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RESEARCH ARTICLE

Characterizing organic matter inputs to sediments of small, intermittent, prairie streams: a molecular marker and stable isotope approach

Oliva Pisani[1] · Walter K. Dodds[2] · Rudolf Jaffé[1]

Abstract Small rivers and streams are ecologically important because they contribute to the export of organic carbon to coastal environments, likely influencing the global carbon cycle. While organic matter (OM) dynamics in large rivers has been studied in quite some detail, less is known about small streams. Sources of OM in streams ultimately determine its availability to the food web and downstream transport. In this study, sediment samples were collected from the King's Creek watershed in Konza Prairie (Kansas, USA) and analyzed using molecular biomarkers and bulk ^{13}C stable isotopes with the objective to comparatively assess OM inputs between riparian forest vegetation and watershed grassland to small, intermittent streams. We are interested in the potential influence of woody riparian expansion that has been ongoing at the site. Biomarkers typical of the local C_4 grasses (branched n-alkanes, phytadienes) were more abundant in some of the sediments of the upper reaches. The sediments of the lower reaches contained biomarkers of algae (short-chain aliphatic compounds, $C_{25:5}$ highly branched isoprenoid, brassicasterol) and vascular plant-derived material (triterpenols). Degraded OM (triterpene/triterpenol ratio) was found throughout the watershed with no pattern between the upper and lower reaches. Bulk ^{13}C isotope analysis showed that the upper reaches of the watershed receive significant OM inputs from the C_4 grasses (74–99 %) while the lower reaches are more strongly influenced by riparian trees (26–27 %) and algae (21–22 %). These results suggest that the environmental dynamics of bulk OM and the biomarker composition of small prairie streams are highly complex and likely a function of several factors such as light availability, riparian vegetative composition and density, and varying degrees of OM storage, retention and transport along the river continuum.

Keywords Small streams · Konza Prairie · Riparian · Watershed · Biomarkers · ^{13}C stable isotopes

Introduction

Rivers can export significant amounts of total suspended solids (TSS) to coastal environments discharging more than 2000×10^6 tons of suspended materials per year (Farnsworth and Milliman 2003). The transport of large amounts of TSS and its associated organic carbon (OC) can influence coastal/estuarine nutrient dynamics and aquatic ecosystem productivity and is important in the context of carbon cycling (Eglinton 2008). Although there have been many studies and improved knowledge on fluvial TSS fluxes, only the larger world rivers have usually been taken into account when studying the transfer of materials from land to sea (Meybeck et al. 2003).

The ecological importance of small rivers and streams is now well recognized (Peterson et al. 2001; Farnsworth and Milliman 2003; Dodds et al. 2004; Medeiros and Simoneit 2008; Jaffé et al. 2012; Rosemond et al. 2015). Small rivers have a smaller drainage basin for storing flood-driven sediments (Milliman and Syvitski 1992) and they are more likely to respond to event-driven floods (Farnsworth and Milliman 2003). Compared to their larger counterparts,

✉ Rudolf Jaffé
jaffer@fiu.edu

1   Southeast Environmental Research Center and Department of Chemistry & Biochemistry, Florida International University, Miami, FL 33199, USA

2   Division of Biology, Kansas State University, Manhattan, KS 66506, USA

small basins are more responsive to episodic events and can discharge large portions of their sediment loads in relatively short periods of time, affecting the dispersal and fate of the event-derived sediments (Farnsworth and Milliman 2003). Furthermore, because the number of small rivers is much greater than that of large ones, these small streams collectively can be responsible for a substantial portion of sediment and OM delivery from land to oceans (Farnsworth and Milliman 2003).

Several recent studies have focused on the characterization of OC exported from small rivers (Blair et al. 2003; Komada et al. 2004, 2005; Hwang et al. 2005; Leithold et al. 2006). While most of these studies focused on the bulk particulate OC (POC) isotopic composition, a more detailed characterization, through the molecular identification of source-specific biomarkers (Jaffé et al. 2001; Medeiros and Simoneit 2008; Medeiros et al. 2012; Cooper et al. 2015; Giri et al. 2015; Grewer et al. 2015), could provide valuable information on the OM sources to and transport by small rivers. While detrital OM representative of the watershed could dominate supply to the stream network (Allan and Castillo 1995), a large portion of this material can originate from the vegetation comprising the riparian zone (Medeiros and Simoneit 2008).

One conceptual view of OM sources from headwaters to larger receiving waters is the River Continuum Concept (RCC; Vannote et al. 1980). In part, the RCC suggests that closed canopy headwater streams have OM inputs dominated by riparian vegetation, and that downstream, as streams get wider and are exposed to more sunlight, a greater portion of the OM can originate from algal production, though transport from upstream and riparian inputs still can be important. This view has been modified for streams that are naturally open canopy and predicts more algal-derived OM in smaller headwater streams, though with net heterotrophy suggesting that terrestrial carbon sources still are important (Dodds et al. 2004).

Global ecological changes complicate these views. Woody expansion along wet areas is occurring worldwide (Saintilan and Rogers 2014) and these rapid rates of expansion can lead to a transition from C_4 to C_3 dominated vegetation (Veach et al. 2014), resulting in part from increased competitive ability of C_3 species with greater atmospheric CO_2. The consequences of these changes and how they relate to the historic conditions (i.e., the historic stream biome gradient; Dodds et al. 2015) of many streams are difficult to understand with respect to OM transport and supply without the ability to trace both allochthonous and autochthonous sources of carbon in streams.

Only a few studies have used biomarker composition to assess the relative contributions of allochthonous and autochthonous sources of POC to small stream sediments (Jaffé et al. 2001; Mead et al. 2005; Medeiros and Simoneit 2008; Medeiros et al. 2012). These studies have increased our knowledge of OM transport and cycling in small streams, but assessing the environmental dynamics in such systems can be very challenging (Medeiros and Simoneit 2008; Giri et al. 2015). Longitudinal changes described for lotic systems by the RCC can be more pronounced for small streams compared to larger rivers (Houser et al. 2010), making it difficult to study OC dynamics in these environments.

The main goal of this study was to determine the contribution of autochthonous and allochthonous OM inputs to sediments of small, intermittent, prairie streams. An effort was made to distinguish the allochthonous inputs from an extensive C_4 grass-dominated watershed from those of a C_3 vascular plant-dominated riparian area. The King's Creek watershed located in Konza Prairie (Kansas, USA) offers the ideal venue for combining the use of biomarkers and bulk ^{13}C isotopic determinations in an attempt to distinguish between different OM inputs to small prairie stream sediments.

Materials and methods

Site description and sample collection

Konza Prairie is located in the Flint Hills region of the Central Plains, about 10 km southeast of Manhattan, Kansas, USA. The Flint Hills region is a large area (1.6 million ha) of unplowed, native tallgrass prairie (more than 90 % of the vegetation is composed of grasses). The grassland is characterized by several species of C_4 grasses with big bluestem (*Andropogon gerardii*; Freeman 1998) dominating. In Konza Prairie, the two main watersheds are King's Creek and Shane Creek that converge at McDowell Creek, a tributary of the Kansas River. The riparian area of the downstream areas of these creeks is characterized by continuous 10- to 300-m-wide bands of deciduous forest that extends onto the prairie, covering about 7 % of the site (Abrams 1986). These riparian forests are dominated by several species of trees, overstory associates and understory shrubs (Freeman 1998). The King's Creek watershed (1060 ha) is located entirely within the Konza Prairie boundaries (3487 ha) and its geology, hydrology and biology have been investigated by the Long Term Ecological Research program since 1980 (Knapp and Seastedt 1998; KNZ LTER; www.konza.ksu.edu).

Samples were collected in the southern branch of the King's Creek watershed (Fig. 1). Typical vegetation, including fresh leaves and grasses (both C_3 and C_4) was cut from the plant and placed in zip-lock bags. Leaves from the following trees were collected: bur oak (*Quercus macrocarpa*), chinkapin oak (*Quercus muehlenbergii*), hackberry

Fig. 1 Map of the King's Creek watershed showing the sediment and soil sampling sites along the South Branch at the Konza Prairie, Kansas. The tree leaves were collected from the riparian area bordering the streams and the grasses were collected from areas adjacent to the streams. The moss and algae samples were scraped from rocks in the stream channel
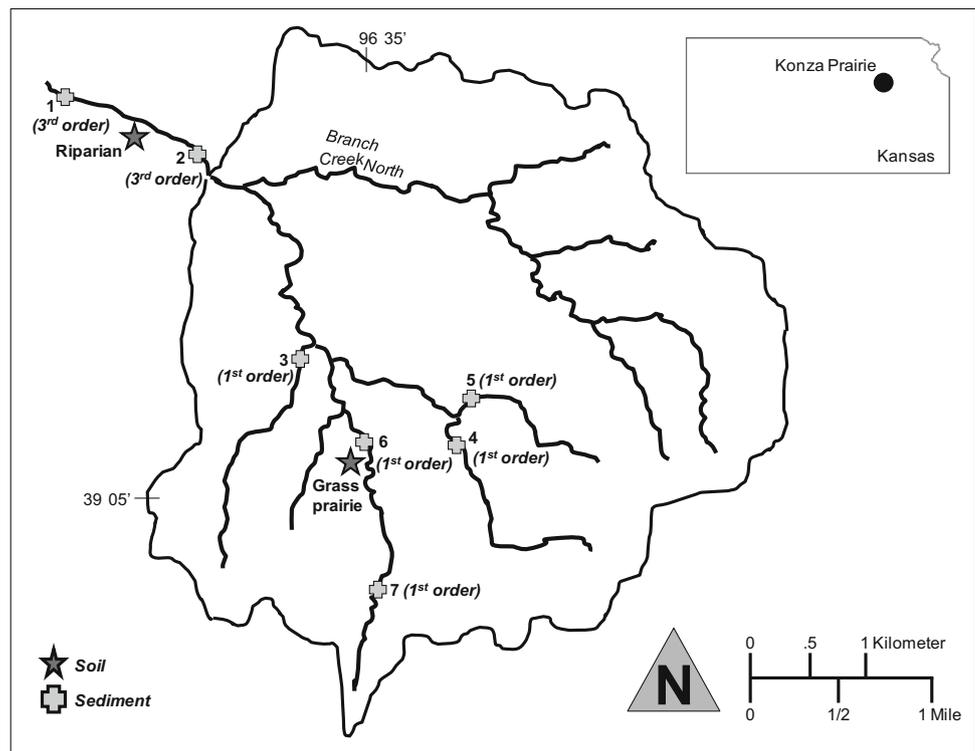
(*Celtis occidentalis*), cottonwood (*Populus deltoides*), wild plum (*Prunus americana*), black walnut (*Juglans nigra*) and roughleaf dogwood (*Cornus drummondii*). The grasses included johnson grass (*Sorghum halepense*; C_3), prairie cordgrass (*Spartina pectinata*; C_3), eastern gamagrass (*Tripsacum dactyloides*; C_4) and big bluestem grass (*Andropogon gerardii*; C_4). Three algae samples and one moss sample were scraped from the rocks in the stream channel and placed in glass jars. Sediment samples were collected in the stream channel with a stainless steel spoon and immediately placed in glass jars. Four sediment samples were collected in 1st order streams (sites #3–7) and two were collected in 3rd order streams (sites #1–2). Two soil samples were collected outside the stream channel. One was from the riparian area dominated by deciduous trees and other C_3 vascular plants; the other was from the prairie environment dominated by C_4 grasses. All samples were kept on ice and transported to the laboratory. The vegetation samples were rinsed, dried and frozen. All the samples were freeze-dried and ground prior to analysis.

Bulk parameters

About 2–10 mg of sample (vegetation, sediments and soils) were weighed in silver cups and de-carbonated by exposure to hydrochloric acid vapors overnight (Harris et al. 2001). Samples were dried in a 60 °C oven overnight and analyzed for total organic carbon (TOC) and total nitrogen (TN)

concentrations. Triplicate samples were measured on a Carlo Erba NA 1500 Nitrogen/Carbon Analyzer with a reproducibility of 0.73 % for TOC and 0.02 % for TN on average. Bulk stable isotope measurements ($\delta^{13}C$) were performed on triplicate samples using standard Elemental Analyzer Isotope Ratio Mass Spectrometry (EA-IRMS) methods on a Finnigan MAT Delta C IRMS. Carbon isotopic values are reported in the standard delta (δ) notation relative to the internal standard, Vienna Pee Dee Belemnite (PDB):

$$\delta^{13}C(\text{‰}) = \left[\left({}^{13}C/{}^{12}C \right)_{\text{sample}} \Big/ \left({}^{13}C/{}^{12}C \right)_{\text{PDB}} - 1 \right] \times 1000$$

Sample reproducibility for bulk $\delta^{13}C$ was 0.22 ‰ on average. The bulk ^{13}C isotope data was fit into a three end-member model using the computer program IsoSource (version 1.3.1; Phillips and Gregg 2003) to quantitatively determine the proportional contribution of three OM sources to the sediments of these prairie streams (C_4 grasses from the watershed, C_3 trees from the riparian forest and algae from the stream bed). The IsoSource program allows the determination of source contributions when the number of sources is too large to permit unique solutions from stable isotope mixing models. The estimated ranges depend on the mixing space and the similarity of source and mixture of isotopic signatures. The variation in estimated ranges is reported to be small when using different choice of source increment and mass balance tolerance parameter values (Phillips and Gregg 2003).

Sample extraction and biomarker analysis by gas chromatography-mass spectrometry

Samples (vegetation: ~ 0.5 g and sediments/soils: ~ 15 g) were Soxhlet extracted with 300 mL of pure methylene chloride for 24 h (Jaffé et al. 2001). Activated copper was added to the extract to remove elemental sulfur. The extracts were concentrated on a rotary evaporator and dried under a stream of N_2 gas. The total extracts were saponified twice using 25 mL of freshly prepared 1 N KOH solution to separate the acid from the neutral fraction. Anhydrous sodium sulfate was added to the resulting fractions to eliminate traces of water (12 h). The neutral fraction was concentrated on a rotary evaporator, further concentrated under a stream of N_2 gas to about 1 mL of extract and fractionated using silica gel adsorption chromatography (7 g of 5 % deactivated silica gel, 100–200 mesh, Fisher Scientific). A total of eight fractions were obtained: aliphatic and aromatic hydrocarbons, wax and methyl esters (not analyzed), aliphatic and triterpenoid ketones and alcohols, sterols, and a polar fraction (not analyzed). The alcohol and sterol fractions were derivatized with N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA; 50 μL) and anhydrous pyridine (20 μL; 60 °C for 1 h) prior to analysis by gas chromatography-mass spectrometry (GC–MS).

The sample extract (1 μL) was analyzed by GC–MS on an HP 6890 GC coupled with an HP 5730 quadrupole mass selective detector. The GC was fitted with a DB-5MS capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) and helium was used as the carrier gas (flow rate: 1.2 mL min⁻¹). For the analysis of the aliphatic hydrocarbon fraction, a DB1-MS capillary column was used. The GC oven temperature was kept at 60 °C for 1 min and then ramped to 300 °C at a rate of 6 °C min⁻¹ and held at 300 °C for 20 min. The column was fed directly into the EI source which was operating at an ionization potential of 70 eV. The injector temperature was maintained at 280 °C. Samples were injected in the splitless mode (splitless time: 2 min) and the mass scan range was set from 50 to 550 Da at a rate of 2.94 scan s⁻¹. Data were acquired and processed with the Agilent MSD Productivity ChemStation software (version B.00.01). The identification of compounds was achieved by comparison with reported mass spectra of authentic standards and with the mass spectral library on the GC–MS data system. All compounds were quantified using the total ion current peak area and converted to compound mass with the addition of a known amount of internal standard (Squalane; 2,6,10,15,19,23-hexamethyl-tetracosane). Blanks were run between samples showing no background interferences.

Results and discussion

Bulk parameters

For sediments that receive OM contributions from algae and both C_3 and C_4 vascular plants, such as those of the Konza Prairie streams, the combined use of elemental carbon to nitrogen ratios (C/N) and $\delta^{13}C$ stable isotopic determinations may aid in the identification of OM sources (Fig. 2). A benefit of using these bulk OM source proxies is that they are representative of the whole sample (Meyers 1997). Elemental C/N ratios can be used to estimate the contribution of OM from different sources to sediments and soils (Jaffé et al. 2001; Otto and Simpson 2005). Terrestrial plants, which contain large amounts of cellulose, generally have high C/N values of 20 or more while algae have a lower proportion of inert structural C and generally have low values between 4 and 10 (Meyers 1997). The riparian trees and C_3 grasses from the King's Creek watershed had lower C/N values (22-41) compared to the C_4 grasses (53–55; Table 1; Fig. 2) as the latter contain low amounts of N in their tissues (Dornbush 2007). The moss and two of the algae samples had C/N values similar to the C_3 vegetation (20–22) while the other algae sample had a much lower value (10). The higher C/N values obtained for the moss and two of the algae samples may derive from the incorporation of higher plant detrital leaf material in the moss and algal mats. Alternatively, the involvement of mosses in the cycling of nitrogen in these streams has been reported as minimal (Dodds et al. 2000) possibly leading to a low N content. The C/N values of the stream sediments were not very different between the 1st and 3rd order streams (Table 2; Fig. 2). The slightly higher value
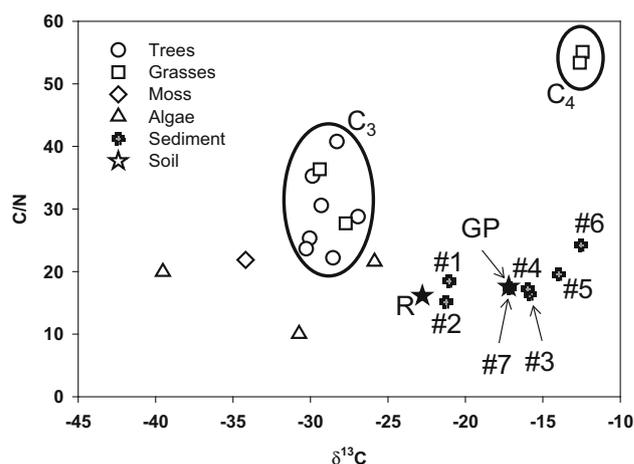
Fig. 2 Elemental carbon to nitrogen ratios (C/N) and bulk ^{13}C isotopes for the riparian trees, grasses, moss, algae, sediments (#1–7) and soils (*R* riparian, *GP* grass prairie)

Table 1 Elemental carbon to nitrogen ratios (C/N), bulk ^{13}C isotopes (‰) and major compound classes (mg g^{-1}OC) identified in the extracts of the tree leaves, grasses, moss and algae samples from the King's Creek watershed at Konza Prairie

	Trees							Grasses				Moss	Algae		
	Bur Oak	Hackberry	Cottonwood	Wild plum	Chinkapin oak	Black walnut	Roughleaf dogwood	Johnson	Prairie cordgrass	Eastern gama	Big Bluestem		#1	#2	#3
C/N	25	24	35	29	31	22	41	28	36	55	53	22	10	20	22
^{13}C (‰)	−30	−30	−30	−27	−29	−28	−28	−28	−29	−12	−13	−34	−31	−39	−26
Aliphatics															
n-alkanes	C_{29} 0.13	C_{29} 0.74	C_{29} 0.67	C_{29} 0.12	C_{29} 0.52	C_{31} 0.50	C_{29} 0.16	C_{31} 0.22	C_{29} 0.13	C_{31} 0.45	C_{27} 3.9	C_{29} 0.028	C_{17} 0.53	C_{29} 0.93	C_{29} 1.7
n-alkenes	C_{28} 0.0059	C_{26} 0.0022	C_{28} 0.17	C_{30} 0.0050	C_{28} 0.012	C_{26} 0.0012	C_{30} 0.015	C_{28} 0.0044	nd	C_{30} 0.19	C_{26} 0.36	C_{28} 0.00074	C_{17} 0.17	C_{17} 0.016	C_{29} 0.36
br. n-alkanes[a]	nd	nd	nd	nd	nd	nd	nd	nd	nd	C_{32} 0.0075	C_{28} 0.56	nd	C_{28} 0.010	C_{30} 0.026	C_{28} 0.24
Phytadienes[b]	nd	nd	nd	nd	nd	nd	nd	0.015	nd	nd	0.69	0.014	nd	nd	nd
$C_{25:2}$ HBI	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.034	0.022	0.015
$C_{25:5}$ HBI	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.0055	0.0031	n.d.
n-alkan-2-ones	C_{29} 0.0035	C_{29} 0.0022	nd	C_{33} 0.0058	C_{29} 0.00026	C_{33} 0.0018	C_{33} 0.0028	C_{31} 0.046	C_{31} 0.00043	C_{31} 0.0067	C_{29} 0.013	nd	C_{20} 0.0035	C_{15} 0.024	C_{15} 0.013
n-alkanals	C_{26} 0.10	C_{17} 0.016	C_{30} 0.077	C_{15} 0.017	C_{26} 0.13	C_{26} 0.0048	C_{30} 0.0094	C_{30} 0.032	C_{23} 0.00051	C_{30} 0.00052	C_{28} 0.028	nd	nd	nd	nd
n-alkanols	C_{24} 0.12	C_{28} 0.23	C_{28} 0.071	C_{26} 0.099	C_{24} 0.15	C_{26} 0.27	C_{26} 0.071	C_{30} 0.36	C_{30} 0.019	C_{32} 0.010	C_{32} 0.11	C_{30} 0.011	nd	C_{30} 0.23	C_{30} 0.0050
Phytone	0.0026	0.0011	0.0018	0.0058	0.0013	0.0019	0.0030	0.022	0.0030	0.0036	0.0046	0.023	0.11	0.28	0.22
Phytol	0.0072	0.0048	0.013	0.019	0.011	0.033	0.066	0.066	0.039	0.23	0.078	0.15	0.71	0.0030	0.13
Σ Aliphatics	0.36	0.99	1.0	0.28	0.82	0.80	0.33	0.76	0.19	0.89	5.7	0.23	1.6	1.5	2.6
Cyclics															
Sterols[c]	st5 0.051	st5 0.24	st5 0.074	st5 0.17	st5 0.028	st5 0.13	st5 0.11	st5 0.13	st5 0.20	st5 0.11	st5 0.063	st4 0.17	st2 1.6	st5 0.50	st5 0.72
Triterpenols[d]	t5 0.063	t2 3.6	nd	t4 0.11	t4 0.22	t5 0.11	t4 0.12	t5 0.038	t5 0.0075	t4 0.053	t3 0.0026	t3 0.0010	nd	t3 0.029	t5 0.065
Σ Cyclics	0.11	3.8	0.074	0.27	0.25	0.24	0.23	0.17	0.20	0.16	0.066	0.17	1.6	0.53	0.79
Total	0.47	4.8	1.1	0.55	1.1	1.0	0.55	0.93	0.39	1.1	5.8	0.40	3.2	3.4	2.1

Compounds indicate the most abundant compound within the series

[a] br. n-alkanes are branched (monomethyl) n-alkanes

[b] Phytadienes include neophytadiene, (Z)-1,3-phytadiene and (E)-1,3-phytadiene

[c] Sterols are identified as cholesterol (st1), brassicasterol (st2), stigmasterol (st3), campesterol (st4) and β-sitosterol (st5)

[d] Triterpenols are identified as taraxerol (t1), δ-amyrin (t2), β-amyrin (t3), α-amyrin (t4) and lupeol (t5)

nd not detected

Table 2 Elemental carbon to nitrogen ratios (C/N), bulk ^{13}C isotopes (‰) and major compound classes (mg g^{-1}OC) identified in the extracts of the sediment and soil samples from the King's Creek watershed at Konza Prairie

	Sediments							Soils	
	#1	#2	#3	#4	#5	#6	#7	Riparian	Grass Prairie
C/N	15	18	16	17	20	24	17	16	18
^{13}C (‰)	−21	−21	−16	−16	−14	−12	−17	−23	−17
Aliphatics									
n-alkanes	C_{29}	C_{29}	C_{29}	C_{29}	C_{29}	C_{29}	C_{29}	C_{31}	C_{31}
	0.16	0.13	0.25	0.23	0.21	0.37	0.16	0.24	0.20
n-alkenes	C_{17}	C_{28}	C_{28}	C_{16}	C_{28}	C_{17}	C_{28}	C_{28}	C_{30}
	0.0026	0.0038	0.0081	0.018	0.0051	0.027	0.0042	0.0031	0.0021
br. *n*-alkanes[a]	C_{28}	C_{28}	C_{28}	C_{30}	C_{30}	C_{28}	nd	nd	C_{28}
	0.0011	0.0016	0.00099	0.0034	0.0015	4.7*			0.0017
Phytadienes[b]	0.029	0.0058	0.019	0.13	0.0037	0.069	0.035	0.0079	0.0059
$C_{25:2}$ HBI	0.010	0.0045	0.00096	0.0088	nd	0.014	0.0024	nd	nd
$C_{25:5}$ HBI	0.00052	0.00022	nd	nd	nd	nd	nd	nd	nd
n-alkan-2-ones	C_{33}	C_{31}	C_{33}	C_{31}	C_{31}	C_{29}	C_{31}	C_{31}	C_{33}
	0.098	0.090	0.20	0.0075	0.0042	0.0012	0.0019	0.0059	0.031
n-alkanals	C_{16}	C_{16}	C_{30}	C_{16}	C_{28}	C_{28}	C_{28}	C_{30}	C_{28}
	0.061	0.043	0.037	0.020	0.0022	0.0023	0.0065	0.0092	0.015
n-alkanols	C_{32}	C_{28}	C_{32}	C_{28}	C_{32}	C_{28}	C_{28}	C_{30}	C_{32}
	0.053	3.4*	0.022	0.055	0.031	0.045	0.071	0.13	0.057
Phytone	0.0093	0.0088	0.011	0.0013	0.00044	nd	nd	0.0016	0.0043
Phytol	0.0014	nd	nd	0.0034	0.0034	0.0010	0.00083	0.00014	nd
Σ Aliphatics	0.43	3.7	0.55	0.49	0.26	5.3	0.28	0.39	0.32
Short/long[c]	0.15	0.030	0.025	0.082	0.017	0.070	0.040	0.0038	0.076
Cyclics									
Sterols[d]	st2	st5	st5	st5	st5	st5	st5	st5	st5
	0.065	0.31	0.0085	0.019	0.0017	0.0093	0.022	0.021	0.0012
Triterpenes[e]	tr2	tr3	tr2	tr2	tr2	tr2	tr2	tr2	tr2
	0.0042	0.0043	0.017	0.011	0.011	0.011	0.0071	0.014	0.0046
Triterpenols[f]	t5	t3	t3	t3	t3	t3	t3	t5	t5
	0.067	1.3	0.0024	0.0068	0.0044	0.014	0.016	0.0044	0.023
Σ cyclic	0.14	1.6	0.028	0.036	0.017	0.035	0.045	0.040	0.029
Triterpene/Triterpenol[g]	0.063	0.0033	7.1	1.6	2.4	0.80	0.43	3.2	0.20
Total	0.56	5.3	0.58	0.52	0.28	5.3	0.33	0.43	0.35

Compounds indicate the most abundant compound within the series

[a] br. *n*-alkanes are branched (monomethyl) *n*-alkanes

[b] Phytadienes include neophytadiene, (Z)-1,3-phytadiene and (E)-1,3-phytadiene

[c] Short/long ratio is calculated as the sum of short-chain aliphatics ($<C_{20}$) divided by the sum of long-chain aliphatics ($\geq C_{20}$)

[d] Sterols are identified as cholesterol (st1), brassicasterol (st2), stigmasterol (st3), campesterol (st4) and β-sitosterol (st5)

[e] Triterpenes are identified as olean-13(18)-ene (tr1), olean-12-ene (tr2) and olean-18-ene (tr3)

[f] Triterpenols are identified as taraxerol (t1), δ-amyrin (t2), β-amyrin (t3), α-amyrin (t4) and lupeol (t5)

[g] Triterpene/triterpenol ratio is calculated as the sum of triterpenes divided by the sum of triterpenols

nd not detected

* These unexpectedly high concentration values may be due to the co-elution of other compounds using GC–MS and should be interpreted with caution

obtained at site #6 may suggest more C_4 grass (particularly eastern gamagrass and big bluestem) watershed-derived inputs to the sediments at this site compared to the other sites. The grass prairie soil and the riparian soil had very similar C/N values and in the same range as the sediments at sites #1 to #4. The lower C/N values of the soils and

sediments compared to the vegetation samples are suggestive of OM degradation, as it has been reported that the C/N ratio decreases with heterotrophic degradation of OM. The observed decrease in C/N ratios likely involves the microbial immobilization of nitrogenous material accompanied by the mineralization of carbon compounds (Gallardo and Merino 1992; Meyers 1997). The reduction in the C/N ratio is much larger between the C_4 grasses and the sediments/soils compared to the ratio for the C_3 vegetation (Fig. 2) likely due to the more labile character of the C_4-derived carbon (herbaceous) compared to its C_3 counterpart (woody; Wynn and Bird 2007).

The application of $\delta^{13}C$ stable isotopes can be very useful to identify OM from biomass using different photosynthetic pathways (Meyers 1997; Fry 2006). Plants that follow the Calvin pathway (C_3) such as trees, shrubs and many grasses, have lower, more negative $\delta^{13}C$ values averaging near -28 ‰, whereas plants that follow the Hatch-Slack pathway (C_4) such as sugar cane, corn and many grasses, have higher, less negative values averaging near -13 ‰ (Meyers 1997). In this study, bulk $\delta^{13}C$ values for the riparian trees and the C_3 grasses were more negative (-27 to -30 ‰) compared to the two C_4 grasses (-12 and -13 ‰; Table 1; Fig. 2). The moss and algae samples also showed more negative isotopic values ranging between -26 and -40 ‰. The variability in ^{13}C isotope values observed for the algae may be attributed to the isotopic signature of the carbon they take up (carbon dioxide versus bicarbonate), photosynthetic fractionation and physiological characteristics such as growth rate and cell geometry (Laws et al. 1997; Popp et al. 1998; Marty and Planas 2008). In addition, greater water velocity can result in depleted ^{13}C isotope values for algae in small streams (Trudeau and Rasmussen 2003). Sediments collected in the 1st order streams of the upper reaches had a less negative isotopic signature than those collected in the 3rd order lower reaches of the streams (Table 2; Fig. 2). In agreement with the isotopic values for the vegetation samples and for the riparian and the prairie soils, the larger values of the upper reaches could be indicative of preferential OM inputs from the extensive C_4 grasses in the prairie-dominated watershed, while the smaller values of the lower reaches indicate a mixed input from the greater watershed and the riparian area. Based on the ^{13}C isotope results, the three end-member model showed that 74–99 % of the OM in the sediments of the upper reaches is derived from C_4 grasses (Table 3). The sediments of the lower reaches are also dominated by inputs from C_4 grasses (52–53 %), but receive more OM from the C_3 riparian trees (26–27 %) and from the algae (21–22 %) compared to the upper reaches (0.4-14 and 0.3–11 %, respectively). The riparian soil showed mixed inputs from higher plants although a significant portion of its OM is derived from the C_4 grasses

Table 3 Organic matter contributions (%) to the sediments and soils from King's Creek using bulk ^{13}C isotopes (three end-member model; algae versus C_3 and C_4 plants)

	Algae (%)	C_3 (%)	C_4 (%)
Sediments			
1	22	27	52
2	21	26	53
3	8	10	82
4	8	11	81
5	4	5	92
6	0.3	0.4	99
7	11	14	74
Soils			
Grass Prairie	12	14	74
Riparian	26	31	43

(43 %). The higher isotopic signal of the grass prairie soil suggests inputs from the C_4 grasses (74 %) dominating the prairie landscape. The decomposition of litter derived from C_3 and C_4 grasses can result in shifts in $\delta^{13}C$ values in opposite directions where C_4 species show a more negative signal (1.5 ‰ decrease) and C_3 species a less negative signal (0.6 ‰ increase; Wedin et al. 1995). If different OM decomposition patterns are occurring in the Konza Prairie sediments, the calculated OM contributions using the three end-member model may be resulting in an underestimation of different vegetation type inputs.

Biomarkers for organic matter characterization and degradation patterns

Aliphatic compounds

A series of aliphatic compounds were identified in the samples from the King's Creek watershed (n-alkanes, branched n-alkanes, n-alkenes, phytadienes, highly branched isoprenoid hydrocarbons (HBI), n-alkanals and n-alkanols; Tables 1, 2). These biomarkers are useful for OM source characterization because long-chain compounds ($\geq C_{20}$) are considered to derive from the epicuticular waxes of higher plants (Eglinton and Hamilton 1967; Simoneit 2005), while short-chain compounds ($<C_{20}$) are presumed to be mainly from algal/planktonic origin (Cranwell 1982; Gogou and Stephanou 2004). As such, the riparian trees, grasses and the moss from the King's Creek watershed were dominated by long-chain aliphatic compounds while the algae showed enrichment in the shorter chain homologues (Table 1). Although long-chain aliphatics have been observed in several species of microalgae (Volkman et al. 1998; Zegouagh et al. 1998) their presence in the algae samples from King's Creek could be the result of plant debris trapped in the algal mat (see above).

Based on the distribution of aliphatic compounds, the sediment samples showed a mixed source of OM with no clear pattern from the upper to the lower reaches of the watershed (Table 2). The molecular distribution for most of the aliphatic compound classes were not different between the riparian trees and the grasses and thus were not source-specific to any particular higher plant-derived material. However, the *n*-alkanal distribution for the big bluestem grass showed a C_{max} at C_{28} (Table 1) which was also observed for the grass prairie soil and the sediments from sites #4, #5 and #6 (Table 2). The abundance of the C_{28} *n*-alkanal may reflect OM contributions from this C_4 grass to the sediments at these sites. The *n*-alkanol distribution was less clear than the *n*-alkanals and was different between the C_3 ($C_{max} = C_{30}$) and the C_4 grasses (C_{32}; Table 1). The sediments from sites #1, #3 and #5, as well as the grass prairie soil, also showed a C_{max} at C_{32} (Table 2) suggesting inputs from the C_4 grasses.

The ratio of short- ($<C_{20}$) to long-chain ($\geq C_{20}$) aliphatics potentially indicates microbial inputs to stream sediments (Pisani et al. 2013). Based on this ratio, the sediments at site #1 receive more such fresh, autochthonous contributions compared to the other sites (Table 2). According to the RCC as modified to apply to prairie streams (Dodds et al. 2004), lower order reaches are dominated by riparian forests. However, the streams at sites #1 and #2 are wider than the ones in the upper reaches, allowing light penetration to the stream bed and favoring algal growth. In fact, algae sample #1 was collected near site #1 as a filamentous assemblage attached to a limestone outcrop and totally exposed to sunlight. In addition, low order reaches are perennial (Dodds et al. 2004) and these conditions may favor not only the production but also the preservation of algal OM. The sediments at sites #4 and #6 also had relatively high short- to long-chain aliphatic ratios compared to the other sites, suggesting high inputs from the algae growing in the stream bed. The riparian soil, which receives litterfall inputs enriched in long-chain aliphatic compounds, had a lower ratio compared to the grass prairie soil.

Branched (monomethyl) *n*-alkanes occur as natural products in plant leaf waxes (Eglinton and Hamilton 1967; Huang et al. 2011) and in cyanobacteria (He et al. 2015). In the present study, the greatest abundances of these compounds were found in the big bluestem grass (Table 1), with a C_{max} at C_{28}. Much smaller amounts were detected in the eastern gamagrass and in the three algae samples. Based on these data, it was assumed that the big bluestem grass is the main contributor of these compounds in this environment and they can therefore be used as markers for this vegetation. All the sediments, with the exception of site #7, contained branched *n*-alkanes in similar concentrations (Table 2) and no specific trend was observed

between the sediments of the upper and the lower reaches of the watershed.

Three phytadiene isomers were detected in the samples from King's Creek: neophytadiene (7,11,15-trimethyl-3-methylene-1-hexadecene), (Z)- and (E)-1,3-phytadiene. The highest concentration of these compounds was found in the big bluestem grass (Table 1), suggesting that they could serve as indicators of grass-derived OM inputs to sediments in small prairie streams. In fact, none of the riparian trees or algae contained these compounds. The phytadiene concentrations in sediments were highest at the upper reaches (#4, 6 and 7), particularly at site #4 (Table 2). Their presence may suggest direct inputs of big bluestem grass to these low order streams. In the high order streams, smaller amounts of phytadienes were detected, with smallest concentration found at site #2. The two soil samples also contained small amounts of phytadienes. Interestingly, although big bluestem is the most abundant grass in the watershed adjacent to the riparian areas, the concentrations of phytadienes in the riparian soil were similar to those in the prairie soil, and carbon-normalized concentrations in the sediments were much higher than in the soils. This suggests that big bluestem is a significant source of phytadienes to the sediments, but also that accumulation of these compounds is preferred in the sediments (flooded conditions) while their preservation in soils (open air conditions) is not favored. As such, their presence in sediments may suggest a direct source from grass detritus rather than from remobilized soil OM. In addition, if the riparian vegetation was established over the last century, there may not have been enough time for a significant composition shift in the present day riparian soils. It is possible that frequent fires that characterize the Konza Prairie environment (Ding et al. 2013) may reduce the accumulation of OM in prairie soils.

The three algae samples contained several poly-unsaturated C_{25} highly branched isoprenoids ($C_{25:2}$ and $C_{25:5}$ HBI; Table 1) that have been assigned a diatom source (Wraige et al. 1997; Belt et al. 2001). The $C_{25:2}$ HBI, identified as 2,10,14-trimethyl-6-methylene-7-(3′-methyl-pent-1-enyl)-pentadecane, was present in all the sediment samples except for site #5. Site #6 showed the highest inputs from algae followed by sites #1, #2 and #4 (Table 2). This compound was not detected in sediments at site #5, probably because of insignificant algal growth in the stream at that site. Furthermore, the $C_{25:2}$ HBI was not detected in the soil samples. Another poly-unsaturated HBI, namely the $C_{25:5}$ HBI 2,6,10,14-tetramethyl-7-(3-methylpent-4-enyl)-pentadec-2,5,9,13-ene, was found in two of the algae samples and in the sediments from the lower reaches (#1 and #2), indicating fresh algal inputs to the higher order stream sites. Since this compound features a high degree of unsaturation, it may be expected to be less

stable compared to the $C_{25:2}$ HBI, suggesting that these permanently flooded locations preferentially accumulate fresh OM in their sediments or feature better environmental conditions for OM preservation.

The ketone 6,10,14-trimethylpentadecan-2-one (phytone) is believed to be an oxidation product derived from the microbial alteration of phytol (Ikan et al. 1973, Brooks and Maxwell 1974). Because the algae samples from King's Creek contained two orders of magnitude more phytone than the rest of the vegetation samples (Table 1), they can be considered significant sources of this isoprenoid compound to sediments (Rontani and Volkman 2003). The concentrations of phytone increased from the sediments of the upper reaches to those of the lower reaches of the watershed (Table 2). Site #3 contained the largest amount of this compound, suggesting the accumulation of degraded OM at this site (in agreement with the triterpene data discussed below) as well as autochthonous inputs to the sediments. The sediments at sites #6 and #7 did not contain phytone, which could have been transported further downstream during a flash flood event. In agreement with data presented above on C_{25} HBIs and phytadienes, it seems that the lower reaches of the system preferentially accumulate OM from soil erosion, detritus and algal sources.

Cyclic compounds

The samples from the King's Creek watershed contained a series of cyclic compounds including pentacyclic triterpenols (taraxerol, δ-, β- and α-amyrin, and lupeol) and sterols (cholesterol, brassicasterol, stigmasterol, campesterol and β-sitosterol; Tables 1, 2). The triterpenols identified in the samples are characteristic biomarkers originating from higher plants (Simoneit 1986; Ten Haven et al. 1992; Medeiros and Simoneit 2007). As such, the riparian tree leaves contained relatively high concentrations of triterpenols, followed by the grasses, the algae and the moss (Table 1). The small amounts of α- and β-amyrin detected in the algae samples are likely due to higher plant leaf litter detritus that can get trapped in filamentous algal mats. The triterpenols were found in all the sediments with sites #1 and #2 containing the highest concentrations (Table 2). Lowest amounts of these higher plant markers were found at site #3. The riparian vegetation of the lower reaches of this watershed is composed mainly of higher plants, such as bur oak and hackberry. On the other hand, the riparian vegetation of the upper reaches is also composed of higher plants, but is less wide and thus with lower standing biomass. The smaller amounts of triterpenols found in the upper reaches may be indicative of a higher contribution of OM from grass relative to riparian vegetation derived sources. This pattern might also be associated with the fact that flash floods may remobilize riparian detrital particles from the upper reaches to the deeper, higher order streams. The soils were very different in their total triterpenol distributions and were dominated by lupeol instead of β-amyrin as for the sediments. Strangely, the grass prairie soil contained higher abundances of these compounds compared to the riparian soil.

Several mono-unsaturated triterpenes were detected in the sediment and soil samples from King's Creek (Table 2). The compounds identified belonged to the oleanane (olean-13(18)-ene, olean-12-ene and olean-18-ene) class and are early diagenetic products of 3-*oxy*-triterpenoids (ten Haven et al. 1992). The triterpene/triterpenol ratio (Table 2) can be used to estimate the degree of OM degradation in stream sediments. Based on this ratio, the sediments of some of the upper reaches (particularly sites #3 and #5) of the watershed appear to accumulate degraded plant-derived OM. This process may be favored by the hydrological conditions of these prairie streams. The streams of the upper reaches are intermittent and the OM in the sediments at these sites may undergo enhanced aerobic respiration during dry periods. Subsequently, the smaller amounts of these compounds present in the lower reaches indicate poor environmental conditions for OM degradation. The riparian soil had a higher triterpene/triterpenol ratio compared to the grass prairie soil, suggesting the low accumulation of these higher plant-derived degradation products in soils from this prairie watershed.

Sterols can distinguish aquatic contributions from plant-derived material to sedimentary OM (Huang and Meinschen 1979; Meyers 1997). All the samples from King's Creek contained various types of C_{27}, C_{28} and C_{29} sterols, and the carbon number distributions are displayed in a ternary diagram (Fig. 3). Although zooplankton are rare in these prairie streams, other crustaceans such as isopods are present (Edler and Dodds 1996) and may contribute to the sterol signature of the sediments. The major sterols identified were cholesterol, brassicasterol, campesterol, stigmasterol and β-sitosterol (Tables 1, 2). Cholesterol (C_{27}) has been attributed an algal source, as it is present only in small amounts in higher plants compared to aquatic organisms (Smittenberg et al. 2004). Sterols with a C_{28} structural unit, such as brassicasterol are known biomarkers for algal inputs (Volkman and Maxwell 1986; Volkman et al. 1998) and were quite abundant in one of the algae samples from King's Creek (Table 1; Fig. 3). Campesterol, stigmasterol and β-sitosterol (C_{29}) are constituents of higher plants (Hartmann 1998) and the riparian tree leaves and grasses contained relatively high amounts of these phytosterols (Fig. 3) with β-sitosterol being the most abundant (Table 1). This sterol was also very abundant in two of the algae samples, showing that this sterol is widely distributed and should be used with caution to distinguish inputs from different sources (Volkman et al. 1998).
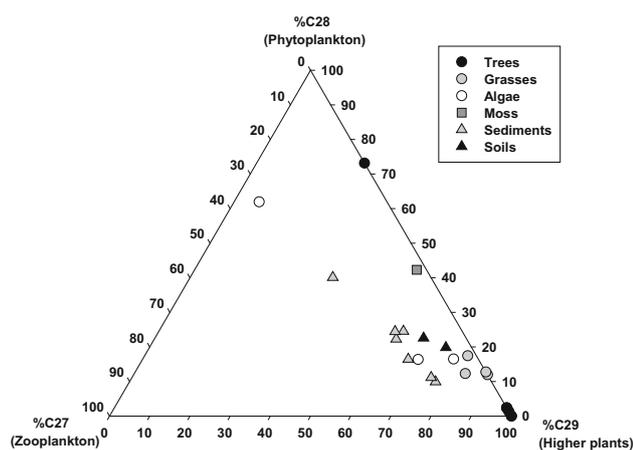
Fig. 3 Ternary plot showing the C_{27} (zooplankton), C_{28} (phytoplankton) and C_{29} (vascular land plants) sterol distribution in the samples from King's Creek

However, the presence of β-sitosterol in two of the algae samples may also derive from detrital leaf material trapped in the algal mat. The sediments at site #1 are separated from the sediments at the other sites and are highly influenced by algal-derived OM (brassicasterol; Table 2; Fig. 3). The contribution of autochthonous OM inputs to the sediments at this site is in agreement with the $C_{25:5}$ HBI and the short-/long-chain aliphatic ratio data presented above. The sediments of the other sites had a sterol distribution similar to the grasses and riparian trees (Fig. 3) with the most abundant sterol being β-sitosterol (Table 2). The sterol distribution of the two soil samples was quite similar and confirms mixed higher plant inputs.

Conclusions

Sediment and soil samples from the King's Creek watershed at Konza Prairie were found to contain organic compounds from different biogenic sources as well as products indicative of early diagenetic alterations. The sediments of the upper reaches (sites #3–7) of the watershed are highly influenced by grasses (especially site #6) while the lower reaches (sites #1 and #2) receive more balanced inputs from grasses, riparian vegetation (including trees) and algae. The presence of partially degraded, "older" OM in the sediments of the upper reaches may due to enhanced aerobic degradation during dry periods. These hydrologic trends complicate the characterization of OM transport in this dynamic environment.

The inputs of autochthonous material to stream sediments can be related to the RCC, which has been re-defined for small prairie streams (Dodds et al. 1996 and 2004). The streams at Konza Prairie are characterized by a downstream change in vegetation cover which can greatly

influence the growth of stream algal communities. The upstream reaches have historically been characterized by minimal canopy cover and low shading of the stream, but are progressively more dominated by woody cover (Veach et al. 2014). The canopy openness allows the growth of algal biofilms in the stream channel. As stream order increases, so does the amount of canopy cover and consequent shading of the stream bed. Eventually, as the stream channel widens, more light reaches the stream and algal growth can be substantial in the absence of grazing. The enhanced presence of autochthonous OM in the sediments of the lower reaches suggests either instream production in the lower reaches or transport of autochthonous OM. As algal OM is generally thought to be labile, the former explanation is more likely for the occurrence of algal biomarkers.

The present study shows that the bulk OM and biomarker composition of small prairie streams is very complex and is a function of light, riparian vegetative composition, and variable degrees of storage/retention and transport of labile and recalcitrant OM fractions. The importance of small streams is now recognized in the context of POM export from terrestrial to coastal environments, contributing to the estimations of the global ocean carbon cycle. However, while there are a growing number of studies on the detailed characterization of OM in small rivers (Jaffé et al. 2001; Mead et al. 2005; Medeiros and Simoneit 2008; Medeiros et al. 2012; Cooper et al. 2015; Giri et al. 2015; Grewer et al. 2015), more work is needed to characterize this material and link its sources, transport and transformations to spatially and temporally variable conditions that occur in stream networks. As we begin to understand how stream biogeochemistry varies across biome gradients at continental scales (Dodds et al. 2015), a more complete model of OM sources, processing and transport may become possible and allow predictive ability related to anthropogenic changes such as woody vegetation expansion, climate change, and land use/land cover change.

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