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Hydrologic and forest management controls on dissolved organic matter characteristics in headwater streams of old-growth forests in the Oregon Cascades

Baek Soo Lee [a,*], Kate Lajtha [b]

[a] Water Resources Engineering, Oregon State University, 116 Gilmore Hall, Corvallis, OR 97331, USA
[b] Crop and Soil Science, Oregon State University, 3059 Ag Life Sciences Bldg, Corvallis, OR 97331, USA

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ABSTRACT

Dissolved organic matter (DOM) is a critical component of the carbon cycle linking terrestrial and aquatic ecosystems. Although many factors have been identified as influencing DOM fluxes and biochemical quality in rivers with varying land cover types, controls on DOM composition in forested headwater catchments of the western U.S. are poorly understood. This study examined the effect of hydrologic patterns and forest management history on stream DOM chemistry at watersheds located in the H.J. Andrews Experimental Forest of the Oregon Cascades. Specific UV absorbance at 254 nm ($SUVA_{254}$), generally indicative of aromaticity, increased in streams during storms with increasing surficial soil horizon and litter DOM inputs. Fluorescence excitation and emission matrices (EEMs) with Parallel Factor Analysis (PARAFAC) identified a protein-like DOM fluorescent component as well as several other components associated with terrestrial plant material. Correlation analysis between the protein-like DOM component and hydrologic patterns, $SUVA_{254}$, and DOC concentrations suggest that DOM during dry seasons represents more microbially-processed sources, such as protein-rich, deeper soil or DOM with greater in-stream microbial processing, compared to more plant-like surface soil sources observed during high flow. The base flow index (the proportion of base flow to total flow) showed a high correlation with the relative proportion of protein-like DOM indicating that deep soil water is a source of the protein-like signal. The relative proportions of the protein-like DOM and humic DOM were also influenced by the abundance of coarse woody debris (CWD), but not live tree biomass, with the proportions of protein-like DOM highest in harvested watersheds with low surficial CWD. This study shows UV and fluorescent spectroscopy is a viable finger printing method to elucidate DOM sources in pristine headwater streams at the western Cascades of Oregon.

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1. Introduction

Dissolved organic matter (DOM) is a critical component of the global carbon (C) cycle linking the terrestrial and aquatic ecosystems through in-stream microbial metabolism of terrestrial DOM (Battin et al., 2008). Although headwater streams make up the longest river length (53%) in the U.S. excluding Alaska (Nadeau and Rains, 2007), little is known about the contributions of small headwater streams to the global C cycle (Cole et al., 2007; Raymond et al., 2013). To better characterize this role, it is important to understand hydrologic pathways transporting DOM from terrestrial to aquatic ecosystems in headwater watersheds. It is known that DOM transport from small watersheds increases with storm and snowmelt (Frank et al., 2000; Meyer et al., 1983; Raymond and Saiers, 2010; Wilson et al., 2013). Similarly, DOM compositions may change under different hydrologic scenarios. For example, Wilson et al. (2013) found that bioavailable, less recalcitrant DOM increased with storm events. However, during storm events, van Verseveld et al. (2008) saw increases in specific UV absorbance at 254 nm ($SUVA_{254}$), widely used as an indicator of aromaticity of DOM samples (Weishaar et al., 2003) and potentially indicative of more recalcitrant DOM. Further examining changes in DOM chemistry with hydrologic events may help to better characterize DOM transport in small headwater streams.

Fingerprinting fluorescent spectroscopy techniques can be used to identify DOM chemistry in freshwater samples using optical signals created by unique chemical structures of DOM (McKnight et al., 2001; Weishaar et al., 2003). Chemical structures and

* Corresponding author.
E-mail address: baeksoolee@gmail.com (B.S. Lee).

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quantities of DOM create unique 3-D fluorescent spectra at distinctive wavelengths defined as excitation and emission matrices (EEMs) (Stedmon and Bro, 2008). The matrices are a complex combination of DOM fluorescent signals. Identification of the chemical structure of the DOM components from the EEMs require statistical analysis, e.g. a multivariate statistical parallel factor analysis (PARAFAC) modeling and principal component analysis (PCA) (Stedmon and Bro, 2008). Output from a PARAFAC model results in percentages of DOM signals or identified components, which makes PARAFAC more advantageous for looking at DOM characteristics in natural waters than PCA (Stedmon and Bro, 2008). Fluorescent spectroscopy with PARAFAC has been widely used recently to identify and quantify DOM sources in many freshwater ecosystems (Cawley et al., 2012; Cory and McKnight, 2005; Hosen et al., 2014; Stedmon et al., 2003). Fluorescent DOM components have been associated with varying land uses, landscape features, or effluent sources (Cawley et al., 2012; Hosen et al., 2014; Stedmon et al., 2003). Redox states of quinone-like components have been identified in disparate ecosystems of the Arctic, the Antarctic, Botswana, and Colorado (Cory and McKnight, 2005). Technically simple and relatively rapid fluorescent spectroscopy can be useful compared to more complicated and expensive infrared (IR) or nuclear magnetic resonance (NMR) spectroscopy to determine DOM chemistry (Cory et al., 2011).

Studies from eastern forests indicate that DOM optical properties vary seasonally and respond to forest management. In the Coweeta Experimental Forest located in western North Carolina, increased amounts of a protein-like component in forested headwater streams in the early summer and fall were attributed to higher biological activity in the forest floor and/or riparian zone (Yamashita et al., 2011). In the Hubbard Brook Experimental Forest in New Hampshire, streams in previously harvested forests had lower dissolved organic carbon (DOC) concentrations and a higher protein-like fluorescence component compared to reference streams (Cawley et al., 2014). These studies were conducted on the East Coast of the U.S. where forests and streams historically have received relatively high inputs of acidity and pollutants (Evans et al., 2005; Monteith et al., 2007) especially compared to the Pacific Northwest (Lajtha and Jones, 2013) that can affect both fluxes and composition of DOM. Controls on DOM chemistry in forested headwater ecosystems of the Pacific Northwest with different environment, climate, and forest types compared to the East Coast are less well studied, and it is not clear if DOM chemistry will respond in similar ways to land management and climate variability.

This study was conducted in nine experimental watersheds containing old-growth forest (450-yr-old) and regenerating (50 ~ 60-yr-old) forest in the H.J. Andrews Experimental Forest (HJAEF) in Oregon. At the HJAEF, DOM chemical characterization has been limited to the fluorescent index (FI) (McKnight et al., 2001) and/or $SUVA_{254}$ during storm events in the limited number of watersheds (Hood et al., 2006; van Verseveld et al., 2009, 2008). Hood et al. (2006) and van Verseveld et al. (2008) found DOC was more aromatic during storm events, compared to base flow season in the streams. Hood et al. (2006) did not see the variation in FI during a week-long storm event. van Verseveld et al. (2009) found declining $SUVA_{254}$ in soil water in the following order respectively: an organic layer, shallow soil water (20 cm), deep soil water (70–110 cm) as well as stream water, and deep groundwater. Shallow, mineral soils preferentially adsorb aromatic and carboxyl DOM (Kaiser et al., 1997). This results in deep soil layers with highly hydrophilic, more microbially processed, labile DOM (i.e. less aromatic DOM) (Lajtha et al., 2005), and thus deep soils may be sources of increased proportion of bioavailable and protein-like, DOM to streams. At the HJAEF, overland flow is rarely observed during fall and winter storm seasons (Harr, 1976), but the seasonal flows can be characterized as shallow subsurface flow, vertical preferential flow, deep groundwater, and/or deep soil water (van Verseveld et al., 2008). The dry summer is characterized by base flow with a residence time of 0.8–3.5 years (McGuire et al., 2005). Here, we call fall and winter flows "shallow subsurface flow" and summer base flow "deeper subsurface flow". Hence, DOM aromaticity and recalcitrant DOM in streams may be high (high $SUVA_{254}$) during high flow events at the HJAEF, when there are increased shallow subsurface flow paths through surface soil horizons resulting in limited interaction with deep soils. The proportion of bioavailable and protein-like DOM in streams may be high (with low $SUVA_{254}$) during summer deeper flow periods, when base flow dominantly contributes to streams through deep mineral soil horizons allowing longer exposure to microbially processed deep soil and greater interaction of DOM with soil minerals and active microbes.

The objectives of this study were to (1) examine the role of seasonality and hydrology on DOM chemistry and (2) investigate the potential role of forest management history on DOM chemistry using UV and fluorescent spectroscopy. We hypothesized that the proportion of aromatic and terrestrial DOM in streams would be higher during high flow compared to base flow conditions and in watersheds with a low base flow index (BFI) (Santhi et al., 2008). This hypothesis is based on shifts in dominant flowpaths from deeper subsurface flow (in summer, between storm events, and in low-gradient watersheds) to shallow subsurface flow (in winter, during storm events, and in steep watersheds). We also hypothesized that DOM in streams draining watersheds whose coarse woody debris (CWD; i.e. woody detritus) pools have been depleted by forest harvest in the last 50–60 years would have lower $SUVA_{254}$ and a lower proportion of humic-like DOM, but greater relative percentages of protein-like DOM, compared to old-growth watersheds with high CWD loads on the forest floor.

2. Materials and methods

2.1. Sample sites

This study examined stream water samples collected between May 2013 and June 2015 (36 events) at the H. J. Andrews Experimental Forest (HJAEF) located in the western Cascades of Oregon (Fig. 1). The forest is a 6400-ha LTER site and encompasses the forested Lookout Creek watershed filled with old-growth Douglas fir and western hemlock (400–500 years) (Swanson and Jones, 2001; Vanderbilt et al., 2003). The stream water data were collected as a part of the long-term water quality monitoring effort started in 1968 (Swanson and Jones, 2001).

The climate of the HJAEF is marine temperate and characterized by dry, warm summers and wet, cool winters (Fig. 2) (Swanson and Jones, 2001). Elevation ranges between 434 and 1627 m (H.J. Andrews Experimental Forest, 2015), which contributes to different precipitation patterns within the forest (Vanderbilt et al., 2003). The average annual precipitation is about 2500 mm, falling mainly as rain, and a seasonal snow pack accumulates above 1000 m (Swanson and Jones, 2001).

The experimental watersheds observed for this study were seven headwater watersheds (WS) 1, 2, 6, 7, 8, 9, and 10 as well as the Mack Creek (MACK, 3rd order) and Lookout Creek (LOOK, 5th order) watersheds (Fig. 1, Table 1). All the experimental watersheds except 1, 9, and 10 are nested within LOOK. Each watershed underwent various forest management practices. Northwest-facing WS 1 and 2 are adjacent to each other; WS 1 was clear-cut between 1962 and 1966 and slash was burned in 1966, and WS 2 is a reference watershed with old-growth forest. South-facing WS 6 and 7 are adjacent to each other; WS 6 was

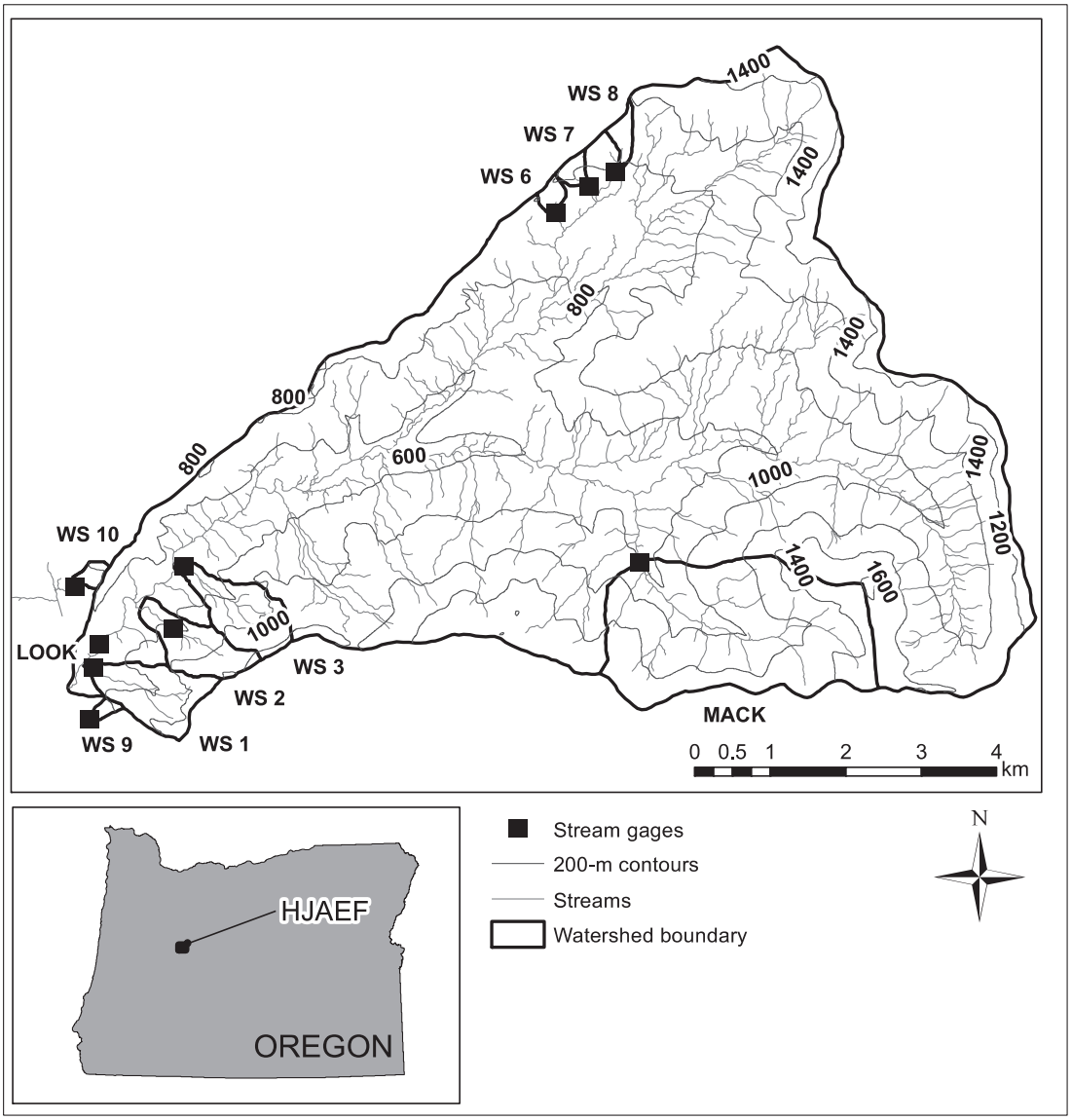

Fig. 1. Map of the H.J. Andrews Experimental Forest showing the location of 10 experimental watersheds and their stream gages (Projection: NAD 1983 UTM Zone 10 N). WS 3 is not monitored for chemistry, and thus only the remaining nine watersheds were analyzed in this study.

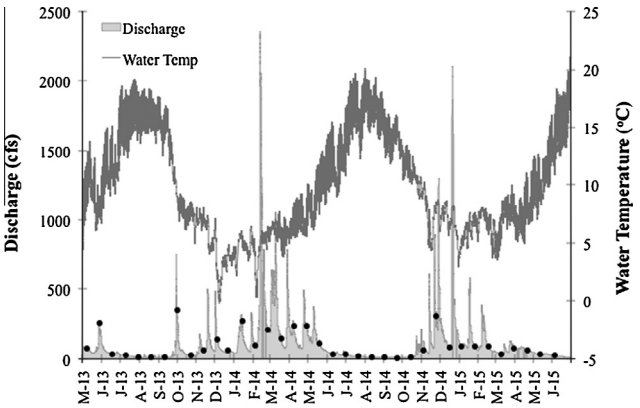

Fig. 2. Flow rate and stream temperature at the Lookout Creek Watershed (LOOK) between May 2013 and June 2015. Each dot indicates a sample collecting date that occurred every three weeks. Flow rate and stream temperature were measured by the U.S. Geological Survey (USGS National Water Information System at Lookout Creek Near Blue River, OR (14161500)).

clear-cut and slash was burned in 1975, WS 7 received two canopy removal treatments (60% selective-cut in 1974 and the removal of the remainder of the canopy in 1984), and WS 8 is the reference watershed for WS 6 and 7. West-facing WS 9 is the reference watershed for west-facing WS 10 that was clear-cut in 1975 with no burning. The northwest-facing MACK has not been altered significantly aside from moderate cutting (13% est.) between 1957 and 1982 and fire that occurred 120 years ago (H.J. Andrews Experimental Forest, 2015). Approximately 25% of the west-facing LOOK has been patch-cut between 1948 and present. Coarse woody debris (CWD) stocks within watersheds were measured by Fasth et al. (Unpublished Results) using the line intercept method and further described in their report (Table 1).

2.2. Field methods

Composited three-weekly samples of stream water are collected by automated samplers at gaging stations located at the outlet of experimental watersheds as part of the HJAEF long-term water quality monitoring program. The sampling method is

Table 1
Experimental watersheds properties and history at the Andrews Experimental Forest (Swanson and Jones, 2001; H.J. Andrews Experimental Forest, 2015) as well as biomass (Mg/ha) of total, live tree, and logs (coarse woody debris) in each watershed (Fasth and others, Unpublished Data).

WS no.	Area (ha)	Elevation min (m)	Elevation max (m)	Slope (%)	Management history & remarks	Biomass (Mg/ha)		
						Total	Live tree	Logs (CWD)
Look	6242	434	1627	40	1948 ~ Present: 25% patch-cut between	–	–	–
Mack	581	765	1626	48	Control	–	–	–
1	96	450	1027	60	1957–1982: 8 units (about 13%) partially or fully cut 1962–1966: 100% clear cut 1966: Logging debris burn No roads	267	142	72
2	60	572	1079	53	Undisturbed control for WS 1	894	654	103
6	13	893	1029	25	1974: 100% clear cut 1975: Logging debris burn 1976: Planted with Douglas-fir seedlings A road	191	110	33
7	15	931	1102	34	1974: 60% selective canopy removal 1975: Logging residue burn at lower half 1976: Planting 1984: Remaining canopy removal 2001: Thinning	130	55	29
8	21	968	1182	26	Undisturbed control for WS 6 and 7	906	652	115
9	8.5	438	731	58	Undisturbed control for WS 10	791	585	108
10	10	471	679	58	1975: 100% clear cut	232	134	29

detailed at the HJAEF web-site (http://andrewsforest.oregonstate.edu/lter/; Johnson, 1984).

2.3. Laboratory methods

Analyses for nutrient and DOC were conducted at the Cooperative Chemical Analytical Laboratory (CCAL) at Oregon State University using standard analytical procedures (http://andrewsforest.oregonstate.edu/lter/). Samples were filtered through GF/F filters (0.7 μm), poured into acid-rinsed and pre-combusted (4 h at 490 °C) glass vials, and stored in a dark refrigerator (0–4 °C) until analysis. Inorganic nitrogen (N) species, nitrate-N (NO_3^--N) and ammonia-N (NH_3-N), and total dissolved nitrogen (TDN) were measured with a Technicon auto-analyzer II; DOC concentrations were measured with a Shimadzu TOC-VCSH combustion analyzer. The concentrations of DON are obtained by subtracting dissolved inorganic nitrogen N (NO_3^--N and NH_3^+-N) from TDN. The ratio between DOC and DON (DOC:DON) was used as an indicator of microbial influence. The method detection limits were as follows: DOC = 0.05 mg L^{-1}, NO_3^--N = 0.001 mg L^{-1}, NH_3^+-N = 0.010 mg L^{-1}, and TDN = 0.01 mg L^{-1} (CCAL, 2014). Maximum holding times at CCAL were as follows: DOC = 14 days, inorganic N = 48 h, and TDN = 28 days (Motter and Jones, 2013).

The optical properties of the samples, absorbance at 254 nm (Abs_{254}) and excitation and emission matrices (EEMs), showing fluorescent spectra at the distinctive combinations of excitation and emission wavelengths, were measured on the same day within 14 weeks of sample collection dates at the HJAEF. The effect of varying holding times is assumed to be minimal for this study, as no significant spectral change for DOM was observed in samples stored for two months in a refrigerator by Jaffé et al. (2008). The fluorescent index (FI), developed as an indicator of *terrestrial* versus *microbial* sources (McKnight et al., 2001), stayed stable throughout a five-month refrigerator storage experiment (Ebert, 2013), and absorbance, EEMs, and FI remained the same for 70 days for samples stored in a refrigerator and collected downstream of this study site (Lee, 2015).

Absorbance over a range of 240–560 nm was measured with a Cary 300 UV–Visible spectrophotometer to obtain $SUVA_{254}$ and to correct EEMs for the inner-filter effect (Lakowicz, 2006; Miller et al., 2010). Values of $SUVA_{254}$ (L mg C^{-1} m^{-1}) were calculated as UV absorbance at 254 nm (Abs_{254}) normalized for DOC concentrations (Weishaar et al., 2003). Samples with Abs_{254} > 0.2 cm^{-1} were diluted to correct for inner-filter effects before EEMs measurements (Miller et al., 2010). The range of absorbance necessary for inner-filter correction was not measured between May and October 1st, 2013; therefore, the inner-filter effect was not corrected for the samples. The values of Abs_{254} for all the samples collected during the period were less than 0.2 cm^{-1} hence the effect of the inner-filter effects on those samples were assumed to be minimal. Additionally, samples collected between October 23rd, 2013 and April 2014 were compared for the inner-filter effect. There was no difference for FI and protein identified by the Cory and McKnight (2005) PARAFAC model (r^2 = 1.0 and 0.99, respectively) between inner-filter corrected samples and non-inner-filter corrected samples, and Abs_{254} of samples was less than 0.2 cm^{-1}.

Excitation and emission matrices (EEMs) were measured over an excitation range of 250–400 nm with 10 nm intervals and an emission range of 350–550 nm with 2 nm intervals with a band slit of 3 nm by a Fluorolog® spectrofluorometer (HORIBA Jobin Yvon, Inc.) (Cory and McKnight, 2005). An EEM of Milli-Q™ water was subtracted from EEMs of samples for removing Raman scattering effects (Cory and McKnight, 2005; Stedmon and Bro, 2008). The MilliQ EEM was also used to calculate the Raman curve to normalize sample EEMs and report EEMs in Raman units (R.U., nm^{-1}) and enable the direct comparison of samples from different dates (Lawaetz and Stedmon, 2009; Stedmon et al., 2003). The EEMs were corrected for instrument-specific errors using the correction file provided by HORIBA Jovin Yvon, Inc. All optical properties were measured while the lights above the instruments were turned off. The Milli-Q™ water (Millipore Corporation) was used to calibrate samples for both Abs_{254} and EEMs.

2.4. EEM analysis

The updated FI (EM 470 nm/EM 520 nm at EX 370 nm) for EEMs with instrument-specific corrections (Cory et al., 2010) was used for our analyses. The updated FI values of 1.46 or greater are reported to indicate *microbially* derived sources, and 1.21 or lower to indicate *terrestrially* derived sources (Cory et al., 2010; McKnight et al., 2001). A FI value difference of 0.1 can be used to indicate a different DOM source (McKnight et al., 2001).

Characterization and quantification of fluorescent DOM from a total of 322 EEMs was conducted with the PARAFAC model using the DOMFluor Toolbox (ver. 1.7) (Stedmon and Bro, 2008) and the N-way Toolbox (ver. 3.31) (Andersson and Bro, 2000) with

MATLAB® (ver. R2013b). The model was validated with split half analysis (Stedmon and Bro, 2008). Four components identified by the PARAFAC were visually compared to the components determined by previous studies (Table 2). Correlation among DOM parameters was calculated using Pearson's r with SPSS (v. 22) for samples collected from May 2013 to June 2015 (322 samples).

2.5. Hydrological analysis

In order to investigate the effect of soil moisture and flow rate on DOM characteristics, the average daily flow rate was summed for the sampling collection date as well as three days (Qsum3), 14 days (Qsum14), 21 days (Qsum21), and 30 days (Qsum30) prior to the sampling collection date. Stream flow is measured at MACK, WS 1, 2, 6, 7, 8, 9, and 10 using trapezoidal flumes and automated stage height recorders; data were obtained from the HJAEF (http://andrewsforest.oregonstate.edu/lter/). Stream flow at Lookout Creek is measured using an automated stage height recorder at a controlled section; data were obtained from the U.S. Geological Survey (USGS; http://waterdata.usgs.gov/nwis/uv?). Missing values were estimated as the average stream flow of the previous and following day. Regression analysis was conducted on DOM optical parameters against Qsum3, Qsum14, Qsum21, and Qsum30 using SPSS (v. 22). The base flow index (BFI) was calculated for the study period at each watershed using the lfstat package in R (v 3.1.1.) (Gustard and Demuth, 2009) to examine the base flow influence on DOM chemistry.

3. Results

3.1. DOM components

Four fluorescent DOM components were identified with the PARAFAC model created for the study site (Table 2). Component 4 (C4) was visually associated with an EEM region identified as a protein-like or, more specifically, a tryptophan-like EEM signal (Coble, 1996; Cory and McKnight, 2005; Murphy et al., 2014; Yamashita et al., 2011). This EEM region also has been associated with protein-rich, autochthonous DOM (Stedmon and Markager, 2005).

Table 2
Four DOM components identified by this study and their previously identified characteristics. Values in the parenthesis indicate the second peak.

C	Ex max (nm)	Em max (nm)	Characteristics
1	260	486	Similar to humic-like DOM (Murphy et al., 2014) commonly found in forested streams (C1, Stedmon and Markager, 2005)
2	250 (310)	410	Humic-like DOM (Murphy et al., 2014) common in forested streams (C3, Stedmon and Markager, 2005)
3	250 (330)	454	Fulvic acid and found in various environments (C4, Stedmon and Markager, 2005)
4	250 (280)	350	Tryptophan-like (Cory and McKnight, 2005; C7, Stedmon and Markager, 2005; C4, Hosen et al., 2014; Murphy et al., 2014) and protein-like component (T, Coble, 1996; Stedmon et al., 2003). Originated from aromatic amino acids, an indicator of total hydrolysable amino acids, and labile or semi-labile aquatic DOM (C5, Yamashita et al., 2011). Autochthonous source and correlated to terrestrial DOM from forested catchments (Stedmon and Markager, 2005)

3.2. Correlations of DOM components with other parameters

DOC concentrations ranged between 0.3 and 4.0 mg L^{-1} with an average of 1.2 mg L^{-1} and showed a positive and strong correlation ($r > 0.5$, $\alpha = 0.01$) with the percentage of DOM components 1 and 2 (C1 (%) and C2 (%)) and a negative and strong correlation with C4 (%) ($r = -0.6$, $\alpha = 0.01$) (Tables 3 and 4). The concentrations of DON ranged between 0.00 and 0.12 mg L^{-1} with an average of 0.03 mg L^{-1} and was moderately and positively correlated with C1 (%) and C2 (%) ($r = 0.3–0.5$, $\alpha = 0.01$) and moderately and negatively correlated with C4 (%) ($r = -0.47$, $\alpha = 0.01$). The ratio of DOC to DON concentrations ranged between 9.3 and 288.3, with an average of 41.9 and was not correlated with the percentage of any DOM component. Values of $SUVA_{254}$ were strongly and positively correlated with C1 (%) and C2 (%) ($r > 0.5$, $\alpha = 0.01$) and strongly and negatively correlated with C4 (%) ($r = -0.53$, $\alpha = 0.01$). C4 (%) and the biomass of coarse woody debris (CWD) were negatively and strongly correlated ($r = -0.72$, $\alpha = 0.07$) (Fig. 3a).

3.3. Temporal variations

3.3.1. DOM optical properties

The FI values did not vary significantly among reference watersheds over the sampling season. However, FI at harvested watersheds (WS 1, 6, 7, and 10) increased during low flow seasons and warm months compared to high flow seasons and cold months (Fig. 4a).

The standard errors for the average of the reference watersheds (N = 3) are shown. Average daily flow rate of the sampling date was measured by USGS at Lookout Creek (USGS National Water Information System at Lookout Creek Near Blue River, OR (14161500)).

$SUVA_{254}$ ranged between 0.2 and 8.1 L mg^{-1} m^{-1} with an average of 3.5 L mg^{-1} m^{-1} (Table 3 & Fig. 4b). Overall, WS 6 and 10 showed the lowest and highest $SUVA_{254}$ throughout the study period, respectively.

The temporal variations of C1, C2, and C3 in absolute Raman units (R.U.) were similar to the temporal variations in DOC concentrations especially during the first storm event of the high flow season. When a harvested watershed and its corresponding reference watershed were compared, the absolute C1, C2, and C3 in R.U. were lower in harvested, WS 6, 7, and 10, than their reference watersheds (WS 8, 8, and 9, respectively) (Fig. 5). The absolute C1, C2, and C3 in R.U. were similar in WS 1 (harvested) and WS 2 (reference). Values for C4 in absolute R.U. were similar between all combinations of harvested and reference watersheds.

The relative contribution of C1 (%) decreased over summers at high elevation sites (WS 6–8) (Fig. 4c). The relative contributions of C2 (%) and C3 (%) had low temporal variability (Fig. 4d and e). The relative contribution of the protein-like component, C4 (%), showed the most temporal variation among the four fluorescent

Table 3
Statistics of measured parameters in water samples from the nine experimental watersheds at the H.J. Andrews Experimental Forest (N = 322).

Parameter	Min	Max	Mean	Median	St dev
DON (mg L^{-1})	0.00	0.12	0.03	0.03	0.02
DOC (mg L^{-1})	0.3	4.0	1.2	1.0	0.6
DOC:DON	9.3	288.3	41.9	34.4	28.7
FI	1.3	2.1	1.4	1.4	0.1
$SUVA_{254}$ (L mg^{-1} m^{-1})	0.2	8.1	3.5	3.7	1.0
Abs_{254} (m^{-1})	0.2	15.6	4.2	3.6	2.6
C1 (%)	13.1	37.7	28.8	29.4	5.3
C2 (%)	9.2	27.9	18.7	19.2	3.1
C3 (%)	16.1	47.1	26.7	26.6	2.9
C4 (%)	13.8	46.0	25.7	24.4	7.2

Table 4
Linear correlations (Pearson's R) among key parameters in water samples from the nine experimental watersheds at the H.J. Andrews Experimental Forest. (N = 322, Two-tailed significance test, **: $\alpha = 0.01$, *: $\alpha = 0.05$).

	DOC	DON	DOC/DON	FI	$SUVA_{254}$	C1 (%)	C2 (%)	C3 (%)	C4 (%)
DOC	1	0.60**	0.23**	−0.21**	0.19**	0.60**	0.55**	−0.19**	−0.60**
DON		1	−0.44**	−0.06	0.19**	0.45**	0.35**	−0.02	−0.47**
DOC/DON			1	0.05	−0.11*	−0.04	0.06	−0.08	0.04
FI				1	−0.37**	−0.47**	−0.27**	0.20**	0.39**
$SUVA_{254}$					1	0.55**	0.51**	−0.23**	−0.53**
C1 (%)						1	0.74**	−0.31**	−0.94**
C2 (%)							1	−0.54**	−0.76**
C3 (%)								1	0.06
C4 (%)									1

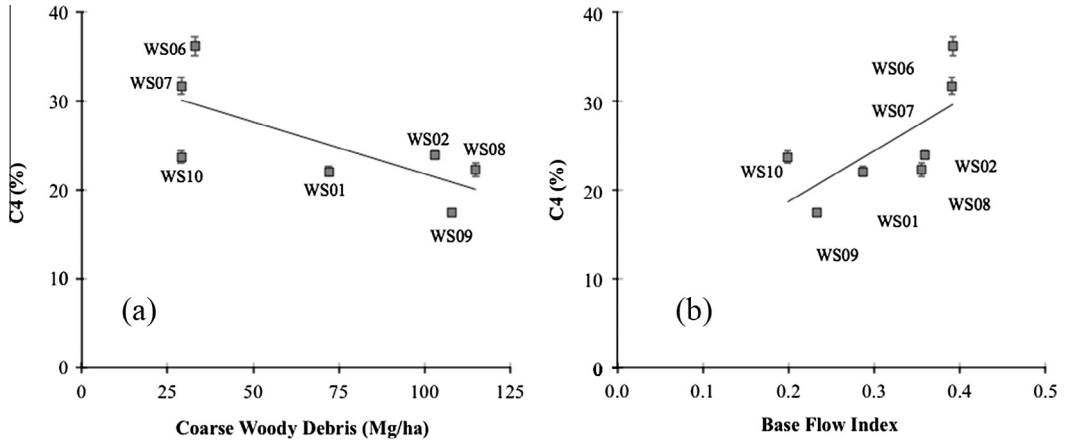

Fig. 3. Correlation of the relative contribution of a tryptophan-like DOM component, C4 (%), and (a) coarse woody debris (CWD) biomass (N = 7; Y = −0.12x + 34; $r^2 = 0.52$) and (b) the base flow index (BFI) (N = 7; Y = 57x + 7.3; $r^2 = 0.48$) at the seven small experimental watersheds at the H.J. Andrews Experimental Forest. Error bars (when visible) show the standard error. Each point represents the average of C4 (%) for all water samples collected at each location (36 sampling events total).

components (Fig. 4f). Mean C4 (%) was the lowest in the reference watersheds. Among harvested watersheds, samples from WS6 and 7 showed higher C4 (%) than those from WS1 and 10 overall. However, C4 (%) in samples from these watersheds decreased and became about the same during the first storm event of each year. When a harvested watershed and its corresponding reference watershed were compared, C4 (%) in samples from WS 6, 7, and 10 were higher than those from their reference watersheds (WS 8, 8, and 9, respectively) and C4 (%) in samples from WS 1 and 2 (control) were highly correlated (Fig. 6).

3.3.2. Hydrologic events

Correlation analysis between all flow parameters and C4 (%) and $SUVA_{254}$ was conducted at each watershed (Table 5). Values of $SUVA_{254}$ were positively correlated with Q, Qsum3, Qsum14, Qsum 21, and Qsum 30 at all sites. There was a strong linear correlation for $SUVA_{254}$ against all flow parameters at LOOK, WS 1, and WS 10, ($r > 0.5$). A moderate and positive linear correlation for $SUVA_{254}$ against all flow parameters was observed at WS 2, 6, 8, and 9 ($r = 0.3–0.49$). There was a moderate and positive correlation for $SUVA_{254}$ against Q and Qsum3 at WS 7 ($r = 0.3–0.49$). There was a moderate and positive correlation for $SUVA_{254}$ against Qsum14 and Qsum30 at WS 9 ($r = 0.36, 0.38$, respectively).

The relative contribution of C4 (%) was negatively correlated with Q, Qsum3, Qsum14, Qsum 21 and Qsum30 (Table 5) at all sites. There was a strong negative linear correlation for C4 (%) against all flow parameters at LOOK and MACK (absolute $r > 0.5$). Between C4 (%) against Q and Qsum3, a strong negative correlation was observed at WS 1, 7, 9, and 10 ($r < −0.5$); a moderate negative correlation was observed at WS 2, 6, and 8 ($r = −0.37$ to $−0.42$). A moderate correlation was observed for C4 (%) against Qsum14, Qsum21, and Qsum30 at WS1, 7, and 9 ($r = −0.38$ to $−0.46$). A regression analysis revealed more logarithmic than linear trends with a negative correlation for C4 (%) against all flow parameters at LOOK, MACK, WS1, WS9, and WS10 (not shown in the paper). The relative contribution of C4 (%) was positively and strongly correlated with the base flow index (BFI) ($r = 0.69$, $\alpha = 0.08$) (Fig. 3b).

4. Discussion

4.1. Overall DOM sources

Although an average FI value of 1.4, as found in this study, has been interpreted as indicative of "microbial" or autochthonous sources (Cory et al., 2010; McKnight et al., 2001), other studies of forested headwater streams have reported FI values ranging from 1.2–1.4 (Yamashita et al., 2011) to 1.4–1.6 (Cawley et al., 2014). The original FI scale was based on end-members that represent a "terrestrial" source (Suwanee River water) and a "microbial" or algal source (McKnight et al., 2001). However, most DOM produced in upland watersheds will be more microbially decomposed and altered than DOM from the low-pH, poorly oxygenated Suwanee River water, and thus we suggest that the FI indices in most stream samples are actually more reflective of microbial processing of terrestrial inputs than of autochthonous sources. DOM sources in forested headwater streams have generally been reported to be allochthonous (Vannote et al., 1980), given that they are characterized by significant inputs of forest litter and significant shading of the headwater streams. It is also possible that whole water samples of neutral pH with high humic acids may not necessarily result in a FI index on the same scale as a FI index developed with separated fulvic acids (McKnight et al., 2001) that are soluble at any pH.

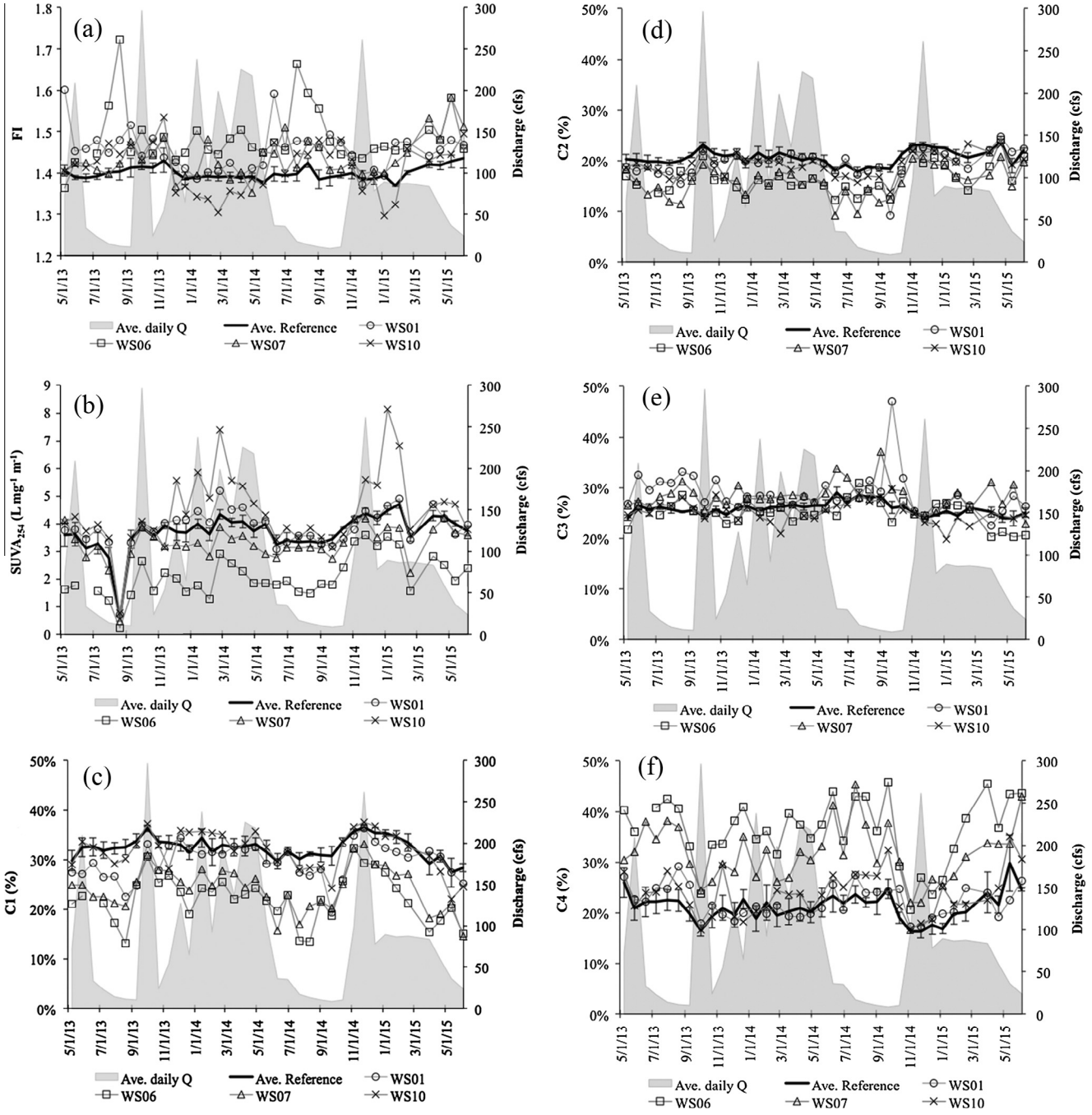

Fig. 4. Time-series of (a) fluorescence index (FI), (b) $SUVA_{254}$ ($L\,mg^{-1}\,m^{-1}$), (c) DOM component 1 (C1 (%)), (d) component 2 (C2 (%)), (e) component 3 (C3 (%)), and (f) component 4 (C4 (%)) of the four harvested watersheds at the H.J. Andrews Experimental Forest.

Hence we restrict our interpretations to relative changes in FI, rather than absolute values.

4.2. Protein-like DOM and hydrologic flowpaths

An increase in C4 (%) identified as a protein-like DOM was observed over summers compared to during high flow conditions. One possible explanation for the increase could be an increase within in-stream biological activity with increased temperature, resulting in greater autochthonous inputs. FI values similarly increased in harvested headwater watersheds over summers. In alpine and subalpine lakes with low plant inputs, algal and microbial production during low-flow seasons in summer has been shown to increasingly influence DOM chemistry as indicated by elevated FI values (Hood et al., 2003). Contrary to those lakes, our streams are shaded, small, first-order streams draining relatively well-developed forests (50–450 years). Hence, we suggest that autochthonous inputs are extremely low compared to allochthonous inputs during all seasons, as has been shown in other shaded headwater streams (Vannote et al., 1980). These phytoplankton-derived autochthonous inputs are also significantly more labile than allochthonous inputs derived from lignified, high C:N terrestrial plant materials (Thorp and Delong, 2002; Toming et al., 2013), and thus likely make up only a small percentage of residual DOM measured in headwater streams. Microbial activity and microbial processing of soil organic matter also increases with

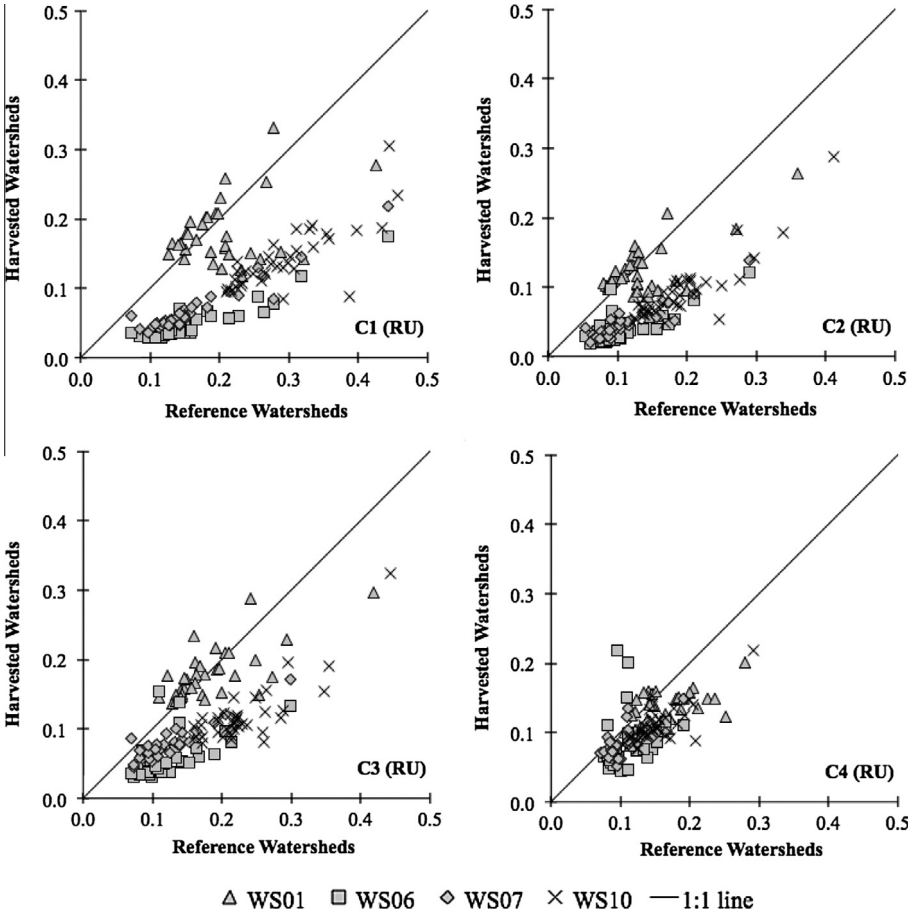

Fig. 5. Comparison of each DOM component identified in the PARAFAC model in Raman Units (RU) between harvested and reference watersheds (N = 36 for each pair of watersheds).

temperature (Kaiser et al., 2001), and thus it is possible that DOM appears more microbially-derived during summer months due to increased microbial activity and release of soil-derived DOM. Because the C4 component can either be phytoplankton-derived or represent soil microbial processing of DOM, an increased FI value alone cannot differentiate in-stream autochthonous production from soil microbial processing during summers.

The proportion of the protein-like component (C4 (%)) was inversely related to DOC and DON concentrations, $SUVA_{254}$, and flow parameters of Q and Qsum 3 through Qsum 30. This suggests that protein-like DOM increases during low-flow conditions, and decreases during seasons of shallow subsurface flow. As previous studies in this study area report, antecedent soil moisture strongly influences DOC and DON exports, and the exports increase with flow rate during the first precipitation event of the season (van Verseveld et al., 2009; Vanderbilt et al., 2003). High $SUVA_{254}$ values of highly vegetated U.S. river basins coincide with high flow conditions (Butman et al., 2012), indicating a relatively less microbially-processed DOM source. Also, high $SUVA_{254}$ during high flow seasons may indicate that highly aromatic DOM that is preferentially adsorbed to shallow soil surface (Kaiser et al., 1997) is mobilized by shallow subsurface flow or travels through preferential flow. These findings imply that increased flow during the fall flushes DOC, DON, and highly aromatic or refractory DOM accumulated in soils and valley floors over the summer along with leachate from accumulated leaf litter in and near the stream, producing increased DOC and DON concentrations as well as less microbially-processed, aromatic DOM in stream water. The negative correlation of C4 (%) with DOC and DON concentrations, $SUVA_{254}$, and flow parameters, thus, suggests that shallow subsurface flow carries lower protein-like DOM component than deeper subsurface flow.

The positive correlation between C4 (%) and the base flow index (BFI) suggests that C4 originates from deeper subsurface flow, groundwater, or deep soil sources, characteristic of low flow seasons. This is consistent with a study conducted in forested headwater of the mid-Atlantic region (Inamdar et al., 2011). Soil organic matter at depth is highly enriched in microbial compounds and is significantly more microbially-processed than surface soil organic matter (Rumpel and Kögel-Knabner, 2011; Sollins et al., 2009). Deep soils in the HJAEF contain higher free amino acids and protein than surface soils (Yano et al., 2004). Protein or protein-like fluorescent DOM is higher in deep soil and/or groundwater than in surface water (Huang et al., 2015; Inamdar et al., 2012; Sollins et al., 2009; Yano et al., 2004). Higher fluorescent protein % in groundwater and water-extractable soil organic matter (WESOM; 0–40 cm deep) compared to more surficial water has been reported from first-order forested catchments (Huang et al., 2015; Inamdar et al., 2012; Johnson et al., 2011). Additionally, several studies have found lower $SUVA_{254}$ in groundwater than surface water (Inamdar et al., 2012; van Verseveld et al., 2009); Gabor et al. (2014) reported lower $SUVA_{254}$ at depth than in surface soils. These studies are consistent with the study of Fellman et al. (2014) that found that streams with high groundwater sources had a greater contribution of old (i.e. depleted ^{14}C) and bioavailable DOM from microbial sources in western Australia.

Although DOC:DON commonly decreases with depth in soil at sites including the HJAEF (Rumpel and Kögel-Knabner, 2011; Yano et al., 2004), DOC:DON of stream water did not decrease in

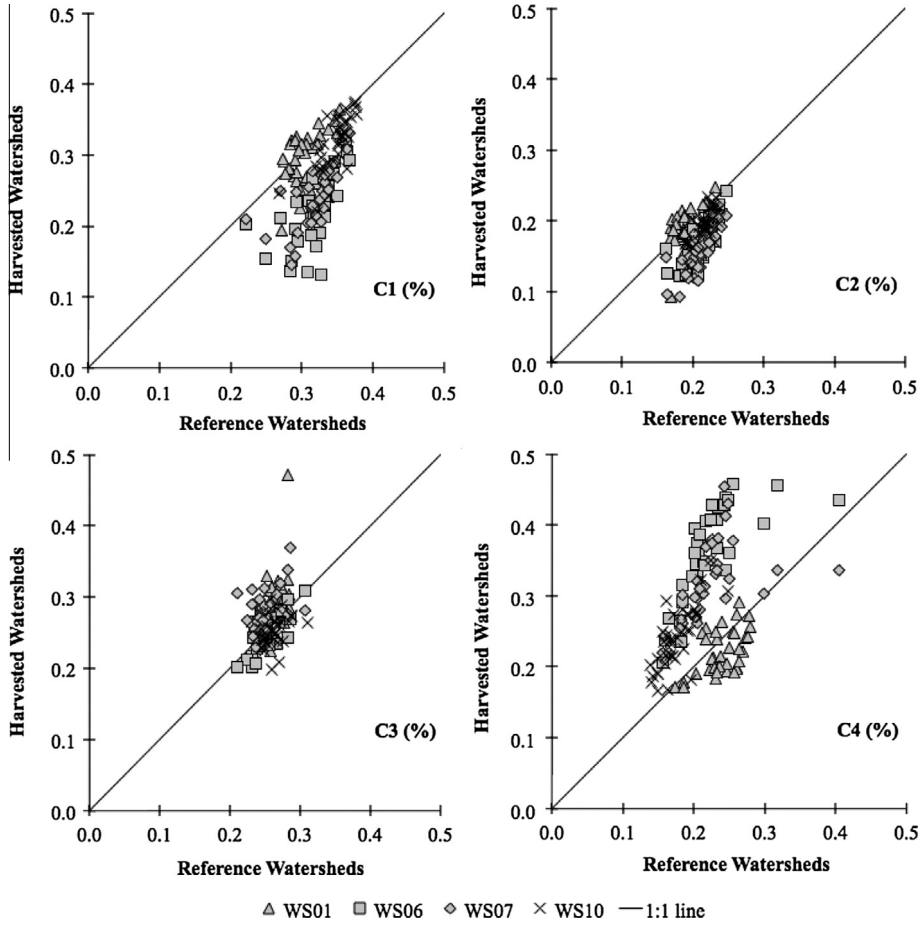

Fig. 6. Comparison of relative contributions of each DOM component (%) identified in the PARAFAC model in percentage between harvested and reference watersheds (N = 36 for each pair of watersheds).

Table 5
Linear correlations (Pearson's R) of C4 (%) and $SUVA_{254}$ with flow parameters at each of the nine watersheds at the H.J. Andrews Experimental Forest. (Two-tailed significance test, **: $\alpha = 0.01$, *: $\alpha = 0.05$).

Site		C4 (%)	$SUVA_{254}$	Q	Qsum3	Qsum14	Qsum21	Qsum30
LOOK	C4 (%)	1	−0.59**	−0.57**	−0.62**	−0.59**	−0.65**	−0.66**
	$SUVA_{254}$		1	0.51**	0.55**	0.60**	0.64**	0.62**
MACK	C4 (%)	1	−0.16	−0.67**	−0.64**	−0.62**	−0.65**	−0.65**
	$SUVA_{254}$		1	0.13	0.13	0.04	0.08	0.07
WS01	C4 (%)	1	−0.62**	−0.62**	−0.59**	−0.39**	−0.43**	−0.44**
	$SUVA_{254}$		1	0.54**	0.49**	0.59**	0.61**	0.60**
WS02	C4 (%)	1	−0.39*	−0.42*	−0.42*	−0.11	−0.10	−0.04
	$SUVA_{254}$		1	0.48**	0.45**	0.38*	0.40*	0.40*
WS06	C4 (%)	1	−0.61**	−0.37*	−0.39*	−0.21	−0.26	−0.19
	$SUVA_{254}$		1	0.42*	0.45**	0.40*	0.45**	0.39*
WS07	C4 (%)	1	−0.47**	−0.56**	−0.57**	−0.39*	−0.42*	−0.38*
	$SUVA_{254}$		1	0.36*	0.36*	0.24	0.27	0.25
WS08	C4 (%)	1	−0.14	−0.42*	−0.42*	−0.31	−0.33	−0.27
	$SUVA_{254}$		1	0.41*	0.41*	0.45**	0.49**	0.46**
WS09	C4 (%)	1	−0.23	−0.52**	−0.57**	−0.41*	−0.43**	−0.46**
	$SUVA_{254}$		1	0.37*	0.31	0.33*	0.36*	0.37*
WS10	C4 (%)	1	−0.26	−0.52**	−0.50**	−0.20	−0.22	−0.21
	$SUVA_{254}$		1	0.55**	0.53**	0.68**	0.79**	0.75**

this study during base flow. The ratio of DOC to DON is often used as an indicator of microbial activity, but did not correlate with C4 (%), our protein-like and microbial component. This could be explained by the low DON in atmospheric deposition and in streams in the HJAEF compared to other sites in the U.S. (Vanderbilt et al., 2003), resulting in DON concentrations at detection limits and with significant noise. Thus, we suggest that a protein-like or specifically a tryptophan-like EEM signal can be

used as an indicator of DOC that originates from microbial processing of terrestrial C either in the soil profile or in streams in similar low-N environments.

4.3. Forest management and landscape

We predicted that watersheds with young (50–60-yr) forests would have less abundant humic-like components (C1 to C3) and a greater contribution from a protein-like and microbial-like component (C4) in stream water compared to old-growth watersheds (500-yr-old forests). This is because DOC concentrations are still depressed in the streams of harvested watersheds even 50–60 years after harvest (Lajtha and Jones, Unpublished Results) and inventories of coarse woody debris (CWD), a source of humic DOM in watersheds with young (50–60-yr) forests have been reduced by harvest, slash removal, slash burning, site preparation, and low wood recruitment to the forest floor (Fasth et al., Unpublished Results).

This prediction was supported at harvested watersheds, WS 6, 7, and 10, where higher relative contributions of a protein-like component (C4 (%)) were observed compared to their reference watersheds (i.e. WS 8, 8, and 9, respectively). This observation is consistent with other studies conducted on the East Coast of the U.S. (Cawley et al., 2014; Yamashita et al., 2011). The high proportion of the protein-like, microbial component is likely due to the low absolute values of C1, C2, and 3 (R.U.), associated with terrestrially derived DOM, in those harvested watersheds compared to their corresponding reference watersheds; the absolute value of C4 (R.U.) remained relatively the same between all the pairs of harvested and reference watersheds. Moreover, C4 (%) in a harvested watershed, WS 1, was similar to its reference watershed (i.e. WS 2) and lower than other harvested watersheds (i.e. WS 6, 7, and 10). This is probably a result of the logistical difficulty of harvesting large, old-growth trees without roads in the early 1960s in WS 1 that resulted in relatively high amounts of CWD left on the forest floor compared to other harvested watersheds (Fasth et al., Unpublished Results). Hence, the abundance of CWD and decomposed logs, not live tree biomass, in a watershed also appears to control stream DOM characteristics by increasing highly aromatic, humic-like components in a stream and diluting the protein-like signature from older, deeper and more microbial sources. Although we also hypothesized that the presence of all relatively young trees, found in harvested watersheds, might result in lower DOC supply due to reduced fine root turnover and root exudation, the lack of difference in DOC between WS 1 and 2 suggests that this is not a significant factor explaining differences in DOM optical properties across watersheds (Lajtha and Jones, Unpublished Results).

Another possibility for the decreased C4 (%) in WS 1 is the steep slope of WS 1. The steep slope may have resulted in higher shallow subsurface flow contribution to streams compared to other harvested watersheds which then diluted the deep flow signal of C4 in WS 1. However, WS 10 is equally as steep as WS 1, and BFI of WS 1 was not the lowest (i.e. not the highest shallow flow contribution), and BFI of the HJAEF remained relatively constant between harvested and reference watersheds. Additionally, forest floor biomass could have resulted in the decreased C4 (%) in WS1; however, the forest floor biomass did not vary between control watersheds and their paired reference watersheds (Fasth et al., Unpublished Results). Hence, either the shallow flow contribution or forest floor biomass cannot be the sole reason for the low C4 (%) in WS 1.

Our correlation analysis showed that CWD and BFI individually are significant predictors of the protein-like DOM contribution. However, adding both parameters in a multiple linear regression did not improve the prediction. Of more concern is the observation that both significant correlations appear to be driven by WS 6 and 7, and both of these watersheds have high BFI and low CWD. However, CWD and BFI were not autocorrelated, and WS 8 also has a gentle slope, high BFI, but is a reference watershed with significant stocks of CWD. It is possible that WS 6 and 7 may be showing the perfect scenario to have a high protein-like DOM in streams: high base flow index (i.e. high deeper flow influence) and low CWD (i.e. low humic-like DOM), and that both of these factors need to be present in order to detect a significant difference in DOM chemistry.

5. Conclusions

In summary, this study shows that a tryptophan-like (protein-like) DOM identified with the fluorescent spectroscopy helps identify sources of DOM and shows important implications of the linkage between terrestrial and aquatic ecosystems. We attribute the increase in a protein-like DOM contribution during summer months to an increased contribution from deeper soil horizons that have an increased microbial (and thus protein) signature. Similarly, the decrease in protein-like signals during the winter can be attributed to increased shallow subsurface flow and/or increased preferential flow that is known to have a more terrestrial, humic and aromatic DOM signal. Increased in-stream microbial activity degrading organic matter inputs to the streams during the warmer summer months at our site also could increase the microbial signature of DOM; our current data cannot distinguish among these hypotheses.

A relatively higher proportion of protein-like DOM was observed among harvested watersheds compared to their reference watersheds even though DOC concentrations were lowered in harvested watersheds after 50 years of the harvest treatment. We attributed the main cause to less coarse woody debris (CWD) contributions (i.e. less humic-like component contributions) on the harvested forest floor compared to old-growth watersheds. Although the combination of CWD and BFI partially explained the fluorescent signature of DOM across these watersheds, our results suggest that the relative contributions of microbially processed, bioavailable DOM (protein), whether due to decreased terrestrial inputs such as CWD or else due to decreased water flux through surface horizons, can be detected. Our results also show that the imprint of forest harvest, and the reduction in CWD inputs to the forest floor, can be detected for many decades, with implications for the metabolism of DOM in downstream receiving ecosystems.

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