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RESEARCH AND OBSERVATORY CATCHMENTS:
THE LEGACY AND THE FUTURE

Amount and reactivity of dissolved organic matter export are affected by land cover change from old-growth to second-growth forests in headwater ecosystems

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Abstract

Headwater forest ecosystems of the western USA generate a large portion of the dissolved organic matter (DOM) transported in streams across North America. Land cover changes that alter forest structure and species composition affect the quantity and composition of DOM transferred to aquatic ecosystems. Clear-cut harvesting affects ~1% of the forest area of North America annually, leaving most western forests in varying stages of regrowth and the total area of old-growth forest is decreasing. The consequences of this widespread management practice on watershed carbon cycling remain unknown. We investigated the role of land cover change, because of clear-cut harvesting, from mixed-species old-growth to lodgepole pine-dominated second-growth forest on the character and reactivity of hillslope DOM exports. We evaluated inputs of DOM from litter leachates and export of DOM collected at the base of trenched hillslopes during a 3-year period (2016–2018) at the Fraser Experimental Forest in north-central Colorado, USA. Dissolved organic carbon and total dissolved nitrogen were higher in lateral subsurface flow draining old- versus second-growth forest. Fluorescence spectroscopy showed that the DOM exported from the old-growth forest was more heterogeneous and aromatic and that proteinaceous, microbially processed DOM components were more prevalent in the second-growth forest. Biological oxygen demand assays revealed much lower microbial metabolism of DOM in litter leachate and subsurface exports from the old-growth forest relative to second growth. Old-growth and second-growth forests are co-mingled in managed ecosystems, and our findings demonstrate that land cover change from a mixture of conifer species to lodgepole pine dominance influences DOM inputs that can increase the reactivity of DOM transferred from terrestrial to aquatic ecosystems.

KEYWORDS
disturbance, DOM reactivity, experimental forest, headwater ecosystem, land cover change, timber harvest

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1 | INTRODUCTION

Dissolved organic matter (DOM) derived from vegetation and soils accounts for up to 90% of the organic carbon (C) found in surface water (Aitkenhead-Peterson, McDowell, & Neff, 2003) and DOM character regulates microbial C processing in aquatic environments (Benner, 2003; D'Andrilli, Junker, Smith, Scholl, & Foreman, 2019; Lennon & Pfaff, 2005). While encompassing less than 1% of the global land surface, inland waters regulate carbon cycling from landscape to continental scales (Battin et al., 2009; Cavallaro et al., 2018; Cole et al., 2007; Raymond et al., 2013), and headwater streams drain 70% of North American land area (Colvin et al., 2019). Changes to forest land cover that affect terrestrial DOM character will influence aquatic ecosystem metabolism (Cawley, Campbell, Zwilling, & Jaffé, 2014; Lajtha & Jones, 2018; Williams, Yamashita, Wilson, Jaffé, & Xenopoulos, 2010), and deciphering these relationships are crucial for predicting C cycling in inland waters.

Vegetation responses to land management can alter watershed hydrology and biogeochemistry for decades to centuries (Chantigny, 2003; Lee & Lajtha, 2016; Rhoades, Hubbard, & Elder, 2017; Troendle & King, 1985; Wilm & Dunford, 1948). In the mountain ranges of the American West, where the short growing season and cold, dry climate limit forest regrowth, the consequences of timber harvesting on snowpack, stream flow and nutrient export as well as on potential wildfire behaviour and susceptibility to insect outbreaks are long-lasting (Rhoades et al., 2017; Stottlemyer & Troendle, 1999; Wilm & Dunford, 1948). Timber harvesting decreases canopy interception and evapotranspiration resulting in more snowpack water storage, and increased soil moisture and stream flow (Troendle & King, 1985) with effects that remain measurable for more than 50 years. Timber harvesting also shifts the species composition of these forests and their development trajectory for more than a century (Collins, Rhoades, Hubbard, & Battaglia, 2011; Lotan & Perry, 1983).

Harvested stands of subalpine old-growth forests comprised of subalpine fir (*Abies lasiocarpa*), Engelmann spruce (*Picea engelmannii*) and lodgepole pine (*Pinus contorta*) typically regenerate into lodgepole pine-dominated second-growth stands (Collins et al., 2011). While the effects of land cover, age and species change on terrestrial nutrient cycling and organic matter decomposition are well studied (Chantigny, 2003 for a review), whereas, their consequences on adjacent aquatic ecosystem C cycling are not. The chemical characteristics of litter in second-growth forests alter hillslope DOM inputs relative to those in old-growth forest (Beggs & Summers, 2011; D'Andrilli et al., 2019), likely regulating the reactivity of DOM exported to streams at watershed scales. The soluble polyphenolic and protein-like DOM released from lodgepole pine litter in second-growth stands, for example, is more biologically reactive than the more aromatic DOM generated by old-growth, mixed-species forests (Beggs & Summers, 2011; Yavitt & Fahey, 1984 and 1986). Connecting the effects of land cover type on the reactivity of the forest floor to the reactivity of hillslope DOM exports will increase understanding of the effects of land cover change on watershed-scale C cycling.

Understanding the consequences of land cover and tree species shifts on watershed-scale DOM dynamics benefits from techniques that differentiate DOM reactivity of hillslope inputs and exports. Analysis of fluorescing components of DOM (FDOM) has become a routine, low-cost approach to characterize the relative abundance of biologically reactive organic molecules (Smith et al., 2018). Correlation between fluorescing and non-fluorescing DOM molecules of similar chemical structures and biological reactivities expands the utility of FDOM as an index of overall DOM quality (Stubbins et al., 2014). Optical characterization can be used in conjunction with heterotrophic microbial oxygen consumption assays to identify which DOM components are microbially created or utilized (D'Andrilli et al., 2019).

In this study, we compare DOM inputs from litter leachate and the concentration, character and biological reactivity of DOM exports in subsurface flow between adjacent old-growth subalpine and second-growth pine forests. Early work at these sites documented that clear-cut harvesting resulted in lasting increases in snow accumulation, subsurface discharge and nutrient export (Reuss, Stottlemyer, & Troendle, 1997; Starr, 2004; Troendle & Reuss, 1997). The amount of dissolved organic carbon (DOC) exported from forests is determined by O horizon C content, with old-growth forests exporting more DOC compared to regenerating ones (Cawley et al., 2014; Lajtha & Jones, 2018; Pacific, et al., 2010). However, DOC reactivity is affected by DOM character and processing within subsurface flow paths (Lehmann & Kleber, 2015). Because old-growth forests generally have deeper O horizons composed of more recalcitrant DOM (Jandl et al., 2007; Johnson, Johnson, Huntington, & Siccama, 1991), we expect greater flux but lower biological reactivity of DOM from these forests. We hypothesize that DOM exported from the pine-dominated, second-growth forest will be proportionally more biologically reactive, typical of the water-soluble proteins and polyphenolics found in pine needle litter (Beggs & Summers, 2011). Western conifer forests often require a century or longer to regrow to their pre-harvest stand structure (Burns & Honkala, 1990). The extent of old-growth forest cover has decreased during more than a century of timber harvesting and most forests are in intermediate stages of recovery (Anderson-Teixeira et al., 2013; Hurtt et al., 2011; McDowell et al., 2020). This study evaluates how forest change following clear-cut harvesting alters the reactivity of DOM transferred from the terrestrial landscape to aquatic ecosystems.

2 | METHODS

2.1 | Site description

Some of the earliest research on the effects of land cover change and forest management on stand and watershed-scale hydrology was conducted at the Fraser Experimental Forest (FEF), 137 km west of Denver, Colorado (Goodell, 1952; Hoover & Leaf, 1966; Troendle & King, 1985; Wilm & Dunford, 1948). The snowmelt-dominated hydrologic regime of Fraser's high-elevation subalpine forests is representative of a large extent of the mountainous western United States. The trenched hillslope study approach helps characterize the subsurface processes that link terrestrial landscapes to the aquatic environment. Like other trenched hillslope studies, some of which appear in this special issue (Coweeta Hydrologic Laboratory [Hewlett & Hibbert, 1963], H.J. Andrews Experimental Forest [Crampe, Segura, & Jones, 2021], Maimai New Zealand [McDonnell et al., 2021], Panola Mountain Research Watershed [Aulenbach et al., 2021]), findings from this experimental scale can be validated and strengthened by long-term catchment scale hydrology and climate data.

Mean annual temperature at FEF headquarters (elevation 2725 m) is 0.5°C, and ranges from monthly averages of -10°C in January to 12.7°C in July. Mean annual precipitation is 610 mm (range 427–902 mm; 1981–2010), nearly two-thirds of which falls as snow from October to May. Annual inorganic N deposition averaged 2.6 kg N ha^{-1} over the last decade (Argerich et al., 2013). The Fraser area was extensively glaciated and FEF is underlain by metamorphosed rock, most commonly biotite schist and hornblende or calc-silicate gneiss (Shroba, Bryant, Kellogg, Theobald, & Brandt, 2010). Soils are skeletal, sandy loam Dystric and Typic Cryochrepts (Alstatt & Miles, 1983) with 20%–30% gravel and 30%–50% cobble-sized materials. In 1979, trenches were installed on adjacent hillslopes to evaluate the role of forest cover on hillslope hydrologic processes, including quantifying the timing and amount of subsurface flow. The paired 3 ha hillslopes are adjacent to each other on a glacial moraine that is underlain at 4 m by a clay aquaclude (Reuss et al., 1997; Troendle & Reuss, 1997). Subsurface flow is collected by slotted PVC pipe installed at 4 m depth in lined trenches at the base of the hillslopes and piped to individual gauging stations (HS flumes) where water level is recorded at 10-min intervals. These water level data are then converted to subsurface flow rates using known relations between water depth and discharge (Bos, 1989). Areas of accumulation above each trenched hillslope were estimated at 1.62 ha for the old-growth hillslope and 0.12 ha for the second-growth hillslope using seismic studies and a decade of precipitation and discharge monitoring and modelling (Troendle & Reuss, 1997). In December 1984, after 5 years of pre-treatment calibration of subsurface flow rates, the entire 3 ha area of one of the trenched hillslopes was clear cut harvested, while the other was left intact.

Old-growth subalpine forests at FEF are comprised of a mixture of equal proportions of lodgepole pine, subalpine fir and Englemann spruce, respectively 32%, 34% and 34% of overstory basal area (Table S1). Low-stature shrubs (*Vaccinium scoparium*, *Vaccinium myrtillus*, *Vaccinium caespitosum and Shepherdia canadensis*) form a dense understory beneath the coniferous overstory (Popovich, 1993). The two hillslopes were identical in the stand structure before harvest (Troendle, 1985). The clear-cut hillslope has regenerated into a pine-dominated second-growth stand (82% of overstory basal area) with 9 cm mean diameter and 4 m mean height (Table S1). Mountain pine bark beetles (*Dendroctonus ponderosae*) preferentially attack larger trees (Rhoades et al., 2017), and an outbreak of beetles in 2008 killed 18% of the old-growth basal area but did not infest the second-growth stand.

2.2 | Sampling and analysis

Lateral subsurface flow begins mid to late April at the start of snowmelt, increases to the peak in early to mid-May, then declines and halts by mid to late June (Figure 1(a), Troendle & Reuss, 1997). We collected hillslope export samples as lateral subsurface flow at the base of each hillslope (i.e. at the piped trenches) weekly in 2016–2018. Hillslope export samples were analysed for DOC, total dissolved nitrogen (TDN) and DOM chemical characteristics. Samples were collected in pre-combusted (heated for 3 h at 500°C) amber glass bottles then filtered through 0.7 μm pore-size glass fibre filters (Millipore Corp, Burlington, MA) within 24 h of collection and analysed for DOC, TDN and DOM fluorescence spectroscopy. We collected DOM reactivity samples in 250 ml pre-combusted amber

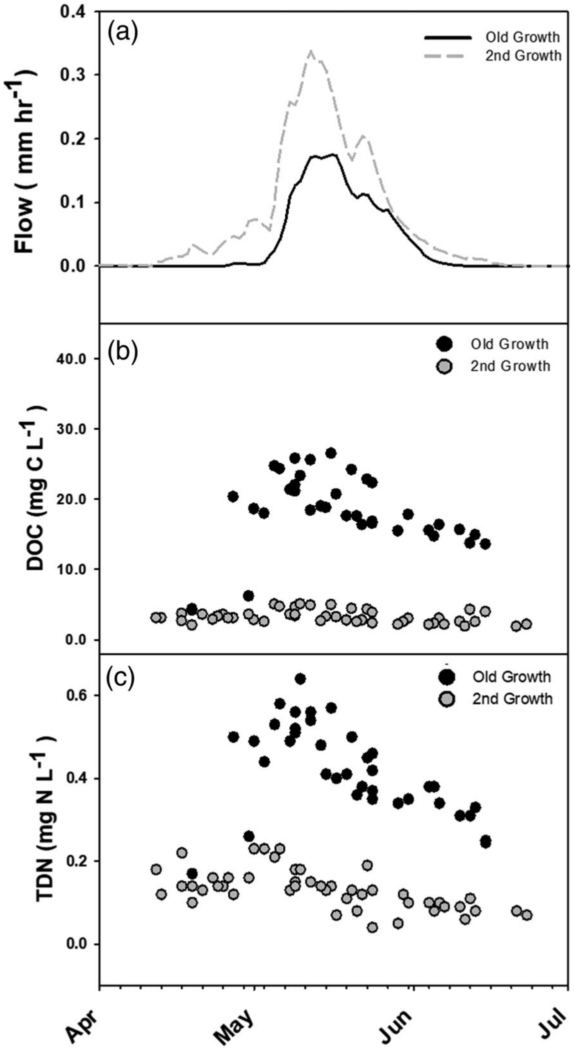

FIGURE 1 Average daily subsurface flow (a) from adjacent old-growth and second-growth hillslopes at the Fraser Experimental Forest for 2016, 2017 and 2018. Dissolved organic carbon (b) and total dissolved nitrogen (c) in subsurface flow (old-growth $n = 36$; second-growth $n = 48$)

glass bottles, and then filtered through glass fibre filters (GF/C Whatman®, 1.2 μm effective pore size) within 3 h of collection to remove bacterial grazers. DOC and TDN were determined using a Shimadzu TOC-V_{CPN} total organic carbon analyser, with 2 M HCl addition before analysis to remove mineral C (Shimadzu Corporation Columbia, MD). Detection limits for DOC and TDN were 50 μg L^{-1}.

The optical properties of DOM exported from each hillslope (i.e. lateral subsurface flow) were analysed using UV–Visible fluorescence spectroscopy on a Horiba Scientific Aqualog (Horiba-Jobin Yvon Scientific Edison, New Jersey, USA). Samples with greater than 5 mg C L^{-1} concentration were standardized to 5 mg C L^{-1} using deionized water (>18 mΩ), while all other samples were undiluted. Ultraviolet absorbance was analysed at the 254 nm wavelength. Excitation emission matrix (EEM) fluorescence scans were completed from 240 to 600 nm excitation and emission wavelengths, with 5 nm bandpass, 3 nm increments and 1 s integrations. Scans were blank corrected using deionized water and corrected for inner filter effects (Kubista, et al., 1994). First- and second-order Rayleigh scattering were masked (10 nm width masking), and samples were normalised by the area of the deionized water Raman scattering peak (Lawaetz & Stedmon, 2009).

$SUVA_{254}$ (L mg C^{-1} m^{-1}) was calculated by dividing ultraviolet absorbance at 254 nm by DOC concentration (Weishaar et al., 2003). Humification index (HIX) is an indicator of DOM humicity and aromaticity and was calculated as the area of spectra collected under 435–480 nm emission divided by the area under the peak 300–345 nm emission at 254 nm excitation; higher HIX values represent more complex DOM (Zsolnay, Baigar, Jimenez, Steinweg, & Saccomandi, 1999). Fluorescence index (FI) was calculated as the ratio between emission at 470 and 520 nm at 370 nm excitation; higher FI values are associated with DOM of microbial origin (Cory & McKnight, 2005). Fluorescence regional integration modelling (FRI) was applied to EEM data (Chen, Westerhoff, Leenheer, & Booksh, 2003). Briefly, EEM scans were separated into five regions associated with distinct DOM chemical components. Total fluorescence intensity for each region was divided by total intensity of the entire scan, resulting in percentages of total FDOM derived from each DOM chemical component region. Differences in individual peak indices (HIX and FI) between our hillslope treatments were large enough for clear interpretation, there was minimal fluorophore tailing and peak overlap, and the FRI approach effectively characterized these samples (Figure S1).

We sampled the organic (O horizon) and mineral (A horizon; 10 cm depth) soil layers at 10 locations distributed across the old-growth and second-growth hillslopes ($n = 20$). O horizon material was sampled within a 30 cm by 30 cm quadrat and total O horizon depth was measured in each quadrat corner. O horizons were separated into litter and duff layers as follows (FOREST INVENTORY AND ANALYSIS [FIA] 2019): needles and recognizable plant material (<6 mm diameter) were classified as litter, while unrecognizable, fragmented material between the litter and mineral soil layers was considered duff. There was no measurable duff in the second-growth forest. Mineral soil (0–10 cm depth) was collected using a 7.5 cm diameter corer after the O horizon was removed. Mineral soils had rocks, mosses and lichens removed, and were then sieved to 2 mm. Organic horizon samples were mixed well and moss, lichen and rocks were removed by hand. Organic horizon samples were dried for 6 days at 60°C and the total mass was recorded. Total bulk density for mineral and organic soils was calculated by dividing the dry weight of the total soil (including >2 mm fraction in mineral soils) by the sample volume. A subset of each sample was dried for 48 h at 60°C, then ground and analysed for total C and N by dry combustion (LECO 1000 CHN analyser, LECO Corporation). Total C and N pools were calculated by multiplying C and N concentrations by the associated O- and A-horizon masses. Water extractable soil organic matter (WEOM) samples were created by leaching a litter layer sample from each hillslope's O horizon to replicate DOM inputs (Sparling, et al., 1998). Litter samples were air dried for 3 days; then 10 g subsamples were steeped in 50 ml of deionized water (DI) (>18 mΩ) at 70°C for 18 h, shaken and filtered through 0.7 μm pore size glass fibre filters.

Biological oxygen demand assays were performed to assess the reactivity of DOM inputs (WEOM litter leachates) and DOM exports (lateral subsurface flow). DOM input incubations were diluted and standardized to 30 mg C L^{-1} to replicate C concentrations of DOM export incubations. Each DOM input sample was inoculated with 88 ml of water from an adjacent stream (Sparling, Vojvodić-Vuković, & Schipper, 1998), and export DOM was incubated with microbes that occurred naturally in the subsurface flow. Relationships in reactivity between input and output DOM should be considered tentative correlations, as different microbial cultures were used in litter and subsurface leachate incubations. Experimental controls contained the stream water microbial culture with no additional DOM and deionized water controls (>18 mΩ) were incubated simultaneously with the oxygen demand assays. Microbial dissolved oxygen consumption (mg O_2 L^{-1}) was measured at 15-s intervals using oxy-4 probes (PreSens, Precision Sensing GmbH, Regensburg, Germany). Input and export samples were incubated in the dark at 20°C and the hourly oxygen consumption rate (mg O_2 L^{-1} h^{-1}) was averaged over the 24-h incubation period. No samples approached hypoxic conditions (<4 mg O_2 L^{-1}). Oxygen consumption rates were normalized per gram of C to remove any bias of C quantity on consumption rate. Post-incubation samples were filtered to remove microbial biomass (Nucleopore®, polycarbonate filter, 0.2 μm). The concentration of C mineralized (Δ mg C L^{-1}) was calculated as the difference between measured pre- and post-incubation DOC concentrations; then converted to CO_2 loss (ΔCO_2, in mg CO_2 L^{-1}), under the assumption all CO_2 produced by incubations was removed by acidification during C measurement. The respiratory quotient (RQ), was calculated by dividing C lost to respiration (ΔCO_2, in mg CO_2 L^{-1}) by the change in O during the incubation (ΔO_2 in mg O_2 L^{-1}).

DOC and TDN concentrations, and FDOM indices in subsurface flow exports were compared between old-growth and second-growth land cover types using Welch-Satterthwaite unequal variance *t*-test with significance assigned at $p < 0.01$ (R Studio Team, 2019). Regional percentages for FDOM components (FRI modelling) in export samples were logit transformed before statistical analyses to remove biases inherent in proportional data. We compared nutrient concentrations and pools in organic and mineral horizon soils and oxygen consumption and respiratory quotients for DOM leachate and subsurface export between old-growth and second-growth hillslopes using the Student's *t*-tests for parametric data, with significance assigned at $p < 0.01$ (*t*-test function, R Studio Team, 2019).

3 | RESULTS

3.1 | C and N inputs to the hillslope from soil O horizons

For the old-growth hillslope, O horizon mass, total C and total N content were 6, 4 and 11 times higher, respectively than the adjacent second-growth stand (Table 1). The C:N ratio of the O horizon for the old-growth was roughly half that of the second-growth hillslope. Mass and C content of litter layers were similar between hillslopes, but the N concentration was twice as high in litter on the old-growth hillslope. The C concentration of the uppermost mineral soil (10 cm depth) was 1.3 times higher in the second-growth forest but N concentration did not differ (Table 1).

3.2 | C and N exports in lateral subsurface flow

Lateral subsurface flow from the second-growth forest started earlier, ran later and generated twice the total runoff compared to the old growth forest (Figure 1(a), Table 2). Concentrations of DOC and TDN exported in lateral subsurface flow from the old-growth forest were 5 and 3 times higher than those from the second-growth forest and C:N (DOC/TDN) was also higher in old-growth exports (Table 2, Figure 1(b),(c)). Peak DOC and TDN concentrations for the old-growth forest export coincided with the mid-May peak in subsurface runoff (Figure 1). In contrast, the DOC and TDN concentrations in subsurface export from the second-growth hillslope were uniformly low. Annual subsurface flux of DOC and TDN were 3 and 1.5 times higher from the old-growth hillslope (Table 2).

3.3 | Characteristics of dissolved organic matter exported in hillslope lateral subsurface flow

DOM exported from the old-growth forest was more aromatic with a >15% higher mean SUVA_{254} (3.46 vs. 3.00) and twice the mean humification index (HIX) (12.24 vs. 6.63) of the second-growth forest. The DOM exported from the old-growth hillslope had a mean FI of 1.14 compared to 1.52 from the second-growth hillslope. Fluorescence regional integration modelling (FRI) confirmed the patterns shown by the EEM indices (Figure 2). FDOM corresponding to amino acids (RI and RII) and microbial exudates (RIV) were higher in exports from the second-growth hillslope. Conversely, plant-derived fulvic-like and humic-like hydrophobic organic acids (RIII and RV) were higher in exports from the old-growth hillslope.

TABLE 1 Soil horizon mass, carbon (C) and nitrogen (N) pools, C and N concentrations, and C:N ratios in organic and mineral (0–10 cm) soil horizons on adjacent old-growth and second-growth forest hillslopes at the Fraser Experimental Forest, Colorado, USA

		Old growth		2nd growth		Old growth		2nd growth	
		(%)				(Mg ha^{-1})			
		Mean	SE	Mean	SE	Mean	SE	Mean	SE
Soil horizon Mass	Litter	–	–	–	–	7.91	1.01	7.73	1.02
	Duff	–	–	–	–	36.63	3.61	–	–
	Total O horizon	–	–	–	–	44.54**	3.73	7.73	1.02
Carbon	Litter	53.28	0.97	55.25	0.33	4.21	0.52	4.24	0.57
	Duff	34.05	1.84	–	–	12.19	1.08	–	–
	Total O horizon	43.67*	2.41	55.25	0.33	16.40**	1.13	4.24	0.57
	Mineral	3.05	1.30	4.04	1.43	20.42	5.25	23.44	6.06
Nitrogen	Litter	1.12**	0.11	0.60	0.02	0.10**	0.01	0.04	0.01
	Duff	1.01	0.12	–	–	0.40	0.04	–	–
	Total O horizon	1.07**	0.11	0.60	0.02	0.50**	0.04	0.04	0.01
	Mineral	0.11	0.13	0.10	0.04	0.60	0.10	0.90**	0.10
C:N ratio	Litter	50.33**	2.59	94.28	9.98	–	–	–	–
	Duff	35.11	2.28	–	–	–	–	–	–
	Total O horizon	42.72**	2.41	94.28	9.98	–	–	–	–
	Mineral	26.69	6.24	28.04	6.17	–	–	–	–

Note: Values are means with standard errors ($n = 10$ per hillslope type). Total O-horizon concentrations are averages of litter and duff. Total O-horizon pools are sums of litter and duff horizons. Within each horizon, * and ** denote differences at $p < 0.01$ and <0.001 using a Student's parametric *t*-test.

TABLE 2 Discharge, dissolved organic carbon (DOC), total dissolved nitrogen (TDN) concentrations, and annual fluxes in subsurface flow and DOC and TDN in water extractable organic matter (WEOM) litter leachates from adjacent old-growth and second-growth hillslopes at the Fraser Experimental Forest, Colorado, USA

		Old growth		2nd growth	
WEOM litter leachates		Mean	SE	Mean	SE
DOC	(g C L^{-1})	3.22	0.08	3.24	0.14
TDN	(g N L^{-1})	0.08	0.01	0.15**	0.01
DOC:TDN		46.35**	4.30	22.51	1.33
Exports from subsurface flow					
Annual subsurface discharge	(mm $year^{-1}$)	76.98	15.19	158.88	26.73
DOC	(mg C L^{-1})	20.55**	4.84	3.60	0.89
TDN	(mg N L^{-1})	0.47**	0.14	0.14	0.05
C:N		44.50**	6.49	28.6	8.67
Annual subsurface DOC flux	(kg C ha^{-1} $year^{-1}$)	16.49**	4.44	5.16	0.46
Annual subsurface TDN flux	(kg N ha^{-1} $year^{-1}$)	0.37**	0.08	0.21	0.02

Note: Subsurface export values are means with standard errors for the 2016, 2017 and 2018 snowmelt seasons from the old-growth and second-growth hillslopes. Subsurface flow sample numbers for DOC and TDN were $n = 36$ for the old-growth and $n = 48$ for second-growth. WEOM values are means with standard errors for samples collected in 2018 ($n = 10$ for each hillslope type). Differences between hillslopes are noted by ** at $p < 0.001$, using a Welch-Satterthwaite non-parametric t-test for the subsurface export data and a Student's parametric t-test for WEOM samples.

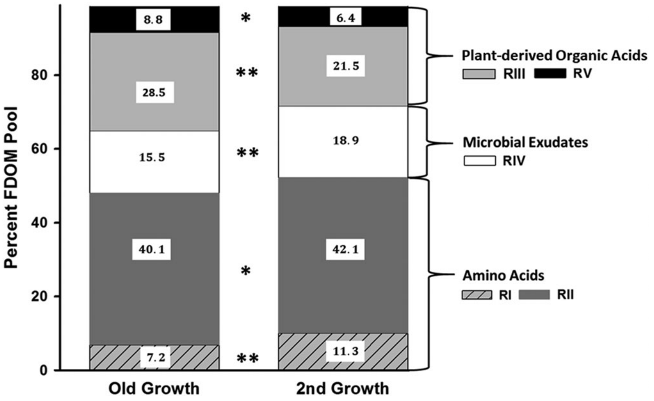

FIGURE 2 Components of fluorescing dissolved organic matter (FDOM) in subsurface flow differentiated by fluorescence regional integration (FRI) modelling. Values are means from 2016, 2017 and 2018 for adjacent old-growth ($n = 23$) and second-growth ($n = 35$) hillslopes. Differences between FRI regions (RI-RV) on logit transformed data were noted by * at $p < 0.01$ and ** at $p < 0.001$ using a Welch-Satterthwaite non-parametric t-test

FDOM optical character (FI and HIX) was similar in exports from the two hillslopes at the onset of subsurface flow but diverged over time (Figure 3(a),(b)). Across the subsurface flow season, FI decreased by half the possible range in the old-growth hillslope. The proportion of complex organic acids (based on HIX) in FDOM exported from the old-growth hillslope increased threefold during the flow period. In contrast, the optical character of FDOM exported from the second-growth hillslope remained relatively uniform (Figure 3(a),(b), Figure S1).

3.4 | Reactivity of litter dissolved organic matter inputs and lateral subsurface flow dissolved organic matter exports

Patterns of biological reactivity in DOM inputs in litter leachate between hillslopes matched those of DOM exports in subsurface flow. DOM inputs and exports on the second-growth hillslope had dissolved oxygen consumption rates more than twice those from old-growth, reflective of higher DOM reactivity (Figure 4).

4 | DISCUSSION

Forest recovery following timber harvesting and wildfire often shifts mixed-species subalpine forests to pine-dominant stands (Collins et al., 2011), and in our study, the second-growth forest had 69% less hillslope DOM export than the old-growth forest (Table 2, Figure 1). The amount of C contained within the O horizon determines the amount of DOM available for microbial processing and subsurface transport (Lee, Park, & Matzner, 2018; Nave, Vance, Swanston, & Curtis, 2010). Pre-harvest soil C content was similar between the hillslopes (Table S2, Reuss et al., 1997; Stottlemyer & Troendle, 1999). However, as seen elsewhere, we found higher O horizon C stock, DOC concentrations and annual export in the old-growth compared to the second-growth forest that regenerated on the harvested hillslope (Chatterjee, Vance, Pendall, & Stahl, 2008; Chatterjee, Vance, & Tinker, 2009). The higher DOC exported from the old-growth (likely resulting from direct leaching of O horizon and transport through shallow, subsurface flowpaths) underscores the importance of subsurface transport of organic C from soil O horizons to shallow mineral layers.

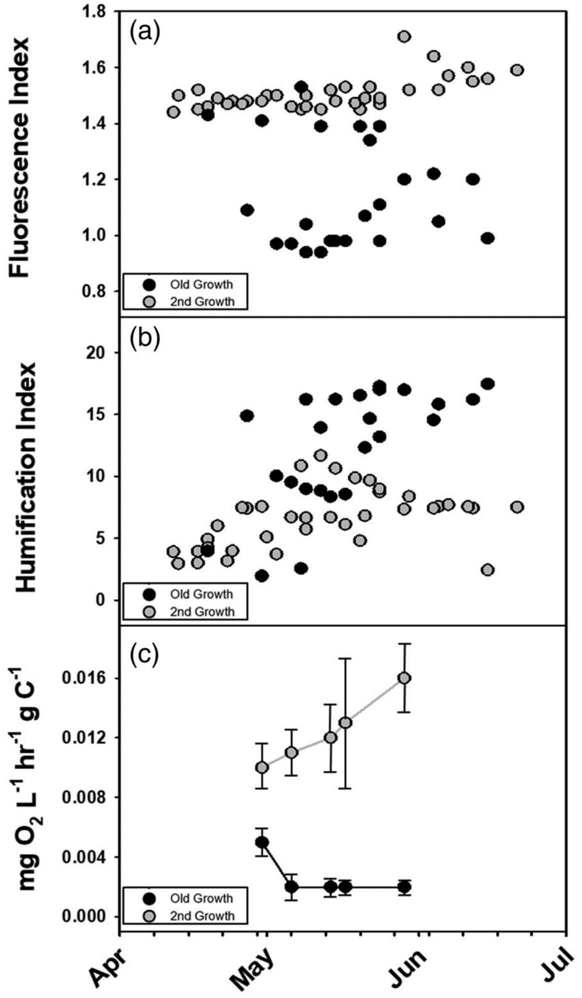

FIGURE 3 Dissolved organic matter (DOM) quality and reactivity in subsurface leachate for adjacent old-growth and second-growth hillslopes. DOM quality examined through fluorescence index (a), and humification index (b) for samples collected during 2016, 2017 and 2018 flow periods ($n = 23$ for second- and $n = 35$ for old-growth). Biological oxygen demand assays of DOM reactivity report oxygen consumption during the 2018 flow period (c)

Our findings suggest that land cover shifts following forest disturbance (McDowell et al., 2020) and harvesting is likely to decrease the amount of organic C exported to headwater streams.

Our hillslope-scale findings agree with those from nearby paired old-growth (East Saint Louis) and mixed-aged (Fool Creek) forest watershed studies (Troendle & King, 1985; Table S3). Like our trenched old-growth hillslope, export of DOC and TDN were higher from the old-growth watershed during the study period and matched those reported for the previous decade (Rhoades et al., 2017). Exports of DOC in the mixed-age watershed were 63% greater than those of the second-growth hillslope, likely due to time since treatment (64 years watershed; 33 years trenched hillslope), the proportion of the watershed harvested (40% watershed; 100% trenched hillslope) and other factors. Similar to the hillslope scale, the extent of old-growth stands within the mixed-age watershed (i.e. 60% of the area) is likely to elevate DOC exports compared to the 100% harvested second-growth hillslope. The conditions from the old- and second-growth trenched hillslopes represent land cover endmembers. However, managed catchments and landscapes are comprised of complex and dynamic combinations of forest composition and ages that remain a challenge to characterize.

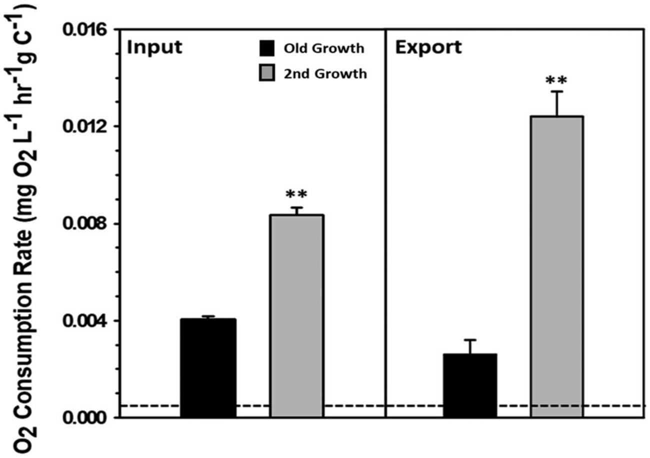

FIGURE 4 Reactivity measured as oxygen consumption rates for dissolved organic matter (DOM) extracted from O horizon litter inputs and subsurface flow exports ($n = 10$ per hillslope treatment with standard error bars). The dashed line shows oxygen consumption for a sample of the native microbial culture without hillslope DOM added (experimental control). Differences between hillslope treatments are noted by ** at $p < 0.001$ using Student's parametric *t*-test

The chemical character and biological reactivity of DOM inputs from organic horizons also differed between forest types (Table S1, Figure 4). While the old-growth had more recalcitrant DOM inputs, the more reactive DOM compounds of the second-growth inputs (Figures 3(c) and 4) and associated fluorescence indicators (Figure 3 (a),(b)) were typical of DOM released from pine litter (Beggs & Summers, 2011; Berg & McClaugherty, 2014; Reckhow, et al., 1990; Yavitt & Fahey, 1984). The similar forest composition and soil C content of the adjacent hillslopes suggest that pre-harvest DOM differences would have been minimal (Table S2, Reuss et al., 1997; Stottlemyer & Troendle, 1999). Calculation of respiratory quotients (RQ, $\Delta CO_2/\Delta O_2$) allows for inference of stoichiometric ratios (C:O) of respired DOM (Berggren, et al., 2012) and the RQ of the DOM released from second-growth forest litter (1.25) was consistent with microbial utilization of proteins or sugars. The lower RQ (0.18) of DOM from the old-growth site, in contrast, suggests metabolism of humic acids, fulvic acids and tannins.

The lower C:N ratio of the old-growth organic horizons compared to the second-growth forest (42.7 vs. 94.3; Table 1) contrasts with the higher C:N ratio of the DOM released from old-growth litter (46.4 vs. 22.5; Table 2). The higher N contained in old-growth organic horizons, combined with lower subsurface TDN export indicates limited microbial utilization of recalcitrant, N-containing organic compounds and low release of soluble N forms (Rillig, Caldwell, Wösten, & Sollins, 2007; Schimel & Bennet, 2004; Schulten & Schnitzer, 1997). Nitrate export from the second-growth hillslope was consistently higher relative to the old-growth hillslope for more than a decade following harvesting and stands regeneration (Reuss et al., 1997; Starr, 2004). Further, higher dissolved oxygen consumption from the second-growth site is an indicator of greater DOM reactivity in pine litter leachate (Figure 4). As opposed to the thin needle litter of the second-growth pine stand, the deep, stratified, O horizon of the old-growth forest generates less reactive DOM (Table 1).

Reactivity of subsurface DOM exports differed between forest cover types. The predominantly pine litter of the second-growth hillslope produced biologically reactive DOM (Figure 4) that was subject to microbial transformation as it infiltrated into soils and moved along subsurface flowpaths (Figures 2 and 3). The greater prevalence of microbially processed DOM we found in second-growth hillslope exports was consistent with numerous other studies of DOM composition and export after post-harvest and subsequent forest change (Cawley et al., 2014; Lee & Lajtha, 2016; Williams et al., 2010; Yamashita, Kloeppel, Knoepp, Zausen, & Jaffé, 2011). In contrast, the DOM exported from old-growth forest was less biologically reactive (Figure 3(b), Figure 4), consistent with fluorescence indicators of DOM recalcitrance and complexity (Figure 3(a),(b)).

We found that DOM reactivity changed in distinct ways in the two forest types as it moved along subsurface flowpaths (Figure 4). Like the most high-elevation forests (Bockheim, 2002), the majority of DOM from the trenched hillslopes originates from organic soil horizons. While the reactivity of DOM deeper in the soil profile is unknown, lower soil C concentration at depth (Table 1, Table S2), the well-drained soils (Alstatt & Miles, 1983), and synchronous peaks of hillslope discharge and DOM at these sites are consistent with leaching from surface soils (Figure 1). The thick O horizons in the old-growth forest released more DOC, though its recalcitrant, aromatic composition limited the degree of subsurface DOM processing (Figure 4). In contrast, the more reactive DOM of the second-growth forest changed substantially along subsurface flowpaths (Figure 4). Both our FRI modelling and earlier works (Córdova et al., 2018; Yano, Lajtha, Sollins, & Caldwell, 2005) demonstrate the conversion of reactive DOM from litter into microbial biomass and release of increasingly reactive compounds in hillslope exports (Figure 2). The highly reactive nature of second-growth DOM inputs, along with changes in soil microbial communities (Chatterjee et al., 2008) and root exudate production (Douglas, Parker, & Cullings, 2005) associated with regenerating forest may stimulate turnover of C stored in mineral soil (Evans, Pierson, & Lajtha, 2020; Kuzyakov, 2010). This agrees with studies that indicate that microbially processed C may contribute to vertical C movement from surface litter into the mineral soil profile (Córdova et al., 2018; Cotrufo, Wallenstein, Boot, Denef, & Paul, 2013).

The optical properties of DOM exported from the old-growth hillslope shifted over the course of the snowmelt season (Figure 3(b),(c)) and indicated a decline in relatively reactive byproducts of microbial processing and an increase in recalcitrant compounds. This pattern suggests the presence of distinct DOM sources in this forest type. The DOM transported early in the snowmelt season may be comprised of reactive metabolic byproducts that accumulated during overwinter microbial transformation of recalcitrant organic compounds from old-growth litter (Schmidt et al., 2007). After this initial flush, DOM export may originate from unprocessed compounds leached directly from the recalcitrant O horizon of the old-growth forest floor (Figure 3(b)). In contrast, the DOM exported from the second-growth forests was both more reactive and increased in reactivity through the snowmelt season (Figure 3(c)). This increase in DOM reactivity may result from input and turnover of leachates of reactive litter to microbial biomass that increases rates of oxygen consumption.

5 | CONCLUSION

Forested headwater streams drain much of the land area in North America (Colvin et al., 2019) and are a major contributor of C to the atmosphere (Cavallaro et al., 2018). Regeneration of pine stands following harvest of old-growth forests is a common land cover change in the western United States (Collins et al., 2011), one that has long-term consequences on the quantity and composition of DOM exported from forest hillslopes and watersheds. We found that the DOM exported from second-growth hillslopes was five times more reactive than that from old-growth, though the total amount of DOC released was three times lower. As such, export of bioavailable DOM from second-growth was 67% more than that released from old-growth forest, increasing the amount of DOM available to stream microbes. The slow recovery of these forests following harvest and other ecosystem disturbances extends the persistence of these land cover changes on DOM composition and reactivity in headwater ecosystems.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of the article at the publisher's website.

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