important food web subsidy in riverine systems in general, as well as in other freshwater systems. Significant subsidization of aquatic food webs by aged terrestrial sources would indicate that contemporary primary production within the aquatic system or even the surrounding watershed may not limit consumer production or the stability of aquatic communities (Nowlin et al. 2007). Instead, these aquatic consumers, like contemporary humans, would be released from the material and energy constraints of modern primary production through the use of previously sequestered and highly aged sources of organic matter.

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APPENDIX A

[14]C overview and units (*Ecological Archives* E091-170-A1).

APPENDIX B

Seasonal variability (*Ecological Archives* E091-170-A2).