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Abstract

A number of rivers have been found to transport highly aged organic matter [OM]; however, the sources of this aged material remain a matter of debate. One potential source may be erosion and weathering of headwater lithologies rich in ancient sedimentary OM. In this study, waters, suspended particulates, streambed sediments, rocks and soils from fourteen small headwater watersheds of a mid-size, temperate, passive margin river were sampled and characterized by $\Delta^{14}\text{C}$, $\delta^{13}\text{C}$, and POC/TPN ratios to identify sources of particulate and dissolved OM delivered to the river mainstem. These headwater sites encompass a range in lithology (OM-rich shales, OM-lean carbonate/mudstone facies, and OM-free crystalline rocks) and land use types (forested and agricultural), and allow investigation of the influence of agriculture and bedrock types on stream OM characteristics. Streams draining large areas of both agricultural land use and OM-rich lithology contain particulate OM [POM] that is more ^{14}C -depleted than streams draining forested, shale-free watersheds. However, this is not sufficient to account for the significantly lower $\Delta^{14}\text{C}$ -POC measured in the river mainstem. Dissolved OM [DOM] $\Delta^{14}\text{C}$ are in all cases enriched compared to POM from the same stream, but are otherwise highly variable and unrelated to either land use or lithology. POC/TPN ratios were likewise highly variable. POC and DOC $\delta^{13}\text{C}$ signatures were similar across all watersheds. Based on isotope mass balance, ^{14}C -free fossil OM sources contribute 0–12% of total stream POM. Although these results do not unequivocally separate the influences of land use and lithology, watershed coverage by shale and agriculture are both important controls on stream $\Delta^{14}\text{C}$ -POC. Thus export of aged, particle-associated OM may be a feature of river systems along both passive and active continental margins.

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1. INTRODUCTION

Rivers are an important component in both the long-term geologic and shorter term surficial carbon cycles. They expose and erode ancient carbon buried in sedimentary rocks, and are the primary export path for all terrestrial carbon sources to the ocean. While much of the organic

matter [OM] contained in rocks is degraded within the outcrop and oxidized to CO_2 during weathering (Petsch et al., 2000, 2001; Wildman et al., 2004; Bolton et al., 2006), a portion is transported downstream with little or no alteration (Dickens et al., 2004). This recycled ancient OM may escape remineralization in rivers or in nearshore marine environments and be reburied in modern marine sediments. Burial fluxes of OM in modern sediments may, in some settings, comprise a mixture of ancient OM and recent primary production, contributing to increased estimates of burial efficiencies where OM burial is contrasted against autochthonous inputs (Blair et al., 2003, 2004).

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Additionally, because reconstructions of OM burial fluxes and growth of the crustal carbon inventory over geologic time depend largely on isotope mass balance models and 100% efficiency of OM remineralization during weathering (Berner, 1989), recycled ancient OM plays an important but as yet undefined role in the long-term geochemical cycles of carbon and atmospheric oxygen (Bolton et al., 2006).

The age and source of OM exported to the ocean by rivers are important factors for understanding the global cycling of modern and ancient carbon. Approximately 90% of organic carbon burial is associated with river-dominated continental margins (Berner, 1982, 1989; Berner and Raiswell, 1983; Hedges and Keil, 1995). OM burial efficiency is at least in part related to its association with mineral particles (Mayer, 1994a,b; Hedges and Keil, 1995; Keil et al., 1997; Mayer, 1999; Kennedy et al., 2002, 2006; Dickens et al., 2006). The delivery of fine-grained particles by rivers therefore plays an important role in controlling the burial of OM in marine sediments, by limiting the amount of particle surfaces contributed to the ocean. This control may be most pronounced in river systems with high sediment yields such as those draining small, mountainous watersheds (Blair et al., 2003, 2004; Gomez et al., 2003; Carey et al., 2005; Leithold et al., 2005). Recent work has shown that a number of rivers export aged OM (Kao and Liu, 1996; Masiello and Druffel, 2001; Raymond and Bauer, 2001a,b; Blair et al., 2003; Komada et al., 2004), and that the source of this aged material is a combination of slow-cycling pools of soil OM with long residence times and ancient OM released by eroding sedimentary rock (Gomez et al., 2003; Gordon and Goñi, 2003, 2004; Dickens et al., 2004; Raymond et al., 2004; Goñi et al., 2005; Komada et al., 2005; Leithold et al., 2005; Leithold et al., 2006). Pre-loading of river-borne particulates with aged, particle-associated soil-derived and rock-derived OM may in fact restrict the addition of young terrestrial and marine OM to particles during transport, thus limiting the burial of recent primary production compared with particle-associated fossil OM (Blair et al., 2003).

Along active margins, extensive reburial of aged carbon exported by small, mountainous rivers such as the Eel (Blair et al., 2003), the Santa Clara (Masiello and Druffel, 2001; Komada et al., 2004, 2005), the Waipaoa (Gomez et al., 2003), the Waiapu (Leithold et al., 2006) and the Lanyang Hsi (Kao and Liu, 1996) is driven by rapid erosion of OM-rich rocks and regolith coupled with high rates of sediment export to the shelf (Leithold et al., 2006). However, highly aged OM has also been detected in POM and river-mouth sediments of major rivers (Goñi et al., 1997, 1998, 2000; Gordon and Goñi, 2003, 2004; Mayorga et al., 2005; Perkey et al., 2007) as well as smaller, passive margin rivers (Megens et al., 2001; Raymond and Bauer, 2001a,b; Raymond et al., 2004). Relief, erosion, transport, and sedimentation are less clearly linked to the export of aged, rock-derived OM along passive margins, indicating that internal modification of particle-associated OM by processes such as degradation of aged OM and loading of terrestrial and autochthonous river OM may exert greater control in these systems.

While most previous research has focused on the discharge of carbon from river mouths, this study examines

small tributaries of larger river systems, to establish if headwater catchments of modest relief receive POM from aged soil and rock sources. Smaller tributaries with greater relief and velocity receive proportionately greater amounts of allochthonous OM compared to in stream autochthonous production, and are proportionately less affected by downstream transformations than large rivers (Vannote et al., 1980). Therefore, headwaters provide valuable information on the sources of allochthonous OM input to river systems and their contributions to downstream OM pools and fluxes.

2. STUDY AREA

In this study, OM inputs to the Hudson–Mohawk River system were characterized in a suite of headwater tributaries and watershed materials. Multiple isotopic and elemental tracers were used investigate three objectives: (1) to examine the sources of OM to Hudson River headwaters; (2) to determine whether ancient sedimentary OM is a recognizable contributor to the Hudson system; and (3) to assess the role that land use (in particular, agriculture) may play in the flux and composition of OM exported to streams draining similar lithologies.

The Hudson–Mohawk watershed (New York, USA) provides an ideal location to study the behavior of ancient OM in a passive-margin river system. Over its 500 km course, the Hudson River (Fig. 1) drains an area of approx-

Fig. 1. Map of the Hudson–Mohawk River watershed and major tributaries. Lithologic units rich in ancient sedimentary OM (gray) dominate much of the watershed of the Mohawk River. Box indicates study area. C, Mohawk River at Cohoes, NY; G, Hudson River at Germantown, NY; W, Upper Hudson River at Waterford, NY. Inset map, small tributary watersheds of the Hudson–Mohawk River system included in this study.

imately $3.5 \times 10^4 \text{ km}^2$, and descends from headwater elevations of 1200 m to sea level, ultimately discharging in New York Harbor (Limburg et al., 1986). A tidal freshwater estuary with extended water residence times extends 300 km up the river to near Albany, NY, USA. Mean annual discharge of the Hudson is $\sim 12.3 \times 10^9 \text{ m}^3 \text{ y}^{-1}$ as measured 4 km below the confluence of the Mohawk and Upper Hudson at Green Island Dam, and above the northern limit of tidal influence (Butch et al., 2003). Peak flows are associated with spring rains and snowmelt during March–April. The Mohawk River joins the Hudson north of Albany, and contributes $\sim 43\%$ of total discharge measured at Green Island Dam; the remainder derives from the Upper Hudson and its tributaries. Rainfall over the study area averages 88 cm annually and is evenly distributed seasonally and across the basin (New et al., 1999, 2000), and annual sediment discharge at Green Island is $265 \times 10^3 \text{ ton y}^{-1}$ (Butch et al., 2003). For contrast, small mountainous rivers such as the Eel and Santa Clara are characterized by overall shorter courses, steeper slopes that are more prone to mass wasting, discernible tectonic uplift, substantially greater sediment yields, and lower but more episodic discharge (Masiello and Druffel, 2001; Blair et al., 2004; Leithold et al., 2005; Komada et al., 2005).

Fourteen streams were sampled to provide a range of tributary and watershed types. The sites are spread throughout the Hudson drainage basin, and encompass a range of lithologies and land uses (Fig. 1 inset, also Table 1). Of the fourteen, a subset of six sites was selected for repeated sampling. Within these six sites, four drain the Devonian and Ordovician black shales of the Mohawk Valley in upstate New York, and two sites drain the OM-free metamorphic rocks of the southern Adirondacks.

2.1. Geologic setting of the Hudson–Mohawk watershed

The lithology of the Hudson–Mohawk watershed may be divided into the metamorphic and igneous facies of the Adirondack Mountains to the north, metamorphosed foreland basin deposits between Albany east to the Taconic Range, and sedimentary lithologies of the Mohawk Valley. The latter two features were formed as siliciclastic sediments were shed from the eroding Taconic and subsequent tectonic highlands into the compensatory foreland basin during the multiple orogenic events that punctuated the early Paleozoic throughout New England (Coch and Boku-niewicz, 1986; Isachsen et al., 2000). These dominantly terrigenous sequences comprise the Ordovician Trenton Group and Devonian Hamilton Group of interbedded shales, siltstones, and carbonates.

Shale organic carbon contents increase to the west through the study area (Sageman et al., 2003). While units such as the Ordovician Utica Shale and the Devonian Marcellus Formation may contain upwards of 3–8% TOC, other shale, siltstone and carbonate units in the region contain substantially less. Paleozoic metasedimentary slates, schists and phyllites from Albany east through the Taconic Range are generally devoid of OM, resulting from both OM dilution due to deposition proximal to the eroding highlands and subsequent low-grade metamorphism. The

Adirondacks are composed of high-grade metamorphosed Grenville basement rocks, primarily gneiss, amphibolite and granitic gneiss later uplifted by post-Taconic block faulting. During the last glacial maximum the entire field area was covered by the Laurentide Ice Sheet. Other than pockets of remnant paleosols and organic material mixed with tills, soil inception in the study area occurred no earlier than 15,600 ^{14}C -yr BP, the approximate time of glacial retreat (Mickelson and Colgan, 2004).

2.2. Land use

Land use across the study area ranges from completely forested in the Adirondacks to mostly agricultural in the Mohawk Valley (Supplementary material Fig. EA-1). Uplands surrounding the Mohawk Valley and the Taconic Highlands exhibit mixed forest/agricultural uses, while the region at the confluence of the Mohawk and Hudson is highly urbanized. Agriculture has been in decline in New York for much of the 20th century, and formerly tilled fields are being replaced by fallow fields, pasture and forest (Ramankutty and Foley, 1999). The “agricultural” designation in this study reflects the most recent land cover database available, and includes pasture and fallow fields. Small wetlands are a limited feature of the landscape most common towards the north and east of the field area, in highlands of the Adirondacks and Taconic Range.

3. METHODS

3.1. Geographic Information Systems

A Geographic Information Systems (GIS) approach was employed for both site selection and the analysis of the land use and geology of sampled watersheds. For site selection, a GIS was constructed using publicly available digital spatial datasets for bedrock geology (New York State GIS Clearinghouse, Bedrock Geology of New York State—Hudson Mohawk Sheet, <http://www.nysgis.state.ny.us>), land use (Multi-Resolution Land Characteristic Consortium, National Land Cover Database, <http://landcover.usgs.gov/natl/landcover.php>) and hydrology (U.S.G.S. National Hydrography Dataset, <http://nhd.usgs.gov>). Data on lithology and land use were attached to each watershed as defined by the NHD watersheds layer. This permitted selection of watersheds in the study area according to substrate attributes of land use and lithology. Watersheds representing the following four characteristics were chosen: (1) forest overlying OM-rich shales, (2) forest overlying OM-free rocks, (3) agriculture overlying OM-rich shales, and (4) agriculture overlying OM-free crystalline/metamorphic rocks. From the selection of watersheds satisfying each condition, a small number with similar area, slope, and morphology were chosen, and watersheds with potential contamination problems or access issues were avoided.

A handheld GPS unit was used to record the exact location of each sampling site. These locations were converted to a GIS layer and used to determine total area and extent of the watershed area upstream from the sampling site. Using digital elevation data from the National Elevation

Table 1
Site information for sampled watersheds in the Hudson–Mohawk drainage

Watershed			Lithology					Land use			
	Area (km ²)	Map symbol	OM-rich ^a (%)	OM-poor ^b (%)	Sed _{other} ^c (%)	Crystalline ^d (%)	OC- weighted ^e	Agricultural ^f (%)	Forest ^g (%)	Wetlands ^h (%)	Urb/Res ⁱ (%)
<i>OM-rich and OM-poor watersheds (shale)</i>											
Danascara Cr.	24	DC	0	100	0	0	0.30	61	32	1	5
Gordon Cr.	16	GC	0	100	0	0	0.30	20	72	5	3
Nowadaga Cr.	82	NC	45	44	11	0	0.45	49	50	0	0
Otsuago Cr.	149	OC	55	37	8	0	0.55	65	35	0	0
Schoharie Trib.	21	ST	0	95	5	0	0.39	19	80	1	0
West Cr.	142	WC	0	76	24	0	0.35	47	51	1	0
Winnie's Hollow Br.	23	WH	0	100	0	0	0.35	7	93	0	0
<i>OM-free watersheds (sedimentary, metamorphic and crystalline rocks)</i>											
Beaverdam Cr.	29	BC	0	0	100	0	0	46	51	2	1
Caroga Cr.	46	CC	0	0	39	61	0	1	86	10	2
Couch Hollow Br.	24	CH	0	0	100	0	0	6	89	2	2
Fly Br.	31	FB	0	7	93	0	0	46	52	2	0
S. Br.	21	SK	0	0	47	53	0	7	90	3	0
Kayaderosseras Cr.											
Schafer's Br.	25	SB	0	0	16	84	0	0	98	2	0
Wampecack Cr.	50	WA	0	8	92	0	0	61	35	2	1

All sites were sampled in April 2003; sites in bold were selected for repeated sampling in May, June, July, and September, 2003. Areas and fractional coverages were calculated using a GIS.

^a OM-rich rocks are limited to the Utica Shale (Trenton Group).

^b OM-poor rocks include shales, cherts, siltstones, and carbonates of the Hamilton, Helderberg, Trenton, and Black River Groups.

^c Sed_{other} includes metamorphosed slates and schists of the Taconic Range, as well as siltstones, cherts and carbonates (no shale) of the Helderberg Gp.

^d crystalline rocks include pyroxene-hornblende-quartz-plagioclase gneiss, granitic gneiss, quartz-syenite gneiss and amphibolite.

^e OC-weighted fraction reflects the % area of OM-rich and OM-poor rocks multiplied by rock % TOC.

^f Agriculture includes pasture and row crops.

^g Forest includes deciduous, evergreen, and mixed forest.

^h Wetlands includes woody wetlands, herbaceous wetlands, and open (still) water.

ⁱ Urban/Residential includes commercial/industrial, low-intensity residential and high-intensity residential land uses.

Dataset, watershed modeling in ArcGIS 8 (ESRI, Redlands, CA) was used to produce a layer of the sampled watersheds. This layer was then spatially joined to the lithology and land use layers to provide the fractional areal extent of each type of land use and lithology in the study watersheds.

3.2. Sampling

Stream water samples were collected during peak spring runoff in April 2003 at fourteen sites, and again in June, July, and September 2003 at six of these sites (Table 3). Stream waters were collected in pre-combusted (480 °C) 4 L glass jugs with Teflon lined caps. Samples from the Hudson (near Germantown, NY), Mohawk (near Cohoes, NY) and Upper Hudson (near Waterford, NY) Rivers were collected in May 2003 as part of an ongoing, multi-year monitoring of variability in OM sources and ages at sites described in Raymond and Bauer (2001b). River water samples were collected at ~0.5 m water depth in acid-cleaned polycarbonate bottles that were submerged inverted to avoid collecting any surface film.

Soil sampling sites were chosen to represent the dominant land use for a given watershed, and were sampled close to streams, but outside of frequently flooded areas. Soils were sampled ~500 m upstream of stream water sampling sites, and ~5 m away from the stream bank and on level ground. Soil profiles were obtained using a 100 cm coring auger. Deep soil samples were compiled from 40–50 cm depth, shallow from 0–10 cm depth, and litter from the soil surface. These depths were chosen to represent the likely sources of interfluvial (shallow) and stream bank (deep) erosion. Samples of outcropping rocks and stream sediments were collected from a subset of study watersheds for elemental and isotopic analysis. Periphyton in streams was obtained from material attached to submerged rocks. All samples were immediately stored in the dark at 4 °C, and processed for further analyses within 24 h of collection.

3.3. Laboratory analyses

A volume of 0.5–1 L of each 4 L water sample was filtered through pre-combusted 25 mm glass fiber filters (Whatman GF-F, ~0.7 µm pore size) to collect POM for elemental and $\delta^{13}\text{C}$ analysis, and the remainder was filtered through pre-combusted 47 mm quartz filters to separate POM for $\Delta^{14}\text{C}$ analysis (Whatman QM-A, ~1 µm pore size). Filters were immediately frozen at –35 °C, lyophilized, and stored airtight at room temperature until analysis. The first liter of filtrate was used as a rinse for collection vessels and discarded. Subsequently, 125 mL of filtrate were collected in glass bottles for $\Delta^{14}\text{C}_{\text{DOC}}$ and preserved with concentrated H_3PO_4 . 50 mL were collected in pre-cleaned glass vials and acidified for DOC assay, and 125 mL were collected unacidified and overfilled for determination of alkalinity and anions. Stream sediments, rocks and soil samples were immediately frozen at –35 °C, lyophilized, and stored airtight at room temperature until analysis.

DOC concentrations were measured using a Shimadzu TOC-V carbon analyzer. Carbon and nitrogen elemental abundance and $\delta^{13}\text{C}$ of POM, stream sediments, outcrop samples and soils were determined using an elemental analyzer coupled to an isotope ratio mass spectrometer (EA–IRMS). Dried samples were powdered in a ball mill and weighed into Ag sample boats. Weighed samples were then acidified with repeated application of H_2SO_3 and drying at 55 °C to remove carbonates (Hedges and Stern, 1984). Filters bearing stream particulate matter were acidified over fuming HCl for 24 h, freeze-dried and packed whole into large tin capsules. Samples were combusted at 1020 °C in a Costech ECS140 elemental analyzer (EA) interfaced with a Finnigan Delta XL mass spectrometer for continuous flow determination of $\delta^{13}\text{C}$ (Werner et al., 1999). Results for carbon are reported in standard delta notation ($\delta^{13}\text{C}$) as the per mil deviation in $^{13}\text{C}/^{12}\text{C}$ relative to the Pee Dee Belemnite standard. The analytical precision of these analyses is better than 0.3‰, and analysis of replicates shows samples to be reproducible to within 0.5‰. The precision for elemental analysis is 5% C and 10% N, based on the mean standard error for all samples run in triplicate.

Radiocarbon analysis of stream POC, DOC, and watershed materials was performed at the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory (LLNL). Hudson and Mohawk River DOC and $\Delta^{14}\text{C}$ -POC analyses were conducted at the NSF-Arizona Accelerator Mass Spectrometry Laboratory of the University of Arizona. POC filters were acidified in glass vials over fuming HCl for 24 h, and then dried at 55 °C. Rock, sediment and soil samples were acidified over fuming HCl for 24 h to remove inorganic carbon, and then dried in a Jouan vacuum centrifuge.

Samples were combusted in sealed, evacuated quartz tubes with CuO wire and Ag powder at 850 °C for 4 h. The resulting CO_2 was purified cryogenically before reduction to graphite. For $\Delta^{14}\text{C}$ -DOC analysis, 100 mL of filtered stream water were acidified in quartz reactor tubes with H_3PO_4 and sparged with ultra-high purity N_2 gas to remove inorganic carbon, saturated with ultra-high purity O_2 , and exposed to UV light to oxidize DOC to CO_2 (Raymond and Bauer, 2001a; Raymond et al., 2004). This CO_2 was then purified cryogenically before graphitization. All CO_2 produced from various samples was graphitized over iron catalyst (Vogel et al., 1987) and analyzed for $\Delta^{14}\text{C}$ by AMS. Results were corrected for process and instrument blanks, and for isotopic fractionation using measured $\delta^{13}\text{C}$ values. Data are expressed as $\Delta^{14}\text{C}$ relative to the NBS oxalic acid standard (Stuiver and Polach, 1977) with an average reported error of $\pm 4\text{‰}$ (CAMS) or $\pm 5\text{‰}$ (Arizona).

3.4. Statistical analyses

The watersheds for this project were selected to include different combinations of shale and agriculture (i.e., no shale, no agriculture; shale, no agriculture; agriculture, no shale; and shale, agriculture). Differences among sites were tested for significance using an analysis of variance (ANOVA), reported as the ratio (F) of observed versus predicted averages among groups and as the probability (p) that

groups of samples are not distinct. Single and multiple regressions of data were performed using land use (% agriculture or forest) and lithology (weighted % shale) as predictors and OM characteristics as dependent variables. The fraction of shale within each watershed was weighted by the OC content of each shale type, as determined from samples taken in this study and values from the literature (Petsch et al., 2000; Peucker-Ehrenbrink and Hannigan, 2000). A principal components analysis (PCA) was performed to examine correlations between watershed factors and stream OM character. Statistical analyses were performed using Excel or R (R Development Core Team, 2006). Source mixing models used a combination of simple mass balance calculations and software packages produced by Phillips and Gregg (2001, 2003). The IsoError package was used to examine the effect of variability in stream $\Delta^{14}\text{C}$ -POC on potential source contributions, and IsoSource was used to estimate possible ranges of source contributions in systems with more than two isotopically distinct OM sources.

4. RESULTS

4.1. Watershed land use and lithology

Land use and lithology for each sampled watershed are presented in Table 1. Figures of the field area, showing the bedrock geology and distribution of land use types derived from the GIS, are provided in [Supplementary material](#). Agriculture (cropland and pasture) ranges from 0% to 65% by area in the sample watersheds (Fig. EA-1). Most agriculture is concentrated in regions underlain by sedimentary rock, and the highest coverage by agricultural land use is generally coincident with the greatest abundance of OM-rich shales. Forests cover 30–98% of the studied watersheds throughout the Hudson–Mohawk drainage area. Wetlands are limited to $\leq 3\%$ of land use in each watershed, except at Caroga and Gordon Creeks. Urban and industrial areas are very limited throughout the watersheds. This distribution of land use types allowed division of the sampled headwater streams into two dominant land use groups: “agricultural”, in which agricultural uses make up $>40\%$ of the land use; and “forested”, in which forests make up $>70\%$ of the land use and agriculture is limited to $\leq 20\%$.

In two watersheds, Nowadaga Creek and Otsquago Creek, OM-rich shales of the Trenton Group make up 45% and 55% of the drainage basin area, respectively (Fig. EA-2). In contrast, OM-rich shales are absent from the other sampled watersheds, but low-TOC shales, carbonates and siltstones are abundant (up to 100% of land area) in a number of these. OM-free rocks including slates and schists of the Taconic Range and crystalline rocks in the Adirondacks comprise nearly 100% of the land area in seven of the fourteen sampled watersheds. This distribution of lithologies and their extent in each watershed allowed division of the sampled headwater streams into three lithology groups: “OM-rich”, in which high-TOC Utica Shale makes up $>40\%$ of the lithology in the watershed; “OM-poor”, which contains no Utica Shale but does contain between 75–100% of OM-poor interbedded shales, carbonates

and siltstones; and “OM-free”, which includes crystalline and metamorphic rocks.

4.2. Watershed POM and DOM elemental and isotopic characteristics

The 14 small watersheds were highly variable in POM and DOM elemental and isotopic signatures among samples collected during high spring run-off in April 2003 (Table 2). POC concentrations averaged $28\text{ }\mu\text{M}$ (range $12\text{--}47\text{ }\mu\text{M}$, $n = 14$). The average POC concentration in streams in OM-rich watersheds was $26\text{ }\mu\text{M}$ (18 and $33\text{ }\mu\text{M}$, $n = 2$), OM-poor watersheds averaged $17\text{ }\mu\text{M}$ ($12\text{--}24\text{ }\mu\text{M}$, $n = 5$), while streams draining OM-free lithologies averaged $37\text{ }\mu\text{M}$ ($21\text{--}47\text{ }\mu\text{M}$, $n = 7$). Streams draining watersheds with $>40\%$ agricultural coverage averaged $23\text{ }\mu\text{M}$ POC ($12\text{--}33\text{ }\mu\text{M}$, $n = 7$), while forested watersheds averaged $34\text{ }\mu\text{M}$ ($17\text{--}47\text{ }\mu\text{M}$, $n = 7$). Stream $\Delta^{14}\text{C}$ -POC values ranged from -109‰ to 95‰ , with a mean of 9‰ ($n = 13$), which was ^{14}C -enriched relative to POC in the Mohawk and Hudson River mainstems (Fig. 2). The average $\Delta^{14}\text{C}$ -POC from OM-rich watersheds was -83‰ ($n = 2$) and from OM-poor watersheds was -20‰ ($n = 5$) which is 135‰ and 72‰ more depleted than average POC in watersheds draining OM-free lithologies, respectively. POC in streams draining agricultural watersheds was also more ^{14}C -depleted (average -31‰ , $n = 7$) compared with forested streams (average $+55\text{‰}$, $n = 7$). Total particulate nitrogen [TPN] averaged $4.5\text{ }\mu\text{M}$ (range $1.6\text{--}8.2\text{ }\mu\text{M}$, $n = 14$). Stable carbon isotopic values ($\delta^{13}\text{C}$) of POC for all sites averaged -27.3‰ (range -28‰ to -25.5‰ , $n = 13$). POC:TPN among all sites averaged 8.7 (range $1.5\text{--}28.8$, $n = 14$). Extremely low ($1.5\text{--}4.9$) POC:TPN ratios were obtained for several sites draining shales and/or agricultural land use. A positive y -intercept for a linear regression of POC versus TPN likely suggests incorporation of inorganic N in stream suspended matter. Additionally, accurate detection of nitrogen in POM is difficult to achieve at very low concentrations. These POC:TPN ratios do not solely reflect the composition of stream POM, but rather include stream POM, particulate inorganic N, and analytical detection limits associated with samples low in POC. The mean molar POC:TPN ratio in streams with $[\text{POC}] > 25\text{ }\mu\text{M}$ was 13.7. River mainstem POC:TPN ratios (Upper Hudson, Mohawk and Hudson) ranged from 7.3–8.5, which may indicate that POM delivered to streams was modified during transport as more C-rich components of POM were degraded or deposited upstream of the mainstem sampling locations. However, given the low apparent POC:TPN ratios in most of these streams, no further conclusions regarding the influence of land use or lithology can be drawn.

DOC concentrations for all April 2003 small watershed samples averaged $432\text{ }\mu\text{M}$ (range $152\text{--}1938\text{ }\mu\text{M}$, $n = 14$) (Table 2). This yielded a mean DOC:POC ratio of 17, which was greater than the ratios measured in the Hudson, Upper Hudson and Mohawk Rivers (DOC:POC of 5, 4, and 4, respectively). A high DOC:POC ratio in headwaters may indicate that particle production was limited in many headwater streams. Stream $\Delta^{14}\text{C}$ -DOC ranged from -5‰ to

Table 2
Concentrations and isotopic characteristics of river mainstem and watershed DOM and POM, collected April 2003

Site name	POC (μM)	$\delta^{13}\text{C}_{\text{POC}}$ (‰)	$\Delta^{14}\text{C}_{\text{POC}}$ (‰)	DOC (μM)	$\delta^{13}\text{C}_{\text{DOC}}$ (‰)	$\Delta^{14}\text{C}_{\text{DOC}}$ (‰)	TPN (μM)	POC/TPN	DOC:POC
<i>OM-rich watersheds</i>									
<u>Nowadaga Cr.</u>	33	-26.1	-109	213	n.d.	47	3.3	10	6
<u>Otsquago Cr.</u>	18	-26.5	-57	299	-28.2	68	6.2	2.9	17
<i>OM-poor watersheds</i>									
<u>Danascara Cr.</u>	14	-27.1	-28.5	386	-27.9	83	7.1	2.0	27
Gordon Cr.	24	-28.5	72.8	561	-27.7	124	5.5	4.4	23
Schoharie Trib.	17	-26.9	-29	261	-27.2	89	5.0	3.4	16
<u>West Cr.</u>	12	-27.4	-96	282	-28.6	104	8.2	1.5	23
Winnie's Hollow Br.	19	-27.3	n.d.	194	n.d.	-5	2.6	7.3	10
<i>OM-free sedimentary watersheds</i>									
<u>Beaverdam Cr.</u>	21	-27.9	13.7	401	n.d.	91	4.3	4.9	19
Couch Hollow Br.	46	-27.5	94.9	152	n.d.	22	1.6	28.8	3
<u>Fly Br.</u>	30	-27.9	23.4	1938	n.d.	n.d.	3.7	8.1	65
<u>Wampecack Cr.</u>	32	-25.5	35.6	327	-27.5	68	4.3	7.4	10
<i>OM-free crystalline rock watersheds</i>									
Caroga Creek	40	-28.3	44	330	-27.1	103	2.7	14.8	8
Kayaderosseras	44	-27.4	81.3	235	n.d.	118	6.0	7.3	5
Schafer's Br.	47	-27.8	68	464	n.d.	31	2.4	19.6	10
Average, all streams	28	-27.3	9	432	-27.7	73	4.5	8.7	17
Average agricultural	23	-26.9	-31	549	-28.1	77	5.3	5.3	24
Average forested	34	-27.7	55	314	-27.3	69	3.7	12.2	11
Average, OM-rich	26	-26.3	-83	256	-28.2	58	4.8	6.5	12
Average, OM-poor	17	-27.4	-20	337	-27.9	79	5.7	3.7	20
Average, OM-free	37	-27.5	52	550	-27.3	72	3.6	13.0	17
Hudson River (Germantown, NY)	39	-27.0	-150	187	-26.4	45	5.3	7.3	5
Upper Hudson River (Waterford, NY)	60	-27.6	-20	212	-26.8	70	7.1	8.5	4
Mohawk River (Cohoes, NY)	56	-26.8	-191	207	-26.9	26	7.1	7.8	4

n.d., Not determined. Watersheds in bold are characterized by >70% forest cover. Underlined sites are characterized by >40% agricultural land use. Nitrogen measurements on samples with [POC] < 25 μM may reflect contributions from inorganic N.

Fig. 2. Comparison of $\Delta^{14}\text{C}$ of stream POM and DOM for all sampled watersheds, demonstrating distribution among lithology and land use types in each watershed. Watersheds with $>40\%$ agricultural uses are “Agricultural”. Watersheds with $>70\%$ coverage by forests are “Forested”. H, Hudson River mainstem at Germantown, NY; M, Mohawk River at Cohoes, NY; UH, Upper Hudson River at Waterford, NY.

124‰ , with a mean of 73‰ ($n = 13$). These values are similar to $\Delta^{14}\text{C}$ -DOC in the Hudson and Mohawk Rivers. The average $\Delta^{14}\text{C}$ -DOC for OM-rich or OM-poor watersheds compared to OM-free watersheds, or in forested compared with agricultural systems, was statistically indistinguishable from the average for all watersheds. Stream $\delta^{13}\text{C}$ -DOC averaged -27.7‰ , and had smaller range than $\delta^{13}\text{C}$ -POC (range -28.6‰ to -27.1‰ , $n = 7$).

4.3. Temporal variability of POM and DOM

A subset of six streams was sampled three additional times during 2003 to evaluate temporal variability in OM characteristics (Table 3). These small streams are not gauged; however, repeat sampling of the watersheds was timed to coincide with periods of high (April 2003) and low (June, July, and September 2003) flow. Flows recorded in a nearby stream with a similar drainage area to that of the sampled watersheds ranged from $10 \text{ m}^3 \text{ s}^{-1}$ during the April sampling to $0.2 \text{ m}^3 \text{ s}^{-1}$ during the September sampling (Canajoharie Cr., area = 155 km^2 , data from USGS National Water Information System, <http://waterdata.usgs.gov/nwis/>). Trends in stream OM characteristics related to time of sampling or streamflow were not apparent, but characteristics such as $\Delta^{14}\text{C}$ -POC, $\Delta^{14}\text{C}$ -DOC, POC/TPN, and DOC:POC ratios did vary through time (Table 3). This variability shows that single samples are unlikely to fully represent the time- and flow-weighted averages of different stream OM compositions. For example, variability in $\Delta^{14}\text{C}$ -POC over six months of sampling spanned a range of over 200‰ in the case of West Creek and over 100‰ in the other streams draining OM-rich and OM-poor lithologies, but only spanned a $40\text{--}50\text{‰}$ in the two streams draining OM-free rocks. The $\delta^{14}\text{C}$ -POC enrichment in West Creek and other OM-rich and OM-poor streams observed

during June sampling likely indicates influence of recent production, either autochthonous or from terrestrial vegetation, mixed with post-bomb soil carbon; of these, terrestrial vegetation inputs were more consistent with the observed $\delta^{13}\text{C}$ -POC.

Mean values of $\Delta^{14}\text{C}$ -DOC in this subset of six watersheds were 25‰ more depleted in watersheds draining shale/carbonate than in streams draining crystalline rocks (Table 3). In these same repeatedly sampled watersheds, $\Delta^{14}\text{C}$ -DOC ranged from -40‰ to 104‰ in streams draining OM-rich and OM-poor rocks, and ranged from 31‰ to 103‰ in streams draining OM-free rocks. The average POC:TPN ratio in the repeatedly sampled watersheds draining OM-free rocks was greater than that of POM from streams draining OM-rich and OM-poor rock, and ranged from 2.0 to 10.3 in streams draining OM-rich and OM-poor rock, and from 8.6 to 19.6 in streams draining OM-free rocks. Extremely low POC/TPN ratios were observed in three streams (Otsquago Creek, Schoharie Trib., West Creek in April, 2003, and Schoharie Trib. again in September 2003). Agricultural land use makes up 65%, 19%, and 47% of these watersheds, respectively, and all three drain either OM-rich or OM-poor rocks. The low POC/TPN ratios may indicate addition of inorganic nitrogen as fertilizer or analytical detection limits associated with samples low in POC. Stream POM and DOM $\delta^{13}\text{C}$ exhibited little temporal variability in this study. The observations of ^{14}C -depleted POC and lower POC/TPN in streams draining OM-rich and OM-poor rocks compared to OM-free rocks upon repeated sampling of a subset of streams are broadly similar to results from the larger survey of streams sampled once.

4.4. Watershed source materials

Rocks and soil OC in watersheds draining OC-bearing sedimentary rocks were ^{14}C -depleted compared with analogous samples from watersheds draining crystalline rocks (Table 4). This indicates a link between the low $\Delta^{14}\text{C}$ values in stream POC and ^{14}C -depleted OC sources (Fig. 3). In contrast, stream $\Delta^{14}\text{C}$ -DOC did not correlate directly with the $\Delta^{14}\text{C}$ values for rock and soil OC examined in this study. Instead, DOC may reflect a younger and more rapidly cycling pool of watershed OC. Extensive biogeochemical processing affects DOC inputs, transformations and degradation in streams (Frost et al., 2006), obscuring relationships between DOC and source materials.

Sediments from Nowadaga Creek were more ^{14}C -depleted than Nowadaga Cr. POC and DOC (Tables 3 and 4). These same sediments were also highly ^{14}C -depleted compared with sediments from Schafer's Brook. The low sediment $\Delta^{14}\text{C}$ values may reflect contributions from soils and weathered rocks in the watershed. In the Nowadaga Cr. watershed, where OC-rich shales underlie 45% of the drainage, both shallow and deep soil horizons were ^{14}C -depleted compared to soils from the Schafer's Brook watershed which drains crystalline rock (Table 4). Shallow soils from both of these watersheds were enriched by $\sim 150\text{‰}$ relative to deep soils, although the shallow Nowadaga Creek soil was still 83‰ depleted in $\Delta^{14}\text{C}$ relative to the Schafer's Brook soil. Molar C:N ratios at all levels of the

Table 3
Concentrations and isotopic composition DOM and POM in stream waters, collected April–September, 2003

Site name	POC (μM)	$\delta^{13}\text{C}_{\text{POC}}$ (‰)	$\Delta^{14}\text{C}_{\text{POC}}$ (‰)	DOC (μM)	$\delta^{13}\text{C}_{\text{DOC}}$ (‰)	$\Delta^{14}\text{C}_{\text{DOC}}$ (‰)	TPN (μM)	POC:TPN	DOC:POC
<i>OM-rich watersheds</i>									
<u>Otsuquago Creek</u>									
Average	19	−27.3	−97	224	−26.9	2	3.3	7.5	12
4/03	18	−26.5	−57	299	−28.2	68	6.2	2.9	17
6/03	20	−26.7	−32	230			2.4	8.2	12
7/03	22	−28.4	−151	193	−25.8	−40	2.8	7.7	9
9/03	17	−27.4	−148	174	−26.8	−22	1.6	11	10
<u>Nowadaga Creek</u>									
Average	28	−27.1	−103	199	−27.9	39	3.2	8.8	8
4/03	33	−26.1	−109	213		47	3.3	10	6
6/03	31	−26.2	−84	191			3.8	8.3	6
7/03	30	−26.6	−97	204	−28.2	39	3	10	7
9/03	18	−29.4	−123	189	−27.6	30	2.5	7	11
<i>OM-poor watersheds</i>									
Schoharie Trib.									
Average	26	−28.1	1	242	−27.7	69	3.7	6.0	47
4/03	17	−26.9	−29	261	−27.2	89	5	3.4	16
6/03	58	−28	25	254			5.6	10.3	4
7/03	26	−27.2	11	183	−28.1	60	3.1	8.4	7
9/03	2	−30.2	−2	269	−27.7	57	0.9	2	161
West Cr.									
Average	49	−29.4	−3	343	−28.5	70	7.9	6.1	13
4/03	12	−27.4	−96	282	−28.6	104	8.2	1.5	23
6/03	42	−33.3	132	317			5.4	7.7	8
7/03	121	−29.2	−41	408	−28.6	58	14.6	8.3	3
9/03	22	−27.6	−6	365	−28.3	49	3.2	7	16
<i>OM-free watersheds</i>									
Caroga Creek									
Average	42	−27.8	20	352	−27.6	76	3.3	12.2	12
4/03	40	−28.3	44	330	−27.1	103	2.7	14.8	8
6/03	84	−27.9	15	351			6.2	13.5	4
7/03	23	−27.9	17	291	−27.9	66	2.7	8.6	12
9/03	19	−27	4	435	−27.7	60	1.6	12	23
Schafer's Br.									
Average	116	−28.6	35	265	−28.1	65	4.5	15.7	6
4/03	47	−27.8	68	464		31	2.4	19.6	10
6/03	170	−28	19	216			10.1	16.7	1
7/03	53	−28.5	33	185	−28	86	3.6	14.4	4
9/03	195	−29.9	20	195	−28.2	77	1.9	12	9

(continued on next page)

Table 3 (continued)

Site name	POC (μM)	$\delta^{13}\text{C}_{\text{POC}}$ (‰)	$\Delta^{14}\text{C}_{\text{POC}}$ (‰)	DOC (μM)	$\delta^{13}\text{C}_{\text{DOC}}$ (‰)	$\Delta^{14}\text{C}_{\text{DOC}}$ (‰)	TPN (μM)	POC:TPN	DOC:POC
Average, all streams	47	-28.0	-24	271	-27.8	53	4.3	9.4	16
Average, OM-rich	24	-27.2	-100	212	-27.3	20	3.2	8.1	10
Average, OM-poor	38	-28.7	-1	292	-28.1	70	5.8	6.1	30
Average, OM-free	79	-28.2	28	308	-27.8	71	3.9	14.0	9
Average, agricultural	32	-27.9	-68	255	-27.8	37	4.8	7.5	11
Average, forested	61	-28.1	19	286	-27.7	70	3.8	11.3	22

Underlined sites are categorized as “agricultural”, with >40% of land use assigned to agriculture; watersheds in bold are categorized as “forested”, with no more than 20% of land use assigned to agriculture.

Schafer’s Brook watershed soil were enriched relative to soil from the Nowadaga Creek watershed. Differences in soil OC $\delta^{13}\text{C}$ among these sites are not statistically significant, and these data likely reflect C_3 vascular plant material as the dominant initial source of OM in these watersheds.

5. DISCUSSION

5.1. Contributions of watershed materials to stream POM

The sources of river OM include weathering, erosion, and leaching of watershed materials (rocks, soils, plants, streambed and floodplain sediments) as well as internal production. Therefore, OM in rivers and streams should exhibit characteristics that are diagnostic of its particular watershed attributes. For example, ^{14}C -depleted rocks and soils occur in watersheds exhibiting more ^{14}C -depleted POC and stream sediment signatures, suggesting that erosion and weathering of these materials contribute to the aged materials in downstream reservoirs. Weathered outcrops of Utica shale found in the Otsquago and Nowadaga Creek watersheds contained 2–3.5% OC, and these samples contained no modern carbon (Table 4). Previous studies have determined that unweathered samples of Utica and Marcellus Shale may contain up to 10% and 6% OC, respectively (Petsch et al., 2000; Peucker-Ehrenbrink and Hannigan, 2000). Outcrops of the Marcellus Formation within the West Creek watershed contained only 0.4% OC, and although geologic maps show Marcellus underlying the Schoharie tributary site, no dark-colored shale outcrops were located in the watershed, and the sampled shale had only 0.1% OC. This indicates that sites located north and east of the Schoharie watershed, such as Beavercreek Creek and Gordon Creek, may be underlain by shales that are more OM-lean than geologic maps would suggest.

While lithology is linked to stream $\Delta^{14}\text{C}$ -OM signatures through the weathering and erosion of ancient sedimentary OM, agriculture may increase the mean age of surface soil OM by mixing with deeper, older soil pools during tilling. If exported to streams, soil OM may then influence the $\Delta^{14}\text{C}$ signatures of stream OM in the water column, sediments, or both. In many systems, tilling decreases soil permeability and increases runoff, thereby increasing rates of soil OM erosion and export (Lal, 2003). However, in this study, stream POC concentration and percent agricultural land use exhibit a weak inverse correlation ($r^2 = 0.33$, $p = 0.03$). This suggests that agricultural practices are not associated with an increased rate of litter or soil OM export in these watersheds unless streams in the study area presently exhibit higher discharge than they did prior to conversion to agricultural land use. While leaf and twig litter in heavily forested watersheds could contribute to an inverse relationship between POC and % agriculture, litter sources should also be important in agricultural watersheds.

Tilling also mixes deep, aged soil horizons and regolith with younger surface material, increasing the average age of exposed soil OC available for export and causing a decrease in the $\Delta^{14}\text{C}$ range between shallow and deep soil horizons (Paul et al., 1997). This may in part explain the low soil OC $\Delta^{14}\text{C}$ values and reduced range between deep

Table 4
Organic carbon and total nitrogen concentrations and isotopic composition of watershed OM

Site	Sample description	TOC (%)	$\delta^{13}\text{C}$ (‰)	$\Delta^{14}\text{C}$ (‰)	N_{tot} (%)	C:N
<i>Rocks</i>						
Schoharie Trib.	Grey shale	0.10	−28.7		0.04	2
West Cr.	Marcellus shale	0.37	−26.4		0.09	3
Otsquago Cr.	Utica shale	2.04	−25.2	−997	0.10	17
Nowadaga Cr.	Utica shale	3.55	−32.2	−977	0.17	18
Nowadaga Cr.	Frankfort shale	0.12	n.d.		0.08	1
Schafer's Br.	Gneiss	0.04	n.d.		0.02	2
<i>Soils</i>						
West Cr.	Deep	2.70	−26.2		0.30	8
West Cr.	Shallow	3.98	−26.2		0.42	8
West Cr.	Litter	42.94	−29.7		1.56	24
Nowadaga Cr.	Deep	2.13	−27.9	−127	0.25	7
Nowadaga Cr.	Shallow	3.98	−28.7	20	0.43	8
Nowadaga Cr.	Litter	14.21	−27.8		0.80	15
Caroga Cr.	Deep	3.47	−26.1		0.26	12
Caroga Cr.	Shallow	2.80	−46.7		0.22	11
Caroga Cr.	Litter	23.38	−28.5		0.78	26
Schafer's Br.	Deep	2.65	−25.7	−84	0.14	16
Schafer's Br.	Shallow	10.74	−27.4	103	0.78	12
Schafer's Br.	Litter	45.72	−27.8		1.90	21
Schafer's Br.	Deep	1.29	−27.3		0.09	12
Schafer's Br.	Shallow	1.76	−27.2		0.10	15
Schafer's Br.	Litter	37.62	−28.2		1.57	21
<i>Streambed sediments</i>						
Nowadaga Cr.		1.8	−23.9	−185	0.2	10
		1.2	−27.6	−193	0.14	10
Schoharie Trib.		2.2	−27.2	−14	0.19	13
		20.9	−18.0	−103	2.7	9
Caroga Cr.		0.8	−27.0	24	0.07	14
Schafer's Br.		0.8	−18.0	1	0.06	14
		0.5	−28.1	−7	0.06	9

Samples from watersheds draining OM-rich or OM-poor shales are in bold.

Fig. 3. Comparison of stream $\Delta^{14}\text{C}$ -POC and POC/TPN ratios for all sampled watersheds, demonstrating distribution among lithology and land use types in each watershed. Also shown is the range of POC/TPN ratios and $\Delta^{14}\text{C}$ values for soils, plants, shales and stream sediments that may contribute to stream POM.

and shallow soil OC from the Nowadaga Cr. watershed (Table 4). However, POC in Nowadaga Cr. was at least as ^{14}C -depleted as deep soils in the Nowadaga Cr. watershed, while POC from Schafer's Br. was more ^{14}C -enriched than the Schafer's Br. deep soil (Table 4). Either POC delivery to streams draining shale derives primarily from deep soil horizons with little contribution from shallow soils, or other POC sources such as erosion of the bedrock, resuspension of bedrock-bearing stream sediments or fossil fuel contamination are required to explain the observed values. Future efforts may reveal if these trends, based on comparisons of only two soils, hold in general across the Hudson–Mohawk drainage basin as well as in other regions.

5.2. Factors influencing stream OM composition

Analysis of variance (ANOVA) may be used to evaluate the significance of means and variances among groupings of subsets of sample populations. Single-factor ANOVA revealed a significant probability that the ^{14}C -depleted POC in streams draining shales were significantly different than the $\Delta^{14}\text{C}$ -POC in streams draining other lithologies (Table 5, Fig. 4a). ^{14}C -depleted POC in agricultural watersheds

Table 5

Single-factor analysis of variance (ANOVA) comparing variance in chemical characteristics among lithology and land use groupings of the 14 survey watersheds

	[POC]	$\delta^{13}\text{C-POC}$	$\Delta^{14}\text{C-POC}$	[DOC]	$\delta^{13}\text{C-DOC}$	$\Delta^{14}\text{C-DOC}$	TPN	POC/TPN	DOC/POC
<i>Lithology: OM-rich shale (n = 2), OM-poor shale/carbonate (n = 5) and OM-free rock types (n = 7)</i>									
p^a	0.0060	0.20	0.0095	0.64	0.39	0.83	0.178	0.097	0.84
$F/(F_{\text{critical}})^b$	2.12	0.48	1.87	0.12	0.17	0.05	0.51	0.73	0.04
<i>Land use: >40% agriculture (n = 7) and others (n = 7)</i>									
p^a	0.093	0.088	0.013	0.34	0.073	0.73	0.12	0.087	0.12
$F/(F_{\text{critical}})^b$	0.70	0.73	1.81	0.20	0.78	0.03	0.58	0.73	0.60

^a p is the probability for the null hypothesis (groups of samples are indistinguishable at 95% confidence for the given characteristic).

^b $F/(F_{\text{critical}})$ is the ratio of observed over expected group averages, with values >1 indicating real differences between groups.

Fig. 4. Box-and-whisker plots of $\Delta^{14}\text{C-POC}$ of repeat sampled sites grouped by (a) lithology, and (b) land use. Samples from sites with OM-rich Utica shale are classed as OM-rich ($n = 2$), samples from sites with other shales are OM-poor ($n = 4$), and sites without shale are in the OM-free group ($n = 7$). Watersheds with more than 40% agricultural land use are in the agriculture category ($n = 7$), and sites with <40% agriculture are in the forested category ($n = 7$).

were also significantly different than those in streams draining watersheds with little or no agriculture (Table 5, Fig. 4b). Additionally, the lower POC concentrations measured in

streams draining mainly shales were also significantly different than concentrations in streams draining other lithologies (Table 5). There were no significant differences between these groupings in other stream chemical characteristics ($\delta^{13}\text{C-POC}$, DOC concentration, $\delta^{13}\text{C-DOC}$, $\Delta^{14}\text{C-DOC}$, TPN, POC/DOC and POC/TPN) (Table 5). These findings serve as a guide towards further understanding of lithologic and land use influences on stream OM composition. However, care must be taken not to over interpret ANOVA results from unbalanced groupings of the small overall number of samples in this study.

The relationship between watershed lithology, land use and stream water OM characteristics was examined in more detail using regression analysis. When each factor (land use and lithology) was compared to $\Delta^{14}\text{C-POC}$ in a simple regression, the extent of OC-weighted shale explained 60% of the variance ($p = 0.002$, Fig. 5a), and the extent of agriculture accounted for 43% of variance ($p = 0.015$, Fig. 5b). $\delta^{13}\text{C-DOC}$, and $\delta^{13}\text{C-POC}$ were not significantly correlated with the extent of agriculture or shale. There was no significant relationship between $\Delta^{14}\text{C-POC}$ and $\Delta^{14}\text{C-DOC}$ for the spring sampling. The relationships between $\Delta^{14}\text{C-POC}$ and both agriculture and lithology had a negative slope (Fig. 5), indicating that more agriculture and more shale both result in export of more ^{14}C -depleted POC. Within watersheds of this study, the extents of agriculture and shale were not significantly correlated ($r^2 = 0.14$, $p = 0.19$), suggesting that land use and lithology are important but separate controls on stream OM composition. Combining OC-weighted shale and agriculture in a multiple regression produced the best model to explain the variation in $\Delta^{14}\text{C-POC}$ ($r^2 = 0.71$, $p = 0.008$).

A principal components analysis (PCA) was used to explore relationships between watershed attributes and stream water OM character (Fig. 6). Prior to the analysis, the data were scaled to unit variance and centered to allow comparison between variables with differing ranges (Maradia et al., 1979). The subsequent PCA analysis shows strong relationships between $\Delta^{14}\text{C-POC}$ and the extents of watershed agriculture and OM-rich shale (Fig. 6). These factors load heavily on the first component and act similarly on all components. Observations are generally well grouped by lithology, with samples from high-OM shale streams clustered to the right (Fig. 6) in the area defined by high agriculture and shale contents and low $\Delta^{14}\text{C}$, and samples from forested and shale-free sites grouped to the lower left.

Fig. 5. Regressions of (a) OC-weighted watershed shale and (b) agriculture on $\Delta^{14}\text{C}$ -POC for the 14 sites sampled in this study. Calculation of OC-weighted shale is described in Section 3.4.

Analysis of variance, linear regressions and PCA all indicate that headwater stream POM composition is influenced by watershed attributes such as land use and lithology. In contrast, a link between aged watershed materials and headwater DOM composition is not apparent. While combinations of watershed attributes such as lithology (OM-bearing sedimentary rocks), land use (intensive agriculture) or geomorphology (high relief and sediment yield) may control export of aged POM, DOM export does not appear to be influenced by these features but instead may be more closely associated with rapidly cycling litter and shallow soil pools. This decoupling of DOM and POM export could be an important feature of terrestrial OM export, and similarities or differences between DOM and POM may be mostly due to very different watershed controls on each.

5.3. Estimating source material contributions to POM using isotopic mass balances

Given known stream water POM and potential POM source compositions, linear mixing models provide an addi-

Fig. 6. Principal components analysis of stream water POM. Measured compositional and GIS-derived watershed variables and individual observations are plotted on the first two principal components. Variables are represented by vectors labeled in bold type. Individual samples from both survey and repeat samplings are labeled by land use and lithology, with squares representing sites with OM-rich shale, triangles as OM-poor shale, and circles for OM-free rocks. Filled symbols represent sites dominated by agricultural land use (>40%) and unfilled symbols are forested sites.

tional approach for evaluation of different source contributions to the POM pool. This technique has been used to evaluate the relative contributions of changing vegetation to soil OM (Vitarello et al., 1989; Lichtfouse et al., 1997), and contributions of autochthonous and allochthonous OM to rivers (McCallister et al., 2004), estuaries (Raymond and Bauer, 2001a) and ocean margins (Bauer et al., 2002). Here, mixing models are used to establish the relative contributions of allochthonous soil and shale OM to headwaters in systems with and without shale.

A mass balance model of the following form describes the composition of a mixture:

$$I_t = \sum_{i=1}^n f_n I_n \quad (1)$$

where I_t is the isotopic signature of the mixture and f_n is the fraction of end member n with isotopic signature I_n . If mixing models are to be applied with an explicit solution, for every $n + 1$ OM sources, n compositional variables are required. In this study, limited variability in stream $\delta^{13}\text{C}$ -POC and the $\delta^{13}\text{C}$ of source OM preclude the use of a two-isotope model. However, when there are too many potential OM sources to solve the model explicitly, the range of possible solutions to a one-isotope model can still be determined iteratively (Fig. 7). Both explicit and iterative methods were used to investigate possible shale contributions to $\Delta^{14}\text{C}$ -POC by comparing single isotope mixing model results from shale and nonshale systems.

Fig. 7. Isotopic mixing models representing (a) watershed source contributions to headwater streams and (b) estimated relative contributions of different headwater stream types to the Hudson–Mohawk main stem. Horizontal box-and-whisker plots indicate the range of possible contributions from each source type to the bulk $\Delta^{14}\text{C}$ -POC value of the system. The width of these plots represents an estimate of compositional range based on measurement variability for Schafer's Brook, and the range of possible solutions for underdetermined models for other systems. Vertical lines indicate median values for each source. A ^{14}C -free shale OC input of 0–12% is possible for Nowadaga Cr., and 5–10% produces a reasonable balance of other components. The Mohawk and Hudson estuary require an additional source of ^{14}C -free OC, or POC from tributaries with POC more ^{14}C -depleted than those measured here. These values may also be explained by preferential removal of younger POC during downstream transport.

A simple mixing model was therefore constructed to estimate source contributions to riverine POM using $\Delta^{14}\text{C}$ as a compositional variable. Two sources provided an explicit solution, while possible solutions could be solved iteratively if a third source was added. If deep and shallow soil horizons were assumed to be the two sources of riverine POM, this system was described by the following equations:

$$I_t = f_{ss}I_{ss} + f_{sd}I_{sd} \quad (2)$$

$$f_{ss} + f_{sd} = 1 \quad (3)$$

where I and f represent isotopic compositions and fractions of river POC (t), shallow (ss) and deep (sd) soil OC, respectively. When solved to find the fraction of shallow soil OC, f_{ss} this becomes:

$$f_{ss} = \frac{I_t - I_{sd}}{I_{ss} - I_{sd}} \quad (4)$$

Data for soil, shale and river POM from Nowadaga Cr. and Schafer's Br. (Tables 3 and 4) were used to drive the models. Autochthonous production of POM was not considered for these fast-flowing, small-catchment streams, and POM inputs from modern terrestrial plants and plant litter were implicitly included in estimated contributions from shallow soils. Schafer's Br. was modeled as a two component system with deep and shallow soil inputs; there are no potential sources of ^{14}C -free shale OC within this watershed. The variability among measurements of $\Delta^{14}\text{C}$ in stream water POC ($\text{SD} = 22.9\text{‰}$, $n = 4$) and an estimated standard deviation of 20‰ for soil samples was used to provide an estimated error in source contributions (IsoError model, Phillips and Gregg, 2001).

This model projected that Schafer's Br. POM was composed of 64% shallow soil and 36% deep soil, with a standard error of 10% (Fig. 7a). Source contributions to

Nowadaga Cr. were modeled with ^{14}C -free shale OC as a third source, making this an underdetermined model with many possible solutions. All possible combinations of source contributions satisfying the model were found iteratively using IsoSource (Fig. 7a, Phillips and Gregg, 2003). While possible solutions vary over a wide range (deep soil: 0–84%, shallow soil: 16–88%, shale-OC: 0–12%), ^{14}C -free shale OC contributes to Nowadaga Creek POC substantially less than deep and shallow soils overall. The median solution estimates contributions to Nowadaga Creek of 52% shallow soil, 42% deep soil, and 6% ^{14}C -free shale OC (Fig. 7a). This range of solutions produces a ratio of shallow to deep soil input of 1.2 which is lower than the ratio for the Schafer's Br. model (1.8). The Schafer's Brook and Nowadaga Creek watersheds are similar in topography, area, flow and POC content; and differ mainly in land use and lithology, so the assumption of similar shallow/deep soil export ratios is reasonable. If the ratio of shallow and deep soil inputs in Nowadaga Cr. is adjusted to match the soil input ratio of Schafer's Br., the composition of Nowadaga Cr. becomes 60% shallow soil, 33% deep soil and 7% ^{14}C -free shale OC.

5.4. Linkages between OM in headwater streams and river mainstems

The mean age of bulk POC increased as a function of both amount of OM-rich watershed shale and agriculture (Fig. 5a and b). However, both this study and previous work (Raymond and Bauer, 2001b; Raymond et al., 2004) have measured $\Delta^{14}\text{C}$ -POC in the Hudson and Mohawk Rivers proper that were up to 350‰ more depleted than observed in the studied headwater streams, although values similar to headwater $\Delta^{14}\text{C}$ -POC were also observed at specific times and locations. Thus, while headwaters in the Hudson–Mohawk system may be sources of aged POM, these small watersheds are not the sole sources. Somewhere between the mouths of these headwaters as they empty in the Mohawk, and the mouth of the Mohawk as it enters into the Hudson River, other pools of ^{14}C -depleted OM must be at least intermittently delivered to the river.

One potential source of this additional ^{14}C -free OC may be fossil fuel-derived pollutants associated with industrialization within the watershed. The majority of industrial pollution sources in the Hudson watershed, including dredge spoils, spill sites, contaminated landfills and former manufacturing facilities, are located along the Upper Hudson River, which confounds interpretation of the greater ^{14}C -depletion of POC in the Mohawk and Lower Hudson compared to the Upper Hudson (Table 3) as due to fossil OM pollution. Furthermore, an extremely aged signal was not observed in other highly industrialized watersheds such as the James, and Potomac Rivers (Raymond and Bauer, 2001a,b; Raymond et al., 2004), the Rhine-Meuse-Schelde and Ems estuaries (Megens et al., 2001), or the Tyne and Tweed estuaries (Ahad et al., 2006), suggesting that while significant in terms of environmental impact and ecosystem health, fossil fuel contributions may not be sufficient to depress $\Delta^{14}\text{C}$ -POC values in even highly impacted rivers systems.

Isotope mass balance was used to estimate a potential fossil fuel contribution to Mohawk River POM pools (Fig. 7b). As in Eqs. (1)–(4) above, one source of Mohawk POM may be from shale-rich headwater streams ($\Delta^{14}\text{C} \sim -100\text{‰}$), with the other being fossil fuels ($\Delta^{14}\text{C} = -1000\text{‰}$). These calculations are conservative, in that several Mohawk River headwater streams exhibit POM that is more ^{14}C -enriched than -100‰ , and thus would require an even greater fossil fuel contribution to achieve the measured Mohawk $\Delta^{14}\text{C}$ -POC, as would explicitly including a term for addition of modern soil or autochthonous inputs. Nonetheless, to achieve the observed Mohawk $\Delta^{14}\text{C}$ -POC of -150‰ to -450‰ (Raymond et al., 2004; see also Table 2), a minimum of 5% of Mohawk River POM must derive from ^{14}C -free OC contributed downstream of the headwaters; measured Mohawk and Hudson River $\Delta^{14}\text{C}$ -POC of $\sim -450\text{‰}$ recorded during previous sampling (Raymond and Bauer, 2001a,b; Raymond et al., 2004) requires that over 38% of POC derives from ^{14}C -free OC contributions according to this isotope mass balance. On a global scale, rivers deliver an estimated 0.2 Pg OC to the oceans each year (Hedges and Keil, 1995; Schlünz and Schneider, 2000), of which between 20–40% is estimated to derive from ^{14}C -free OC sources (Meybeck, 1993; Blair et al., 2003). In small mountainous rivers with high rates of erosion and sediment discharge, this fraction may approach 50–70% (Blair et al., 2003), while prolonged exposure and contributions from soils and autochthonous production may lower this fraction in temperate, passive margin rivers. 5% ^{14}C -free POC is thus reasonable for the Hudson, while higher percentages may reflect episodic inputs of highly aged soil, sediment or contaminants.

Alternatively, aged POM in the Mohawk and Lower Hudson may derive from selective degradation of more ^{14}C -enriched reactive components, leaving a residual that becomes more ^{14}C -depleted during transit from headwater streams to the rivers. However, selective remineralization of a younger POM pool seems inconsistent with the trend towards more ^{14}C -enriched DOM and POM pools during transport down the Hudson River (Raymond and Bauer, 2001b). Instead, this trend suggests preferential utilization of aged components of river OM. These authors showed that along a 100-km transect of the tidal freshwater Hudson collected during May, 1997, DOC concentrations remained nearly constant while $\Delta^{14}\text{C}$ -DOC increased from -158‰ to -38‰ from upstream to downstream. Increasing $\Delta^{14}\text{C}$ -DOC under constant DOC concentrations can only be achieved if net input (supply minus removal) of aged DOM is outpaced by net input of younger DOM: in other words, if a greater proportion of young DOM supply is remineralized compared with aged DOM.

Finally, resuspension of river sediments, which include soil- and rock-derived OM associated with mineral particles, may provide a source of ^{14}C -free POC throughout the course of the river (Komada and Reimers, 2001; McCallister et al., 2004, 2006). Stream sediments from the shale-dominated Nowadaga Creek watershed had a mean $\Delta^{14}\text{C}$ of -189‰ , lower than either stream water POC or soil OC. Future efforts may reveal if this aged material is stored in floodplain sediments, transported as resuspended

POM, or remineralized *in situ*. Reworking of coarse-grained sediments into fine, suspended particles downstream of headwaters may deliver aged, rock-derived OM to downstream river POM pools at locations far removed from soil and bedrock erosion. Particulate soil-derived OM may also be resuspended following storage and aging in river floodplain sediments.

While the composition of DOM in these headwater streams does not closely relate to the watershed materials measured in this study (Tables 2 and 3), $\Delta^{14}\text{C}$ -POC and C:N ratios are at least in part a reflection of OM sources in the watershed. Future efforts, including coupled analysis of suspended sediment surface area, POM composition and isotopic signatures, may help to disentangle various OM transformations between headwater tributaries and river mainstems. The true control on the ^{14}C signature of river POM likely reflects a contribution from each of these: erosion of rocks and soils, fossil fuel pollution, selective degradation, and resuspension.

6. CONCLUSIONS

In the tributaries of the Hudson–Mohawk river system, lithology and land use are shown to influence $\Delta^{14}\text{C}$ in headwater stream POM pools, with watersheds draining ancient sedimentary OM and high relative abundance of agricultural land use exhibiting ^{14}C -depletion. Other stream POM characteristics such as a concentration, POC:TPN, and $\delta^{13}\text{C}$, as well as $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ of stream DOM, do not correlate with either land use or lithology in this system, and support the idea of decoupling between the controls on POM and DOM characteristics and export from land. The influence that land use and lithology exert on headwater POM characteristics further suggests that POM has the capacity to age significantly within headwater systems prior to export, or to be pre-aged in lithologies rich in ancient sedimentary OM. In contrast, DOM derives from OM that is much more rapidly cycled through litter, soils and sediments. This difference in the controls on POM versus DOM plays an important role in understanding the variability in headwater POM composition, the lack of linkage between watershed land use or lithology and DOM composition, and how the signatures of watershed materials are propagated through headwater streams into the POM and DOM pools that are then exported by rivers to the coastal ocean.

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APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.gca.2007.06.056](https://doi.org/10.1016/j.gca.2007.06.056).

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