Aquat Sci
DOI 10.1007/s00027-014-0344-9

Aquatic Sciences

RESEARCH ARTICLE

Effects of watershed land use on sources and nutritional value of particulate organic matter in temperate headwater streams

Yue Han Lu · Elizabeth A. Canuel · James E. Bauer · R. M. Chambers

Received: 13 June 2013 / Accepted: 5 February 2014

Abstract Suspended particulate organic matter (POM) in headwater streams is an important source of food and energy to stream food webs. In order to determine the effects of watershed land use on the sources and characteristics of POM, we compared the lipid composition of POM (fatty acid, aliphatic alcohol and sterol) from streams influenced by different types of watershed land use. Eight first-order streams discharging to the York River Estuary (Virginia, USA) were sampled during baseflow conditions bi-monthly from February to November 2009, including streams draining forest-dominated, pasture-dominated, cropland-dominated, and urban land-dominated watersheds. Allochthonous vs. autochthonous lipids showed that POM in most of these streams was dominated by allochthonous sources (59.5 ± 14.2 vs. 39.6 ± 14.5 % for aliphatic alcohols and 52.9 ± 11.5 vs. 34.1 ± 10.3 % for sterols). The relative abundance of allochthonous vs. autochthonous lipid inputs to POM varied as a function of land use type. POM in streams draining forest-dominated watersheds contained a higher proportion of allochthonous lipids and a lower proportion of autochthonous lipids than the streams influenced by human land use. The contribution of bacterial fatty acids differed significantly among sampling times ($P = 0.003$), but not among land use types ($P = 0.547$). Stepwise linear regression model selected nitrate and temperature as the best predictors of variation in bacterial inputs to POM. Proxies used to assess the nutritional value of POM potentially available to stream consumers included C:N ratios, and the concentrations of total long-chain polyunsaturated fatty acids, eicosapentaenoic acid, arachidonic acid, and cholesterol. None of these nutritional proxies differed among sampling months ($P \geq 0.171$), but the proxies showed that the nutritional value of POM in forest streams was lower than in urban streams. Collectively, these findings suggest that human land use in upstream watersheds alters the source composition and nutritional value of stream POM, which not only impacts food quality for stream biota, but also potentially changes the characteristics of OM reaching downstream ecosystems.

Keywords Lipid biomarker · Neutral lipid fatty acid · Phospholipid linked fatty acid · Alcohol · Sterol · Watershed · Land use · Particulate organic matter

Introduction

Human modifications to watershed land use have been shown to influence aquatic ecosystems by altering

Y. H. Lu performed field and laboratory work to acquire the data and wrote the main paper. All authors commented on the manuscript of all stages, and contributed substantially to conception and design of the study, and discussion of the results.

Y. H. Lu (✉)
Department of Geological Sciences, University of Alabama, 201 7th Ave, Tuscaloosa, AL 35485, USA
e-mail: yuehan.lu@ua.edu

E. A. Canuel
Department of Physical Sciences, Virginia Institute of Marine Sciences, Gloucester Point, VA 23062, USA

J. E. Bauer
Aquatic Biogeochemistry Laboratory, Department of Evolution, Ecology and Organismal Biology, Ohio State University, Columbus, OH 43210, USA

R. M. Chambers
Department of Biology, College of William and Mary, Williamsburg, VA 23187, USA

Published online: 06 March 2014

microbial processing of carbon and nitrogen (Newcomer et al. 2012; Lu et al. 2013), whole-stream primary productivity and respiration (Maloney et al. 2008; Bernot et al. 2010), and biotic diversity and integrity (Allan 2004; Maloney et al. 2008). These ecosystem-level impacts may be linked, directly or indirectly, to land use-induced changes in the transfer of nutrient and/or organic substrates from terrestrial landscapes to aquatic environments. Previous studies have reported human land use increases inorganic nutrient exports (Carpenter et al. 1998; Niyogi et al. 2003) and modifies stream and river water dissolved organic matter (DOM), including sources, molecular structure and reactivity (e.g., Stern et al. 2007; Sickman et al. 2010; Wilson and Xenopoulos 2009; Lu et al. 2013). Past studies of the effects of land use on particulate organic matter (POM) composition have focused primarily on soils (e.g. Yamashita et al. 2006; Meyer et al. 2012), with little attention given to POM in adjacent aquatic systems.

Particulate organic matter serves as an important source of energy and nutrition to aquatic biota (Anderson and Sedell 1979; Cummins et al. 1989; Allan and Castillo 2007). In streams, two of five invertebrate functional feeding groups rely on POM as the primary food source—shredders convert coarse POM to fine POM and feed on fine POM while collectors/filterers eat fine POM (Anderson and Sedell 1979; Cummins et al. 1989). These two groups dominate in first- and second-order streams (Anderson and Sedell 1979), where POM is primarily derived from terrestrial plants (allochthonous POM, e.g., leaf and wood inputs), with only a small fraction from aquatic organisms (autochthonous POM) (Malas and Wallace 1977; Anderson and Sedell 1979; Wallace et al. 1987). In general, allochthonous POM is considered lower in nutritional value to invertebrates than autochthonous POM due to differences in chemical composition, e.g., leaves and woody debris have higher stoichiometric C:N ratios than algae and aquatic organic matter (Anderson and Sedell 1979; Elser et al. 2000; Atkinson et al. 2009).

Human modifications to land use may alter the sources of POM to streams (i.e., the dominance of allochthonous inputs) and consequently, the nutritional value of POM as a food source for aquatic consumers. Hicks (1997), for example, used bulk stable isotopes of carbon and nitrogen to investigate food webs in forest and pasture streams in New Zealand, and reported that forest stream food webs were subsidized primarily by allochthonous sources of organic matter while food webs in pasture streams were supported by both autochthonous and allochthonous sources. Direct measures of the effects of land use on the sources and nutritional quality of stream water POM, however, are relatively rare.

Lipid content and biomarker distributions, combined with stoichiometric C:N ratios and stable carbon isotopes, are powerful tools for understanding aquatic OM sources and reactivity, and particularly for differentiating autochthonous vs. allochthonous sources (Canuel et al. 1995; Bianchi and Canuel 2011), assessing processing status (e.g., diagenetic status) (Canuel and Martens 1993; Zimmerman and Canuel 2002; Lu and Meyers 2009), providing information about nutritional value of particulates as a food source to biota and understanding aquatic food webs (Ahlgren et al. 1990; Brett and Müller-Navarra 1997; Napolitano 1998; Dalsgaard et al. 2003; Martin-Creuzburg and Von Elert 2009a). For example, elevated concentrations of long-chain polyunsaturated fatty acids and dietary sterols in food sources (POM, seston, algae) have been linked to higher nutritional quality and elevated trophic transfer efficiency between primary and secondary producers (Ahlgren et al. 1990; Brett and Müller-Navarra 1997; Von Elert et al. 2003; Martin-Creuzburg and Von Elert 2009a).

In the present study, we used lipid biomarkers to evaluate how human land use may change POM sources, inputs and potential nutritional value in temperate headwater streams. Previous attempts to link land use to OM in receiving waters have been hindered by confounding factors influencing aquatic OM, such as lithology, climate, and hydrology. To overcome these factors, our study sites consisted of a regional group of streams with similar lithological and climatic parameters sampled under base flow conditions. Because previous studies have demonstrated the importance of seasonal variation in stream water POM inputs and composition (e.g., França et al. 2009), we sampled at five different times between February and November of 2009 to attempt to distinguish between temporal and land use-related variability in POM. A suite of lipid biomarkers including fatty acids (FAs), aliphatic alcohols and sterols were used to evaluate the sources, diagenetic status and potential nutritional quality of stream water POM.

Methods

Sampling sites and watershed land use classification

Eight first-order streams (Strahler scale) discharging to the York River estuary, a sub-estuary of the lower Chesapeake Bay in VA, USA, were chosen for study. They included three forest streams (i.e., F1, F2 and F3) which drained forest-dominated watersheds, two pasture streams (P1, P2) draining pasture-dominated watersheds, one cropland stream (C1) draining cropland-dominated watershed and two urban streams (U1and U2) for urban-land dominated watersheds (Table 1; Fig. 1). The forest, pasture and cropland streams were located in rural areas (population

Table 1 Watershed land use and annual means of environmental parameters for the sampling streams in the present study

Sampling site	Dominant watershed land use	Water temperature[a] (°C)	pH[a]	Dissolved oxygen[a] (mg/L)	Specific conductivity[a] (μS)	Chlorophyll-a[a] (μg/L)	Nitrate[a] (μM)	Ammonium[a] (μM)	Stream length (km)	Watershed size (km^2)
F1	83 % Forest	19 ± 9	6 ± 0.5	8 ± 1	45 ± 9	0.2009 ± 0.1	26 ± 11	BD	0.61	0.27
F2	100 % Forest	14 ± 5	6 ± 1	6 ± 4	105 ± 49	0.03 ± 0.02	3 ± 4	BD	0.68	0.20
F3	100 % Forest	14 ± 10	5 ± 1	8 ± 1	50 ± 15	0.1 ± 0.2	0.4 ± 0.3	BD	1.01	0.28
P1	70 % Pasture	18 ± 9	6 ± 0.4	8 ± 2	156 ± 98	1.9 ± 2.4	13 ± 15	5 ± 7	1.00	0.29
P2	61 % Pasture	16 ± 8	6 ± 1	6 ± 3	71 ± 24	2.3 ± 2.7	9 ± 10	0.2 ± 0.5	1.32	0.44
C1	72 % Cropland	20 ± 9	5 ± 0.5	7 ± 2	83 ± 31	0.3 ± 0.2	275 ± 42	BD	1.88	0.30
U1	81 % Urban	22 ± 7	7 ± 1	8 ± 2	302 ± 94	3 ± 4.8	10 ± 7	1.9 ± 4.3	2.26	0.67
U2	94 % Urban	19 ± 4	7 ± 1	7 ± 3	578 ± 172	0.7 ± 0.5	23 ± 18	BD	0.24	0.12

BD below detection

[a] Data are presented as mean ± SD (standard deviation); Means and SD were calculated from samples collected at the five sampling times

density: 18 per km^2 as of 2000). The urban streams were located in Williamsburg, VA (population density: 564 per km^2 as of 2008) and were ca. 35–39 km from the other streams (Fig. 1). During the study period (February–November 2009), monthly mean precipitation ranged between 7 and 21 cm (mean ± SD = 12 ± 5 cm) based on data from climate observation stations located 1–6 km from the sampling sties (the precipitation data were downloaded from www.sercc.com, Southeast Regional Climate Center: Station West Point 2 SW, VA for forest, pasture and cropland streams and Station Willamsburg 2 N for urban streams).

Watershed delineation and classification were conducted in ArcGIS. Based on topographic maps at a scale of 1:24,000 (USGS 1992), the watersheds were first delineated and overlain on aerial photos (1:1,200 or 1:2,400), then divided into polygons of different land use type. The areas of the polygons were calculated to determine the dominant land use type (Table 1). Only the watershed areas upstream of the sampling locations were calculated, with the assumption that stream OM content and biogeochemical characteristics were driven mainly by upstream sources and processes.

Sample collection

In the sampled watersheds, the time between the storm peak and the termination of overland flow (D) ranged between 13 and 18 h. D was estimated by using $D = 0.827A^{0.2}$, where A represents drainage basin area in square kilometers (Fetter 2001). All streams were sampled ≥24 h after rain events to ensure that the samples were collected during base flow periods. Water samples were collected in acid cleaned (10 % HCl) polycarbonate carboys (20 l) with a Masterflex® E/S™ portable peristaltic pump (Cole-Parmer) equipped with acid-cleaned silicone tubing. Sampling depth ranged between 15 and 30 cm and care was taken to avoid resuspending stream sediments. Samples were stored in the dark on ice for up to 6 h before processing. In the laboratory, ~8–10 l water samples were transferred to stainless steel tanks that were rinsed sequentially with Methanol, Acetone, and Hexane. The tanks were pressurized with ultra-high purity N_2 gas to filter the water through pre-combusted glass fiber filters (142 mm, Gelman A/E, norminal pore size 1 μm) for collecting POM. Filters were folded carefully, wrapped with pre-combusted Al foil and kept frozen at −80 °C until extraction.

Lipid analysis

The POM sample filters were shredded using solvent cleaned forceps and mixed with pre-combusted hydromatrix (Varian®) to remove water. Lipid extraction followed the method described by Poerschmann and Carlson (2006) using a Dionex accelerated solvent extraction system (ASE 350). To separate neutral and polar lipids, ~500 mg of cyanopropyl sorbent (Supelco®, Discovery-CN, 7 % 3-cyanopropyl) was placed into each ASE cell. Each sample filter was then added to an individual ASE cell, followed by addition of a mixture of surrogate standards consisting of a C_{19} FA methyl ester (FAME; methyl nonadecanoate), a C_{19} alcohol (nonadecanol), a wax ester (myristyl arachidate) comprised of a C_{20} FA and a C_{14} alcohol, and androstanol. Some of the standards were used to provide extraction recoveries for different lipid compound classes (e.g., C_{19} FAME, C_{19} alcohol and androstanol) while the wax ester (myristyl arachidate) was used to evaluate the recovery of the saponification and subsequent steps in the procedure. Neutral lipids (NL) were extracted with hexane:acetone (9:1, v:v) at 50 °C, and polar phospholipids (PL) were extracted with $CHCl_3$:MeOH (1:4, v:v) at 80 °C. Following extraction, samples were concentrated and saponified with

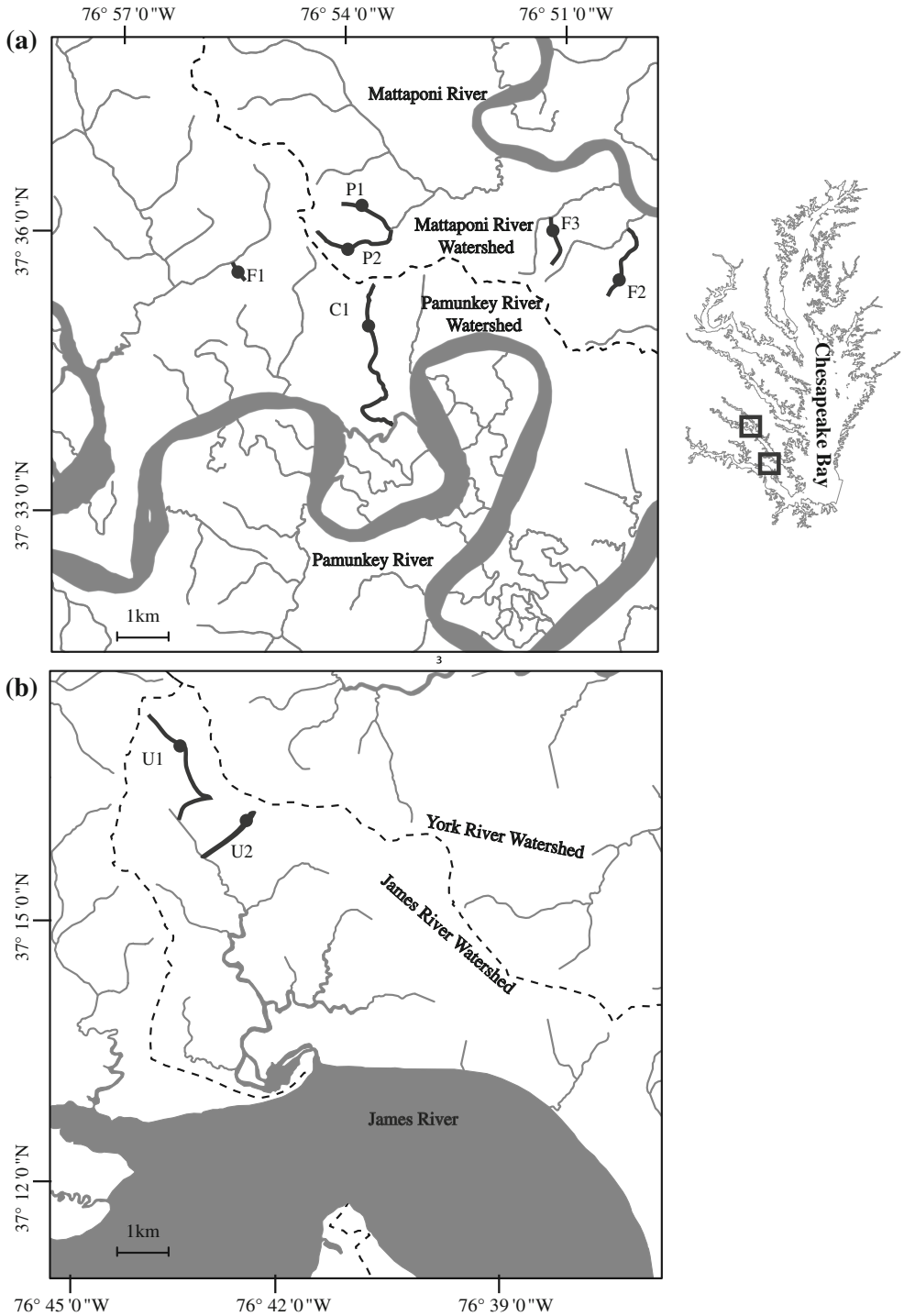

Fig. 1 Locations of study sites within the **a** York River estuary and **b** James River watersheds in Virginia (USA). Sampling streams are indicated by *heavy black lines* and sampling sites are indicated by *solid black dots*. Other streams in this area that were not sampled are indicated by *grey lines*. The *black dashed line* delineates watershed boundaries of the major rivers

1 N KOH in aqueous MeOH at 110 °C for 2 h, followed by sequential extraction with hexane under basic and acidic conditions yielding saponified neutral lipids (SAP-NL) and neutral and polar lipid fatty acid fractions (NLFA and PLFA, respectively) (Waterson and Canuel 2008; Palomo and Canuel 2010).

The SAP-NL fractions were separated into four main constituent classes using a silica gel column. Alkanes,

aromatics, ketones/aldehydes and aliphatic alcohols/sterols, were eluted using hexane, 25 % toluene in hexane, 5 and 10 % EtOAc in hexane, and 15 and 20 % EtOAc in hexane, respectively. Results from the aliphatic alcohols, sterols and FAs from the NL and PL fractions (i.e., NLFA and PLFA) are presented here.

Prior to gas chromatography (GC) and GC-mass spectrometry, NLFA and PLFA fractions were methylated to FAME using BF_3/MeOH (3 %) and alcohols were derivatized to trimethylsilyl (TMS) ethers using bis(trimethylsilyl)trifluroacetamide. FAME and TMS ethers were quantified using a GC (Hewlett-Packard 5890 Series II Plus) equipped with a 30 m × 0.32 mm DB-5 column and flame ionization detector, and peaks were identified using relative retention times and mass spectral fragmentation patterns (Hewlett-Packard 6890 GC coupled to a mass selective detector). GC conditions for FAME analysis were: 60–110 °C at 20 °C min^{-1}, then to 280 °C (held 5 min) at 3 °C min^{-1}. For TMS ethers, they were: 100–170 °C at 3 °C min^{-1}, then at 3 °C min^{-1} to 310 °C (held 10 min). The carrier gas (He) flow was 0.9 ml min^{-1}. Compounds were quantified from their peak areas relative to the peak areas of internal standards (methyl heneicosanoate for FAME and 5α-cholestane for TMS ethers) added prior to GC injection. The GC response of the two internal standards was evaluated daily using a mixture of 37 FAME compounds (Supelco 37-Component FAME Mix, Sigma) and a customized alcohol mixture consisting of a myristyl alcohol, phytol, nonadecyl alcohol, 5α-androstan-3β-ol, lignoceryl alcohol, 5α-cholestane, cholesterol, campesterol and β-sitosterol (Sigma).

Ancillary measurements

Quartz fiber filters (type QMA, 47 mm, nominal pore size 1 μm) were used to collect POM for elemental and stable isotopic analyses. The POM collected on QMA filters was fumed using concentrated hydrochloric acid in a glass desiccator to remove inorganic carbon (Lorrain et al. 2003). Particulate organic carbon (POC) and particulate nitrogen (PN) concentrations were measured using a Costech elemental analyzer interfaced to a Finnigan Delta Plus Advantage (4th generation) isotope ratio mass spectrometer with a CONFLO-III at the Ohio State University Stable Isotope Facility. All $\delta^{13}C$ values are reported relative to the PDB standard, as $\delta^{13}C = [(R_{sample}/R_{standard}) - 1] \times 1{,}000$, where R is $^{13}C/^{12}C$. The standard deviation (SD) of concentration measurements of duplicate or triplicate filters was $\leq$1.67 μM for POC, $\leq$ 0.21 μM for PN.

Chlorophyll-a (Chl-a) measurements followed Parsons et al. (1984) using a Turner Designs TD-700 fluorometer. Dissolved nutrient species including PO_4^{3-}, NO_3^-, NO_2^- and NH_4^+ were measured using an ion chromatograph (Dionex LC20). Anion and cation mixtures (Alltech anion Mix5 and Dionex six cation-1 standards) were used for constructing calibration curves and Ion-96.3 river water (Environment Canada) was used to determine accuracy. The relative standard deviations for duplicate measurements were within 14.4 % for NO_3^- and 6.6 % for NH_4^+. PO_4^{3-} and NO_2^- concentrations for all samples were below the detection limit for this method (0.8 μM for PO_4^{3-} and 1 μM for NO_2^-).

Statistical analysis

Pearson correlation coefficients (r) were used to examine relationships between variables. Mann–Whitney U tests (for 2 groups) or Kruskal–Wallis tests (for $\geq$3 groups) were used to compare data across land use types and sampling times. A stepwise linear regression model was used to determine the environmental parameter(s) that best predict lipid variability and the model selection was based on R-square (RSQ). Error assumptions, including constant variance, linearity, and normality, were examined using residuals vs. fitted plots and Q–Q plots. The significance level, α, was set at 0.05 for all statistical analyses.

Results and discussion

Our study assesses POM at baseflow conditions, which may differ in chemical makeup and nutritional quality from POM associated with elevated flow or stormflow conditions. For example, Atkinson et al. (2009) found that high flows may transport particles of higher quality to the streams while during baseflow conditions particles showed greater in-stream variability. However, differences in POM between stormflow vs. baseflow conditions are difficult to generalize because they can be influenced by stream parameters varying at local levels, e.g., the distribution of riparian vegetation and channel morphology (Brookshire and Dwire 2003; Atkinson et al. 2009), as well as by antecedent conditions (Vidon et al. 2009). Therefore, our assessment is only applicable to baseflow conditions, which dominate these streams temporally.

Concentrations of lipids associated with POM

Phospholipid linked fatty acids and NLFA concentrations in stream water POM from the eight streams varied between 1.7 and 140.4 μg/mg POC and 0.7–29.5 μg/mg POC, respectively (Table 2), and were positively correlated (Pearson $r = 0.523$, $P < 0.004$). POM showed highly variable concentrations of total aliphatic alcohols and sterols, ranging between 0.6 and 16.4 μg/mg POC and

Table 2 Total concentrations of phospholipid linked fatty acids (PLFA) and neutral lipid fatty acids (NLFA) associated with POM and relative concentrations of the dominant compounds (or groups of compounds) in POM of the study streams

Site	Dominant watershed land use	Sampling date (day/month/year)	PLFA (μg/l)	PLFA (μg/mg POC)	NLFA (μg/l)	NLFA (μg/mg POC)	PLFA: NLFA	Abundance relative to total FA (%)				
								*n*SAFA[a]	MUFA[a]	PUFA[a]	BrFA[a]	LCFA[a]
F1	Forest	01/03/2009	2.0	NA	3.7	NA	0.5	67.4	18.8	12.0	1.8	10.9
F1	Forest	15/05/2009	2.4	7.1	3.7	11.0	0.6	66.6	25.4	4.1	3.9	10.7
F1	Forest	01/07/2009	2.1	7.6	2.1	7.6	1.0	73.5	16.4	4.6	5.6	19.7
F1	Forest	11/09/2009	10.3	27.7	3.7	9.9	2.8	56.9	33.5	2.4	7.2	23.0
F1	Forest	08/11/2009	3.3	10.2	1.1	3.4	3.0	62.3	23.4	6.6	7.8	21.6
F2	Forest	13/03/2009	5.9	18.2	6.6	20.4	0.9	87.2	9.8	1.8	1.3	5.8
F2	Forest	22/05/2009	6.6	7.1	NA	NA	NA	NA	NA	NA	NA	NA
F2	Forest	24/07/2009	NA	NA	2.9	0.7	NA	NA	NA	NA	NA	NA
F2	Forest	08/11/2009	3.8	6.3	1.1	1.8	3.5	54.6	17.7	3.4	24.3	12.8
F3	Forest	13/03/2009	3.6	8.1	1.8	4.1	2.0	77.1	16.6	3.9	2.4	18.4
F3	Forest	22/05/2009	2.3	1.7	6.9	5.0	0.3	60.6	22.1	7.6	9.6	27.8
F3	Forest	24/07/2009	4.7	2.2	2.9	1.3	1.6	60.5	24.3	3.8	11.4	21.0
F3	Forest	08/11/2009	3.3	3.7	0.8	0.9	4.1	66.6	18.5	2.9	12.0	25.9
P1	Pasture	01/03/2009	17.3	8.6	22.9	11.4	0.8	67.0	20.3	12.1	3.6	4.9
P1	Pasture	15/05/2009	10.1	4.5	24.2	10.9	0.4	58.0	30.6	6.8	4.6	7.6
P1	Pasture	07/07/2009	50.0	29.6	41.4	24.5	1.2	35.2	40.4	19.5	4.9	1.4
P1	Pasture	11/09/2009	6.3	5.3	3.1	2.6	2.0	54.1	33.3	0.7	11.9	9.3
P1	Pasture	08/11/2009	7.5	7.2	4.5	4.3	1.7	27.4	67.0	2.5	3.1	6.0
P2	Pasture	01/03/2009	40.6	96.7	12.4	29.5	3.3	82.1	9.0	8.1	0.8	1.2
P2	Pasture	15/05/2009	98.6	NA	61.4	NA	1.6	75.9	16.3	2.4	5.4	16.3
P2	Pasture	01/07/2009	3.5	11.2	3.1	9.9	1.1	57.9	27.0	6.0	9.1	12.0
P2	Pasture	11/09/2009	91.0	140.4	9.2	14.2	9.9	65.9	11.4	8.2	14.5	27.3
P2	Pasture	08/11/2009	4.9	NA	1.7	NA	2.9	62.8	25.4	2.5	9.3	15.2
C1	Cropland	13/03/2009	4.3	NA	2.6	NA	1.7	62.8	21.0	13.6	2.6	7.5
C1	Cropland	24/07/2009	4.3	5.3	2.2	2.7	2.0	60.9	26.6	3.4	9.1	18.1
C1	Cropland	11/09/2009	1.8	5.2	2.6	7.5	0.7	63.1	23.6	4.1	9.2	21.8
C1	Cropland	06/11/2009	7.8	10.5	5.1	6.9	1.5	44.7	38.3	7.0	10.1	7.0
U1	Urban	16/02/2009	3.0	10.4	5.9	20.5	0.5	43.9	34.5	19.0	2.6	2.3
U1	Urban	28/05/2009	1.0	NA	5.4	NA	0.2	62.4	25.3	6.1	6.1	10.9
U1	Urban	06/07/2009	4.4	26.2	3.4	20.2	1.3	55.1	31.0	7.4	6.5	9.1
U1	Urban	08/09/2009	5.9	13.3	6.1	13.7	1.0	44.3	34.9	15.1	5.7	4.2
U1	Urban	03/11/2009	42.7	20.5	17.6	8.4	2.4	42.8	35.8	16.2	5.2	1.6
U2	Urban	19/02/2009	2.1	NA	4.1	NA	0.5	46.3	39.4	8.1	6.2	3.4
U2	Urban	28/05/2009	3.6	13.6	2.4	9.1	1.5	58.2	30.2	6.8	4.8	8.5
U2	Urban	06/07/2009	4.8	25.0	3.0	15.6	1.6	60.0	27.0	7.6	5.3	7.3
U2	Urban	08/09/2009	NA	NA	2.7	8.7	NA	NA	NA	NA	NA	NA
U2	Urban	03/11/2009	2.5	7.7	2.5	7.7	1.0	55.8	34.1	4.4	5.8	4.2

NA data not available because of sample loss during the lipid or POC analyses

[a] *n*SAFA = ∑straight-chain 12:0–32:0; MUFA = ∑14:1, 16:1ω7, 16:1ω5, 18:1ω9c, 18:1ω9t, 19:1, 20:1, 22:1; PUFA = ∑16:4, 16:3, 18:4, 18:3ω6, 18:2ω6, 18:3ω3, 20:4ω6, 20:5ω3, 20:3ω6, 20:3ω3, 22:6ω3, 22:2; BrFA = ∑ iso-, anteiso- 13, 15, 17, 19; LCFA = ∑ *n*-22:0–32:0 FAs

0.4–245.2 μg/mg POC, respectively (Table 2). Land use was an important factor determining the variability of PLFA and NLFA concentrations. Relative to forest streams, urban streams had significantly higher concentrations of PLFA and NLFA (Fig. 2a, b) and pasture streams had higher concentrations of NLFA (Fig. 2b). In contrast, the concentrations of total aliphatic alcohols and sterols were similar across all land use types (Fig. 2c, d). Pasture streams exhibited the greatest variation in concentrations of PLFA and sterols (Fig. 2a, b), largely owing

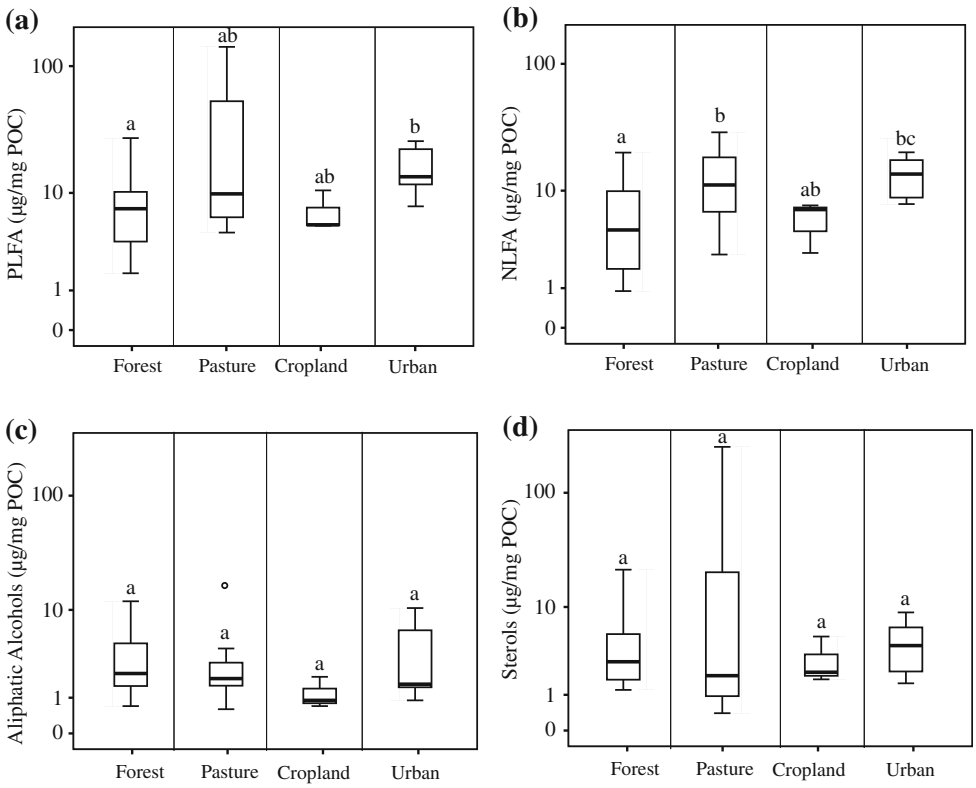

Fig. 2 *Box plot* comparison of the concentrations of different compound classes in POM between watershed land use types for **a** PLFA and NLFA and **b** aliphatic alcohols and sterols. *Open circles* represent outliers (i.e., data beyond the upper/lower quartile ± 1.5 interquartile range). *Different letters above the boxes* signify significant differences in the variables across the land use types, e.g., in *panel* **a**, forest streams differed from urban streams but were not significantly different from pasture and cropland streams

to the exceptionally high values for stream P2 in May and September (Tables 2, 3, 4). These high lipid concentrations may reflect erosion of soil materials due to grazing, since cattle were actively grazing in pastures immediately adjacent to the P2 stream during these 2 months, and/or associated responses of autochthonous stream biota.

Lipid distributions in POM and source assignment of lipids

Fatty acids

Source-specific lipids provide additional information regarding OM sources in streams. The main FA classes found in the stream water POM samples included straight chain, saturated FA (*n*SAFA), monounsaturated FA (MUFA), polyunsaturated FA (PUFA) and branched FA (BrFA) (Table 2). These four classes had similar distributions in PLFA and NLFA, as evidenced by a positive correlation between the relative abundance of these main FA classes in NLFA and PLFA ($r \geq 0.52$, $P \leq 0.002$). Since NLFA and PLFA showed similar distributions, they were combined for estimating the relative contribution of each class to total FA.

Saturated FA ranged between C_{12} and C_{32} and comprised a relatively large portion of the total FA (27.4–87.2 %; mean ± SD = 59.7 ± 12.5 %) (Table 2). Overall, 16:0 and 18:0 were the dominant *n*SAFA in most samples, with 16:0 accounting for 12.5–57.9 % (mean ± SD = 41.7 ± 10.0 %) of total FA and 18:0 comprising 2.9–50.7 % (16.0 ± 10.8 %) of total FA. Since 16:0 and 18:0 are prevalent in both aquatic and terrestrial organisms (Cranwell 1982), their relative abundances are not helpful for providing information about the proportions of allochthonous vs. autochthonous sources of POM. In contrast, long chain *n*-FAs $\geq C_{22}$ (i.e. LCFA) are derived from leaf waxes of terrestrial plants and hence commonly used for representing contributions from terrestrial vascular plants to water and sediment (Eglinton and Hamilton 1967; Cranwell 1982). Long chain *n*-FAs $\geq C_{22}$ accounted for 1.2–27.8 % (mean ± SD = 11.9 ± 8.0 %) of total FA (Table 2).

Monounsaturated FA, generally dominated by 16:1ω7, 18:1ω9c and 18:1ω9t (Table 2), was the second most abundant FA group in most samples and showed high variability across samples, constituting 9.0–67.0 % (mean ± SD = 26.4 ± 10.8 %) of total FA. Polyunsaturated FA were less abundant than *n*SAFA and MUFA, accounting for levels ranging from 1.8 to 19.5 % (7.2 ± 4.8 %) of total FA (Table 2). Polyunsaturated FA compounds included 16:4, 16:3, 18:4, 18:3ω6, 18:2ω6, 18:3ω3, 20:4ω6, 20:5ω3, 20:3ω6, 20:3ω3, 22:6ω3 and 22:2. C_{16} and C_{18} MUFA and PUFA are abundant in a variety of sources including terrestrial plants (Millar et al.

Table 3 Total concentrations of aliphatic alcohols associated with POM and relative concentrations of the compounds (or groups of compounds) in POM of the study streams

Site	Dominant watershed land use	Sampling date (day/month/year)	Total alcohols (μg/L)	Total alcohols (μg/mg POC)	Abundance relative to total aliphatic alcohols (%)									
					15:0	16:1	16:0	17:0	18:0	20:0	22:0	24:0	26:0	∑22:0-30:0
F1	Forest	01/07/2009	3.3	12.0	1.6	1.4	10.6	2.7	6.1	7.6	0.3	36.4	19.3	70.0
F1	Forest	11/09/2009	1.5	4.0	2.0	1.1	14.6	2.7	8.4	0.0	0.2	31.1	18.1	71.3
F1	Forest	08/11/2009	0.7	2.2	1.5	1.2	11.5	6.4	24.0	0.0	12.3	18.6	18.4	55.4
F2	Forest	13/03/2009	1.8	5.6	1.3	0.0	5.8	2.3	14.8	0.0	31.7	10.1	34.1	75.8
F2	Forest	24/07/2009	2.7	0.6	0.7	0.7	12.7	4.9	7.6	0.0	29.7	26.3	12.4	73.5
F2	Forest	08/11/2009	0.4	0.7	2.3	0.0	9.2	7.9	25.3	0.0	12.4	16.9	14.7	55.5
F3	Forest	13/03/2009	0.5	1.1	0.6	1.7	6.5	2.3	15.4	0.0	30.3	24.9	15.3	73.6
F3	Forest	24/07/2009	2.7	2.0	0.7	0.7	12.7	4.9	7.6	0.0	29.7	26.3	12.4	73.5
P1	Pasture	01/03/2009	3.8	1.9	2.3	0.0	14.7	4.5	33.2	0.1	23.8	9.9	5.9	45.2
P1	Pasture	01/07/2009	3.3	2.0	14.9	0.0	40.0	0.0	10.7	0.9	20.1	8.2	0.0	33.5
P1	Pasture	11/09/2009	1.4	1.2	0.5	1.0	9.9	4.5	11.3	0.3	31.9	11.1	11.3	72.7
P1	Pasture	08/11/2009	0.6	0.6	1.4	0.9	16.9	3.2	28.0	0.0	11.1	12.0	21.3	49.6
P2	Pasture	01/03/2009	0.8	1.9	4.3	1.1	24.6	2.7	18.6	0.0	19.3	9.2	7.1	48.8
P2	Pasture	01/07/2009	1.3	4.2	0.8	3.3	21.4	12.4	9.3	4.5	27.3	7.9	8.3	48.4
P2	Pasture	11/09/2009	10.6	16.4	8.1	0.7	22.8	2.3	12.1	0.0	18.1	18.6	17.4	54.0
P2	Pasture	08/11/2009	0.8	NA	12.2	0.7	26.8	1.0	21.2	0.0	9.7	7.4	10.7	38.1
C1	Cropland	13/03/2009	0.8	NA	0.0	0.6	24.9	3.7	18.8	0.1	28.6	11.5	9.4	51.9
C1	Cropland	24/07/2009	0.7	0.9	9.0	0.0	0.0	0.0	1.2	0.0	57.4	28.7	0.0	89.8
C1	Cropland	11/09/2009	0.7	2.0	0.6	0.0	9.7	4.0	17.9	0.0	34.7	10.7	8.8	67.8
C1	Cropland	06/11/2009	0.5	0.7	5.4	0.0	24.2	0.0	32.9	0.0	0.0	16.9	0.0	37.4
U1	Urban	16/02/2009	0.4	1.4	2.2	1.7	16.2	7.0	19.0	0.0	32.3	6.6	4.5	54.0
U1	Urban	06/07/2009	1.3	7.7	2.2	3.0	2.2	6.6	13.1	0.0	43.8	14.3	12.9	72.9
U1	Urban	08/09/2009	0.7	1.6	0.4	1.0	10.6	4.1	13.2	0.0	28.4	9.9	12.3	70.8
U1	Urban	03/11/2009	1.9	0.9	1.9	1.4	8.1	0.0	6.5	6.8	19.6	7.4	6.7	75.3
U2	Urban	19/02/2009	0.4	NA	4.0	1.2	16.4	5.0	20.2	0.0	27.5	5.8	7.6	53.1
U2	Urban	28/05/2009	1.4	5.3	1.2	1.1	24.8	9.1	10.9	0.0	42.4	6.2	4.4	52.9
U2	Urban	06/07/2009	2.0	10.4	3.5	3.5	27.1	8.5	6.9	4.0	31.9	4.8	4.3	46.5
U2	Urban	03/11/2009	0.5	1.5	3.9	1.1	16.6	5.6	17.5	1.4	38.9	4.5	4.2	53.9

NA data not available because POC data were not available

2000), diatoms (Sicko-Goad et al. 1988, Volkman et al. 1989; Canuel and Martens 1993; Canuel 2001), some cyanobacteria (Napolitano 1998 and references therein; Ahlgren et al. 1992), and aquatic animals (Sargent 1976; Wakeham and Canuel 1990; Napolitano 1998), and therefore were not used for source identification in the present study. Long-chain PUFAs (carbon number ≥20) were used, however, to indicate nutritional quality of POM (see details in "The quality of POM as a potential food source to stream consumers").

BrFA included *iso*- and *anteiso*-13, 15, 16, 17, 19, which together comprised 0.8–24.3 % (26.4 ± 10.8 %) of total FA (Table 2). These compounds are synthesized by some gram-positive and sulfate reducing bacteria (Kaneda 1991), and are commonly attributed to heterotrophic bacterial sources with the caveat that not all bacteria synthesize these compounds (e.g. Waterson and Canuel 2008 and references therein).

Aliphatic alcohols

Aliphatic alcohols ranged between C_{15} and C_{30} and were dominated by even-numbered homologues (*n*-C_{14} and *n*-C_{19} were not quantified because the former was contributed via saponification of the surrogate standard myristyl arachidate and the latter was present in the surrogate). Most samples were dominated by even-numbered aliphatic alcohols ≥C_{22} (long chain alcohols, LCOL), which accounted for 33.5–89.8 % (mean ± SD = 59.5 ± 14.2 %) of total aliphatic alcohols (Table 3). Aliphatic alcohols ≥C_{22} (LCOL) with strong even dominance are derived primarily from plant waxes (Tulloch 1976;

Table 4 Total concentrations of sterols associated with POM and relative concentrations of the dominant compounds in POM of the study streams

Site	Dominant watershed land use	Sampling date (day/month/year)	Sterols (μg/L)	Sterols (μg/mg POC)	Abundance relative to total sterols (%)									
					$27\Delta^{5,22}$	$27\Delta^{5}$	$27\Delta^{0}$	$28\Delta^{5,22}$	$28\Delta^{5}$	$28\Delta^{0}$	$29\Delta^{5,22}$	$29\Delta^{22}$	$29\Delta^{5}$	$29\Delta^{0}$
F1	Forest	01/03/2009	0.5	NA	0.0	24.3	0.0	3.6	4.7	0.0	17.6	0.0	44.5	5.3
F1	Forest	15/05/2009	0.6	1.8	0.0	31.2	1.9	5.1	6.5	0.0	9.7	0.0	40.0	5.7
F1	Forest	01/07/2009	6.0	21.7	1.4	17.5	4.6	1.8	6.3	1.7	7.6	4.4	38.9	15.9
F1	Forest	11/09/2009	3.2	8.6	0.0	24.5	3.0	3.6	9.4	0.0	8.4	0.0	51.1	0.0
F1	Forest	08/11/2009	1.1	3.4	0.9	19.9	2.1	3.6	6.5	0.0	7.8	2.5	40.0	16.7
F2	Forest	13/03/2009	0.9	2.8	0.0	60.9	0.0	0.0	1.8	0.0	5.1	2.9	29.3	0.0
F2	Forest	22/05/2009	0.7	0.8	0.0	34.6	0.0	3.1	3.5	0.0	12.3	0.0	46.5	0.0
F2	Forest	08/11/2009	0.7	1.2	0.0	24.8	2.4	3.5	6.4	1.8	8.2	1.3	35.6	15.9
F3	Forest	13/03/2009	0.6	1.4	1.0	42.2	0.0	0.0	2.7	0.0	19.9	0.9	31.3	2.1
F3	Forest	22/05/2009	2.8	2.0	0.0	19.3	1.2	4.4	6.7	0.0	11.4	11.4	39.1	6.5
F3	Forest	24/07/2009	3.7	1.7	2.2	22.2	2.0	3.8	6.8	1.0	10.1	2.7	41.8	7.7
P1	Pasture	01/03/2009	7.9	8.9	0.0	10.2	1.3	21.4	36.3	0.0	8.9	0.2	17.9	3.9
P1	Pasture	15/05/2009	1.9	0.9	0.0	40.0	2.1	6.9	0.0	0.0	14.9	0.0	36.1	0.0
P1	Pasture	01/07/2009	7.0	3.2	0.9	19.3	2.3	8.7	7.1	0.8	39.3	0.7	17.2	3.9
P1	Pasture	11/09/2009	1.7	1.0	0.0	26.5	4.7	4.1	9.8	0.0	11.6	0.0	31.0	12.4
P1	Pasture	08/11/2009	0.5	0.4	0.0	38.3	4.9	3.1	6.9	2.7	8.3	0.0	30.4	5.5
P2	Pasture	01/03/2009	3.4	3.3	0.0	7.1	1.3	19.6	37.7	0.0	12.9	1.8	14.2	5.5
P2	Pasture	15/05/2009	45.1	107.4	0.0	13.0	5.7	5.1	41.3	0.0	2.9	1.9	16.9	13.2
P2	Pasture	01/07/2009	1.7	NA	0.6	36.6	3.3	4.6	12.0	0.0	8.5	0.3	27.5	6.7
P2	Pasture	11/09/2009	76.5	245.2	0.0	9.5	7.0	6.3	32.6	0.0	4.6	4.3	35.8	0.0
P2	Pasture	08/11/2009	1.2	1.9	1.2	19.7	6.0	9.0	13.8	0.0	11.8	0.0	23.8	14.7
C1	Cropland	13/03/2009	1.0	NA	0.8	34.9	1.2	4.8	4.0	0.0	16.3	1.0	33.1	4.0
C1	Cropland	22/05/2009	1.1	NA	0.0	31.0	0.0	3.9	8.6	0.0	10.5	0.0	39.3	6.7
C1	Cropland	24/07/2009	1.7	2.1	0.8	24.6	6.0	3.0	8.2	2.0	9.0	0.6	33.6	12.3
C1	Cropland	11/09/2009	1.8	5.2	0.0	11.7	1.7	10.4	46.3	0.0	3.9	3.9	17.5	4.6
C1	Cropland	06/11/2009	1.3	1.7	0.0	12.4	0.0	6.2	10.1	0.0	27.2	0.0	29.2	14.8
U1	Urban	16/02/2009	1.6	5.6	0.0	11.1	1.3	23.7	43.0	0.0	5.4	0.0	13.5	2.0
U1	Urban	28/05/2009	1.2	NA	0.0	30.9	3.4	4.1	14.5	0.0	7.7	0.0	30.3	9.2
U1	Urban	06/07/2009	1.5	8.9	0.0	37.3	5.5	3.2	7.8	0.0	9.2	0.2	28.1	8.7
U1	Urban	08/09/2009	1.0	2.3	0.0	38.0	3.4	5.7	10.3	0.0	11.1	0.2	26.3	5.1
U1	Urban	03/11/2009	4.2	2.0	2.4	32.2	0.0	13.5	18.5	0.0	14.0	0.4	19.1	0.0
U2	Urban	19/02/2009	1.0	NA	0.0	15.3	2.6	18.2	36.1	0.0	0.0	4.5	18.6	4.7
U2	Urban	28/05/2009	1.1	4.2	0.5	40.2	4.0	5.2	4.8	0.0	6.9	0.0	33.8	4.7
U2	Urban	06/07/2009	1.4	7.3	0.0	35.3	2.8	5.5	3.5	0.0	9.7	4.5	38.6	0.0
U2	Urban	08/09/2009	0.6	1.9	0.0	32.4	1.5	3.0	2.6	0.0	6.8	24.7	26.8	2.1
U2	Urban	03/11/2009	0.5	1.5	1.0	49.3	4.5	3.6	4.8	0.0	6.2	0.3	27.5	2.9

NA data not available because POC data were not available

Simoneit 1977; Cranwell 1982) and thus are referred to here as "allochthonous alcohols". Allochothonous alcohols accounted for high relative abundance in most POM samples of, i.e., 33.5–89.8 % (59.5 ± 14.2 %). The *n*-C_{16} and *n*-C_{18} alcohols were also abundant in many samples, comprising 15.8 ± 8.9 and 15.4 ± 8.1 % of total aliphatic alcohols, respectively (Table 3). Short-chain ($C_{\leq 18}$) saturated aliphatic alcohols are found in bacteria (Albro 1976), plants (Simoneit 1977; Simoneit and Mazurek 1982) and algae (Volkman et al. 1998). However, since these compounds are not major constituents of plant waxes (Tulloch 1976; Simoneit 1977; Simoneit and Mazurek 1982), they are often ascribed to aquatic sources (Medeiros and Simoneit 2008). 16:1 was the only

unsaturated aliphatic alcohol found, albeit at low abundance (Below Detection to 3.5 %) (Table 3), likely representing contributions from freshwater algae (Volkman et al. 1998; Ahlgren et al. 1992; Napolitano 1994). We thus assigned $C_{\leq 18}$ aliphatic, saturated alcohols and $C_{16:1}$ to aquatic sources (referred to as "autochthonous alcohols"); these compounds represented 10.2–65.5 % (39.5 ± 14.5 %) of total aliphatic alcohols.

Sterols

The sterols detected in the present study included: cholesta-5,22-dien-3β-ol ($27\Delta^{5,22}$), cholest-5-en-3β-ol ($27\Delta^{5}$), 5α(H)-cholestan-3β-ol ($27\Delta^{0}$), 24-methylcholesta-5,22-dien-3β-ol ($28\Delta^{5,22}$), 24-methylcholest-5-en-3β-ol ($28\Delta^{5}$), 24-methyl-5α(H)-cholestan-3β-ol ($28\Delta^{0}$), 24-ethylcholest-5,22-dien-3β-ol($29\Delta^{5,22}$), 24-ethyl-5α(H)-cholest-22-en-3β-ol ($29\Delta^{22}$), 24-ethylcholest-5-en-3β-ol($29\Delta^{5}$) and 24-ethyl-5α(H)-cholestan-3β-ol ($29\Delta^{0}$) (Table 4). In most samples, $27\Delta^{5}$ and $29\Delta^{5}$ were the most abundant sterols, accounting for 27.2 ± 12.4 and 30.7 ± 9.6 % of total sterols, respectively.

Three sterols, $28\Delta^{5}$, $29\Delta^{5,22}$ and $29\Delta^{5}$, were assigned to allochthonous sources since they are found primarily in higher plants (Bae and Mercer 1970; Wannigama et al. 1981; Volkman 1986; Waterson and Canuel 2008). Three others, $27\Delta^{5,22}$, $27\Delta^{5}$, and $28\Delta^{5,22}$, were considered autochthonous in origin (Table 4) because they have been observed to be prevalent in diatoms, zooplankton and protozoa (Wakeham and Canuel 1990). Allochthonous and autochthonous sterols comprised 15.7–60.9 % (34.1 ± 10.3 %) and 7.3–68.9 % (52.9 ± 11.5 %) of total sterols, respectively.

Two types of source-specific sterols were expected but not found in our samples, perhaps because of the relatively small volumes of water filtered for POM (8–10 l). The first type is fecal sterols, such as 5β(H)-stanols, which are products of microbial degradation of sterols and therefore generally used to indicate the presence of animal fecal matter (Nishimura 1982; Li et al. 1995; Pratt et al. 2007). These compounds were expected to be present in pasture streams due to grazing activities adjacent to the streams but not detected. The second type is the fungal sterol, 22-E-ergosta-5,7,22-trien-3β-ol (ergosterol), which is the predominant sterol in fungi and often used to detect and quantify fungi in biological samples (Gessner and Chauvet 1993; Martin-Creuzburg and Von Elert 2009b). Fungi are generally prevalent in small watersheds as the dominant organisms decomposing leaf litter in headwater streams and mediating energy transfer to other trophic levels (Gulis et al. 2008). However, ergosterol was not detected in our samples.

Changes in stream water POM sources due to human land use

The sources and quality of POM in the study streams were initially evaluated using δ^{13}C-POC and C:N ratio (Lu et al. 2014). δ^{13}C-POC values ranged between −33.3 and −27.6 ‰ (Lu et al. 2014), falling in the general range of values for C_3 terrestrial organic matter, freshwater algae, and petroleum sources of organic matter (Schidlowski et al. 1983; Faure and Mensing 2005; Ogrinc et al. 2008). For C:N ratios, terrestrial higher plants typically have values greater than 20 while algal/microbial sources have values between 4 and 10 (Wetzel 1983; Meyers and Ishiwatari 1993; Kendall et al. 2001). In the study streams, the C:N values of POM ranged from 7.4 to 19.4 (Fig. 3a; Lu et al. 2014), indicating that most POM originated from mixed sources including terrestrial plants, soils and microbes.

The source information from the C:N ratios was corroborated by the lipid biomarkers, which have greater source specificity and thus provide a more quantitative measure of allochthonous vs. autochthonous inputs to POM. Particulate organic matter in most of these headwater streams was dominated by allochthonous sources, as shown by a comparison of aliphatic alcohols and sterols from allochthonous vs. autochthonous sources (59.5 ± 14.2 vs. 39.6 ± 14.5 % for aliphatic alcohols and 52.9 ± 11.5 vs. 34.1 ± 10.3 % for sterols). Note that the sum of these two groups is <100 % since not all compounds were assigned to a source. This observation agrees with many previous studies reporting the preponderance of allochthonous OM in headwater streams, which is delivered to streams through foliage and litter input and soil runoff, and is often the primary energy and food source for stream biota (Webster and Meyer 1997; Mills et al. 2003; França et al. 2009). Additionally, none of the variables representing the relative contributions of autochthonous vs. allochthonous sources to POM (i.e., %LCFA, %allochthonous alcohols; %autochthonous alcohols; %allochthonous sterols; %autochthonous sterols) showed significant correlations with the concentrations of Chl-a, dissolved ammonium or nitrate ($|r| \leq 0.22$, $P > 0.191$), confirming that the source composition of POM was driven primarily by allochthonous inputs.

The predominant contributions of allochthonous OM, however, are influenced by human land use in our study watersheds, as illustrated by the patterns shared by C:N ratios and the three biomarker groups. Although significant differences were not consistently detected for all source proxies across all land use types, streams influenced by human land use had overall lower allochthonous contributions to POM and higher proportions of autochthonous POM than forest streams (Fig. 3a–f). This pattern was most

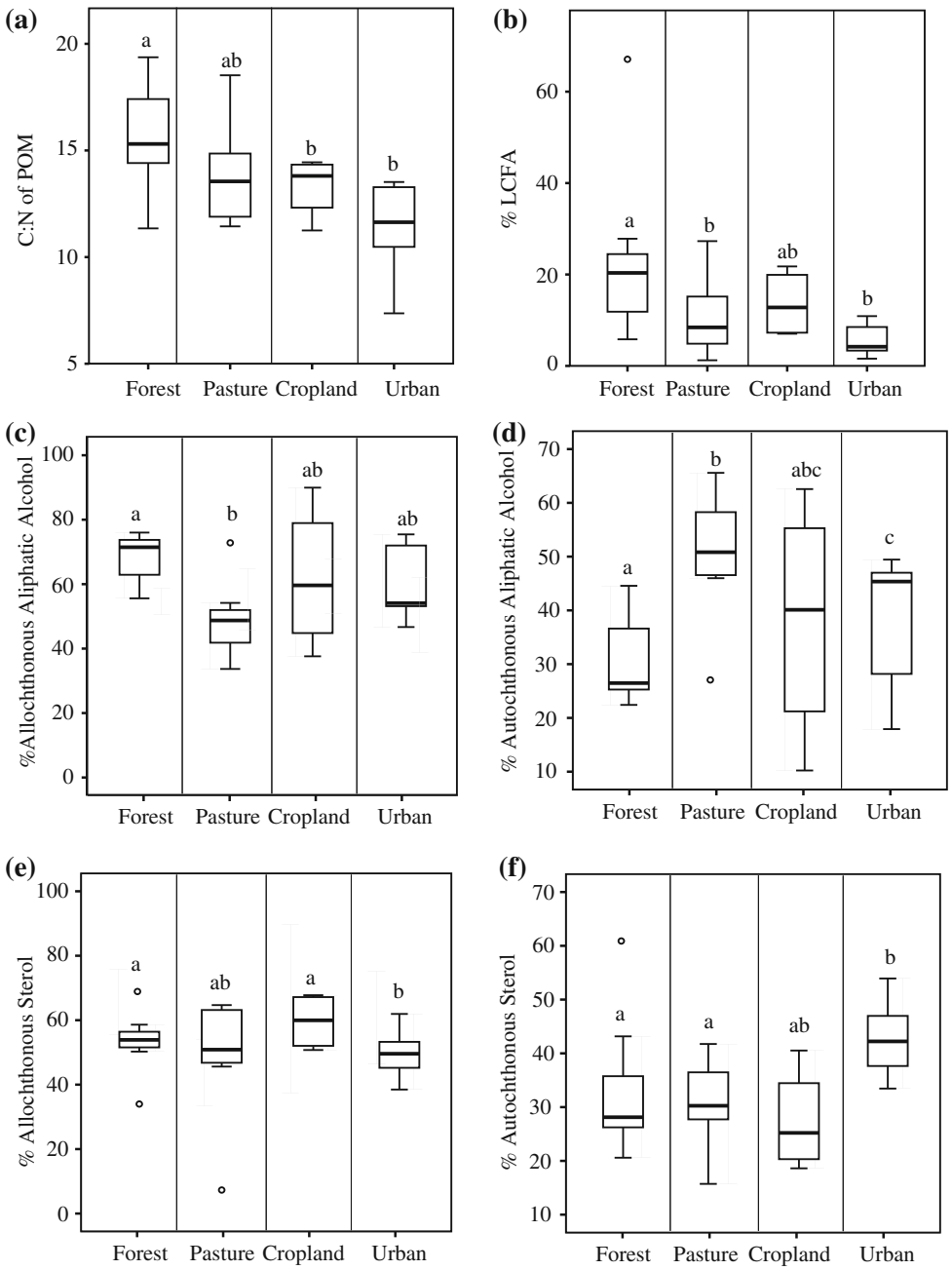

Fig. 3 *Box plot* comparison for different watershed land use types of **a** C:N ratios (from Lu et al. 2014) **b** %LCFA (*n*-22:0–32:0 FAs) **c** %allochthonous aliphatic alcohols **d** % autochthonous aliphatic alcohols **e** % allochthonous sterols, and **f** autochthonous sterols. Kruskal–Wallis tests identified significant differences in values between the four defined land use types ($P < 0.05$). *Open circles* represent outliers (i.e., data beyond the upper/lower quartile ± 1.5 interquartile range); *different letters above the boxes* signify significant difference in the variables across the land use types

evident in urban streams, where all the proxies except %allochthonous aliphatic alcohols differed significantly from forest streams, but was least apparent in cropland streams, where only C:N ratios were significantly lower than forest streams (Fig. 3a–f). These observations demonstrate the importance of watershed development in determining the relative contributions of allochthonous vs. autochthonous sources to POM in stream waters. As a result of converting forested watersheds to human land uses, the proportion of POM of allochthonous origin may decrease while the contribution of POM from autochthonous sources may increase. This change may be attributed to a number of factors associated with watershed development, including reduction of forests, a major source of higher plant derived organic matter, and decreases in forest cover, which increase light penetration to streams, promoting aquatic algal growth and preferentially photo-oxidizing terrestrial compounds over aquatic compounds (Opsahl and Zepp 2001; Osburn et al. 2001; Spencer et al. 2009; Lu et al. 2013). Additionally, increases in watershed exports of anthropogenic nutrients and organic waste may stimulate aquatic productivity and increase the relative abundance of autochthonous OM. This study presents one of the few available lipid datasets demonstrating alterations

to the sources of stream water POM by human land use, and the findings agree with reported changes in the basal carbon sources for stream foodwebs due to human land use—i.e., changing from allochthonous carbon in forest streams to a mixture of allochthonous and autochthonous sources in unshaded pasture streams (Hicks 1997). Similar changes have also been found for the sources of DOM in streams and rivers; that is, watershed development reduces the contributions of terrestrial DOM but increases the contributions of microbial/autochthonous DOM (Wilson and Xenopoulos 2009; Williams et al. 2010; Yamashita et al. 2011; Lu et al. 2013).

Variation in bacterial lipids in POM

Land use was not an important factor influencing variation in the proportion of bacterial lipids associated with POM (Kruskal–Wallis test: $P = 0.547$). Instead, sampling month was found to be the dominant factor driving variation in %BrFA (Kruskal–Wallis test: $P = 0.003$; Fig. 4a). This further suggests that the relative contributions of bacterial lipid to POM were controlled by seasonal factors. Relative to NLFAs that are derived from storage lipids and persist over a longer time, PLFAs in membrane lipids are more susceptible to decomposition, typically degrading soon after cell death (Parkes 1987), and thus represent viable, or recently viable, biomass (Palomo and Canuel 2010). Therefore, we used %BrFA in PLFA (%PBrFA) as a putative proxy for the contribution of viable bacterial biomass to the fresh POM pool and %BrFA in NLFA (%NBrFA) for the contribution of bacteria to the more resistant POM pool. Similar to %BrFA, %PBrFA and %NBrFA both differed among seasons (Kruskal–Wallis test: %PBrFA: $P = 0.002$; %NBrFA: $P = 0.007$; Fig. 4b, c) but not among land use types (Kruskal–Wallis test: %PBrFA: $P = 0.77$; %NBrFA: $P = 0.796$). In particular, POM collected in February–March had lower contributions of bacterial lipids than POM from other months (Fig. 4a–c).

Because stream bacterial communities may be influenced by multiple biotic and abiotic parameters including temperature (Sand-Jensen et al. 2007; Lear et al. 2008), pH (Fierer et al. 2007; Pip and Reinisch 2012), dissolved oxygen (O'Connell et al. 2000), nutrient availability (Barlett and Leff 2010; Pip and Reinisch 2012), OM sources and quality (Koetsier et al. 1997; McArthur and Richardson 2002), and flood/storm events (Holmes et al. 1998), we employed a stepwise linear regression model to identify the main factor(s) driving the variation in %PBrFA and %NBrFA. In the present study, the influence of flood/storm events was not considered because all the samples were collected under baseflow conditions. OM quality, although not directly measured, may be indicated by

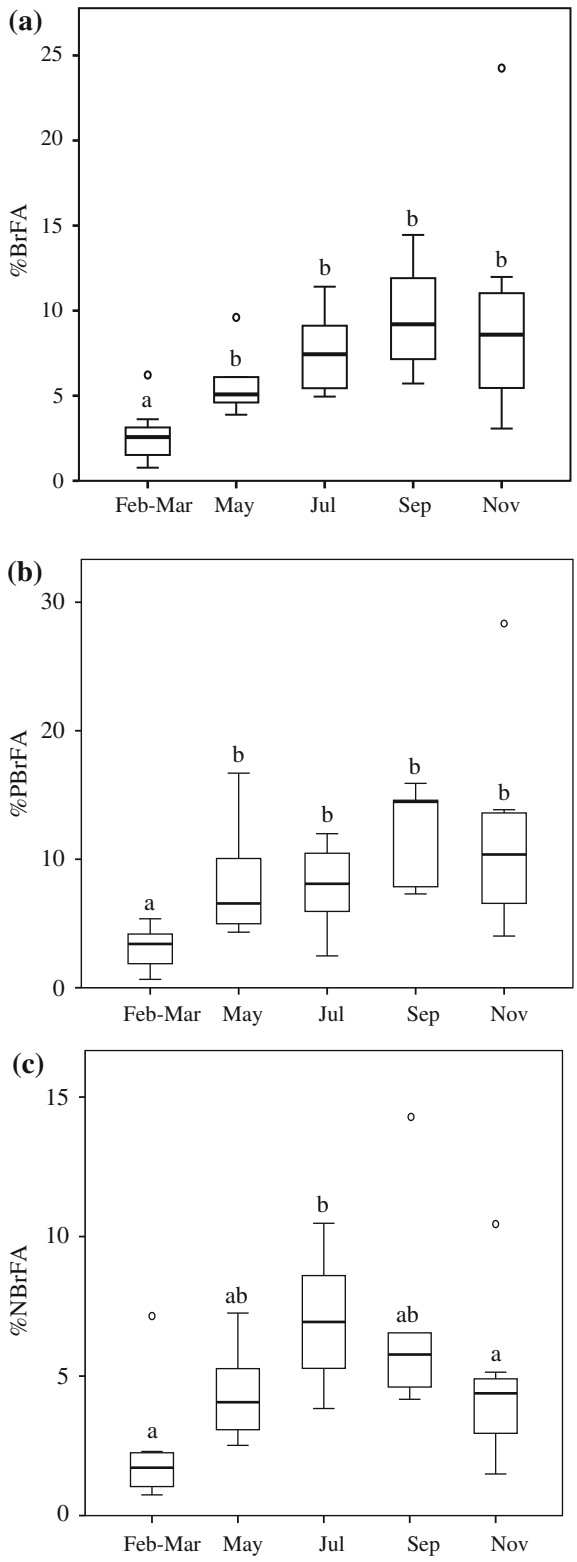

Fig. 4 *Box plot* comparison for the five sampling times of percent abundance of **a** BrFA (iso-, anteiso- 13, 15, 17, 19) **b** phospholipid linked BrFA, and **c** neutral lipid linked BrFA. *Open circles* represent outliers (i.e., data beyond the upper/lower quartile ± 1.5 interquartile range); *different letters* above the *boxes* signify significant difference in the variables across the land use types

%PUFA. Polyunsaturated FAs are overall more reactive than more saturated fatty acids and their abundance may be used to indicate the "freshness" and reactivity of OM in sediment, particles and leaves (Canuel and Martens 1993; McCallister et al. 2006; Torres-Ruiz and Wehr 2010). The model therefore evaluated a series of variables as potential predictors of %PBrFA and %NBrFA, including in situ environmental variables (temperature, pH, DO, conductivity), the concentrations of dissolved inorganic nutrients (nitrate and ammonium), OM reactivity (%PUFA) and OM sources (indicated by Chl-a, C:N ratios, %autochthonous alcohols, %allochthonous alcohols, %autochthonous sterols, %allochthonous sterols). In turn, nitrate and temperature were selected as the best predictors of %PBrFA (%PBrFA = −0.154 + 0.501*(Nitrate) + 0.342*(Temperature), $P = 0.001$, RSQ = 0.643) and temperature was the best predictor of %NBrFA (%NBrFA = −0.432 + 0.385*(Temperature), $P = 0.01$, RSQ = 0.469) (note that both predictors and dependent variables were standardized).

Our results indicate that temperature is an important factor regulating the relative abundances of bacterial lipids in POM and higher temperatures corresponded to greater contributions of bacterial biomass. This observation explains the lower contributions of bacterial lipids to POM in March (Fig. 4) and is consistent with previous studies showing that temperature can regulate stream bacterial community structure and metabolism (Sand-Jensen et al. 2007; Lear et al. 2008). The inputs of viable bacterial biomass were also influenced by dissolved nitrate concentration, in agreement with many previous observations that inorganic nutrient availability is an important factor regulating bacterial growth and metabolism (Bonin et al. 2000; Barlett and Leff 2010; Pip and Reinisch 2012). The positive correlation between nitrate and %PBrFA also implies that watershed development may enhance the contributions of viable bacterial biomass since human land use is generally associated with elevated nitrate inputs (e.g., cropland streams in the present study (Table 1)). This pattern was, however, not systematically observed here (i.e., no significant differences were found in %PBrFA across the watershed land use types), perhaps due to a combination of the confounding influence of temperature and the small sample size.

POM as a potential food source to stream consumers

Particles in headwater streams may serve as an important food source for stream invertebrates. While there is no commonly accepted proxy that alone can evaluate the nutritional quality of food sources to aquatic biota (e.g., Martin-Creuzburg and Von Elert 2009a), biochemical composition of POM may serve as an indicator of nutritional quality of particles as a food source to consumers (Canuel et al. 1995; Hicks 1997; Lau et al. 2008; Newcomer et al. 2012). The most common measure of nutritional quality is elemental composition (C:N), where high values are attributed to lower food quality due to lower levels of protein and other N-rich substrates (Hicks 1997; Elser et al. 2000; Atkinson et al. 2009). In our study, C:N was used to assess relative contributions of allochthonous vs. autochthonous sources to POM, which is an indirect way of using C:N as an indicator of the nutritional value of POM since higher plant OM is generally thought to be lower in nutritional value than OM from aquatic organisms. C:N ratios differed between land use types (Fig. 3a) but not among sampling months (Kruskal–Wallis test: $P = 0.191$), indicating that watershed land use was a more important determinant of the nutritional quality of POM to stream consumers than seasonal variation. On this basis, POM in cropland and urban streams is deduced to have greater nutritional quality to consumers that POM in forest streams (Fig. 3a).

Lipid composition may serve as another proxy for assessing the nutritional value of POM. Results from many previous growth assay experiments have shown that particles containing large amounts of cholesterol ($27\Delta^5$) and long-chain PUFAs may benefit the growth and production of consumers such as *Daphnia magna*, and may increase the efficiency of energy transfer between primary producers and consumers (Muller-Navarra et al. 2000, 2004; Martin-Creuzburg and von Elert 2004, 2009a). These compounds may thus increase the nutritional value of POM due to their being key components of animal cell membranes and precursors of many bioactive molecules with important functions; e.g., eicosapentaenoic acid (EPA; 20:5ω3) is precursor of prostaglandins for arthropod reproduction; $27\Delta^5$ is precursor for steroid hormones (Muller-Navarra et al. 2000; Von Elert et al. 2003; Martin-Creuzburg and Von Elert 2009b). In our samples, we examined four commonly used proxies to assess the nutritional status of POM to stream biota: the concentrations (ng lipid/mg POC) of long-chain PUFA, EPA, arachidonic acid (ARA, 20:4ω6), and $27\Delta^5$ in POM. We did not use DHA (docosahexaenoic acid, 22:6ω3), another typical proxy for nutritional value, because concentrations of DHA were below detection for all samples. None of these four proxies differed among sampling times (Kruskal–Wallis test: long-chain PUFA: $P = 0.265$; $27\Delta^5$: $P = 0.401$; EPA: $P = 0.138$; ARA: $P = 0.171$), indicating that seasonal variability may not be an important factor influencing the nutritional quality of POM in these headwater streams. In contrast, land use was more important for influencing the nutritional quality of POM. Three of the four proxies (i.e., long-chain PUFA, EPA and ARA) suggest that POM in urban streams had greater nutritional value than POM in forest streams (Fig. 5).

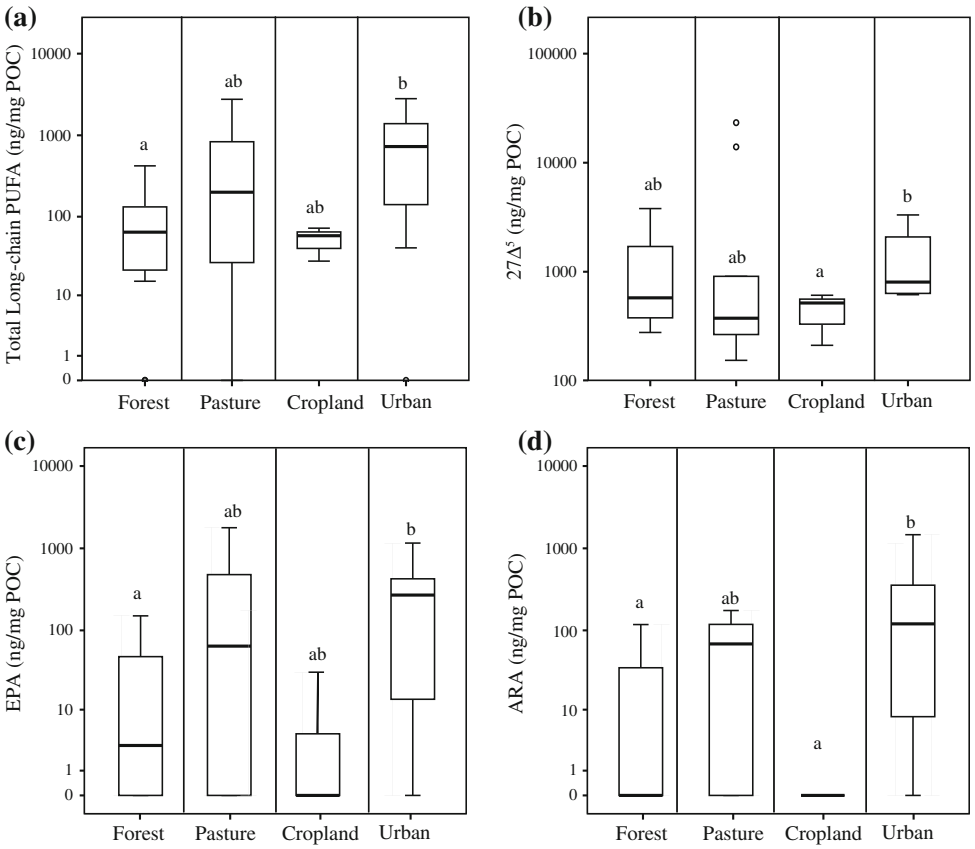

Fig. 5 *Box plot* comparison of the concentrations of **a** Long-chain PUFA (PUFA with carbon numbers ≥20) across the five sampling times **b** cholesterol ($27\Delta^5$) across the five sampling times **c** EPA (20:5ω3) and ARA (20:4ω6) across the five sampling times, and **d** EPA and ARA across the land use types. *Open circles* represent outliers (i.e., data beyond the upper/lower quartile ± 1.5 interquartile range); *different letters above the boxes* signify significant difference in the variables across the land use types

Both C:N values and fatty acid derived proxies suggest that watershed land use was more important than temporal variables in determining the nutritional value of POM. In fact, significant negative correlations were found between C:N and the three fatty acid nutritional proxies (C:N vs. long-chain PUFA: $r = -0.688$, $P = 0.001$; C:N vs. EPA: $r = -0.586$, $P < 0.008$; C:N vs. ARA: $r = -0.509$, $P = 0.026$). Notably, three of the nutritional proxies also correlated significantly with Chl-a concentration (Chl-a vs. long-chain PUFA: $r = 0.577$, $P = 0.002$; Chl-a vs. EPA: $r = 0.616$, $P = 0.001$; Chl-a vs. $27\Delta^5$: $r = 0.665$, $P < 0.001$), suggesting that microalgal inputs to POM may contribute to variability in the nutritional value of POM.

Depending on the proxy used for assessing POM nutritional quality, different conclusions may be drawn with respect to how land use alters the food resources of stream consumers (e.g., statistical differences were found between forest and cropland streams for C:N ratios but not for the other three nutritional proxies). This is consistent with previous studies that have shown that no single measure is capable of comprehensively assessing the nutritional quality of food sources to all types of stream consumers, especially since the putative proxies have generally been developed in growth assay experiments using specific consumer organisms (e.g. Daphnia and Chironomids) (Martin-Creuzburg and von Elert 2004, 2009a; Muller-Navarra et al. 2000, 2004; Rosi-Marshall 2004).

Conclusions and implications

The present study employed lipid biomarker distributions to examine the source composition and potential nutritional value of POM in a set of regional headwater streams in watersheds with differing land uses. We found that POM sources varied as a function of land use type. Streams draining human land use watersheds had a lower proportion of compounds from allochthonous sources and a higher proportion of compounds from autochthonous sources relative to streams draining forested watersheds. The contribution of lipids from bacterial biomass to POM was, however, mainly governed by variations in temperature and nitrate concentration. Our results also indicate that land use plays an important role in determining the nutritional value of POM as a potential food source to in-stream consumers. The C:N ratio and all lipid-based nutritional proxies suggest that POM in urban streams had greater nutritional value than in forest streams.

Our findings that the source composition and nutritional value of stream POM is influenced by watershed land use highlights the impacts of human activities on stream

ecosystems. Relative to previous studies attributing the human-induced changes in stream biota to changes in stream water temperatures (e.g. Hamilton et al. 2010), riparian forest coverage (e.g. Roy et al. 2005), pollutant and nutrient exports (e.g., review by Allan 2004 and references therein), and sedimentation (review by Allan 2004 and references therein), our results suggest that it is equally important to consider the role of anthropogenic activities on OM inputs to stream foodwebs. We propose that increased human modification to watersheds may alter the nutritional quality of particles by shifting stream foodwebs from detritus-based to algal-based systems.

Changes in the source composition of POM in headwater streams due to land use also have important implications for downstream systems. Some headwater stream OM may be delivered to rivers, estuaries and coastal waters (Marutani et al. 2008). During upstream-to-downstream fluvial transport, POM may undergo photodissolution and this process may be enhanced by the degree of aromaticity (Estapa et al. 2012). Since OM derived from higher plants is generally more enriched in aromatic compounds than autochthonous organisms, POM from human-influenced watersheds may be less photosensitive than POM from forested watersheds. As a result, photochemistry, while recognized as a dominant process altering and remineralizing upstream OM during its transit from shaded headwater streams to open-canopied downstream waters (Sulzberger and Durisch-Kaiser 2009), may become less important in human-influenced waterways. Consequently, the characteristics of POM reaching downstream rivers and estuaries may be modified, further impacting downstream food webs that may rely on upstream OM as a subsidiary source of energy and substrate. POM reaching downstream rivers and estuaries may be modified, further impacting downstream food webs that may rely on upstream OM as a subsidiary source of energy and substrate.

Acknowledgments We thank E. Ferer, E. Keesee, C. Pondell, S. Salisbury and S. Schillawski for help with field and laboratory work. T. Russell and S. Hamilton provided invaluable instruction on ArcGIS analysis. The paper is contribution 3352 of the Virginia Institute of Marine Science, College of William and Mary. This work was supported by a Mellon Foundation Grant to the College of William and Mary and by the National Science Foundation (grants OCE0962277, EAR1003529, and DEB 0542645 to E.A.C. and grants DEB0234533, OCE0327423, and EAR0403949 to J.E.B.).

References

Ahlgren G, Lundstedt L, Brett M, Forsberg C (1990) Lipid-composition and food quality of some fresh-water phytoplankton for Cladoceran zooplankters. J Plankton Res 12(4):809–818. doi:10.1093/plankt/12.4.809

Ahlgren G, Gustafsson IB, Boberg M (1992) Fatty-acid content and chemical-composition of fresh-water microalgae. J Phycol 28(1):37–50. doi:10.1111/j.0022-3646.1992.00037.x

Albro PW (1976) Bacterial waxes. In: Kolattukudy PE (ed) Chemistry and biochemistry of natural waxes. Elsevier, Amsterdam, pp 419–445

Allan JD (2004) Landscapes and riverscapes: the influence of land use on stream ecosystems. Annu Rev Ecol Evol S 35:257–284. doi:10.1146/annurev.ecolsys.35.120202.110122

Allan JD, Castillo MM (2007) Stream ecology: structure and function of running waters, 2nd edn. Chapman and Hall, New York

Anderson NH, Sedell JR (1979) Detritus processing by macroinvertebrates in stream ecosystems. Annu Rev Entomol 24:351–377

Atkinson CL, Golladay SW, Opsahl SP, Covich AP (2009) Stream discharge and floodplain connections affect seston quality and stable isotopic signatures in a coastal plain stream. J N Am Benthol Soc 28(2):360–370. doi:10.1899/08-102.1

Bae M, Mercer IE (1970) The effect of long-and short-day photoperiods on the sterol levels in the leaves of *Solanum andigenea*. Phytochemistry 9:63–68

Barlett MA, Leff LG (2010) The effects of N:P ratio and nitrogen form on four major freshwater bacterial taxa in biofilms. Can J Microbiol 56(1):32–43. doi:10.1139/W09-099

Bernot MJ, Sobota DJ, Hall RO, Mulholland PJ, Dodds WK, Webster JR, Tank JL, Ashkenas LR, Cooper LW, Dahm CN, Gregory SV, Grimm NB, Hamilton SK, Johnson SL, Mcdowell WH, Meyer JL, Peterson B, Poole GC, Valett HM, Arango C, Beaulieu JJ, Burgin AJ, Crenshaw C, Helton AM, Johnson L, Merriam J, Niederlehner BR, O'Brien JM, Potter JD, Sheibley RW, Thomas SM, Wilson K (2010) Inter-regional comparison of land-use effects on stream metabolism. Freshw Biol 55(9):1874–1890. doi:10.1111/j.1365-2427.2010.02422.x

Bianchi TS, Canuel EA (2011) Chemical biomarkers in aquatic ecosystems. Princeton University Press, Princeton

Bonin HL, Griffiths RP, Caldwell BA (2000) Nutrient and microbiological characteristics of fine benthic organic matter in mountain streams. J N Am Benthol Soc 19:235–249

Brett M, Müller-Navarra DC (1997) The role of highly unsaturated fatty acids in aquatic foodweb processes. Freshw Biol 38: 483–499

Brookshire ENJ, Dwire KA (2003) Controls on patterns of coarse organic particle retention in headwater streams. J N Am Benthol Soc 22(1):17–34. doi:10.2307/1467975

Canuel EA (2001) Relations between river flow, primary production and fatty acid composition of particulate organic matter in San Francisco and Chesapeake Bays: a multivariate approach. Org Geochem 32(4):563–583

Canuel EA, Martens CS (1993) Seasonal variations in the sources and alteration of organic matter associated with recently deposited sediments. Org Geochem 20(5):563–577

Canuel EA, Cloern JE, Ringelberg DB, Guckert JB, Rau GH (1995) Molecular and isotopic tracers used to examine sources of organic matter and its incorporation into the food webs of San-Francisco Bay. Limnol Oceanogr 40(1):67–81

Carpenter SR, Caraco NF, Howarth RW, Sharpley AN, Smith VH (1998) Nonpoint pollution of surface waters with phosphorous and nitrogen. Ecol Appl 8:559–568

Cranwell PA (1982) Lipids of aquatic sediments and sedimenting particulates. Prog Lipid Res 21:271–308

Cummins KW, Wilzbach MA, Gates DM, Perry JB, Taliferro WB (1989) Shredders and riparian vegetation—leaf litter that falls into streams influences communities of stream invertebrates. Bioscience 39(1):24–30. doi:10.2307/1310804

Dalsgaard J, John M, Kattner G, Muller-Navarra D, Hagen W (2003) Fatty acid trophic markers in the pelagic marine environment. Adv Mar Biol 46:225–340

Eglinton G, Hamilton RJ (1967) Leaf epicuticular waxes. Science 156(3780):1322. doi:10.1126/science.156.3780.1322

Elser JJ, Fagan WF, Denno RF, Dobberfuhl DR, Folarin A, Huberty A, Interlandi S, Kilham SS, McCauley E, Schulz KL, Siemann EH, Sterner RW (2000) Nutritional constraints in terrestrial and freshwater food webs. Nature 408(6812):578–580. doi:10.1038/35046058

Estapa ML, Boss E, Mayer LM, Roesler CS (2012) Role of iron and organic carbon in mass-specific light absorption by particulate matter from Louisiana coastal waters. Limnol Oceanogr 57(1):97–112. doi:10.4319/lo.2012.57.1.0097

Faure G, Mensing TM (2005) Principles of isotope geology, 3rd edn. John Wiley & Sons Inc, Hoboken

Fetter CW (2001) Applied hydrogeology, 4th edn. Prentice Hall, Upper Saddle River

Fierer N, Morse JL, Berthrong ST, Bernhardt ES, Jackson RB (2007) Environmental controls on the landscape-scale biogeography of stream bacterial communities. Ecology 88(9):2162–2173. doi:10.1890/06-1746.1

França JS, Gregorio RS, de Paula JD, Goncalves JF, Ferreira FA, Callisto M (2009) Composition and dynamics of allochthonous organic matter inputs and benthic stock in a Brazilian stream. Mar Freshw Res 60(10):990–998. doi:10.1071/Mf08247

Gessner MO, Chauvet E (1993) Ergosterol-to-biomass conversion factors for aquatic hyphomycetes. Appl Environ Microb 59(2):502–507

Gulis V, Suberkropp K, Rosernond AD (2008) Comparison of fungal activities on wood and leaf litter in unaltered and nutrient-enriched headwater streams. Appl Environ Microb 74(4):1094–1101. doi:10.1128/Aem.01903-07

Hamilton AT, Stamp JD, Bierwagen BG (2010) Vulnerability of biological metrics and multimetric indices to effects of climate change. J N Am Benthol Soc 29(4):1379–1396. doi:10.1899/10-053.1

Hicks BJ (1997) Food webs in forest and pasture streams in the Waikato region, New Zealand: a study based on analyses of stable isotopes of carbon and nitrogen, and fish gut contents. N Z J Mar Fresh 31(5):651–664

Holmes RM, Fisher SG, Grimm NB, Harper BJ (1998) The impact of flash floods on microbial distribution and biogeochemistry in the parafluvial zone of a desert stream. Freshw Biol 40(4):641–654. doi:10.1046/j.1365-2427.1998.00362.x

Kaneda T (1991) Iso-fatty and anteiso-fatty acids in bacteria—biosynthesis, function, and taxonomic significance. Microbiol Rev 55(2):288–302

Kendall C, Silva SR, Kelly VJ (2001) Carbon and nitrogen isotopic compositions of particulate organic matter in four large river systems across the United States. Hydrol Process 15(7):1301–1346

Koetsier P, McArthur JV, Leff LG (1997) Spatial and temporal response of stream bacteria to sources of dissolved organic carbon in a blackwater stream system. Freshw Biol 37(1):79–89. doi:10.1046/j.1365-2427.1997.d01-535.x

Lau DCP, Leung KMY, Dudgeon D (2008) Experimental dietary manipulations for determining the relative importance of allochthonous and autochthonous food resources in tropical streams. Freshw Biol 53(1):139–147. doi:10.1111/j.1365-2427.2007.01873.x

Lear G, Anderson MJ, Smith JP, Boxen K, Lewis GD (2008) Spatial and temporal heterogeneity of the bacterial communities in stream epilithic biofilms. FEMS Microbiol Ecol 65(3):463–473. doi:10.1111/j.1574-6941.2008.00548.x

Li W, Dagaut J, Saliot A (1995) The application of sterol biomarkers to the study of the sources of particulate organic matter in the Solo River system and Serayu River, Java, Indonesia. Biogeochemistry 31(3):139–154

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. doi:10.1016/S0003-2670(03)00815-8

Lu YH, Meyers PA (2009) Sediment lipid biomarkers as recorders of the contamination and cultural eutrophication of Lake Erie, 1909–2003. Org Geochem 40(8):912–921. doi:10.1016/j.orggeochem.2009.04.012

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

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

Malas D, Wallace JB (1977) Strategies for coexistence in three species of net-spinning caddisflies (Trichoptera) in second-order Appalachian streams. Can J Zool 55:1829–1840

Maloney KO, Feminella JW, Mitchell RM, Miller SA, Mulholland PJ, Houser JN (2008) Landuse legacies and small streams: identifying relationships between historical land use and contemporary stream conditions. J N Am Benthol Soc 27(2):280–294. doi:10.1899/07-070.1

Martin-Creuzburg D, Von Elert E (2004) Impact of 10 dietary sterols on growth and reproduction of *Daphnia galeata*. J Chem Ecol 30(3):483–500. doi:10.1023/B:Joec.0000018624.94689.95

Martin-Creuzburg D, Von Elert E (2009a) Good food versus bad food: the role of sterols and polyunsaturated fatty acids in determining growth and reproduction of Daphnia magna. Aquat Ecol 43(4):943–950. doi:10.1007/s10452-009-9239-6

Martin-Creuzburg D, Von Elert E (2009b) Ecological significance of sterols in aquatic food webs. In: Arts MT, Brett MT, Kainz MJ (eds) Lipids in aquatic systems. Springer, New York, pp 43–64

Marutani T, Kikuchi S, Yanai S, Kochi K (2008) The light and dark of Sabo-Dammed streams in steepland settings in Japan. In: Brierley G, Fryirs KA (eds) River futures: an integrative scientific approach to river repair. Island Press, Washington, pp 220–236

McArthur MD, Richardson JS (2002) Microbial utilization of dissolved organic carbon leached from riparian litterfall. Can J of Fish Aqua Sci 59(10):1668–1676. doi:10.1139/F02-135

McCallister SL, Bauer JE, Canuel EA (2006) Bioreactivity of estuarine dissolved organic matter: a combined geochemical and microbiological approach. Limnol Oceanogr 51(1):94–100

Medeiros PM, Simoneit BRT (2008) Multi-biomarker characterization of sedimentary organic carbon in small rivers draining the Northwestern United States. Org Geochem 39(1):52–74. doi:10.1016/j.orggeochem.2007.10.001

Meyer S, Leifeld J, Bahn M, Fuhrer J (2012) Free and protected soil organic carbon dynamics respond differently to abandonment of mountain grassland. Biogeosciences 9(2):853–865. doi:10.5194/bg-9-853-2012

Meyers PA, Ishiwatari R (1993) Lacustrine organic geochemistry—an overview of indicators of organic matter sources and diagenesis in lake sediments. Org Geochem 20:867–900

Millar AA, Smith MA, Kunst L (2000) All fatty acids are not equal: discrimination in plant membrane lipids. Trends Plant Sci 5(3):95–101. doi:10.1016/S1360-1385(00)01566-1

Mills GL, McArthur JV, Wolfe CP (2003) Lipid composition of suspended particulate matter (SPM) in a southeastern blackwater stream. Water Res 37:1783–1793. doi:10.1016/S0043-1354(02)00048-9

Muller-Navarra DC, Brett MT, Liston AM, Goldman CR (2000) A highly unsaturated fatty acid predicts carbon transfer between primary producers and consumers. Nature 403(6765):74–77. doi:10.1038/47469

Muller-Navarra DC, Brett MT, Park S, Chandra S, Ballantyne AP, Zorita E, Goldman CR (2004) Unsaturated fatty acid content in seston and tropho-dynamic coupling in lakes. Nature 427(6969): 69–72. doi:10.1038/Nature02210

Napolitano GE (1994) The relationship of lipids with light and chlorophyll measurements in fresh-water algae and periphyton. J Phycol 30(6):943–950. doi:10.1111/j.0022-3646.1994.00943.x

Napolitano GE (1998) Fatty acids as trophic and chemical markers in freshwater ecosystems. In: Arts MT, Wainman BC (eds) Lipids in freshwater ecosystems. Springer, New York, pp 21–37

Newcomer TA, Kaushal SS, Mayer PM, Shields AR, Canuel EA, Groffman PM, Gold AJ (2012) Influence of natural and novel organic carbon sources on denitrification in forest, degraded urban, and restored streams. Ecol Monogr 82(4):449–466. doi:10.5061/Dryad.4gk00

Nishimura M (1982) 5-Beta-Isomers of stanols and stanones as potential markers of sedimentary organic-quality and depositional paleoenvironments. Geochim Cosmochim Ac 46:423–432

Niyogi DK, Simon KS, Townsend CR (2003) Breakdown of tussock grass in streams along a gradient of agricultural development in New Zealand. Freshwater Biol 48(9):1698–1708. doi:10.1046/j.1365-2427.2003.01104.x

O'Connell M, Baldwin DS, Robertson AI, Rees G (2000) Release and bioavailability of dissolved organic matter from floodplain litter: influence of origin and oxygen levels. Freshw Biol 45(3): 333–342. doi:10.1046/j.1365-2427.2000.00627.x

Ogrinc N, Markovics R, Kanduc T, Walter LM, Hamilton SK (2008) Sources and transport of carbon and nitrogen in the River Sava watershed, a major tributary of the River Danube. Appl Geochem 23:3685–3698

Opsahl SP, Zepp RG (2001) Photochemically-induced alteration of stable carbon isotope ratios (delta C-13) in terrigenous dissolved organic carbon. Geophys Res Lett 28(12):2417–2420

Osburn CL, Morris DP, Thorn KA, Moeller RE (2001) Chemical and optical changes in freshwater dissolved organic matter exposed to solar radiation. Biogeochemistry 54:251–278

Palomo L, Canuel EA (2010) Sources of fatty acids in sediments of the York River estuary: relationships with physical and biological processes. Estuar Coast 33(3):585–599. doi:10.1007/s12237-010-9268-3

Parkes RJ (1987) Analysis of microbial communities within sediments using biomarkers. In: Hetcher M, Gray RTG, Jones JG (eds) Ecology of microbial communities. Cambridge University Press, Cambridge, pp 147–177

Parsons TR, Maita Y, Lalli CM (1984) A manual of chemical and biological methods for seawater analysis. Pergamon Press, Oxford

Pip E, Reinisch A (2012) Stream water quality associated with a livestock/poultry production operation in Southeastern Manitoba, Canada. Soil Water Res 7(1):27–35

Poerschmann J, Carlson R (2006) New fractionation scheme for lipid classes based on "in-cell fractionation" using sequential pressurized liquid extraction. J Chromatogr A 1127(1–2):18–25. doi:10.1016/j.chroma.2006.07.063

Pratt C, Warnken J, Leeming R, Arthur JM, Grice DI (2007) Detection of intermittent sewage pollution in a subtropical, oligotrophic, semi-enclosed embayment system using sterol signatures in sediments. Environ Sci Technol 41(3):792–802. doi:10.1021/Es061450f

Rosi-Marshall EJ (2004) Decline in the quality of matter as a food resource suspended fine particulate for chironomids downstream of an urban area. Freshw Biol 49(5):515–525. doi:10.1111/j.1365-2427.2004.01205.x

Roy AH, Faust CL, Freeman MC, Meyer JL (2005) Reach-scale effects of riparian forest cover on urban stream ecosystems. Can J Fish Aquat Sci 62(10):2312–2329. doi:10.1139/F05-135

Sand-Jensen K, Pedersen NL, Sondergaard M (2007) Bacterial metabolism in small temperate streams under contemporary and future climates. Freshw Biol 52(12):2340–2353. doi:10.1111/j.1365-2427.2007.01852.x

Sargent JR (1976) The structure, metabolism, and function of lipids in marine organisms. In: Malins D, Sargent JR (eds) Biochemical and biophysical perspectives in marine biology. Academic Press, New York, pp 149–212

Schidlowski M, Hayes JM, Kaplan IR (1983) Isotopic inferences of ancient biochemistries: carbon, sulfur, hydrogen and nitrogen. In: Schopf JW (ed) Earth's earliest biosphere: its origin and evolution. Princeton University Press, Princeton

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. doi:10.1007/s10533-009-9391-z

Sicko-Goad L, Simmons MS, Lazinsky D, Hall J (1988) Effect of light cycle on diatom fatty-acid composition and quantitative morphology. J Phycol 24(1):1–7

Simoneit BRT (1977) Diterpenoid compounds and other lipids in deep-sea sediments and their geochemical significance. Geochim Cosmochim Ac 41(4):463–476

Simoneit BRT, Mazurek MA (1982) Organic-matter of the troposphere. 2. natural background of biogenic lipid matter in aerosols over the rural western United States. Atmos Environ 16(9):2139–2159. doi:10.1016/0004-6981(82)90284-0

Spencer RGM, Stubbins A, Hernes PJ, Baker A, Mopper K, Aufdenkampe AK, Dyda RY, Mwamba VL, Mangangu AM, Wabakanghanzi JN, Six J (2009) Photochemical degradation of dissolved organic matter and dissolved lignin phenols from the Congo River. J Geophys Res-Biogeo 114(G3). doi:10.1029/2009jg000968

Stern J, Wang Y, Gu B, Newman J (2007) Distribution and turnover of carbon in natural and constructed wetlands in the Florida Everglades. Appl Geochem 22:1936–1948

Sulzberger B, Durisch-Kaiser E (2009) Chemical characterization of dissolved organic matter (DOM): a prerequisite for understanding UV-induced changes of DOM absorption properties and bioavailability. Aquat Sci 71:104–126

Torres-Ruiz M, Wehr JD (2010) Changes in the nutritional quality of decaying leaf litter in a stream based on fatty acid content. Hydrobiologia 651(1):265–278. doi:10.1007/s10750-010-0305-9

Tulloch AP (1976) Chemistry of waxes of higher plants. In: Kolattukudy PE (ed) Chemistry and biochemistry of natural waxes. Elsevier, Amsterdam, pp 235–287

Vidon P, Hubbard LE, Soyeux E (2009) Impact of sampling strategy on stream load estimates in till landscape of the Midwest. Environ Monit Assess 159(1–4):367–379. doi:10.1007/s10661-008-0635-5

Volkman JK (1986) A review of sterol markers for marine and terrigenous organic matter. Org Geochem 9:83–99

Volkman JK (2003) Sterols in microorganisms. Appl Microbiol Biotechnol 60:495–506. doi:10.1007/s00253-002-1172-8

Volkman JK, Jeffrey SW, Nichols PD, Rogers GI, Garland CD (1989) Fatty-Acid and lipid composition of 10 Species of microalgae used in mariculture. J Exp Mar Biol Ecol 128(3):219–240. doi:10.1016/0022-0981(89)90029-4

Volkman JK, Barrett SM, Blackburn SI, Mansour MP, Sikes EL, Gelin F (1998) Microalgal biomarkers: a review of recent

research developments. Org Geochem 29(5–7):1163–1179. doi:10.1016/S0146-6380(98)00062-X

Von Elert E, Martin-Creuzburg D, Le Coz JR (2003) Absence of sterols constrains carbon transfer between cyanobacteria and a freshwater herbivore (*Daphnia galeata*). Proc R Soc Lond B Biol 270:1209–1214

Wakeham SG, Canuel EA (1990) Fatty-acids and sterols of particulate matter in a brackish and seasonally anoxic coastal salt pond. Org Geochem 16(4–6):703–713

Wallace JB, Benke AC, Lingle AH, Parsons K (1987) Trophic pathways of macroinvertebrate primary consumers in subtropical blackwater streams. Arch Hydrobiol Supplement 74:423–451

Wannigama GP, Volkman JK, Gillan FT, Nichols PD, Johns RB (1981) A comparison of lipid components of the fresh and dead leaves and pneumatophores of the mangrove Avicennia marina. Phytochemistry 20:659–666

Waterson EJ, Canuel EA (2008) Sources of sedimentary organic matter in the Mississippi River and adjacent Gulf of Mexico as revealed by lipid biomarker and delta(13) C(TOC) analyses. Org Geochem 39(4):422–439. doi:10.1016/j.orggeochem.2008.01.011

Webster JR, Meyer JL (1997) Organic matter budgets for streams: a synthesis. J N Am Benthol Soc 16:141–161

Wetzel RG (1983) Limnology, 2nd edn. Saunders College Publishing, Harcourt Brace College Publishers, Fort Worth

Williams CJ, Yamashita Y, Wilson HF, Jaffe R, Xenopoulos MA (2010) Unraveling the role of land use and microbial activity in shaping dissolved organic matter characteristics in stream ecosystems. Limnol Oceanogr 55(3):1159–1171. doi:10.4319/lo.2010.55.3.1159

Wilson HF, Xenopoulos MA (2009) Effects of agricultural land use on the composition of fluvial dissolved organic matter. Nat Geosci 2(1):37–41. doi:10.1038/Ngeo391

Yamashita T, Flessa H, John B, Helfrich M, Ludwig B (2006) Organic matter in density fractions of water-stable aggregates in silty soils: effect of land use. Soil Biol Biochem 38(11):3222–3234. doi:10.1016/j.soilbio.2006.04.013

Yamashita Y, Kloeppel BD, Knoepp J, Zausen G, Jaffé R (2011) Long term effects of watershed disturbance and forest management on dissolved organic matter characteristics in headwater streams. Ecosystem 14:1110–1122. doi:10.1007/s10021-011-9469-z

Zimmerman AR, Canuel EA (2002) Sediment geochemical records of eutrophication in the mesohaline Chesapeake Bay. Limnol Oceanogr 47(4):1084–1093