Aquatic Sciences (2020) 82:23
https://doi.org/10.1007/s00027-019-0691-7

Aquatic Sciences

RESEARCH ARTICLE

Effects of agricultural and tillage practices on isotopic signatures and fluxes of organic and inorganic carbon in headwater streams

Scott A. Kelsey[1] · **Andréa G. Grottoli**[2] · **James E. Bauer**[1] · **Klaus Lorenz**[3] · **Rattan Lal**[3] · **Yohei Matsui**[2] · **Teresa M. Huey-Sanders**[2]

Received: 28 February 2019 / Accepted: 17 December 2019 / Published online: 18 January 2020

Abstract

The amounts and characteristics of carbon (C) transported by streams and rivers are strongly connected to attributes of their associated watersheds. However, the factors controlling how different land uses influence the sources and inputs of organic and inorganic C to headwater streams are not fully understood. In order to assess how land use practices specifically influence headwater stream C, the concentrations and isotopic (natural $\delta^{13}C$ and $\Delta^{14}C$) signatures of dissolved inorganic C (DIC), dissolved organic C (DOC), and particulate organic C (POC) were measured between October 2008 and August 2009 in streams of six small watersheds of differing land use. Bayesian mixing models were used to estimate contributions of potential C sources to stream DIC, DOC, and POC pools. Mixing model results indicate that sources of C to streams in tilled and non-tilled corn watersheds were dominated by C_4 plant biomass and soil organic C. In all other watershed types stream C was dominated by C_3 plant biomass. In addition, $\delta^{13}C$ and $\Delta^{14}C$ values of forested stream C were unique from values in the corn, pasture, and large mixed use watersheds, and showed greater contributions from modern-aged C_3 biomass. Relative to other watershed types, tilled corn agriculture showed the greatest effect on both the sources and amounts of stream C. In the tilled corn watersheds, total C (DIC + DOC + POC) fluxes were 314% higher than in the non-tilled corn watershed and 39–76% higher than in all other watersheds. Thus, land use and agricultural practices can serve as strong controls over the sources and fluxes of organic and inorganic C to streams.

Keywords Headwater streams · Organic carbon · Inorganic carbon · Land use · Carbon export

Introduction

Human activities have fundamentally altered the characteristics and function of many watersheds globally. Specifically, land use change has been implicated as a major factor influencing terrestrial to aquatic carbon (C) exchanges (Butman et al. 2016; Hossler and Bauer 2013a, b; Marín-Spiotta et al. 2014; Regnier et al. 2013). Terrestrial C fluxes to inland waters, estimated at ~ 5.1 PgC year^{-1} (Drake et al. 2017), are an important component of terrestrial, inland water, and global carbon budgets (Aufdenkampe et al. 2011; Battin et al. 2009; Drake et al. 2017; Regnier et al. 2013). Anthropogenic impacts therefore present multiple challenges for assessing alterations to export fluxes of both terrestrial and non-terrestrial carbon in streams and rivers draining their respective watersheds (Aufdenkampe et al. 2011; Bauer et al. 2013; Butman et al. 2016; Drake et al. 2017). The sources and characteristics of organic and inorganic C transported by streams and rivers and to estuaries and coastal

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00027-019-0691-7) contains supplementary material, which is available to authorized users.

Scott A. Kelsey
kelsey.38@osu.edu

Andréa G. Grottoli
grottoli.1@osu.edu

1 Aquatic Biogeochemistry Laboratory, Department of Evolution, Ecology and Organismal Biology, Ohio State University, Columbus, OH 43210, USA

2 School of Earth Sciences, Ohio State University, Columbus, OH 43210, USA

3 Carbon Management and Sequestration, School of Environment and Natural Resources, Ohio State University, Columbus, OH 43210, USA

waters may also be affected by changing land use in associated watersheds (Casas-Ruiz et al. 2017; Fox and Ford 2016; Marín-Spiotta et al. 2014; Stackpoole et al. 2016).

Previous studies have demonstrated that agricultural practices greatly increase the inputs of both terrestrial organic and inorganic C to streams (Graeber et al. 2012), rivers (Raymond et al. 2008; Ren et al. 2016), and coastal waters (Bauer et al. 2013; Regnier et al. 2013) through changes to the dominant forms of terrestrial plant cover and soil disturbance (Drake et al. 2017). Most prior research on terrestrial C loading to streams and rivers has generally focused on larger 3rd–10th order streams, even though 1st-order headwater streams account numerically for more than 90% of all streams and nearly half of all river-miles in the continental United States (Leopold and Leopold 1995; Marx et al. 2017; Strahler 1957). While the characteristics, sources, and fluxes of C have generally been understudied in small headwater streams (e.g., Argerich et al. 2016; Graeber et al. 2012), these systems have the greatest potential for transport and biogeochemical transformations of terrestrial organic and inorganic C loads and therefore serve as key control points for terrestrial-aquatic exchanges (Drake et al. 2017; Hotchkiss et al. 2015; Marx et al. 2017).

Natural abundance C isotopes ($\delta^{13}C$ and $\Delta^{14}C$) can serve as powerful tracers of C sources, fluxes and cycling in streams, rivers and estuaries (Barnes et al. 2018; Butman et al. 2014; Hossler and Bauer 2012, 2013a; Lu et al. 2014a, b; Palmer et al. 2001; Raymond and Bauer 2001; Raymond et al. 2004; Sickman et al. 2010; Townsend-Small et al. 2008). The present study evaluated the role of agriculture and tillage practices on the amounts and $\delta^{13}C$ and $\Delta^{14}C$ signatures of organic and inorganic C in six headwater streams within a long-term experimental watershed in northeastern Ohio, USA using a Bayesian isotopic modeling approach (Butman et al. 2014). Land use practices and individual environmental variables have been documented in this watershed for up to 72 years prior to the present study, providing a detailed historical context for interpreting our findings (Owens et al. 2010). This study is among the few to utilize a Bayesian isotope modeling approach to provide baseline estimates for organic and inorganic C sources and fluxes for numerically dominant headwater streams (see, e.g., Butman et al. 2014), and to our knowledge is the first to incorporate locally measured values of potential C sources.

Methods

Study sites

The study was conducted in six sub-watersheds (hereafter referred to as "watersheds") of the larger North Appalachian Experimental Watershed (NAEW) in Coshocton County, Ohio, USA (40°36.44′ N; 81°79.16′ W; Fig. 1). Information regarding the NAEW, its geology, soils, and forest composition are described in the Online Resource 1(OR1) Text S1. The watersheds consisted of (1) tilled corn, (2) non-tilled corn, (3) large mixed (a combination of meadow, pasture, cropland, and forest) land use, (4) small mixed land use, (5) pasture and (6) hardwood forest (Table 1). Water samples were collected from individual headwater streams between October 2008 and August 2009 (Fig. 1; Table 2), and soil samples were collected in spring 2009 from three of the watersheds (see details in "Soil collection and $\delta^{13}C$ analyses"). Land management rotation and land-use histories from 1997–2009 for the watersheds are also shown in Table 1.

Water sample collection and $\delta^{13}C$ and $\Delta^{14}C$ analyses

Headwater streams were sampled on one base flow day in fall, spring, and summer, and on one storm flow day in spring and winter (Table 2). This sampling strategy enabled us to incorporate as much seasonal variation as possible into our annual estimates of C source contributions, $\delta^{13}C$, and $\Delta^{14}C$ values given the high cost of $\Delta^{14}C$ analyses. The tilled and non-tilled corn watersheds lacked permanent flow (i.e., base flow; classified as 0th-order streams); therefore, water samples from these two watersheds consisted entirely of surface runoff during storm events (see OR1 Text S2 for details). For the corn watersheds, stream water samples from runoff were collected according to Brakensiek et al. (1979) and Parsons (1954) and refrigerated for ≤ 12 h before being filtered and frozen at -20 °C until analysis. For non-corn watersheds (1st-order streams), streamflow was measured by 2:1 broad-crested weirs (Owens et al. 2010), and water samples were collected directly from the stream either above or below the weir (additional details in OR1 Texts S2 and S3).

Water samples were analyzed for concentrations, $\delta^{13}C$ and $\Delta^{14}C$ of DIC, DOC and POC according to methods described in OR1 Text S4. Frozen DOC samples were submitted to the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility at Woods Hole Oceanographic Institution (Woods Hole, Massachusetts, USA) for $\delta^{13}C$ and $\Delta^{14}C$ analysis. For DIC and POC, $\delta^{13}C$ values were measured at the OSU Stable Isotope Biogeochemistry Laboratory (SIBL), and the corresponding $\Delta^{14}C$ analyses were conducted at NOSAMS. Additional analytical details are provided in the OR1 Text S4.

Soil collection and $\delta^{13}C$ analyses

Soil samples were collected from the small mixed use and forested watersheds in May 2009 and from the non-tilled corn watershed in June 2009. Small soil pits (40 cm L × 40 cm W × 60 cm D) were manually excavated in three randomly distributed plots that were ~ 30 m apart

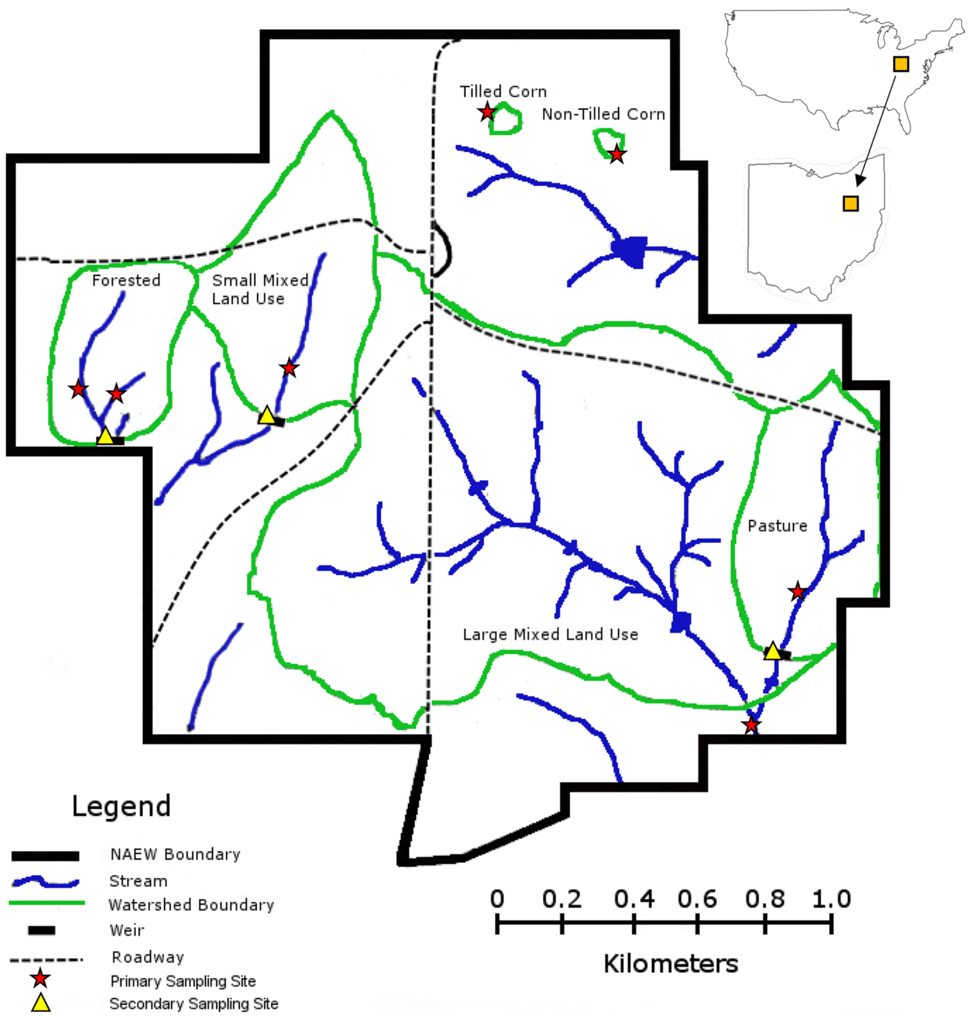

Fig. 1 The North Appalachian Experimental Watershed (NAEW), Coshocton County, Ohio, USA. Stars indicate locations of primary headwater stream sampling sites. When no flowing water was present in the forested, small mixed use, and pasture streams, samples were collected from water discharged from the associated weirs, indicated by the yellow triangles (secondary sampling site). See Methods "Study sites" and Online Resource1 Text S1 and S2 for additional details. Figure adapted from Owens et al. (2010)

within each watershed, and triplicate soil samples were retrieved and the 0–15, 15–30, and 30–50 cm depth intervals were homogenized. The soil samples were acid-fumigated using fresh concentrated HCl in a glass desiccator for 24 h and then dried for 24 h under vacuum to remove acid fumes and residual water. Samples were analyzed at the OSU SIBL for $\delta^{13}C$. The standard deviation (SD) of replicate $\delta^{13}C$ analyses of the graphite standard USGS24 was ±0.05‰ ($n=4$). The average SD of 12 duplicate $\delta^{13}C$ analyses of soil samples was ±0.04‰. Soil samples were not analyzed for $\Delta^{14}C$ due to cost constraints.

Assessment of stream C source contributions using bayesian mixing models

The relative contributions of various potential C sources to stream DIC, DOC, and POC were estimated from $\delta^{13}C$ and $\Delta^{14}C$ values using Bayesian isotope mixing models utilizing the R version 3.4.1 software program MixSIAR (R Core Team 2017; Stock and Semmens 2015). $\delta^{13}C$ and $\Delta^{14}C$ values of the potential C sources identified in the present study as contributing to stream DIC, DOC and POC pools are detailed in OR1 Text S5 and listed in OR1 Table S1. MixSIAR allows for the incorporation of uncertainties in the isotopic signatures of different potential sources and can estimate the relative contributions of multiple potential sources to each C pool by determining the likelihoods of a large number of random combinations of sources with established isotopic values (Stock and Semmens 2015).

Each individual DIC, DOC, and POC sample was assumed to be representative of conditions during the season and flow state (i.e., storm flow or base flow) when it was collected. One mixing model was generated for DIC, DOC, and POC in each watershed using all measured $\delta^{13}C$ and $\Delta^{14}C$ values, thus incorporating variability across seasons and flow state in a given watershed. The $\delta^{13}C$ and $\Delta^{14}C$ values of potential C sources were averaged and the mean ± SD were used in the mixing model (OR1 Table S1, Stock and Semmens 2015). Models generated the range of percent contributions of each possible source to each watershed's DIC, DOC, and POC exports. A minimum of 1,000,000 iterations were run per model in order to ensure an appropriate number

Table 1 Land use characteristics for the six watersheds in the North Appalachian Experimental Watershed (NAEW) used in the present study

Watershed	WS#[a]	Area (ha)	Land use[b]	Period
Corn watersheds[c]				
Tilled Corn	127	0.7	3 year rotation: tilled corn, tilled soybeans, non-tilled wheat and red clover[d]	1997–2005
			Tilled corn	2006–2009
Non-Tilled Corn	115	0.6	3 year rotation: tilled soybeans, non-tilled wheat and red clover, tilled corn[d]	1997–2007
			Non-tilled corn	2008–2009
Non-Corn watersheds[e]				
Large mixed land use	N/A	151.5	52.5 ha meadow (35%)	2000–2009
			46.9 ha wooded (31%)	
			23.6 ha pasture (15%)	
			9.9 ha fertilized cropland (6%)	
			1.5 ha fertilized non-tilled corn (1%)	
Small mixed land use	166	32.1	10.8 ha meadow (34%)	2000–2009
			14.8 ha pasture (56%)	
			10.3 ha fertilized cropland (32%)	
			3.6 ha wooded (11%)	
Pasture	182	28.8	23.6 ha pasture (82%)	2000–2009
			5.2 ha wooded (18%)	
Forested	172	17.7	All wooded (100%)	2000–2009

[a]WS# = NAEW watershed number

[b]Land use definitions: wooded = primarily second-growth C_3 hardwoods and shrubs; meadow = unfertilized grassland; pasture = active cattle grazing; fertilized cropland = agricultural crops (excluding corn) with artificial fertilizer additions

[c]Data from Shipitalo and Owens (2006) and Shipitalo (*unpublished data*)

[d]See OR1 Text S1for further details

[e]Data from Owens et al. (2008) and Shipitalo (*personal communication*)

Table 2 Stream water sampling dates (MM/DD/YY) for the six watersheds evaluated in the present study

Watershed	Fall[a]	Winter[b]	Spring[c]	Summer[a]
Tilled Corn[d]	npfs[e]	02/09/09	05/02/09	npfs[e]
Non-Tilled Corn[d]	npfs[e]	02/09/09	05/02/09	npfs[e]
Large mixed land use	10/25/08	02/09/09	04/25/09	08/18/09
Small mixed land use	10/25/08	02/09/09	04/25/09[f]	08/18/09
Pasture	10/25/08	02/09/09	04/25/09[f]	npfs[e]
Forested	10/25/08	02/09/09	04/25/09	08/18/09

[a]Base flow samples only. See Methods for full description

[b]Storm flow samples only. See Methods for full description

[c]Storm flow sampled on 2 May 2009, base flow sampled on 25 April 2009

[d]"Stream water" consists of surface runoff

[e]npfs = no permanently flowing streams; watersheds had no permanently flowing streams in watershed, therefore no base flow samples were available on these dates

[f]Additional samples collected on 2 May 2009, but analyzed for concentration and $\delta^{13}C$ only

of unique posterior draws (Stock and Semmens 2015), and a final mixing model was generated for each C pool from the median of the posterior distribution. Results from mixing models are presented in the text as the median percent contribution for each source. Full 90% confidence intervals (CIs) are presented in the cited OR1 tables as the 5th and 95th percentiles. Median values were considered to be statistically different from one another when those differences exceeded the 90% CI about each median.

Annual carbon fluxes in headwater streams

Daily discharge rates for each stream were obtained from the NAEW archive for the sampling year time period of 22 September 2008–21 September 2009 (Owens et al. 2010; Martin Shipitalo, *personal communication*). Daily discharges were summed for total annual discharge estimates and to provide annual specific discharges (in mm year^{-1}) for each watershed over the study period (OR2). Stream DIC, DOC, and POC concentrations were averaged across all sampling days, multiplied by annual discharge, and scaled by watershed area to estimate the annual fluxes from each watershed. The SDs for DIC, DOC and POC concentrations were propagated through the flux calculations to provide SDs for each flux. In order to obtain annual area-normalized flux estimates for each potential source of C to the DIC, DOC and POC pools in each stream, the median percent annual contributions of each source (as determined from the MixSIAR output-see "Assessment of stream C source contributions using bayesian mixing models") were multiplied by the corresponding total annual area-normalized stream DIC, DOC, and POC fluxes. Flux SDs were propagated through these calculations.

Statistical analyses

We used a combination of non-parametric statistical tools to determine if stream DIC, DOC, POC and total C differed by land use type. These included analyses of the $\delta^{13}C$ and $\Delta^{14}C$ values, mixing model medians, area-normalized annual C fluxes, and flux estimates for each C source using non-metric multidimensional scaling (NMDS), hierarchical clustering, and similarity profiling (SIMPROF) (Clarke and Gorley 2006). We used NMDS to visualize the data distribution in 2D space. SIMPROF tests whether data clustering by similarity (i.e., distance in two-dimensional NMDS space, determined by hierarchical clustering) is statistically significant (Clarke and Gorley 2006). SIMPER (similarity percentages) analyses were used to determine the percent to which each C variable contributed to the dissimilarity between streams or groups of streams (Clarke and Gorley 2006).

Prior to conducting statistical analyses, annual stream C flux data, mixing model estimates of source contributions to C fluxes, and estimated annual exports of each source were square root-transformed, then normalized. Because only a single watershed of each type was sampled, comparisons of the cumulative specific discharges between each of the six watersheds were limited to subjective comparisons.

For the $\delta^{13}C$ and $\Delta^{14}C$ data, clusters identified by SIMPROF were explored further using a *post-hoc* analysis of similarities (ANOSIM) test (Clarke and Gorley 2006). ANOSIM was used to test whether all $\delta^{13}C$ and $\Delta^{14}C$ sample data grouped by land use were more similar to each other than to data from other land use types (Clarke and Gorley 2006). Data were grouped by watershed land use type (i.e., tilled corn, non-tilled corn, large mixed land use, small mixed land use, pasture, forested). We further explored all pairwise comparisons within the model, including when those pairwise comparisons were non-significant (i.e., $p > 0.05$) but the ANOSIM pairwise test statistic $R > 0.8$. This was done because the value of the ANOSIM pairwise test statistic R (which ranges between 0 and 1) is a better indicator of actual separation between groupings, especially at low sample sizes such as in this study, as long as the overall ANOSIM test statistic R is significant (Clarke and Gorley 2006). For annual C fluxes, mixing models, and estimates of source fluxes, each watershed contained only one data point (i.e., the duration of this study covered one year), so ANOSIM was not possible. All of the above analyses and plots were carried out using Primer 6.6.16 (2013 PRIMER-E Ltd, 3 Meadow View, Lutton, Ivybridge, PL21 9RH, UK). All data used in this manuscript can be found in the included tables and in the Online Resources 1 and 2.

Results

$\delta^{13}C$ and $\Delta^{14}C$ values of headwater stream carbon pools

The $\delta^{13}C$ and $\Delta^{14}C$ values of stream DIC from both corn watersheds averaged −6.4 ± 1.3‰ and 37 ± 7‰, respectively (Fig. 2a, OR1 Table S2). In addition, corn watershed stream DIC was enriched in both $\delta^{13}C$ and $\Delta^{14}C$ by an average of 6.5 ± 1.9‰ and 125 ± 60‰, respectively, compared to all of the other watersheds (Fig. 2a; OR1 Table S2). In the non-corn watersheds, DIC $\delta^{13}C$ values ranged from − 16.6 to − 10.5‰ while $\Delta^{14}C$ values varied between − 164 and 34‰ (1382 years B.P. to modern equivalent ^{14}C ages, respectively; Fig. 2a; OR1 Table S2).

Stream DOC and POC from corn watersheds were enriched in $\delta^{13}C$ compared to non-corn watersheds by an average of 10.4 ± 5.8‰ (Fig. 2b and c; OR1 Table S2). The $\delta^{13}C$ values of DOC for the non-corn watersheds were tightly clustered (mean = − 28.5 ± 1.0‰; Fig. 2b; OR1 Table S2) while POC $\delta^{13}C$ values varied more broadly from − 38.7 to − 26.1‰ (Fig. 2c). The DOC and POC from all watersheds had overlapping $\Delta^{14}C$ values that ranged from − 11 to 77‰ (31 years B.P. to modern equivalent ^{14}C ages) and − 103 to 44‰ (816 years. B.P. to modern equivalent ^{14}C ages), respectively (Fig. 2b, c; OR1 Table S2).

Overall, SIMPROF analysis showed that stream $\delta^{13}C$ and $\Delta^{14}C$ values from the corn watersheds differed significantly from the non-corn watersheds (OR1 Fig. S1), with the $\delta^{13}C$ values of DIC, DOC, and POC accounting for 63% of the dissimilarity (OR1 Table S3). ANOSIM analysis further revealed that $\delta^{13}C$ and $\Delta^{14}C$ values from the forested watershed stream differed from the streams of both large mixed use and pasture watersheds (OR1 Table S4), and this difference was significant ($p = 0.029$).

Relative contributions of potential C sources to stream DIC, DOC and POC

Isotopic mixing models revealed that 94–96% of stream DIC in both the tilled and non-tilled corn watersheds (storm flow only) was derived from atmospheric CO_2 equilibration, while 1–2% was from remineralized organic C and 3–4%

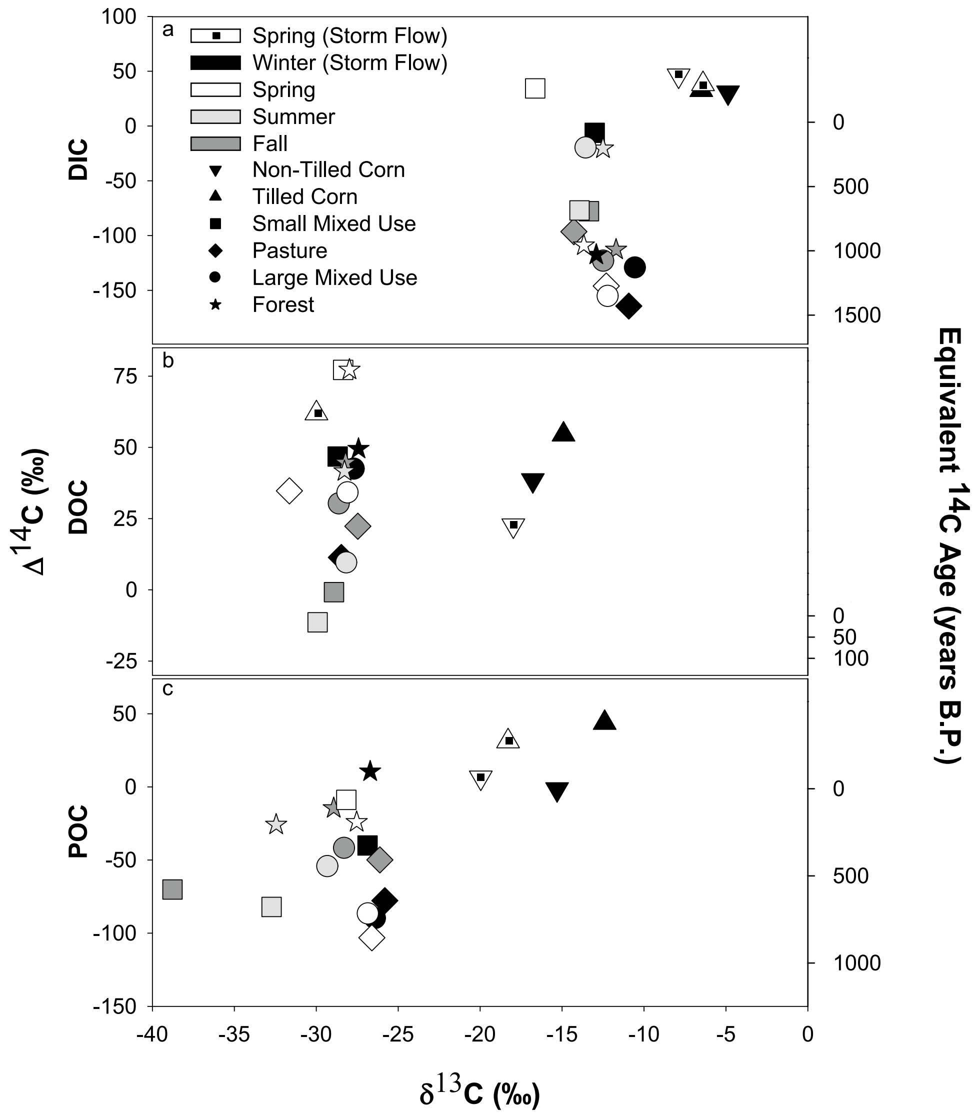

Fig. 2 $\Delta^{14}C$ values, equivalent ^{14}C ages, and stable carbon isotope ($\delta^{13}C$) values of stream water **a** dissolved inorganic carbon (DIC), **b** dissolved organic carbon (DOC), and **c** suspended particulate organic carbon (POC) in the six NAEW watersheds sampled in the present study. Note the different scales on the y-axes of each panel. Raw data are provided in OR1 Table S2. Statistical evaluation of the data is presented in OR1 Fig S1 and Tables S3 and S4

from limestone dissolution (Fig. 3a, OR1 Table S5a). In the non-corn watersheds where baseflow samples predominated, contributions from atmospheric CO_2 also dominated (64–77%) while those from remineralized organic C were lowest among contributing sources (2–4%; Fig. 3a, OR1 Table S5a). Contributions from limestone dissolution were substantially higher (17–33% contribution) than those from remineralized organic C in all watershed types except small mixed land use (Fig. 3a, OR1 Table S5a).

Contributions of shallow soil organic C to DOC export in corn watersheds (40–65%) generally exceeded those in non-corn watersheds (10–33%; Fig. 3b), though there was overlap in the 90% CIs (OR1 Table S5b). C_4 plant biomass was the second greatest contributor to corn watershed DOC export (26–51%) followed by deep soil organic C (4–8%). There were no calculated contributions of POC or C_3 plant biomass to the DOC exported from corn watersheds (no source was present; OR1 Table S1). In contrast, C_3 plant biomass dominated DOC exports across all non-corn watersheds (51–77%), and was higher in the large mixed land use and pasture watersheds than any other source (Fig. 3b, OR1 Table S5b). DOC export was driven about equally by POC (4–9%) and deep soil OC (3–5%) sources across all non-corn watersheds (Fig. 3b, OR1 Table S5b).

Tilled-corn watershed POC exports were dominated by C_4 plant biomass (82%), and this source contributed substantially more than shallow (11%) and deep (5%) soil organic C (Fig. 3c, OR1 Table S5c). In the non-tilled corn watershed, C_4 plant biomass also dominated POC export (56%), but this had overlapping 90% CIs with shallow soil organic C (median of 25%) and deep soil organic C (median of 17%) contributions (Fig. 3c, OR1 Table S5c). Surprisingly, in non-corn watersheds, while C_3 plant biomass contributions dominated POC exports (30–52%), deep soil organic C was the second largest contributor (17–30%, Fig. 3c, OR1 Table S5c). In general, there was a large degree of overlap

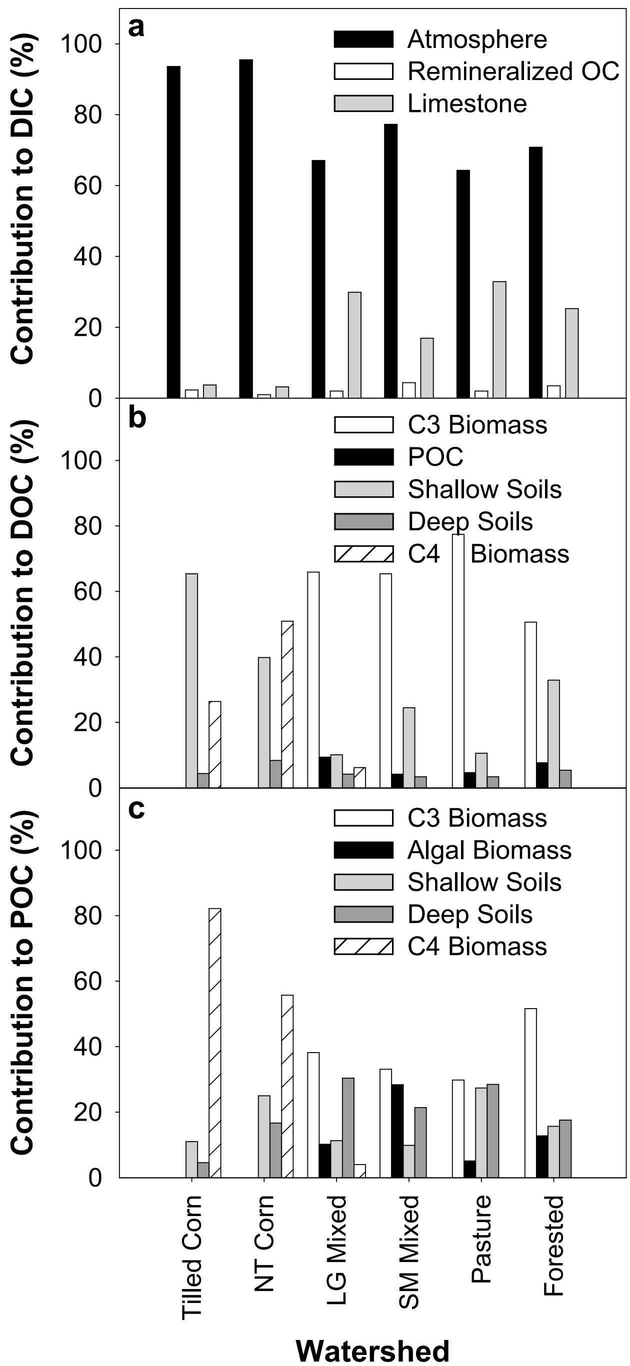

Fig. 3 Mixing model outputs of the average annual percent contributions of various carbon sources to stream water **a** dissolved inorganic carbon (DIC), **b** dissolved organic carbon (DOC) and **c** suspended particulate organic carbon (POC) pools in the tilled corn, non-tilled (NT) corn, large mixed land use (LG Mixed), small mixed land use (SM Mixed), pasture, and forested NAEW watersheds in the present study. Values for percent contributions as well as 5th/95th percentiles are provided in OR1 Table S5. Statistical evaluation of the data is presented in OR1 Fig S2 and Table S6. *OC* organic carbon

in the 90% CIs for all source contributions to non-corn watersheds (indicating a large amount of uncertainty in the models), but the largest contribution of any source to any watershed was C_3 plant biomass to the forested watershed (52%, Fig. 3c, OR1 Table S5c).

Overall, contributions of potential C sources to stream DIC, DOC and POC were significantly different between corn watersheds and non-corn watersheds, but not between tilled and non-tilled corn watersheds or among the non-corn watersheds (Fig. 3 and OR1 S2). The dramatic differences in potential source contributions to stream C observed between corn and non-corn watersheds were driven by the absence or presence of C_3-derived DOC and POC and by the absence or presence of C_4-derived POC in corn vs. non-corn watersheds (Fig. 3, OR1 Table S6).

Annual carbon fluxes from watersheds

The cumulative annual area-specific discharge was greatest from the pasture watershed, lowest from the non-tilled corn watershed, and similar among the other four watersheds (OR1 Fig. S3). Annual stream total C fluxes (i.e., the sum of the DIC, DOC and POC fluxes) were generally dominated by DIC (41–44% for corn, 19–28% for non-corn) (Fig. 4a, d), followed by DOC (37–51% for corn, 19–28% for non-corn; Fig. 4b, d) and POC (8–19% for corn. 3–5% for non-corn) (Fig. 4c, d). DOC fluxes from the tilled-corn watershed stream were the largest in magnitude of all the watersheds (Fig. 4b). The tilled-corn DOC flux contributed most (i.e., of the three C pools) to an annual total C flux (7926 kgC km^{-2} year^{-1}) that was about 314% higher than in the non-tilled watershed stream (2526 kgC km^{-2} year^{-1}), and 39–76% greater than in the non-corn watershed streams (4489–5695 kgC km^{-2} year^{-1}; Fig. 4d).

Overall, total C fluxes in the tilled corn watershed were significantly higher than from all other watersheds, while fluxes in the non-tilled watershed were significantly lower than from all other watersheds (Fig. 4, with statistical results of SIMPROF analyses in OR1 Fig. S4). No significant differences existed among the total C fluxes of any of the non-corn watershed streams (Fig. 4 and OR1 S4). Total C flux contributed most to the statistical dissimilarity between tilled and non-tilled corn watershed streams, whereas both DOC and POC fluxes contributed similarly to the separation between the tilled corn and non-corn watershed streams (OR1 Table S7). DIC flux contributed the most to the statistical dissimilarity between the non-tilled and non-corn watershed streams (OR1 Table S7).

The annual fluxes of individual streamwater C sources (Fig. 5) followed the same patterns as the relative source contributions to the streamwater DIC, DOC and POC pools (Fig. 3) for each watershed. For DIC sources, CO_2 derived from atmospheric equilibration dominated watershed C

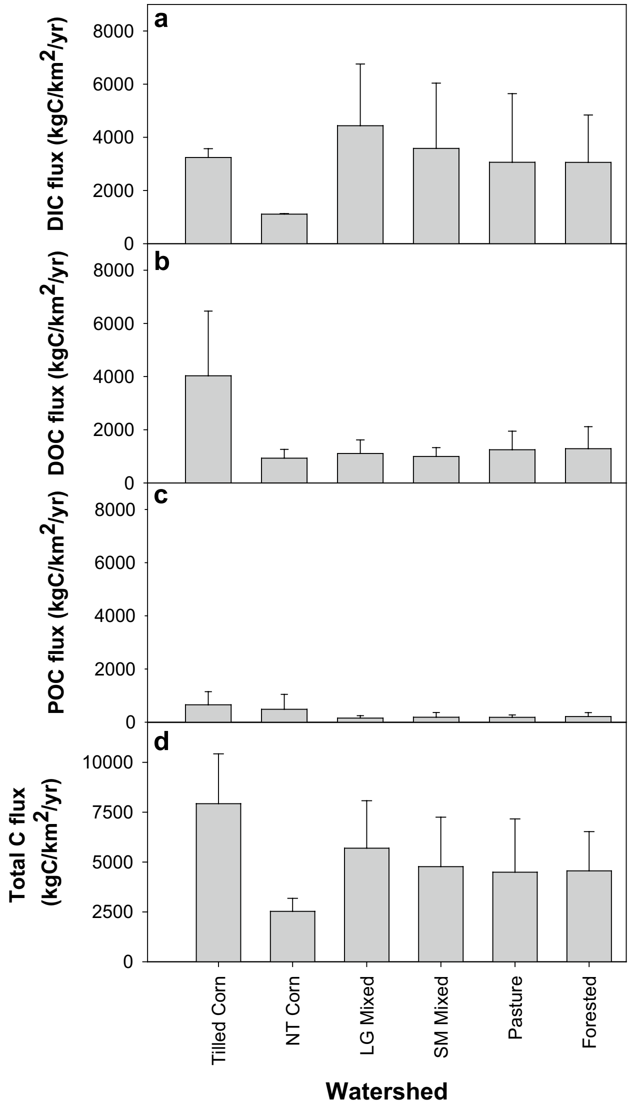

Fig. 4 Annual headwater stream fluxes of **a** dissolved inorganic carbon (DIC), **b** dissolved organic carbon (DOC), **c** stream water suspended particulate organic carbon (POC), and **d** total C (i.e., the sum of the annual fluxes of DIC, DOC, and POC) for the tilled corn, non-tilled corn (NT Corn), large mixed land use (LG Mixed), small mixed land use (SM Mixed), pasture, and forested watersheds in the NAEW during this study. Error bars represent ± 1 standard deviation. Note the different ranges in the y-axes of each panel. Statistical evaluation of the data is presented in OR1 Fig S4 and Table S7

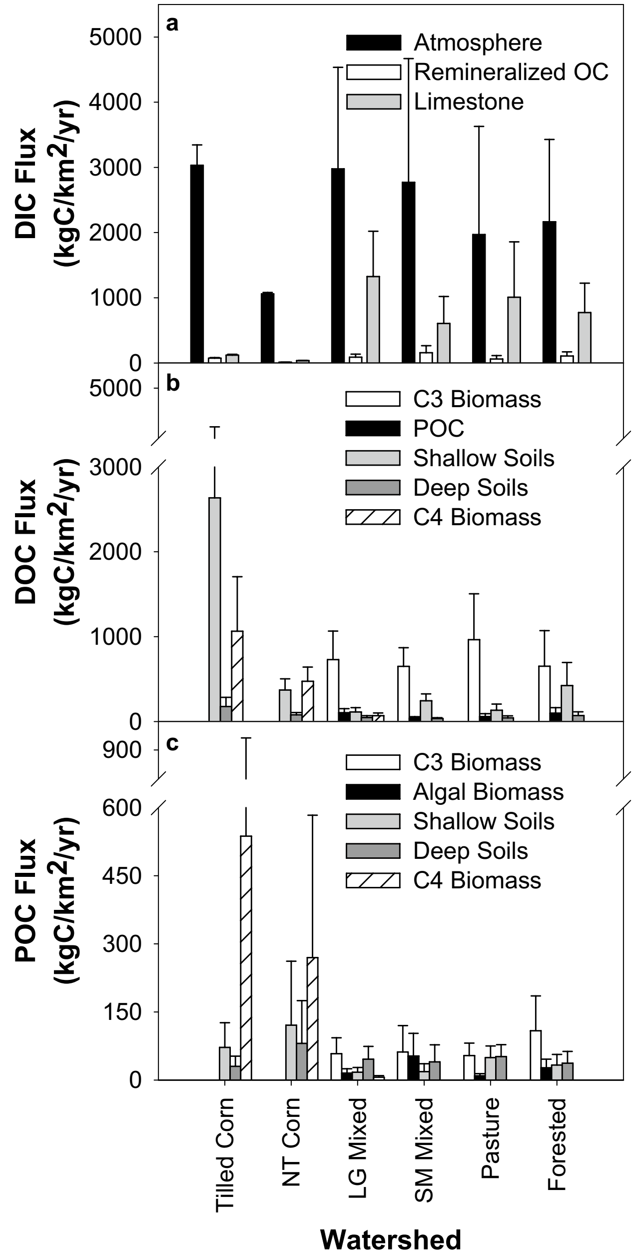

Fig. 5 Average annual source contributions to stream water **a** dissolved inorganic carbon (DIC), **b** dissolved organic carbon (DOC) and **c** suspended particulate organic carbon (POC) fluxes (± 1 SD) in the tilled corn, non-tilled (NT) corn, large mixed land use (LG Mixed), small mixed land use (SM Mixed), pasture, and forested NAEW watersheds in the present study. Note the different scales in the y-axes of each panel. Values are presented in OR1 Table S8. Statistical evaluation of the data is presented in OR1 Fig S5 and Table S9. *OC* organic carbon

export, ranging from 1060 to 3034 kgC km^{-2} year^{-1}, while export fluxes of remineralized organic C were negligible across all watersheds (Fig. 5a, OR1 Table S8a). Relatively large amounts of dissolved limestone were exported from non-corn watersheds (606–1327 kgC km^{-2} year^{-1}), and were one to two orders of magnitude larger than dissolved limestone exports from the corn watersheds (Fig. 5a, OR1 Table S8a). Shallow soil organic C contributed 2636 kgC km^{-2} year^{-1} to the DOC flux from the tilled corn watershed (Fig. 5b, OR1 Table S8b). This was the largest individual organic C flux term for any of the watersheds and was ~ sevenfold higher than the fluxes of shallow soil-derived DOC in the non-tilled corn watershed stream and ~ sixfold higher than the forested watershed stream (Fig. 5b, OR1

Table S8b). C_3 plant biomass, the dominant source of C to DOC export in the non-corn watersheds, ranged between 650 and 964 kgC km^{-2} year^{-1}; Fig. 5b, OR1 Table S8b). C_4 plant biomass dominated contributions to annual stream POC fluxes in the corn watersheds, accounting for 270–537 kgC km^{-2} year^{-1} of the POC flux (Fig. 5c, OR1 Table S8c). C_3 plant biomass dominated the POC fluxes in the forested watershed (108 kgC km^{-2} year^{-1}), whereas a mixture of sources contributed evenly across all other non-corn watersheds (Fig. 5c, OR1 Table S8c).

When all individual C source fluxes from Fig. 5 were taken into account, corn watersheds were significantly different from non-corn watersheds (OR1 Fig. S5). Slightly more than 50% of the dissimilarity between corn and non-corn watersheds was explained by exports of C_3 and C_4 plant biomass as DOC and POC, DOC derived from POC, and limestone dissolution (OR1 Table S9).

Discussion

Headwater streams have been observed in a number of recent studies to respond rapidly to changes in hydrology and to play a critical role in watershed-aquatic-atmosphere C exchanges and downstream transport (e.g., Argerich et al. 2016; Dawson et al. 2011; Kuhn et al. 2017; Marx et al. 2017). These exchanges and transports are impacted by the more intimate and rapid connectivity between headwater streams and the soils, groundwaters and surface runoff of their associated watersheds compared to larger streams and rivers (Kuhn et al. 2017; Marx et al. 2017; Raymond et al. 2016). To evaluate organic and inorganic C sources and dynamics in headwater streams and their associated land use, we investigated the effect of different land-use types and agricultural tillage practices on C fluxes and isotopic signatures in headwater streams of a long-term experimental watershed. Our findings indicate that the C pools and fluxes of these headwater streams respond to (in order of decreasing importance) tillage practices, general land use type, and physical landscape factors.

C sources and exchanges in corn agriculture watersheds

Streams in the corn watersheds (both tilled and non-tilled) differed significantly from streams in all of the other watersheds in their isotopic character (Fig. 2 and OR1 S1) and potential source contributions (Figs. 3, 5, OR1 S2 and S5) to the organic and inorganic C pools. Differences between corn and non-corn watershed DIC were a result of both absences of remineralized organic C contributions and the absence of old (> 1000 years. B.P) inorganic C from weathered limestone contributions (Barnes et al. 2018) to corn watershed DIC (Figs. 2, 3). For the DOC and POC pools, corn vs. non-corn watershed differences were due to inputs of C_4 (i.e., corn) vs. C_3 biomass (Figs. 2, 3, and 5).

Stream total C fluxes in the tilled corn watershed (Fig. 4d) were dominated by DOC export (Fig. 4b) that was comprised largely of shallow soil-derived DOC (Fig. 3b). In fact, the tilled corn watershed yielded an average of ~ 2380 kgC km^{-2} year^{-1} more shallow soil DOC than all other watershed types, including the non-tilled corn watershed (Fig. 5b). This result was heavily influenced by the DOC sample taken in Spring 2009 which occurred immediately following spring tilling (Fig. 2b, OR1 Table S2) (Martin Shipitalo, *personal communication*). The $\delta^{13}C$ value of this DOC sample (− 30.0‰) was also more similar to the $\delta^{13}C$ of shallow soil organic C (− 22.6 ± 0.3‰) and C_3 plant biomass (− 30.3 ± 1.1‰) than to C_4 plant biomass (− 12.3 ± 0.8‰; OR1 Tables S1 and S2). Collectively these findings illustrate the dominant influence of tilling activity on mobilizing shallow soil organic C and enhancing stream organic C exports in the NAEW, and are consistent with earlier findings showing that tilling activities result in significantly higher terrestrial C losses when compared to non-tilling agricultural practices (Beniston et al. 2015; Gao et al. 2016; Jacinthe et al. 2004; Olsen et al. 2013; Owens et al. 2002). The episodic effects of tilling on soil C mobilization to headwater streams could be further confirmed and strengthened by collecting and analyzing samples immediately prior to and after tilling.

C sources and exchanges in non-corn watersheds

Isotopic characteristics of stream inorganic and organic C pools differed between the forested watershed and the pasture and large mixed use watersheds (Fig. 2, OR1 Table S4) due to larger contributions of young leafy and woody debris from C_3 biomass to stream POC in the forested watershed as well as higher contributions of shallow soil-derived OC to DOC in the forested watershed (Figs. 3c, 5c; Table OR1 S8) (Shibata et al. 2001). Despite observed isotopic distinctions between the forested and the pasture and large mixed use streams, neither the calculated contributions of various potential C sources (Figs. 3, 5, OR1 S2), nor the DIC, DOC, POC, and total C fluxes (Fig. 4, OR1 S4) differed among any of the four non-corn watersheds. The relative similarity in sources and fluxes among non-corn watersheds may be a result of riparian buffering along the lengths of the large mixed, small mixed, and pasture watershed streams, offering a similar interface between the land and stream as in the forested watershed (see OR1 Text S1 for details). These macro-vegetated buffers (10 m or more wide along the banks of the streams in many areas, with the small mixed use watershed completely forested on one side of the stream; *personal observation*) may modulate hydrological forcing and C source contributions throughout non-corn watersheds, thus modulating the effect of land use disturbances on DIC (Raymond et al. 2008), DOC (Graeber et al. 2012), and POC (Zaimes et al. 2004) exports from small watersheds. Overall, our findings suggest that pasture grazing or mixed land use may have little effect on total terrestrial C losses compared to undisturbed (i.e., forested) land uses in small watersheds (Fig. 4 and OR1 S4). However, lower impact land uses may still influence the isotopic character of stream DIC, DOC and POC compared to undisturbed forested conditions (OR1 Table S4) by affecting the relative contributions of individual sources (Figs. 3 and 5) (Fox and Ford 2016).

Influence of physical landscape attributes on watershed C fluxes and C isotopes

While land use change and other factors such as topographic relief (i.e., slope) and watershed area can influence the quantities and characteristics of organic and inorganic C transported by headwater streams (Dawson et al. 2011; Finlay 2003; Fortner et al 2012; Shipitalo et al. 2000; Wolock et al. 2013), our data suggests that land use was most likely the dominant driver in the present study. For example, discharge and C fluxes were highest in the tilled-corn watershed even though its slope (2–18%) and watershed size (0.7 ha) were much lower than those of the forested (slope 12–35%, 172 ha) and large mixed land use (slope 18–25%, max 35%, 348 ha) watersheds (Table 1; Figs S3, S4) (Kelly et al. 1975), and discharge only occurred during storm flow events (i.e., ~ 14% of the year) (Table S10). Thus, while our data do not support slope and watershed size as significant drivers of the observed variation in C fluxes, it does support the role of land use.

Any effect of watershed size on the corn watersheds may have been obscured by a lack of permanent streams in the corn watersheds. Ephemeral streams have minimal or no groundwater inputs of limestone-derived aged DIC (resulting in higher Δ^{14}C-DIC values compared to permanent streams) and minimal to no contact time with biogeochemically active sediments (resulting in increased DOC export) (Barnes et al 2018; Wolock et al. 1997). While we found that the ages of C exported from corn watersheds were typically younger than for other watersheds with permanent streams (Fig. 2), DOC exports were only higher for the tilled corn watershed compared to all other watersheds (Fig. 4b). Thus, the discontinuous and ephemeral nature of the corn watershed streams may have influenced the interpretation of the data, but land use was an important factor as well.

Even considering the ephemeral nature of the corn watershed streams, the C flux findings from the present study are consistent with those from Jacinthe et al. (2004) who found that tillage greatly increased C losses from the NAEW watersheds and that this was disproportionately driven by high rainfall events. On a broader scale, our findings are consistent with recent studies that have shown that relatively few large hydrologic events can drive annual watershed organic matter and C exports (the "pulse-shunt" concept; Barnes et al. 2018; Raymond et al. 2016). Furthermore, changes in landscape hydrology (due to land use change) can alter flow paths as well as the amounts and characteristics of C exported from terrestrial to aquatic systems (Barnes et al. 2018). The overall interpretation of the present findings is that, while watershed slope and area may affect watershed C fluxes, tilled agricultural land use has the greatest influence on the amounts and characteristics of C exported from the Coshocton headwater stream watersheds.

Potential impacts of headwater stream land use on downstream processes

The present study demonstrates that land use affected the sources (Fig. 3) and isotopic character (Fig. 2) of organic and inorganic C exported from headwater stream watersheds, especially between corn and non-corn land use. Additionally, our mixing models revealed that tilling activity greatly changed the potential sources of watershed C contributing to overall C fluxes in small, runoff-dominated watersheds (Fig. 3). Specifically, our findings indicate that the upper soil layers of the tilled corn watershed contributed an additional 2266 kgC km^{-2} year^{-1} to the DOC flux compared to the non-tilled corn watershed (Fig. 5) and this was driven primarily by the post-tilling spring sample (Fig. 2) (Beniston et al. 2015; Mishra et al. 2010). Such differences in sources and fluxes of C may also influence the aquatic processing and fates of organic C exported from watersheds having differing land uses. For example, recent studies have shown that the sources of watershed-derived organic C in headwater streams can potentially affect C utilization by stream microbes (Berggren and del Giorgio 2015; Lu et al. 2013, 2014a) and higher consumers (Bellamy et al. 2017; Weber et al. 2017). Future research in this area should strive to connect land use effects on terrestrial-aquatic C fluxes in headwater watersheds with downstream storage, processing and transport of C in order to fully constrain large scale ecosystem C budgets (Butman et al. 2016; Dupas et al. 2017).

Effects of agriculture on ecosystem C budgets, especially due to differences in tillage practices, may extend beyond stream exports to the land–atmosphere interface as well. A prior comparison of NAEW watersheds showed that a tilled corn watershed was a net source of CO_2 to the atmosphere, while non-tilled watersheds (corn and soybean) were net CO_2 sinks (Izaurralde et al. 2007). Reductions in greenhouse gas emissions by altering tillage practices has been demonstrated in other studies as well (e.g., Jin et al. 2017), although this can also be dependent on seasonal climate and soil conditions (Morell et al. 2011).

No-till agricultural practices may therefore also help to offset anthropogenic atmospheric greenhouse gas emissions through soil C sequestration (Jin et al. 2017; Lal 2004a, b), and at the same time maintain or even increase long-term crop yields and soil C retention (Dick and Van Doren 1985; Dick et al. 1991; Jin et al. 2017). However, current models show that land use-associated CO_2 emissions are offset entirely by organic C burial in terrestrial and aquatic systems due to agriculturally-driven soil erosion (Wang et al. 2017). Findings from the present study complement and augment the current community understanding of landscape-scale C sources, transfers and budgets by demonstrating that non-tilled corn watersheds may export far less C (especially in the form of soil organic C) than tilled corn watersheds. However, in order to fully assess and understand the impacts of tilling vs. non-tilling agricultural practices on landscape-scale C budgets, additional studies are needed both on the transport and processing of C in different terrestrial systems as well as on processing and fates of C during transport between headwater streams and the coastal ocean (Bauer et al. 2013; Butman et al. 2016; Drake et al. 2017; Regnier et al. 2013).

Summary

The carbon isotopic characteristics and potential sources contributing to headwater stream C fluxes from anthropogenically altered watersheds in the NAEW are significantly influenced by land use practices. Furthermore, agricultural tilling activities have a major effect on the amounts, isotopic character, and estimated potential source contributions of organic and inorganic C fluxes in streams draining tilled watersheds. As a result, land use disturbance in the watersheds of numerically dominant headwater streams has the potential to alter the biogeochemical cycling and fluxes of C on much larger scales (e.g., Mississippi river basin). The consequences of such large-scale land use alteration for C inputs and cycling in larger streams, rivers, estuaries, and the coastal ocean are only beginning to be understood and incorporated into our conceptual and quantitative models (Bauer et al. 2013; Butman et al. 2016; Regnier et al. 2013; Ren et al. 2016; Stackpoole et al. 2016).

Acknowledgements Sample collection and analyses were funded by the Ohio State University Carbon, Water, and Climate Seed Grant Program to AGG. Support was also provided for SAK by the USDA Forest Service Northern Research Station and by National Science Foundation awards OCE-0961860 and CBET-1236224 to JEB. We thank the NAEW, M. Shipitalo, L. Owens, V. Dreher, and G. Alloway for help and support throughout this project, and R. Moyer, S. Levas, B. Williams, S. Fortner, N. Lorenz, V. Schoepf, J. Baumann, and D. Borg for assistance with fieldwork, analyses, and data interpretation.

References

Argerich A, Haggerty R, Johnson SL, Wondzell SM, Dosch N, Corson-Rikert H, Ashkenas LR, Pennington R, Thomas CK (2016) Comprehensive multiyear carbon budget of a temperate headwater stream. J Geophys Res-Biogeo 121:1306–1315. https://doi.org/10.1002/2015JG003050

Aufdenkampe AK, Mayorga E, Raymond PA, Melack JM, Doney SC, Alin SR, Aalto RE, Yoo K (2011) Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere. Front Ecol Environ 9(1):53–60. https://doi.org/10.1890/100014

Bade DL, Pace ML, Cole JJ, Carpenter SR (2006) Can algal photosynthetic inorganic carbon isotope fractionation be predicted in lakes using existing models? Aquat Sci 68(2):142–153. https://doi.org/10.1007/s00027-006-0818-5

Barnes RT, Butman DE, Wilson HF, Raymond PA (2018) Riverine export of aged carbon driven by flow path depth and residence time. Environ Sci Technol 52:1028–1035. https://doi.org/10.1021/acs.est.7b04717

Battin TJ, Luyssaert S, Kaplan LA, Aufdenkampe AK, Richter A, Tranvik LJ (2009) The boundless carbon cycle. Nat Geosci 2(9):598–600. https://doi.org/10.1038/ngeo618

Bauer JE, Cai W-J, Raymond PA, Bianchi TS, Hopkinson CS, Regnier PA (2013) The changing carbon cycle of the coastal ocean. Nature 504:61–70. https://doi.org/10.1038/nature12857

Beaupré SR, Druffel ERM, Griffin S (2007) A low-blank photochemical extraction system for concentration and isotopic analyses of marine dissolved organic carbon. Limnol Oceanogr-Meth 5(6):174–184. https://doi.org/10.4319/lom.2007.5.174

Bellamy AR, Bauer JE, Grottoli AG (2017) Influence of land use and lithology on sources and ages of nutritional resources for stream macroinvertebrates: a multi-isotopic approach. Aquat Sci 79(4):925–939. https://doi.org/10.1007/s00027-017-0542-3

Beniston JW, Shipitalo MJ, Lal R, Dayton EA, Hopkins DW, Jones F, Joynes A, Dungait JAJ (2015) Carbon and macronutrient losses during accelerated erosion under different tillage and residue management. Eur J Soil Sci 66:218–225. https://doi.org/10.1111/ejss.12205

Berggren M, del Giorgio PA (2015) Distinct patterns of microbial metabolism associated to riverine dissolved organic carbon of different source and quality. J Geophys Res-Biogeo 120(6):989–999. https://doi.org/10.1002/2015JG002963

Brakensiek DL, Osborn HB, Rawls WJ (1979) Field manual for research in agricultural hydrology. Agriculture Handbook, Science and Education Administration, US Department of Agriculture

Butman DE, Wilson HF, Barnes RT, Xenopoulos MA, Raymond PA (2014) Increased mobilization of aged carbon to rivers by human disturbance. Nat Geosci 8:112–116. https://doi.org/10.3038/NGEO2322

Butman D, Stackpoole S, Stets E, McDonald CP, Low DWC, Striegl RG (2016) Aquatic carbon cycling in the conterminous United States and implications for terrestrial carbon accounting. P Natl Acad Sci 113(1):58–63. https://doi.org/10.1073/pnas.1512651112

Caraco N, Bauer JE, Cole JJ, Petsch S, Raymond P (2010) Millennial-aged organic carbon subsidies to a modern river food web. Ecology 91(8):2385–2393. https://doi.org/10.1890/09-0330.1

Casas-Ruiz JP, Catalán N, Gómez-Gener L, von Schiller D, Obrador B, Kothawala DN, López P, Sabater S, Marcé R (2017) A tale of pipes and reactors: controls on the in-stream dynamics of dissolved organic matter in rivers. Limnol Oceanogr 62(S1):S85–S94. https://doi.org/10.1002/lno.10471

Clarke KR, Gorley RN (2006) Primer 6 user manual. Plymouth Marine Laboratory, Plymouth, p 190

Collins HP, Christenson DR, Blevins RL, Bundy LG, Dick WA, Huggins DR, Paul EA (1999) Soil carbon dynamics in corn-based agroecosystems: results from carbon-13 natural abundance. Soil Sci Soc Am J 63:584–591

Dawson JJC, Tetzlaff D, Speed M, Hrachowitz M, Soulsby C (2011) Seasonal controls on DOC dynamics in nested upland catchments in NE Scotland. Hydrol Process 25(10):1647–1658. https://doi.org/10.1002/hyp.7925

Dick W, Van Doren D (1985) Continuous tillage and rotation combinations effects on corn, soybean, and oat yields. Agron J 77(3):459–465. https://doi.org/10.2134/agronj1985.00021962007700030023x

Dick W, McCoy E, Edwards W, Lal R (1991) Continuous application of no-tillage to Ohio soils. Agron J 83(1):65–73. https://doi.org/10.2134/agronj1991.00021962008300010017x

Drake TW, Raymond PA, Spencer RGM (2017) Terrestrial carbon inputs to inland waters: a current synthesis of estimates and uncertainty. Limnol Oceanogr-Lett 3:132–142. https://doi.org/10.10002/lol2.10055

Dupas R, Musolff A, Jawitz JW, Rao PSC, Jäger CG, Fleckenstein JH, Rode M, Borchardt D (2017) Carbon and nutrient export regimes from headwater catchments to downstream reaches. Biogeosciences 14:4391–4407. https://doi.org/10.5194/bg-14-4391-2017

Finlay JC (2003) Controls of streamwater dissolved inorganic carbon dynamics in a forested watershed. Biogeochemistry 62(3):231–252. https://doi.org/10.1023/A:1021183023963

Finlay JC (2004) Patterns and controls of lotic algal stable carbon isotope ratios. Limnol Oceanogr 49(3):850–861. https://doi.org/10.4319/lo.2004.49.3.0859

Fortner SK, Lyons WB, Carey AE, Shipitalo MJ, Welch SA, Welch KA (2012) Silicate weathering and CO_2 consumption within agricultural landscapes, the Ohio-Tennessee River Basin, USA. Biogeosciences 9:941–955. https://doi.org/10.5194/bg-9-941-2012

Fox JF, Ford WI (2016) Impact of landscape disturbance on the quality of terrestrial sediment carbon in temperate streams. J Hydrol 540:1030–1042. https://doi.org/10.1016/j.jhydrol2016.07.016

Gao Y, Dang X, Yu Y, Li Y, Liu Y, Wang J (2016) Effects of tillage methods on soil carbon and wind erosion. Land Degrad Dev 27:583–591. https://doi.org/10.1002/ldr.2404

Graeber D, Gelbrecht J, Pusch MT, Anlanger C, von Schiller D (2012) Agriculture has changed the amount and composition of dissolved organic matter in Central European headwater streams. Sci Total Environ 438:435–446. https://doi.org/10.1016/j.scitotenv.2012.08.087

Hoefs J (2004) Stable isotope geochemistry, 5th edn. Springer, Berlin, p 244

Hossler K, Bauer JE (2012) Estimation of riverine carbon and organic matter source contributions using time-based isotope mixing models. J Geophys Res-Biogeo 117:G03035. https://doi.org/10.1029/2012JG001988

Hossler K, Bauer JE (2013a) Amounts, isotopic character, and ages of organic and inorganic carbon exported from rivers to ocean margins: 2. Assessment of natural and anthropogenic controls. Global Biogeochem Cycle 27(2):347–362. https://doi.org/10.1002/gbc.20034

Hossler K, Bauer JE (2013b) Amounts, isotopic character, and ages of organic and inorganic carbon exported from rivers to ocean margins: 1. Estimates of terrestrial losses and inputs to the Middle Atlantic Bight. Global Biogeochem Cycle 27(2):331–346. https://doi.org/10.1002/gbc.20033

Hotchkiss ER, Hall RO Jr, Sponseller RA, Butman D, Klaminder J, Laudon H, Rosvall M, Karlsson J (2015) Sources of and processes controlling CO_2 emissions change with the size of streams and rivers. Nat Geosci 8(9):696–699. https://doi.org/10.1038/NGEO2507

Hsueh DY, Krakauer NY, Randerson JT, Xu X, Trumbore SE, Southon JR (2007) Regional patterns of radiocarbon and fossil-fuel derived CO_2 in surface air across North America. Geophys Res Lett 34(2):L02816. https://doi.org/10.1029/2006GL027032

Izaurralde RC, Williams JR, Post WM, Thomson AM, McGill WB, Owens LB, Lal R (2007) Long-term modeling of soil C erosion and sequestration at the small watershed scale. Clim Change 80(1–2):73–90. https://doi.org/10.1007/s10584-006-9167-6

Jacinthe PA, Lal R, Owens LB, Hothem DL (2004) Transport of labile carbon in runoff as affected by land use and rainfall characteristics. Soil Till Res 77(2):111–123. https://doi.org/10.1016/j.still.2003.11.004

Jin VL, Schmer MR, Stewart CE, Sindlear AJ, Varvel GE, Wienhold BJ (2017) Long-term no-till and stover retention each decrease the global warming potential of irrigated continuous corn. Global Change Biol 23:2848–2862. https://doi.org/10.1111/gcb.13637

Kelly GE, Edwards WM, Harrold LL, McGuinness JL (1975) Soils of the North Appalachian experimental watershed, US Department of Agriculture. Agricultural Research Service, miscellaneous publication no. 1296, U.S. Government Print Office, Washington D.C., p 160

Kuhn C, Bettigole C, Glick HB, Seegmiller L, Oliver CD, Raymond PA (2017) Patterns in stream greenhouse gas dynamics from mountains to plains in northcentral Wyoming. J Geophys Res-Biogeo 122:2173–2190. https://doi.org/10.1002/2017JG003906

Lal R (2004a) Soil carbon sequestration impacts on global climate change and food security. Science 304(5677):1623–1627. https://doi.org/10.1126/science.1097396

Lal R (2004b) Soil carbon sequestration to mitigate climate change. Geoderma 123(1):1–22. https://doi.org/10.1016/j.geoderma.2004.01.032

Leavitt SW, Follett RF, Kimble JM, Pruessner EG (2007) Radiocarbon and $\delta^{13}C$ depth profiles of soil organic carbon in the US Great Plains: a possible spatial record ofpaleoenvironment and paleovegetation. Quatern Int 162–163:21–34. https://doi.org/10.1016/j.quaint.2006.10.033

Leopold LB, Leopold LB (1995) Fluvial processes in geomorphology. Courier Dover Publications, New York, p 522

Lorrain A, Savoye N, Chauvaud L, Paulet Y-M, Naulet N (2003) Decarbonation and preservation method for the analysis of organic C and N contents and stable isotope ratios of low-carbonated suspended particulate material. Anal Chim Acta 491(2):125–133. https://doi.org/10.1016/S0003-2670(03)00815-8

Lu YH, Bauer JE, Canuel EA, Yamashita Y, Chambers RM, Jaffé R (2013) Photochemical and microbial alteration of dissolved organic matter in temperate headwater streams associated with different land use. J Geophys Res-Biogeo 118(2):566–580. https://doi.org/10.1002/jgrg.20048

Lu YH, Canuel EA, Bauer JE, Chambers RM (2014a) Effects of watershed land use on sources and nutritional value of particulate organic matter in temperate headwater streams. Aquat Sci 76(3):1–18. https://doi.org/10.1007/s00027-014-0344-9

Lu YH, Bauer JE, Canuel EA, Chambers RM, Yamashita Y, Jaffé R, Barrett A (2014b) Effects of land use on sources and ages of inorganic and organic carbon in temperate headwater streams. Biogeochemistry 119(1–3):275–292. https://doi.org/10.1007/s10533-014-9965-2

Marín-Spiotta E, Gruley KE, Crawford J, Atkinson EE, Miesel JR, Greene S, Cardona-Correa C, Spencer RGM (2014) Paradigm shifts in soil organic matter research affect interpretations of aquatic carbon cycling: transcending disciplinary and ecosystem boundaries. Biogeochemistry 117(2–3):279–297. https://doi.org/10.1007/s10533-013-9949-7

Marx AJ, Dusek J, Jankovec J, Sanda M, Vogel T, van Geldern R, Hartmann J, Barth JAC (2017) A review of CO_2 and associated carbon dynamics in headwater streams: a global perspective. Rev Geophys 55:560–585. https://doi.org/10.1002/2016RG000547

McFarlane KJ, Torn MS, Hanson PJ, Porras RC, Swanston CW, Callaham MA Jr, Guilderson TP (2013) Comparison of soil organic matter dynamics at five temperate deciduous forests with physical

fractionation and radiocarbon measurements. Biogeochemistry 112(1–3):457–476. https://doi.org/10.1007/s10533-012-9740-1
Mishra U, Ussiri DAN, Lal R (2010) Tillage effects on soil organic carbon storage and dynamics in Corn Belt of Ohio USA. Soil Till Res 107(2):88–96. https://doi.org/10.1016/j.still.2010.02.005
Mook WG, Bommerson JC, Staverman WH (1974) Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. Earth Planet Sc Lett 22(2):169–176
Morell FJ, Cantero-Martínez C, Lampurlanés J, Plaza-Bonilla D, Álvaro-Fuentes J (2011) Soil carbon dioxide flux and organic carbon content: effects of tillage and nitrogen fertilization. Soil Sci Soc Am J 75(5):1874–1884. https://doi.org/10.2136/sssaj2011.0030
Moyer RP, Bauer JE, Grottoli AG (2013) Carbon isotope biogeochemistry of tropical small mountainous river, estuarine, and coastal systems of Puerto Rico. Biogeochemistry 112(1–3):589–612. https://doi.org/10.1007/s10533-012-9751-y
Olsen KR, Ebelhar SA, Lang JM (2013) Effects of 24 years of conservation tillage systems on soil organic carbon and soil productivity. Appl Environ Soil Sci. https://doi.org/10.1155/2013/617504
Owens LB, Malone RW, Hothem DL, Starr GC, Lal R (2002) Sediment carbon concentration and transport from small watersheds under various conservation tillage practices. Soil Till Res 67(1):65–73. https://doi.org/10.1016/S0167-1987(02)00031-4
Owens LB, Shipitalo MJ, Bonta JV (2008) Water quality response times to pasture management changes in small and large watersheds. J Soil Water Conserv 63(5):292–299. https://doi.org/10.2489/jswc.63.5.292
Owens LB, Bonta JV, Shipitalo MJ (2010) USDA-ARS North Appalachian experimental watershed: 70-year hydrologic, soil erosion, and water quality database. Soil Sci Soc Am J 74(2):619–623. https://doi.org/10.2136/sssaj2009.0196N
Palmer SM, Hope D, Billett MF, Dawson JJC, Bryant CL (2001) Sources of organic and inorganic carbon in a headwater stream: evidence from carbon isotope studies. Biogeochemistry 52:321–338. https://doi.org/10.1023/A:1006447706565
Parsons DA (1954) Coshocton-type runoff samplers: laboratory investigations. US Department of Agriculture, Soil Conservation Service, technical paper 124, p 16
Puget P, Lal R, Izaurralde C, Post M, Owens L (2005) Stock and distribution of total and corn-derived soil organic carbon in aggregate and primary particle fractions for different land use and soil management practices. Soil Sci 170(4):256–279. https://doi.org/10.1097/00010694-200504000-00004
R Core Team (2017). R: a language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. URL https://www.R-project.org/. Accessed 5 Feb 2018
Raymond PA, Bauer JE (2001) Riverine export of aged terrestrial organic matter to the North Atlantic Ocean. Nature 409:497–500. https://doi.org/10.1038/35054034
Raymond PA, Bauer JE, Caraco NF, Cole JJ, Longworth B, Petsch ST (2004) Controls on the variability of organic matter and dissolved inorganic carbon ages in northeast US rivers. Mar Chem 92(1):353–366. https://doi.org/10.1016/j.marchem.2004.06.036
Raymond PA, Oh NH, Turner RE, Broussard W (2008) Anthropogenically enhanced fluxes of water and carbon from the Mississippi River. Nature 451:449–452. https://doi.org/10.1038/nature06505
Raymond PA, Saiers JE, Sobczak WV (2016) Hydrological and biogeochemical controls on watershed dissolved organic matter transport: pulse-shunt concept. Ecology 97(1):5–16. https://doi.org/10.1890/14-1684.1
Regnier P, Friedlingstein P, Ciais P, Mackenzie FT, Gruber N, Janssens IA, Laruelle GG, Lauerwald R, Luyssaert S, Andersson AJ, Arndt S, Arnosti C, Borges AV, Dale AW, Gallego-Sala A, Godderis Y, Goossens N, Hartmann J, Heinze C, Ilyina T, Joos F, LaRowe DE, Leifeld J, Meysman FJR, Munhoven G, Raymond PA, Spahni R, Suntharalingam P, Thullner M (2013) Anthropogenic perturbation of the carbon fluxes from land to ocean. Nat Geosci 6(8):597–607. https://doi.org/10.1038/NGEO1830
Ren W, Tian H, Cai W-J, Lohrenz SE, Hopkinson CS, Huang W-J, Yang J, Tao B, Pan S, He R (2016) Century-long increasing trend and variability of dissolved organic carbon export from the Mississippi River basin driven by natural and anthropogenic forcing. Global Biogeochem Cycle 30(9):1288–1299. https://doi.org/10.1002/2016GB005395
Shibata H, Mitsuhashi H, Miyake Y, Nakano S (2001) Dissolved and particulate carbon dynamics in a cool-temperate forested basin in northern Japan. Hydrol Process 15(10):1817–1828. https://doi.org/10.1002/hyp.241
Shipitalo MJ, Owens LB (2006) Tillage system, application rate, and extreme event effects on herbicide losses in surface runoff. J Environ Qual 35(6):2186–2194. https://doi.org/10.2134/jeq2005.0476
Shipitalo MJ, Dick WA, Edwards WM (2000) Conservation tillage and macropore factors that affect water movement and the fate of chemicals. Soil Till Res 53(3):167–183. https://doi.org/10.1016/S0167-1987(99)00104-X
Sickman JO, DiGiorgio CL, Davisson ML, Lucero DM, Bergamaschi B (2010) Identifying sources of dissolved organic carbon in agriculturally dominated rivers using radiocarbon age dating: Sacramento-San Joaquin River Basin, California. Biogeochemistry 99(1–3):79–96. https://doi.org/10.1007/s10533-009-9391-z
Stackpoole SM, Stets EG, Clow DW, Burns DA, Aiken GR, Aulenbach BT, Creed IF, Hirsch RM, Laudon H, Pellerin BA, Striegl RG (2016) Spatial and temporal patterns of dissolved organic matter quantity and quality in the Mississippi River Basin, 1997–2003. Hydrol Process 31:902–915. https://doi.org/10.1002/hyp.11072
Stock BC, Semmens BX (2015) MixSIAR User Manual, version 3.0. https://github.com/brianstock/MixSIAR/. Accessed 5 Feb 2018
Strahler AN (1957) Quantitative analysis of watershed geomorphology. Eos Trans Am Geophys Union 38(6):913–920. https://doi.org/10.1029/TR038i006p00913
Stuiver M, Polach HA (1977) Discussion: reporting of C-14 data. Radiocarbon 19(3):355–363. https://doi.org/10.1017/S0033822200003672
Townsend-Small A, McClain ME, Hall B, Noguera JL, Llerena CA, Brandes JA (2008) Suspended sediments and organic matter in mountain headwaters of the Amazon River: results from a 1-year time series study in the central Peruvian Andes. Geochim Cosmochim Acta 72(3):732–740. https://doi.org/10.1016/j.gca.2007.11.020
Wang Z, Hoffmann T, Six J, Kaplan JO, Govers G, Doetteri S, Oost KV (2017) Human-induced erosion has offset one-third of carbon emissions from land cover change. Nat Clim Change 7:345–349. https://doi.org/10.1038/nclimate3263
Weber AM, Bauer JE, Watters GT (2017) Assessment of nutritional subsidies to freshwater mussels using a multiple natural abundance isotope approach. Freshw Biol 62(3):615–629. https://doi.org/10.1111/fwb.12890
Wolock DM, Fan J, Lawrence GB (2013) Effects of basin size on low-flow stream chemistry and subsurface contact time in the Neversink River watershed, New York. Hydrol Process 11(9):1273–1286. https://doi.org/10.1002/(SICI)1099-1085(199707)11:9%3c1273:AID-HYP557%3e3.0.CO;2-S
Zaimes GN, Schultz RC, Isenhart TM (2004) Stream bank erosion adjacent to riparian forest buffers, row-crop fields, and continuously-grazed pastures along Bear Creek in central Iowa. J Soil Water Conserv 59(1):19–47