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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

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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

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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