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RESEARCH ARTICLE
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Key Points:

- Terrestrial sourced dissolved organic matter (DOM) dominates drainage waters in a northeast temperate forest
- Typical podzols at lower elevations produced higher fractions of microbially processed organic matter
- DOM within a calcium silicate-treated watershed also exhibited more extensive microbial processing

Supporting Information:

Supporting Information may be found in the online version of this article.

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Dissolved Organic Matter Dynamics in Reference and Calcium Silicate-Treated Watersheds at Hubbard Brook Experimental Forest, NH, USA

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Abstract Dissolved organic matter (DOM) can serve as an indicator of watershed carbon cycling, and links terrestrial to aquatic ecosystems. The extent DOM is microbially processed before it enters aquatic ecosystems is expected to change with soil depth and landscape position, and as some research suggests, in response to recovery from chronic acidification. Here we examined DOM within freely flowing soil pore water and stream water collected from reference and calcium silicate-treated watersheds at the Hubbard Brook Experimental Forest, New Hampshire, USA. Dissolved organic carbon (DOC) and nitrogen (DON) concentrations as well as, absorption and fluorescence properties were analyzed to assess patterns in DOM quantity and quality. Parallel factor analysis was used to identify three predominant fluorescing DOM components (C1-3). All three components were terrestrial in origin, however C3 exhibited spectral properties previously linked to the microbial processing of humic material. Distinct horizonal patterns emerged between genetic soil horizons. DOC quantity decreased with soil depth, so too did, the plant derived lignin-like fraction (C2), while the C3 fraction increased. High-elevation coniferous zones with shallow bedrock contributed to higher DOC concentrations in soil and stream water, while high and low-elevation mineral soils exhibited greater C3 fractions and fluorescence indicators of microbially processed DOM. This pattern suggests these mineral soils are important organic carbon sinks, due to greater rates of microbial DOM processing. DOC in forest floor solutions, C3 fractions, and indicators of smaller molecular size (E_2:E_3) were all higher in the calcium silicate-treated watershed, suggesting greater microbial processing of DOM.

Plain Language Summary Northeast forests are recovering from decades of acid rain, while also impacted by a changing climate. Decaying organisms remains contribute highly variable forms of organic matter in soil, which can serve as an energy source for microbes and other decomposers. A fraction of this organic matter is dissolved and transported by water through the forest soils into streams affecting downstream water quality. Two decades ago, a small watershed at the Hubbard Brook Experimental Forest, in New Hampshire was treated with a calcium-enriched mineral to accelerate recovery from acid rain. Since the application, chemical and biological indicators have seen a marked recovery. The goal of our current study was to examine patterns in dissolved organic matter quantity and quality within reference forest soil and stream water and the response to the calcium treatment. We used spectrofluorometric measurements and modeling to determine different organic matter fractions. One resulting fraction showed evidence of microbial processing, and its relative abundance increased with soil depth, especially at lower elevations in the calcium-treated watershed where mineral soils are deeper and experience more vertical water flow. Greater fractions of unprocessed organic matter were transported through soils into streams at higher elevations in both watersheds.

1. Introduction

Dissolved organic matter (DOM) plays a critical role in the transfer of energy and nutrients within and between terrestrial and aquatic ecosystems (Jaffé et al., 2008). Soils have the capacity to store considerably more carbon than quantities found in either the atmosphere or plant biomass (Schmidt et al., 2011). A fraction of soil carbon is mobilized as DOM to drainage waters, making it one of the largest sources of organic carbon to freshwater and marine ecosystems (Battin et al., 2008).

DOM composition is highly dependent on its source material and the biological and geochemical processes enacted upon it as it is processed through watersheds (Catalán et al., 2014). Studies have found that when DOM is transported through soils, the lignin-like compounds tend to be retained through sorption to Al and Fe oxides-hydroxides (Possinger et al., 2020; Pourpoint et al., 2017; Riedel et al., 2013). In contrast, carbohydrate and protein-like organic matter more readily percolates through soil, where it is available for microbial metabolism (Kaiser et al., 2004). Soil microbes process these compounds, mineralizing organic nitrogen and contributing their own detritus to the dissolved mixture. These processes were synthesized by Kaiser and Kalbitz (2012) into a conceptual model depicting DOM processing throughout the soil profile. This framework for future quantitative measurements suggests patterns of decreased phenolic-like compound fractions coincident with an increase in microbial metabolites with soil depth (Mikutta et al., 2019).

Anthropogenic climate change is altering the processing of DOM withing watersheds (Cawley et al., 2014). In the northeast United States, increases in air temperature have coincided with a lengthening of the growing season (Groffman et al., 2012; USGCRP, 2018). In addition, there has been an increase in annual precipitation, a decrease in the fraction of precipitation occurring as snow and an increase in the intensity of precipitation events. Intense hydrologic events can facilitate the transport of fresh, lignin-like DOM deeper into soils or to streams via bypass soil flow paths (Fröberg et al., 2007; Raymond et al., 2016). At the landscape scale, soils in forested headwater catchments that experience frequent and fluctuating water tables have been found to be zones of carbon accumulation, especially within lower mineral soils where illuvial organic carbon is high but overall dissolved organic carbon (DOC) is low (Bailey et al., 2014; Patel et al., 2021; Possinger et al., 2020). Additional work has shown that during the wetting events, anoxic conditions promote increases in soil CO_2, N_2O, and CH_4 (Werner & Gessler, 2011). Hydrologic events have been found to connect microbial decomposers and sources of carbon within the soil macropore system, resulting in increased CO_2 fluxes and changes in the chemical quality of DOM to more microbially derived content (Bailey et al., 2017; Kravchenko et al., 2021).

An additional factor contributing to DOM transport in watersheds is the recovery from acid deposition. In the eastern U.S., volume-weighted concentrations of sulfate and nitrate in atmospheric deposition have significantly decreased in response to the Clean Air Act and associated rules (Driscoll et al., 2001, 2016). Long-term studies have suggested that decreases in the sulfate concentrations coincide with the release of DOC into surface waters (Driscoll et al., 2003, 2016; Monteith et al., 2007). Another key component of acid deposition is nitrogen derived from nitrogen oxide (NOx) and ammonia emissions (Ukonmaanaho et al., 2014). In the northeastern United States nitrate deposition is decreasing (Lloret & Valeila, 2016). However, in many regions atmospheric nitrogen deposition is increasing, primarily due to increases in ammonia emissions (Lamarque et al., 2013). Elevated inputs of anthropogenic nitrogen have been found to significantly suppress the decomposition of organic matter in forested ecosystems (Tonitto et al., 2014), through either acidification effects or loss of biodiversity in the soil microbial community (Davidson et al., 2012; Gilliam et al., 2019). Therefore, with recent decreases in atmospheric NO_3^-, organic matter decomposition may be enhanced (Driscoll et al., 2016; Groffman et al., 2018).

Soil organic matter is an important regulator of soil pH, while soil pH is an important regulator of DOM. pH and DOM control the solubility of aluminum (Driscoll & Postek, 1995). When mobilized under acidic conditions, aluminum competes with hydrogen ions for binding sites on organic matter colloids, thus enhancing coagulation of DOM and formation of soil organic matter (Cronan & Schofield, 1990; Li & Johnson, 2016). Following reductions in acid deposition, increases in pH decrease the partitioning of DOC to forest soil (Ussiri & Johnson, 2003). Also, a reduction in the ionic strength of soil solution associated with decreases in atmospheric deposition has increased DOM solubility, leading to increased DOC export (Monteith et al., 2007). These findings suggest that recovery from chronic acidification could enhance the quantity of mobile DOM and alter its quality within forested watersheds (Clarholm & Skylberg, 2013). Note that soil organic horizons are characterized by low pH and this pattern may obscure pH-DOM relationships in soil and stream water. As a result, it may be instructive to examine DOM patterns over both horizonal and watershed scales to better elucidate controls on DOM quantity and quality.

New evidence indicates that increased organic carbon transport within forest soils associated with ecosystem recovery from acid deposition and climate change may be connected to nitrogen limitation in forested ecosystems, through a process referred to as "nitrogen oligotrophication" (Groffman et al., 2018). Long-term

observations of watershed stream nitrate export at the Hubbard Brook Experimental Forest (HBEF), NH have shown that declines began in the 1960s, well before NOx emission declines associated with the Clean Air Act, and continue today (Groffman et al., 2018). Additionally, increases in the forest floor C/N ratio have been observed, despite no relative change to the nitrogen pool, suggesting that nitrogen is either being retained by DOM adsorption or metabolized by microbes in lower mineral soils (Yanai et al., 2013). The latter mechanism is supported by significant declines in potential nitrogen mineralization and nitrification, and increases in soil microbial respiration (Durán et al., 2016; Groffman et al., 2018). Thus, the flow of "labile" carbon (DOM) into lower mineral soils could stimulate microbial communities to immobilize reactive nitrogen leading to an overall tightening of available nitrogen cycling within northern forest ecosystems (Groffman et al., 2018).

Recent observations of enhanced mobilization of DOM from soil to surface waters, a phenomenon called "browning," is thought to be a response to recovery from acid deposition and changing climate. Browning has enhanced interest in better understanding DOM processing and how it has manifested a new regime of increased DOM surface water concentrations. Increased mobilization of DOM and associated iron increases the attenuation of light in lakes, which increases upper water temperatures earlier in the summer season, forming shallower thermoclines and strengthening stratification (Brothers et al., 2014; Effler et al., 1985). Nutrients associated with DOM can enhance productivity unless light attenuation becomes so severe that lakes become light limited (Solomon, 2017), although recently Stetler et al. (2021) reported that organic nitrogen and phosphorus have not increased in northern lakes coincident with browning. These changes in water clarity, temperature, stratification, and productivity can decrease oxygen levels and enhance mobilization of sediment phosphorus, causing shifts in lower trophic level zooplankton populations which could impact lacustrine food chains (Williamson et al., 2016). DOM can also complex and facilitate the transport of metals from the forest into surface waters. The mobilization of aluminum and mercury can have negative impacts on terrestrial and aquatic ecosystems (Chiasson-Gould et al., 2014; Li & Johnson, 2016).

There is a poor understanding of how the production and processing of DOM occurs with soil development and is manifested at the landscape scale. Moreover, with interest in the linkage between acid deposition and browning it is unclear how the acid-base status of soils affects DOM production and processing at the watershed scale. We hypothesize that DOC concentrations will decrease, while microbially processed DOM fractions increase, with soil depth. We also hypothesize that a $CaSiO_3$ treated watershed will exhibit greater DOC and dissolved organic nitrogen (DON) concentrations at all soil depths and greater microbial processing of DOM fractions, due to a "deacidification" effect.

To test our hypotheses, we examined patterns of solute (DOC, DON, and dissolved inorganic nitrogen [DIN]) concentrations by horizon, watershed landscape and in a calcium silicate-treated watershed in soil and stream water at the HBEF in the White Mountains of New Hampshire, USA. We also characterized chemically meaningful DOM components, using parallel factor analysis of fluorescence excitation emission matrices (EEM-PARAFAC), as well as additional optical properties, and assessed their relationships with solute measurements from soil and stream water. Effects of recovery from acidification were tested by collecting soil and stream water samples from reference and $CaSiO_3$ treated watersheds. Insights on the evolving characterization of DOM as it is transported through soils, could be valuable to understanding how forest carbon and nitrogen sources and sinks are changing in response to acidification recovery and changing climate.

2. Materials and Methods

2.1. Site Description

HBEF is located within the southern White Mountains of New Hampshire, USA (43°56′N, 71°45′W). The climate is humid-continental, characterized by long cold winters and short cool summers. The mean air temperature is −9° in January, and 19° in July (Bailey et al., 2003; Campbell et al., 2007). Precipitation is evenly distributed throughout the year, with an annual average of 1,400 mm and approximately 30% occurring as snow. The mean annual stream flow from the forest is 905 mm. Approximately 50% of the flow occurs during March, April, and May (Bailey et al., 2003). Low summer stream flows of only 1 or 2 mm per

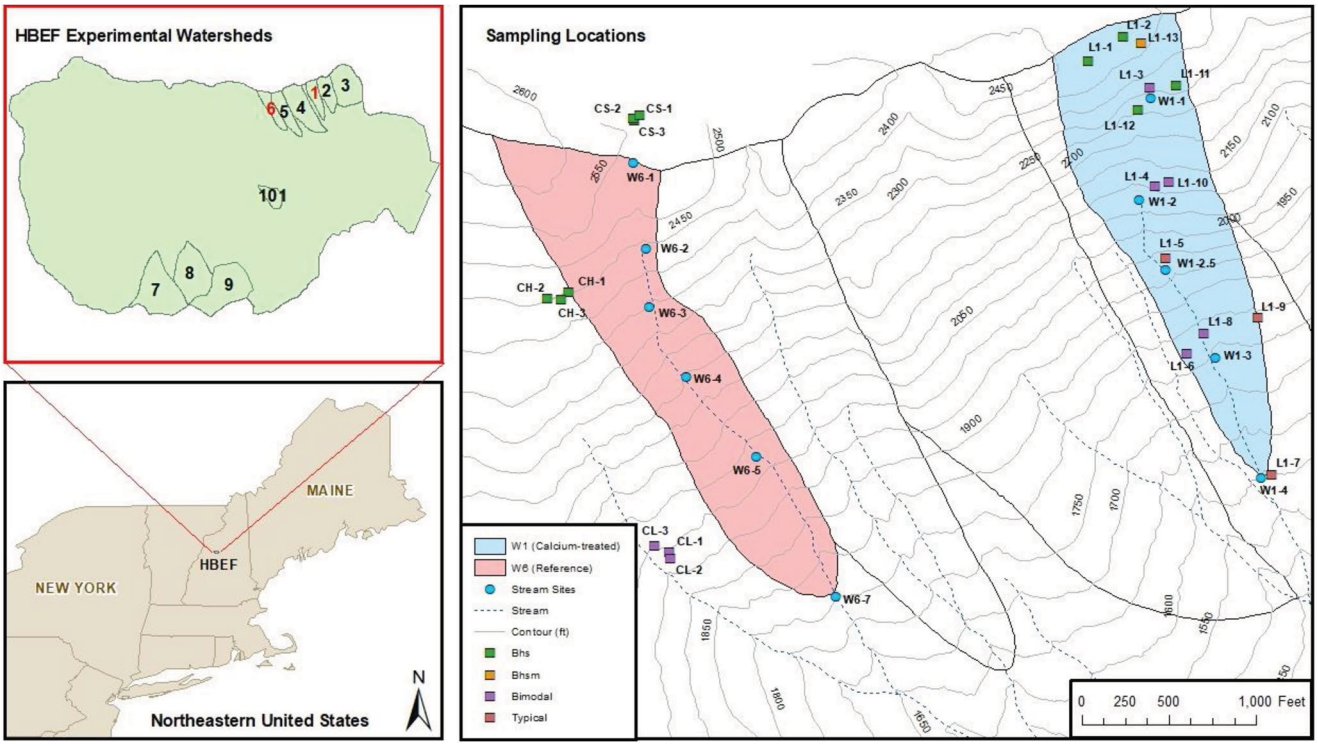

Figure 1. Map of south-facing, experimental watersheds at the Hubbard Brook Experimental Forest (HBEF) in New Hampshire, USA. Circles represent stream water sampling locations, and squares represent lysimeter locations, which are color coded according to soil type.

month have been observed, while streamflow throughout the winter months remains relatively consistent at approximately 50 mm per day, due to snowpack (Bailey et al., 2003).

This study focused on two experimental watersheds on the south-facing slope at the HBEF (Figure 1). Historical land disturbance included heavy logging from 1910 to 1919, but since that period the watersheds have remained relatively undisturbed except for a hurricane in 1938 and an ice storm in 1998 (Houlton et al., 2003). Watershed 6 (W6) is the biogeochemical reference watershed. It has a total area of 13.2 ha, with an elevation range from 540 to 800m (Cho et al., 2009). Watershed 1 (W1) has a total area of 11.8 ha ranging in elevation from 488 to 747 m and was treated with calcium silicate ($CaSiO_3$) in October 1999 to replenish calcium lost from decades of elevated leaching associated with acid deposition. The goal of the W1 experiment was to increase soil base saturation from 10% to 19% (Peters et al., 2004). Changes in the ecosystem structure and function have been observed in response to this treatment (Battles et al., 2014; Cho et al., 2010; Shao et al., 2015).

The watersheds are divided into three elevational subcatchments. The highest is the spruce-fir-birch zone (SFB), which shows a higher density of coniferous trees: red spruce (*Picea rubens* Sarg.) and balsam fir (*Abies balsamea* L.). White birch (*B. papyrifera* var. *cordifolia* Marsh.) is also primarily within this subcatchment. The intermediate high-elevation hardwood zone (HH) and low-elevation hardwood zone (LH) subcatchments are dominated by sugar maple (*Acer saccharum* Marsh.), American beech (*Fagus grandifolia* Britt.), and yellow birch (*Betula alleghaniensis* Britt.). Together, these tree species account for more than 95% of the forest biomass in the experimental watersheds (Battles et al., 2014).

Soils at both experimental watersheds are generally characterized as Spodosols developed in basal and ablation glacial till of sandy loam to loamy sand texture, with a range of drainage classes (Bailey et al., 2014). Average soil depth to the B/C interface is approximately 60 cm. The forest floor, with a mean thickness of 7.1 cm, is deepest in the upper elevations associated with shallow bedrock and outcrops (Bailey et al., 2019; Johnson et al., 2000). Soil pH varies with soil depth, from approximately 3.9 in the organic horizon, to 4.7 in the lower mineral horizon (Johnson et al., 1991). The catchments are steep, averaging 25% slope

(Likens, 2013). Shallow bedrock at the higher elevations of W1 and W6 and accumulating groundwater in deeper soils with higher topographic wetness, promotes lateral flow of groundwater in the soil zone. Varying landscape positions and characteristics result in contrasting soil types, termed hydropedological units (HPUs), differing in patterns of podzolization, carbon storage, and the depth and frequency of water table fluctuations (Bailey et al., 2014; Gannon et al., 2014).

2.2. Sample Collection

Nine lysimeters are located immediately west of W6, grouped in three sets of triplicates along an elevation gradient corresponding with the three landscape zones. Thirteen zero-tension lysimeters are located along an elevation gradient in the calcium silicate-treated watershed, similarly encompassing the three elevational zones (Figure 1). The lysimeters were constructed from PVC troughs placed below the forest floor (Oa horizon) and within the mineral soil (beneath Bh and within Bs horizons). Four hydropedological units were identified at lysimeter locations in watersheds 1 and 6. The Bhs podzol predominantly occurred in the upper catchment elevations (Figure 1) and is characterized by little to no E horizon and a larger Spodic (Bs + Bhs) thickness corresponding to a higher carbon content. The B horizons in these soils are frequently saturated by groundwater during snowmelt and rain events due to relatively shallow bedrock (Bailey et al., 2014). The Bhsm podzol found at lysimeter L1-13, is considered an extreme expression of a Bhs podzol where groundwater saturation has led to partial cementation of the spodic horizon. The Bimodal podzol is morphologically similar to typical podzols but contains a second Bh horizon at the B-C interface, indicative of a fluctuating water table at this interface (Bailey et al., 2014). Bimodal pedons are located at near-stream lysimeters in all elevational subcatchments (Figure 1). Typical podzols are only found in watershed 1 lysimeters, at mid and low elevations. They are characterized by a thin E horizon, and one or two thicker spodic horizons as well as relatively lower carbon content than other podzols. Typical podzols are the best drained of the HPUs defined at Hubbard Brook, with a water table that generally does not rise often or much above the B/C interface (Bailey et al., 2014; Gannon et al., 2014).

Soil solutions were collected using a vacuum hand pump at 4–5 week intervals from January 2015 to December 2016. These collections are a subset of a longer soil solution chemistry record beginning in 1982 in W6, and 1996 in W1 (Driscoll, 2019a, 2019b). Stream water samples were collected at the same monthly intervals from five sites in W1 and six sites in W6 (Figure 1) along the elevational gradients of both watersheds. These collections are also a subset of a longer stream chemistry record beginning in 1982 in W6, and 1991 in W1 (Driscoll, 2019c, 2019d). All samples were placed into acid-washed HDPE bottles, transported back to the laboratory at Syracuse University and stored below 4°C.

2.3. Quantitative Laboratory Methods

Soil solution and stream water samples were analyzed for total nitrogen (TN) concentrations via platinum catalyzed combustion with chemiluminescence detection, using a Teledyne Tekmar Apollo 9000 TOC Analyzer. Ammonium (NH_4^+) was analyzed via the Berthelot reaction, with a Seal Analytical AutoAnalyzer 3. Nitrate (NO_3^-) was analyzed by suppressed ion chromatography with a Dionex IonPAC-AS18 anion-exchange column. DON was quantitatively determined by subtracting the sum of the ammonium and nitrate concentrations (DIN) from the total nitrogen concentration from individual samples. Subsamples were filtered through a Whatman glass microfiber filter 934-AH, then analyzed for DOC concentrations via sodium persulfate oxidation using a Teledyne Tekmar Phoenix 8000 TOC Analyzer.

Quality assurance and quality control measures were used for all sample analyses, including an initial calibration (correlation coefficient >0.995), initial calibration verification (±10% recovery), initial calibration blank, continuing calibration verification (±10% recovery), continuing calibration blank, laboratory control sample made from secondary source (±10% recovery), duplicate sample (10% relative percent difference), and method detection limit (75%–125% recovery) for QA/QC (Cho et al., 2009). All samples that failed these criteria were reanalyzed.

Table 1
Summary of Some Optical Methods for Carbon Quality Analysis in This Study

Measurement	Calculation	Purpose	Reference
Specific ultraviolet absorbance at 254 nm [SUVA254 (L mg-C^{-1} m^{-1})]	Absorption coefficient at 254 nm divided by DOC concentration (mg/L)	Absorbance per unit carbon. Higher values indicate greater aromatic content.	Weishaar et al. (2003)
E2:E3	Ratio of absorbance at 250 nm divided by that at 365 nm	An indicator of DOM molecular size.	De Haan and De Boer (1987)
Fluorescence Index (FI)	Ratio of em intensity at 470 and 520 nm, at ex 370 nm	An indicator of the source of DOM, which is either: microbial (high FI, 1.8, derived from extracellular release and leachate from bacteria and algae) or terrestrially derived (low FI, 1.2, terrestrial plant and soil organic matter).	McKnight et al. (2001); Cory and McKnight (2005)
Redox Index (RIX)	Ratio of Qred over (Qred + Qox), where Qred is the sum of the loadings of reduced quinone-like components (SQ1, SQ2, SQ3, and HQ) and Qox is the sum of the loadings of oxidized quinone-like components (Q1, Q2, and Q3).	An indicator of whether quinone-like components within DOM are more reduced (closer to 1) or oxidized (closer to 0) in character.	Miller et al. (2006)

Abbreviations: DOC, dissolved organic carbon; DOM, dissolved organic matter.

2.4. Optical Measurements

Ultraviolet-visible absorbance of DOM, fluorescence scans, and excitation-emission matrices (EEMs) were measured using a 1 cm quartz cuvette in a Horiba Aqualog spectrofluorometer. The excitation range was set from 240 to 550 at 2 nm increments, with an emission coverage of 247.68–830.02 nm with 2.33 nm increments. The excitation and emission slit widths were set to 10 nm, and the integration time was 0.1 s. EEMs were corrected for instrument-specific correction factors and inner filter effects. All EEMs were also blank-subtracted and normalized against the Raman peak area of fresh Milli-Q water.

Parallel factor analysis (PARAFAC) was conducted on 830 EEMs from samples collected during 2015–2016 calendar years. The model was constructed using the "drEEM" v 0.3.0 toolbox, in Matlab v2016a (Murphy et al., 2013). The component loadings for each sample were then predicted using the model, and the fraction of each PARAFAC component per sample was determined. Additional indicators of carbon quality such as the fluorescence index (FI), redox index (RIX), specific ultraviolet absorbance (SUVA), and E_2:E_3 were also analyzed (Table 1).

2.5. Statistical Analyses

Kruskal-Wallis one-way ANOVA was used to evaluate differences among soil horizon solutions. Wilcoxon signed-rank test was used to evaluate the response of soil solutions and stream water to CaSiO3 treatment compared to reference watershed values. Statistical significance was considered by p-values based on an α-value of 0.05 and a 95% confidence interval. Principal component analysis (PCA) was used as an additional nonparametric method to evaluate the relationships among DOM PARAFAC components, optical indices and solute concentrations. "R" statistical software was used for all statistical analyses.

3. Results

3.1. Patterns by Genetic Soil Horizon

The mean concentration of DOC draining the forest floor of the reference watershed (W6) was 1474.7 ± 1087.5 μmol L^{-1} (Figure 2). DOC concentrations significantly decreased with transport through each subsequent soil horizon and to stream water (Bh: 858 ± 542.9 μmol L^{-1}; Bs: 622.9 ± 583.7 μmol L^{-1};

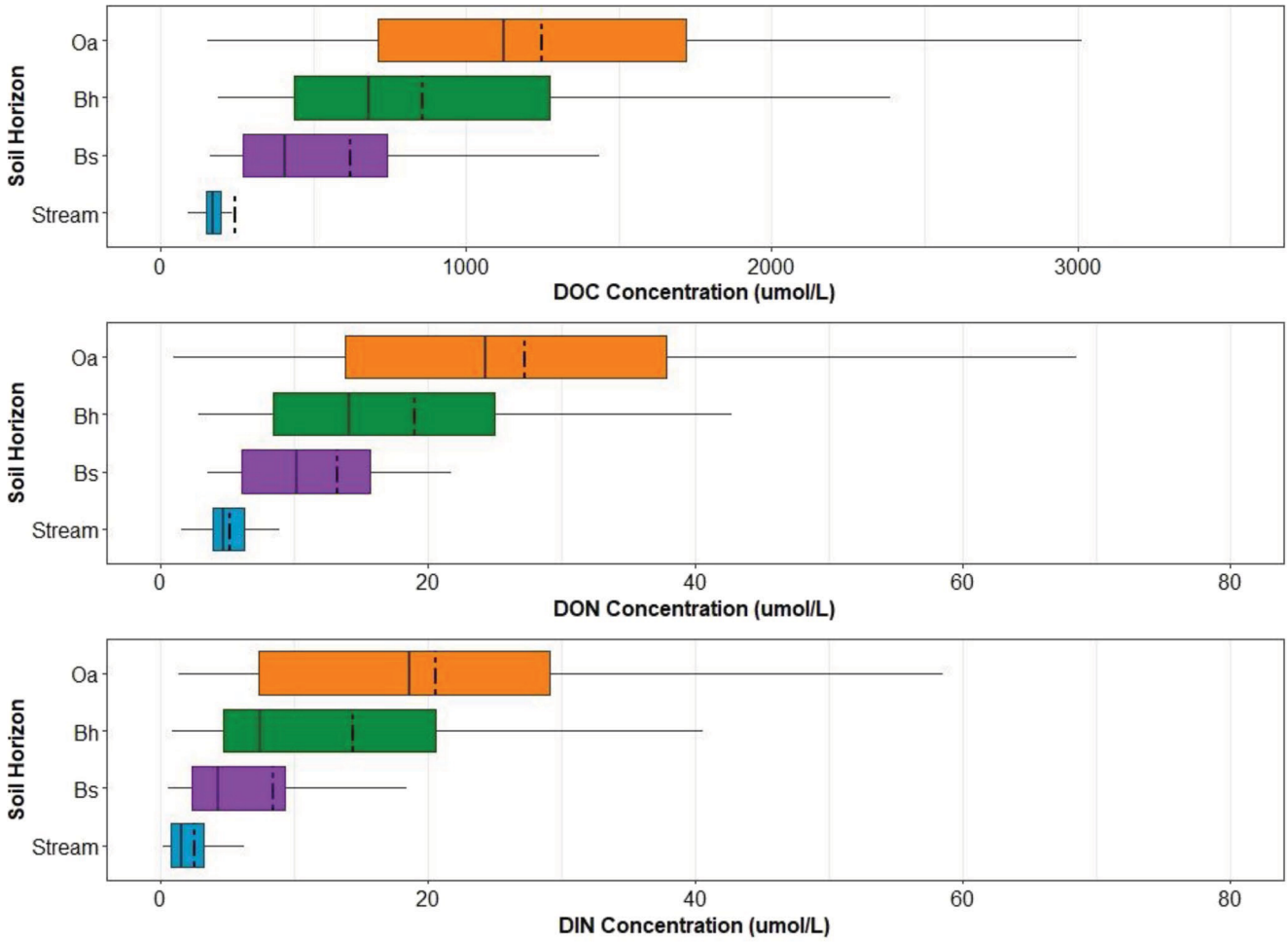

Figure 2. Box and whisker plots presenting: (a) dissolved organic carbon, (b) dissolved organic nitrogen, and (c) dissolved inorganic nitrogen concentrations in stream and soil water, from the reference watershed (W6). Dashed lines represent mean values.

Stream: 243.8 ± 248.9 μmol L^{-1}). DON concentrations in the reference watershed also decreased significantly between all successive horizons with depth and in stream water (Oa: 28.1 ± 18.1 μmol L^{-1}; Bh: 19.0 ± 15.3 μmol L^{-1}; Bs: 13.3 ± 12.7 μmol L^{-1}; Stream: 5.2 ± 2.1 μmol L^{-1}). Consistent with DOC and DON, concentrations of DIN in solutions from W6 (reference) decreased significantly through all soil horizons to the stream (Figure 2). The DOC:DON ratio of drainage waters decreased through all soil horizons from forest floor to the stream in the reference watershed (Oa: 72.4 ± 78.8; Bh: 61.5 ± 45.3; Bs: 57.8 ± 44.2; Stream: 41.0 ± 18.1), with only the decrease between the Bs horizon and the stream statistically significant. Conversely the DOC:DIN ratio in the reference watershed increased from the Oa (134.7 ± 163.8) to the Bs horizon (184.6 ± 244.9), then decreased to 165.7 ± 153.3 in stream water, with none of the horizon values statistically different.

In the reference watershed (W6), the fraction of PARAFAC modeled component 1 (C1) increased through each subsequent soil horizon (Figure 3), yet the overall difference in magnitude was relatively small (0.61%). The C1 fraction in stream water (43.25 ± 0.71%) was lower than the Bs fraction but not significantly. C2 significantly decreased between subsequent soil horizon solutions and stream water, from 34.03 ± 3.33% in the Oa solution, to 28.26 ± 2.25% in stream water (Table S3). Conversely, C3 increased significantly between subsequent soil horizon solutions and stream water (Figure 3) from 23.22 ± 2.66% in the Oa solution to 28.49 ± 2.66% in stream water. Optical properties also exhibited horizonal patterns in W6 (reference). FI increased significantly from the Oa horizon solutions (1.62 ± 0.09) to the Bs horizon solutions (1.76 ± 0.07), but not from the Bs horizon (1.76 ± 0.07) to stream water (1.76 ± 0.06). E_2:E_3 increased significantly with

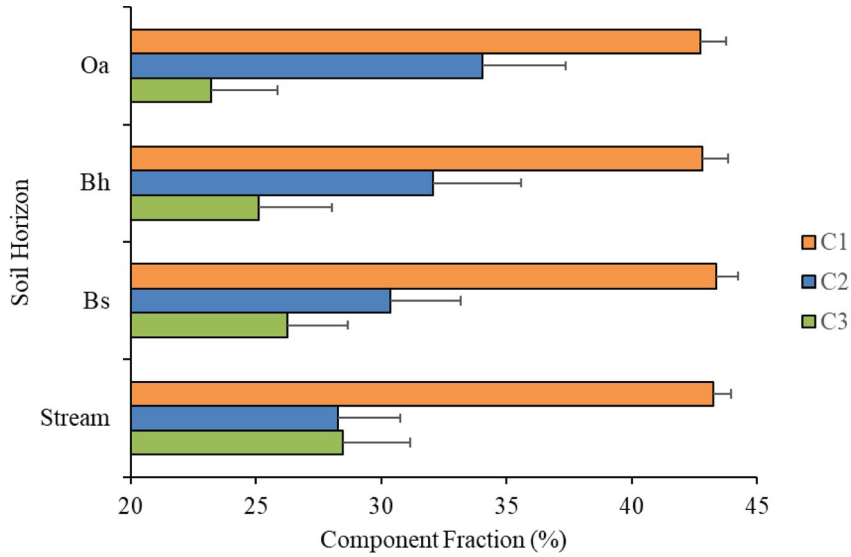

Figure 3. Mean fractions of PARAFAC modeled components (C1, C2, C3) in stream and soil water from the reference watershed (W6). Error bars represent standard deviation.

soil depth (Table S3), while RIX decreased significantly from the Oa leachate (0.71 ± 0.02) to stream water (0.68 ± 0.01). Specific ultraviolet absorbance (SUVA) also decreased significantly through soil solutions from the Oa (4.50 ± 2.67 L mg C^{-1} m^{-1}) to the Bs (2.93 ± 1.32 L mg C^{-1} m^{-1}). SUVA decreased between Bs solutions and stream water (2.78 ± 0.39 L mg C^{-1} m^{-1}), but the difference was not significant (p-value = 0.051).

3.2. Landscape Patterns

In the reference watershed (W6), DOC, DON, and DIN solute concentrations decreased in stream water as elevation decreased. These spatial patterns were not entirely consistent with soil solution chemistry. DOC concentrations decreased in all soil horizon solutions with decreasing elevation, while DIN concentrations were the highest at low elevations (Figure 4). DON landscape patterns did not mirror DOC. DON concentrations were the highest in the high hardwood (HH) zone in both the organic (30.3 ± 23.0 μmol/L) and upper mineral soils (23.3 ± 18.9 μmol/L). In the reference watershed, the DOC:DON and DOC:DIN ratios decreased for all soil solutions and the DOC:DON ratio in stream water decreased as elevation decreased. However, DOC:DIN in stream water from the HH zone contained the highest molar ratio of 130.68, followed by spruce-fir-birch, then low hardwood zones. Additionally, the DOC:DIN ratios were greater than DOC:DON ratios in all upper elevation (SFB & HH) soil solutions, but lower for the LH zone.

C1 fractions in forest floor solutions declined with decreasing elevation. Lower mineral soil (Bs) solutions contained the highest C1 fractions especially at high elevations, with the greatest fraction at the HH zone (43.71% ± 0.53%). Within stream water, there was no elevational pattern in C1 fractions. In all soil solutions, the high hardwood zone presented the lowest C2 fractions and highest C3 fractions among elevational zones. Comparably, FI and E_2:E_3 were also highest in the high hardwood zone. Within stream water, C2 fractions, SUVA, and RIX indicators declined with decreasing watershed elevation, while C3 fractions, FI and E_2:E_3 increased. Mean elevational SUVA values were greatest in spruce-fir-birch zone forest floor (Oa: 6.03 ± 11.86 L mg C^{-1} m^{-1}) and upper mineral horizon (Bh: 4.08 ± 2.30 L mg C^{-1} m^{-1}) solutions, and lowest in the high hardwood zone. In lower mineral soils (Bs), SUVA was highest in the low hardwood zone (3.13 ± 1.87 L mg C^{-1} m^{-1}), but still lowest in the HH zone.

3.3. Calcium Silicate Treatment Effects

Horizonal patterns shifted within calcium silicate-treated soil solutions when compared to the reference watershed. Mean DOC and DON concentrations in W1 (calcium silicate-treated) did not significantly decrease between the Bh and Bs horizons. As at W6 (reference), mean DIN concentrations decreased significantly

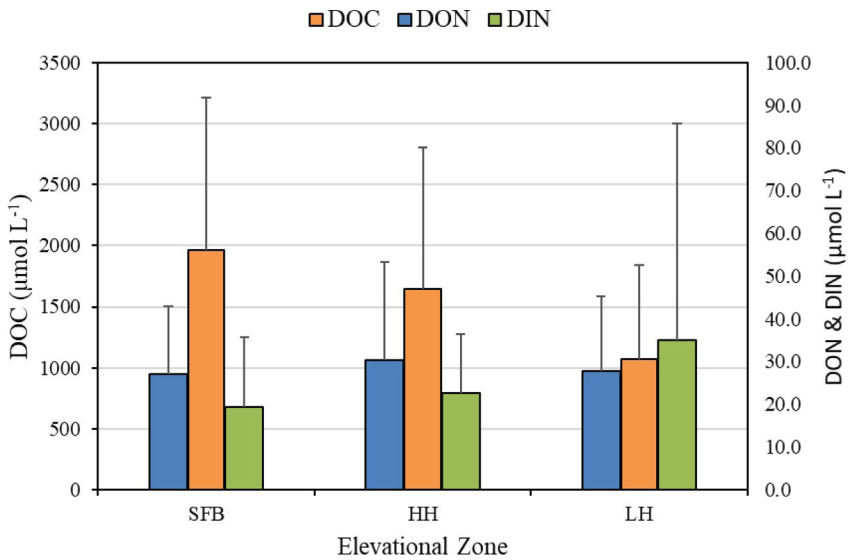

Figure 4. Elevational patterns of dissolved organic carbon, dissolved organic nitrogen, and dissolved inorganic nitrogen mean concentrations in Oa solution soil water for the reference watershed (W6). Subcatchments are presented in order of decreasing elevation: spruce-fir-birch (SFB), high-elevation hardwood (HH), and low-elevation hardwood (LH). Error bars represent standard deviation.

downward through all horizons (Figure 5c). Concentrations of DOC (1881.6 ± 1300.9 μmol L^{-1}), DON (44.8 ± 36.8 μmol L^{-1}), and DIN (56.2 ± 60.5 μmol L^{-1}) were all significantly higher in Oa horizon solutions in W1 than W6 (Figure 5a). DIN concentrations in the Bh horizon (31.6 ± 41.2 μmol L^{-1}), and stream water (14.7 ± 10.2 μmol L^{-1}) were also significantly higher in W1. There was little change in DOC:DON among horizons in W1, unlike at the reference watershed. DOC:DON decreased from 57.5.7 ± 101.2 in the forest floor to 47.7 ± 54.9 in upper mineral, increasing to 53.4 ± 44.6 in lower mineral soil, then finally decreasing to 46.6 ± 26.1 in stream water. In the calcium silicate-treated watershed (W1), the DOC:DIN ratio followed the same soil depth pattern as the reference watershed, increasing (not significantly) from the Oa to the Bs horizons, with a significant decrease between the Bs horizon (125.7 ± 203.0) and stream water (47.6 ± 85.5). In all soil horizons, and stream water, the DOC:DIN ratio in the reference watershed was significantly higher than stream water in the calcium silicate-treated watershed.

Comparisons of the mean C1 fractions between reference and calcium silicate-treated watersheds fell well within the standard deviations of observations, however a comparison of median values reveals the C1 fraction to be significantly higher in Bs solutions in W6 (Figure S2). Mean C2 fractions were higher in the reference watershed (W6) across all soil horizon solutions and stream water, with significant differences between Bh horizon waters and stream water (Table S5). Additionally, while not statistically significant, mean C3 fractions were higher in W1 across all soil horizon solutions and stream water.

Horizonal patterns established among DOM optical properties at the reference watershed (W6) were also evident for W1. SUVA significantly decreased from forest floor solutions (4.44 ± 4.03 L mg C^{-1} m^{-1}) through each soil horizon to stream water (2.51 ± 0.29 L mg C^{-1} m^{-1}). SUVA in the stream water was significantly lower at W1 (2.51 ± 0.29 L mg C^{-1} m^{-1}) than at W6 (2.78 ± 0.39 L mg C^{-1} m^{-1}) (Figure 6a). When compared to W6, FI values at W1 were significantly lower in forest floor solutions (W6: 1.62 ± 0.09; W1: 1.59 ± 0.11), but significantly higher in the Bh horizon waters (Figure 6b) (W6: 1.74 ± 0.09; W1: 1.69 ± 0.08) and in stream water (W6: 1.76 ± 0.06; W1: 1.81 ± 0.05). E_2:E_3 values (indicators of molecular size) were also significantly higher in Bh and Bs solutions, and stream water at W1 than W6 (Figure 6d). The redox index (RIX) values were significantly higher in the Bh and Bs horizon solutions and stream water in W1 than W6 (Figure 6c).

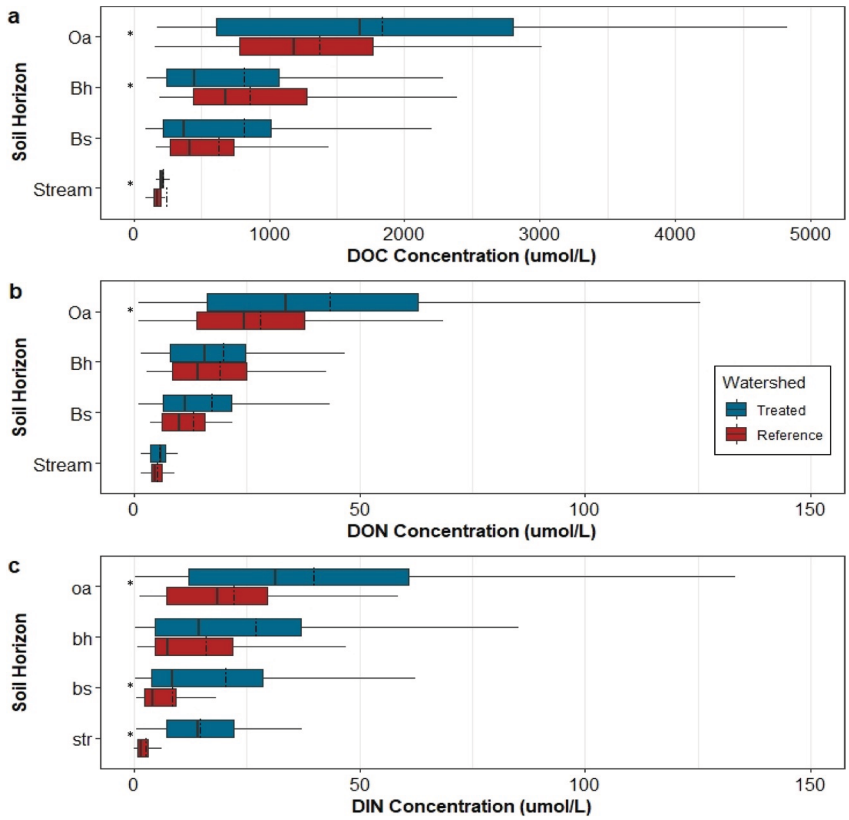

Figure 5. Box and whisker plots of (a) dissolved organic carbon (DOC), (b) dissolved organic nitrogen (DON), and (c) dissolved inorganic nitrogen (DIN) concentrations in stream and soil water, from reference and treated watersheds. Dashed lines represent median values, stream, and soil water, from reference and treated watersheds. Stars represent statistically significant differences between watersheds by Wilcoxon signed-rank test to a significance level of 0.05.

4. Discussion

4.1. Patterns by Genetic Soil Horizon

DOC and DON concentrations in soil solutions at Hubbard Brook exhibited highest concentrations in forest floor leachate and values decreased consistently through the mineral soil to eventual export in stream water, consistent with previous observations (Dittman et al., 2007). This pattern is expected since DOM is mobilized from litter decomposition and fine root turnover and subsequently immobilized in mineral soil. NH_4^+ and NO_3^- are products of mineralization and nitrification process, largely originating from organic nitrogen. Moreover, microbial processing of terrestrial organic carbon can immobilize DIN. A recent NO_3^- tracer study at Hubbard Brook concluded that soil organic matter can be an important sink for inorganic nitrogen, especially within mineral soils (Fuss et al., 2019). It is reasonable to hypothesize that DOC exerts some control over DIN in soil solutions and stream water. Note that the DOC:DON ratio decreased with soil depth in the reference watershed. DIN from both watersheds also decreased with soil depth, and in stream water, leading to increasing DOC:DIN ratios (Table S2).

The conceptual model for DOM processing (Kaiser & Kalbitz, 2012) suggests as DOM is transported through soil with drainage water, microbial processing consumes and transforms organic carbon. Horizonal patterns of DOM quality support this model where microbial metabolites occurred in greater abundance than terrestrial sources in the lower mineral soils. Additionally, DOM was less aromatic, more oxidized with a smaller molecular size, at soil depth. DOM fractions are also consistent with this processing theory. As soil depth increases, lignin-like DOM (C2) abundance decreases, while reprocessed DOM (C3) increases (Figure 2). The relative composition of the ubiquitous DOM fraction (C1) did not change with soil depth suggesting there is a large pool of recalcitrant humic DOM buffering the composition of this fraction in soil solutions.

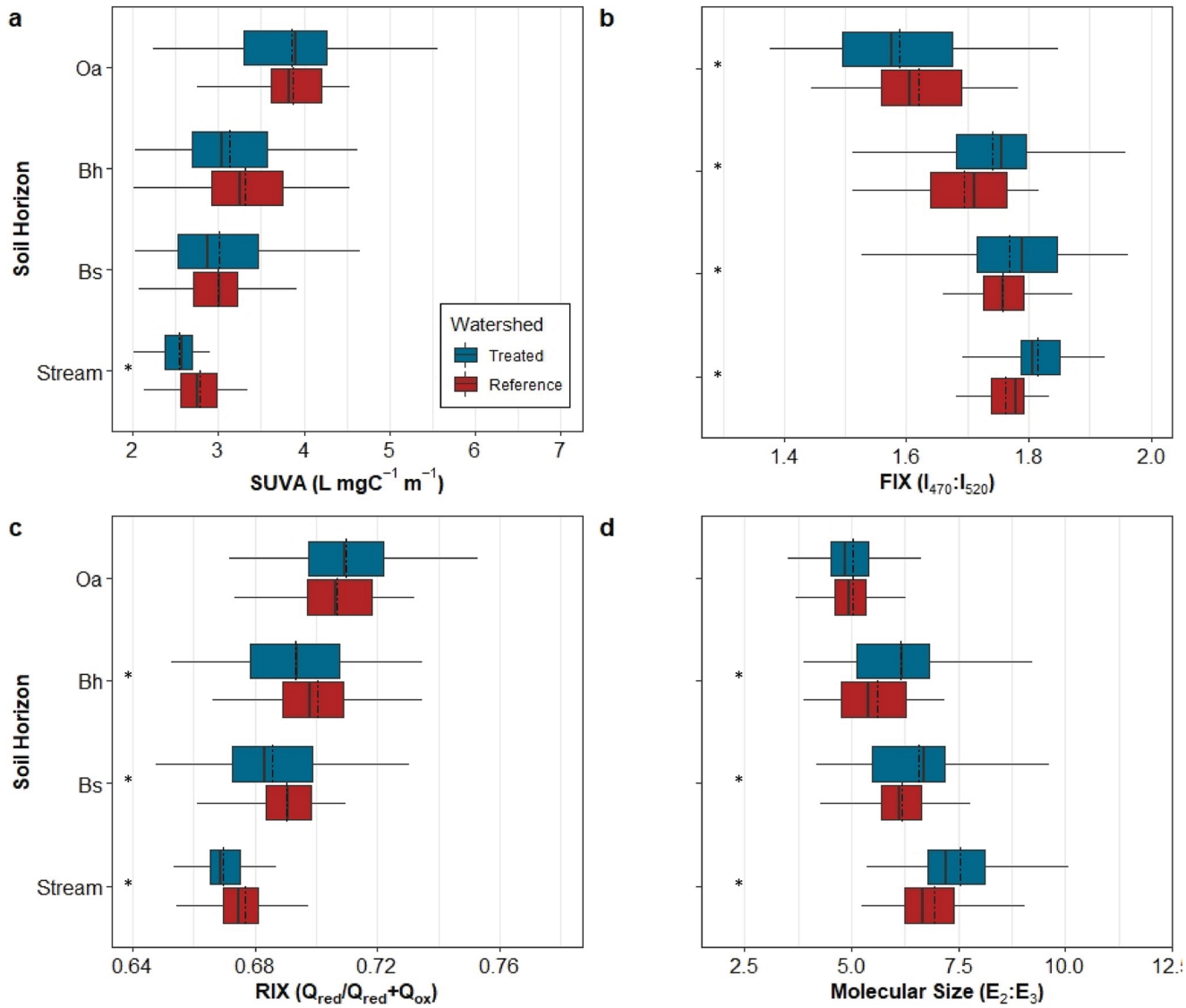

Figure 6. Horizonal patterns in (a) specific ultra-violet absorbance, (b) fluorescence index, (c) redox index, and (d) molecular size, from both reference and treated watersheds. Dashed lines represent mean values. Stars represent statistically significant differences between watersheds by Wilcoxon signed-rank test to a significance level of 0.05.

Previous ^{13}C NMR analysis of soil organic matter at the HBEF found that alkyl C dominated the proportion of organic carbon across the Oa, Bh, and Bs soil horizons. Additionally, O-alkyl C fractions decreased with soil depth (Ussiri & Johnson, 2003). This pattern supports our observations of DOM components and suggests that DOM fractions are dependent on soil carbon composition.

Horizonal patterns were also evident through multivariate analysis of all chemical species, DOM fractions, and DOM optical properties. Observations from the Oa horizon leachate had more negative PC1 scores and were characterized by a lignin-like fraction, reduced and aromatic DOM, and high nutrient concentrations (Figure S3a). In contrast, observations from stream water had exclusively positive PC1 scores, indicating: a higher reprocessed OM fraction, high microbial sourcing, low molecular size, and oxidized DOM. Mineral soil solutions transitioned from negative to positive PC1 scores (Figure S3c). Note that PC1 was not strongly influenced by the C1 humic fraction. However, PC2 was affected by the C1 humic fraction and observations from the Oa horizon solutions had higher PC2 values than those from mineral soil solutions and stream water.

4.2. Landscape Patterns

In the reference watershed, DOC concentrations in all soil solutions and stream water, as well as SUVA in forest floor solutions and stream water, declined with decreases in watershed elevation (Figure 4). This pattern has largely been attributed to shifts in forest tree composition from coniferous to deciduous species (Dittman et al., 2007), since DOM composition is dependent on source material. Experiments comparing carbon quality within coniferous and deciduous forests have found that coniferous forest soils generally have higher DOC concentrations and larger, more aromatic, plant-derived structures (Thieme et al., 2019). Furthermore, our observations of higher DOC and C2 ("lignin-like") fractions in spruce-fir-birch mineral soil solutions and stream water, highlight the importance of shallow soils in transporting relatively unprocessed OM to surface waters at high elevations (Bailey et al., 2014; Johnson et al., 2000). Surprisingly, the highest mean DON concentrations (Figure 4), FI and microbially reprocessed fraction were found in soil water of the transitional high hardwood (HH) zone. In contrast, stream water followed the expected pattern of decreased DON and C2 fraction, coupled with increased C3 fractions and FI with decreased elevation. These patterns in soil solutions diverge from past observations where DON closely mirrored DOC across watershed elevation, and DIN dominated DON concentrations high and low hardwood stands (Dittman et al., 2007).

Repeated wetting and drying cycles which vary with the landscape position associated with hydropedological units (HPUs) have been found to have both biotic and abiotic effects on OM processing. Bhs and Bhsm HPUs found in higher elevations (Figure 1) with shallow bedrock experience flashier water table fluctuations and exhibit stronger lateral flowpaths. We found that mineral (Bh and Bs) soil water from these HPUs, in the SFB zone contained the highest DOC concentrations, as well as "lignin-like" OM fractions characterized by high SUVA and more reduced functional groups. These patterns are consistent with shallow groundwater chemistry where eluvial soil forming processes dominate (Bailey et al., 2019). Additionally, these results were mirrored in stream water, albeit not surprising, given previous work connecting surface water chemistry to surrounding soil type in stream catchments (LoRusso et al., 2020; Zimmer et al., 2013). Repeated wetting and drying cycles in these soils has also been shown to drive OM mobilization and mineralization (Patel et al., 2021), through shifts toward aluminum dominated interactions (Possinger et al., 2020), as well as through the connection of connect labile carbon to microbial communities within soil pore systems leading to further processing (Bailey et al., 2017; Kravchenko et al., 2021). These observations suggest that first order stream catchments play a significant role as carbon sources to downstream water quality (Raymond et al., 2016).

Soils instrumented with lysimeters in the watershed 6 high hardwood zone were also classified as "Bhs" podzols like those found in the SFB, but with significantly different dominant vegetation. Frequent wetting and drying conditions, coupled with a significantly less "lignin-like" OM source could explain the high "reprocessed" OM fractions, FI values suggesting microbially sourced OM, and lowest molecular size observed in all soil horizon solutions. These patterns were not, however, consistent with stream water variation with elevation, suggesting that microbially processed OM is transported more deeply into soils at lower elevations (Bailey et al., 2017; Mikutta et al., 2019)

In contrast, typical and the near-stream bimodal podzols at lower elevations experience more vertical percolation (Bailey et al., 2014). These podzols exhibited lower DOC concentrations and RIX values, indicating more oxidized quinone functions groups. Reprocessed humic-like fractions (C3) were highest at low elevation typical Spodosols, also suggesting a higher rate of DOM microbial processing is occurring in deeper, well-drained mineral soils (Bailey et al., 2014, 2017). These findings are more consistent with the conceptual model proposed by Kaiser and Kalbitz (2012), which indicated deeper more well-drained soils at the lower elevations are important organic carbon sinks when compared to flashier higher elevation catchments (Mikutta et al., 2019; Raymond et al., 2016).

4.3. Calcium Silicate Treatment Effects

Taking advantage of the wollastonite ($CaSiO_3$) experiment in W1, we investigated a "deacidification effect" on DOC and DON concentrations and DOM fractions. We observed significantly higher DOC and DON concentrations in forest floor leachate in the calcium silicate-treated watershed compared to the reference

watershed. Additionally, DIN concentrations were significantly greater in the calcium silicate-treated forest floor, Bh horizon solutions and stream concentrations. Unlike DIN, higher DOC and DON in the calcium silicate-treated Oa horizon leachate did not coincide with comparable increases in DOC and DON concentrations for mineral soil and stream solutions over the period of observation. Rather, DOC concentrations were significantly higher in reference Bh soil solutions and stream water (Figure 6). These observations were further supported by significantly higher fractions of "lignin-like" C2 fractions in reference Bh soil solutions and stream water (Figure S4). While studies have shown that hydrologic events can facilitate the transport of fresh, lignin-like OM deeper into soils (Fröberg et al., 2007; Raymond et al., 2016), precipitation is evenly distributed across the south-facing watershed in HBEF (Bailey et al., 2003). This pattern suggests either DOM is retained more effectively in calcium silicate-treated mineral soils, or more DOM is being processed due to increased microbial activity. Greater fractions of microbially reprocessed OM (C3), albeit not statistically significant, as well as higher concentrations of DON and DIN in calcium silicate-treated Bs soil solutions support the latter. These observations would appear to support theories of higher organic carbon flow to lower mineral soils, contributing to long-term decreases in mineralization and nitrification in deacidified forests (Bailey et al., 2017; Groffman et al., 2018).

Further evidence is provided by comparison of DOM quality between the watersheds. FI was significantly lower in the forest floor at W1 (Figure 6b). This pattern suggests greater inputs of plant-like organic matter in W1 (calcium silicate-treated), which could be driven by increased litterfall (Battles et al., 2014), increased late-stage litter decomposition (Lovett et al., 2016), and fine root mortality (Fahey et al., 2016; Persson, 2012). At the subwatershed scale, the lowest mean FI value (1.55 ± 0.11) was observed in the calcium silicate-treated, high hardwood zone, indicating a greater input of plant-like terrestrial DOM to forest soil solutions than both adjacent elevation zones and those in the reference watershed. Root litter and decaying fine root biomass could be a potential source of carbon to the soil (Persson, 2012). Fine root studies in W1 have found that within the HH zone, fine root biomass has declined significantly since the $CaSiO_3$ treatment in 1999. This decline corresponded with a +5.1% increase in aboveground live biomass in the HH zone, suggesting tree C allocation may be shifting in response to recovery from acid deposition (Fahey et al., 2016).

Within mineral soil solutions (Bh and Bs), FI was significantly higher at the calcium silicate-treated watershed (Figure 6b), an indication of more microbially processed DOM. Additionally, significant differences of E_2:E_3 and RIX were observed between calcium silicate-treated (W1) and reference (W6) mineral soil solutions (Figures 6c and 6d). These indicated a greater degree of DOM quinone oxidation status and lower DOM molecular size within W1 (Table 1). This pattern suggests that DOM at W1 experienced enhanced sorption and reprocessing as it "cycled downward" (Kaiser & Kalbitz, 2012), as research has shown that microbial processing favors more complex, labile compounds (Bailey et al., 2017). There was a significant decrease in DOC and DON concentrations between the reference watershed Bh and Bs soil horizons, while DOC and DON concentrations in calcium silicate-treated Bs soil solutions were not significantly different than Bh horizon solutions. This pattern appears to also support the theory of enhanced OM processing and desorption within calcium silicate-treated mineral soils (Mikutta et al., 2019). Furthermore, stream export of DOM from the calcium silicate-treated watershed was significantly less aromatic (SUVA), of significantly smaller molecular size (E_2:E_3), and more microbially sourced (FI) than the stream export from the reference watershed. Stream W1 export was less linked to DOM in soil water as differences in SUVA and FI in stream water and Bs soil solutions were significantly different, while they were not significantly different in the reference watershed. Our observations have implications for interpreting the source of DOM contributing to recent increases in browning. They suggest that recent influxes of "colored" organic matter in surface waters may not be derived from DOM that has percolated through soils and sorbed to mineral soils (Li & Johnson, 2016; Pourpoint et al., 2017; Riedel et al., 2013), but rather more direct relatively "unprocessed" inputs of OM (Raymond et al., 2016). The more "lignin-like" C2 fraction is strongly associated with SUVA, but this fraction is lower in the calcium silicate-treated watershed. In contrast, C3 is not associated with SUVA increased but produced more prominently in W1. These results might suggest that browning is associated with physiochemical decreases in DOM partitioning associated with increases in pH or decreases in ionic strength rather than changes in microbial processing of OM.

These results differ from a previous study of DOM quality in HBEF stream water from disturbed watersheds (Cawley et al., 2014). While both studies found no significant difference between PARAFAC components identified in W1 and W6, we found significant differences in SUVA, FI, RIX, and molecular size. While our study collected from the stream along an elevational gradient through the watersheds, previous work collected from the stream outlet at the base of the watersheds (Cawley et al., 2014). Additional statistical analysis of samples collected from watershed stream outlets found that the fraction of high MW, "lignin-like" OM, SUVA, and RIX values were significantly lower in the calcium silicate-treated stream when compared to the reference watershed outlet.

4.4. Limitations and Future Analysis

As we only considered two catchments, it is not surprising that there are differences in DOM patterns despite their close proximity. Because there are two catchments (one treatment and one reference) the study is pseudo-replicated. Furthermore, there are no pre-treatment data. As a result, we cannot ascribe the difference between the catchments to the treatment. Future studies might measure DOM prior to and after calcium mineral watershed treatment or examine DOM fractions across a gradient of watershed stream ANC values to gain additional insight in how DOM processing varies with variations in the acid-base status of forest watersheds. Fluorescence spectroscopy is typically conducted on fresh grab samples (Shutova et al., 2014). In this study, soil pore water was collected continuously from passive lysimeters at 4–5 week intervals. Once collected, samples were transported from NH to Syracuse, NY overnight on ice. Water samples were stored in the dark at 4°C until analysis as soon as possible in the laboratory at Syracuse University. As a result, there undoubtedly was some transformation of DOM. We collected and analyzed 2 years ($n = 830$) individual samples to build our PARAFAC model and best represent the landscape and seasonal patterns.

Future work could include statistical analysis of seasonal patterns of DOM processing as well as how those patterns have changed over the long-term. Additionally, focus on organic carbon and nitrogen fluxes between calcium silicate-treated and reference watersheds could determine whether differences in hydrologic/physiochemical or biological factors are driving differences in forest DOM transport. Additionally, collections and analysis of low molecular weight organic acids within fresh organic matter and microbial biomass, as well as litter decomposition studies could help quantify DOM end-members in the aquatic system and provide further insight into DOM sourcing.

5. Conclusions

Our data show that improvements to the calcium status of soil in W1 have potentially caused a shift in DOM quantity and quality. Analyte concentrations, PARAFAC-identified DOM components, fluorescence spectral characteristics have revealed higher concentrations of DOC, DON in forest floor leachate, and DIN throughout the soil profile and in stream water, along with increases microbially processed DOM and declines in DOM molecular size and SUVA suggest enhanced processing within the calcium silicate-treated watershed. Note that although microbial processing of DOM and tree growth have increased (Battles et al., 2014) in W1, these changes have not enhanced ecosystem reactive nitrogen uptake. Rather the sink strength of DIN has decreased in the wollastonite-treated watershed. Horizonal patterns of DOM transformation at the HBEF were consistent with a conceptual model for DOM (Kaiser & Kalbitz, 2012). Unusually high DOC concentrations and characteristics of plant-like DOM inputs in the high elevation hardwood zone suggest fine root turnover contributes to soil organic matter. In catenas where podzols influenced heavily by their landscape position and dominant vegetation give way from Bhs to typical podzols, DOM composition changed from more plant-like, aromatic structures in conifer-dominated high elevation zones to more microbially sourced DOM inputs within both high and low elevation hardwood zones.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The data used for analysis in the study are available at Environmental Data Initiative data portal via: https://doi.org/10.6073/pasta/74691519e5196a7832d73254b88cba69, https://doi.org/10.6073/pasta/3c26b78ca8de3ba3fb79f3fd52d35417, https://doi.org/10.6073/pasta/f4bb35a23b50360800e589647c62a729, https://doi.org/10.6073/pasta/256aaeb2c17ac7c36ea7e3d8170a5af3. (Driscoll, 2019a, 2019b, 2019c, 2019d).

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