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REGULAR ARTICLE

Homogenization of detrital leachate in an old-growth coniferous forest, OR: DOC fluorescence signatures in soils undergoing long-term litter manipulations

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Abstract
Aims Characterizing the relationship between plant detrital inputs and the resulting dissolved organic carbon (DOC) leachate is vital to understanding the ultimate fate of root carbon, fallen wood and needles in forested watersheds. Similarly, elucidating chemical differences in the soil DOC pool may help to explain which DOC fractions are sorbed to mineral surfaces and contribute to accumulation of soil organic carbon, are respired as CO_2, or are exported to nearby catchments.
Methods In order to test the hypothesis that soils with different detrital inputs impart a detectable signal on DOC in mineral soil, soil solution DOC was sampled from the Detrital Input and Removal Treatment (DIRT) plots located in the H.J. Andrews Experimental Forest, OR. Multiple types of fresh litter extracts, along with lysimeter and soil extracts from DIRT treatment plots were characterized using UV-Vis and fluorescence spectroscopy coupled with the Cory and McKnight (Environ Sci Technol 39:8142–8149, 2005) parallel factor analysis (PARAFAC) model.
Results Principal component analysis of 13 unique fluorophores distinguished using PARAFAC show that litter and soil extracts (Douglas-fir needles, wood of decomposition Class 2, Class 3 and Class 5, O-horizon, and 0–5 cm A-horizon) each have distinct fluorescence signatures. However, while litter-leached DOC chemistry varies by litter type, neither lysimeter-collected DOC or soil extracts in the DIRT plots show statistically significant differences in fluorescence signatures among treatments, even after 17 years of litter manipulations. The lack of observed differences among DIRT treatments suggests that both abiotic interactions and microbial activity effectively homogenize organic carbon constituents within the dissolved pool. Minor but observable changes in PARAFAC components and optical indices during a 1-month biodegradation incubation of litter and soil extracts indicate that while biodegradation significantly alters DOC chemistry, abiotic mechanisms are also critical to DOC transformation in these soils with high sorption capacity.
Conclusions Although leachates from different plant detrital sources have distinct carbon chemical signatures, these DOC signatures are effectively homogenized after passage through mineral soil. These results highlight the dominant role of both biotic and abiotic interactions in controlling the chemistry of DOC in shallow soils.

Keywords Dissolved organic carbon · Soil organic matter · Biodegradation · Fluorescence · PARAFAC

Abbreviations

DOC	Dissolved Organic Carbon
C	Carbon
SOC	Soil Organic Carbon

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PARAFAC	Parallel Factor Analysis
DIRT	Detrital Input and Removal Treatment
BDOC	Biodegradable Dissolved Organic Carbon
SUVA	Specific UV Absorbance
EEM	Excitation-Emission Matrix
RI	Redox Index
FI	Fluorescence Index
BIX	Freshness Index
PCA	Principal Component Analysis

Introduction

Soil dissolved organic carbon (DOC) is a vital component of the global carbon (C) cycle (Deb and Shukla 2011; Kindler et al. 2011; Sanderman et al. 2009). Because the retention, movement and formation of soil organic carbon (SOC) are invariably coupled with DOC dynamics, understanding the processes controlling DOC chemistry is essential to modeling the behavior of the large global SOC pool. Losses from SOC in the form of DOC exported to nearby catchments can make up a significant portion of net ecosystem productivity and systematically ignoring these losses can result in overestimation of C stores (Gielen et al. 2011; Cole et al. 2007).

Soil DOC originates from microbial and root biomass, fresh litter inputs, and more processed SOC (Sanderman et al. 2008). While different detrital inputs (e.g. needles, wood, and roots from different species at different stages of decomposition) are known to have unique biochemical compositions (Thevenot et al. 2010; Berg et al. 1982), it is not clear if these differences translate to differences in DOC chemistry and if these differences are preserved in mineral soil solution. While it has been demonstrated that large concentrations of DOC are solubilized from fresh detrital inputs, the contributions of different detrital sources and root leachates relative to the influence of indigenous SOC on DOC in a soil profile are not well understood. Previous research has monitored the impact of litter inputs on soil DOC chemistry for only a few years. In a two-year study, less than 1% of mineral soil DOC was derived from fresh aboveground organic materials as assessed by additions of isotopically-labelled European beech and ash litter to a Luvisol (Scheibe and Gleixner 2014). In a 5-month study, less than 15% of mineral soil DOC was derived from Norway spruce litter added to a Haplic Podzol (Fröberg et al. 2007). However, if long term (i.e. greater than a few years) changes in detrital input amount and chemistry alter the flux of DOC entering the subsoil, there are potentially very significant implications for the accumulation of SOC.

UV-vis and fluorescence spectroscopy have been used extensively to characterize DOC in freshwater, marine and more recently, soil solution. Analyses are relatively cheap, can generally be applied to samples with DOC concentrations typical to field conditions, and have produced promising results as a fingerprinting technique for DOC research. For example, these techniques have aided in identifying DOC source materials in watersheds (Cory and Mcknight 2005), monitoring hydrologic flowpaths, and observing changes as a function of soil depth (Gabor et al. 2014) and land use (Toosi et al. 2014). Separating fluorescence profiles into distinct fluorescing moeities using parallel factor analysis (PARAFAC) allows for identification of subtle changes in spectral signals during decomposition of DOC or differences among leachate source materials.

The Detrital Input and Removal Treatment (DIRT) plots in the H.J. Andrews Experimental Research Forest have undergone a suite of litter manipulation treatments for 17 years and have shown significant changes in total SOC content (Lajtha et al. 2014). Alterations to litter inputs have changed DOC concentrations in lysimeter-collected soil solution, but the impact of needle, wood, and root C on DOC chemistry has not been characterized since the first 3–4 years after H.J. Andrews DIRT plot establishment using resin fractionation (Yano et al. 2005). The aim of this research is to determine whether litter or roots impart a detectable signal on DOC in mineral soil after a longer period (17 years) of litter manipulation than is typically studied.

We hypothesized that fluorescence signatures would show that extractable DOC from roots, needles, and wood have unique chemistries that reflected the distinct compositions of the source materials (Yano et al. 2005), and that these differences could be detected in soil solution DOC from soils that experienced differing detrital input treatments. We used both soil extracts and lysimeter-collected soil solution because each method collects a distinct pool of soil DOC (Sanderman et al. 2008). Several studies have shown clear differences in DOC chemistries in streams draining watersheds with divergent vegetation and detrital inputs, suggesting DOC chemistry should vary in soils undergoing various litter manipulations (Cawley et al. 2014; Williams et al. 2010; Wilson and Xenopoulos

2009). However, we also recognize that DOC in soil can be greatly transformed by microbial activity and through sorption to minerals or organic material, all of which could dampen chemical variation in DOC from different sources of detritus. It has been argued that DOC may be homogenized as it travels though mineral soils (Sanderman and Kramer 2013). A month-long laboratory incubation of litter extracts quantified the impact of biodegradation on DOC composition and the DIRT plots allowed us to examine changes in DOC chemistry in soils where only litter inputs were varied while soil mineralogy and forest type remained constant.

Methods

Field site

The Detrital Input and Removal Treatment (DIRT) site at H.J. Andrews Experimental Forest (OR) was established in 1997 approximately 100 m from Lookout Creek (44°15'N, 122°10'W, 531-m elevation). The mean annual temperature at the H.J. Andrews Headquarters is 7.7°C and mean annual precipitation is 2257 mm. Soils were developed in basaltic parent material and are a complex of Typic Hapludands, Andic Dystrudepts, and Vitrandic Dystrudepts in Douglas-fir, *Pseudotsuga menziesii* and western hemlock, *Tsuga heterophylla* old-growth stands in H.J. Andrews (Dixon 2003). The site has a total of 18 plots and six treatments (Table 1). Each plot is 10 m × 15 m. Three plots were randomly assigned to one of six treatments ($n = 3$).

DIRT soil sampling and extraction

Soils were sampled with a 1.7 cm corer to a depth of 30 cm in March 2014. Within each plot, soil cores were taken from areas at least 1 m from a plot perimeter with approximately 2–4 m separation between cores. If a selected core location happened to be on a decaying log, the sample was discarded and a new location selected. Three cores were taken from each plot and separated into three different depths (0–10 cm, 10–20 cm, and 20–30 cm). Three cores from each depth from each plot were consolidated to homogenize soil variability within a plot. Visible roots and rocks (>5 mm) were removed in the lab. Moist samples were stored at 2°C for several days until extraction. Subsamples were dried at 60°C to determine mean soil moisture contents and to calculate field moist: dry soil ratios.

Soil solution characterization

Moist soils were extracted in 0.5 M K_2SO_4 to give a 1:10 dry soil:solvent w:v ratio. Soils were placed on a horizontal shaker table for 2 h and centrifuged for 45 min at 2400 rpm. Extracts were pre-filtered through combusted, GF/F Whatman filters and subsequently through pre-rinsed 0.45 μm cellulose acetate syringe filters and stored in the dark at 2°C prior to analysis. Control solutions of K_2SO_4 were shaken, centrifuged and filtered. All DOC concentrations of soil and litter extracts were measured on a Shimadzu Total Organic Carbon Analyzer (TOC-V_{CSH} SSM-5000A) with duplicates every 10 samples.

In each of the 18 treatment plots, three Prenart Superquartz tension lysimeters were installed at 30 cm depths in 1997. During a period of high rainfall and soil saturation in December 2014, 15 kbar of tension was placed on each apparatus with clean collection bottles and left in the field to collect soil solution for 24–48 h. Samples were collected, returned to the lab, and refrigerated until analysis within 1 week of collection. Previous research with these soil solutions has shown that

Table 1 DIRT treatment descriptions of plots established in H.J. Andrews in 1997. Three plots were randomly assigned to each of the six treatments

DIRT Treatment	Description
C	Control; No change to aboveground or belowground detrital inputs
DL	Double Litter; Fallen needles onto exclusion plots are added annually to DN plots
DW	Double Wood; Woodchips are added biannually to approximate the amount of C added to DN plots
NL	No Litter; Litterfall consisting primarily of Doug-fir needles are excluded through screening
NR	No Roots; Roots are excluded through living plant removal and lateral ingrowth is prevented through trenching
NI	No Inputs; Combination of NL and NR treatments

filtration did not change DOC concentrations (Lajtha et al. 2005).

Both lysimeters and soil extracts were used because a lysimeter collects a pool of soil DOC that is distinct from a soil extract. DOC extraction procedures mobilize soluble OC into the dissolved pool that may not be accessible to microorganisms in field conditions due to spatial or other constraints. In field-collected solutions, tools may be sampling soil solutions from macropore networks that have particularly active microbial communities ("hot spot" regions) and the sampled solutions have already undergone significant microbial breakdown (Sanderman et al. 2008). Accordingly, lysimeter solutions may capture only the residual DOC pool after initial decomposition.

Litter sampling and extraction for biodegradation study

Needles, wood of different decomposition classes, A-horizon and O-horizon soils were collected from areas adjacent to DIRT treatment plots with soils similar to Control plots for characterization of DOC from different sources of detritus and for the biodegradation incubation (Table 2). Wood was sampled from wood added to Double Wood plots that was obtained from a local commercial wood chip facility. Decomposition Class 2 refers to recently fallen, relatively undecomposed wood (Sollins 1982). Sampled wood chips were placed in the Class 2 category due to lack of bark and minimal decomposition. Decomposition Class 3 is marked by rotting sapwood and bark that has sloughed off from fallen trees and Class 5 includes logs that are no longer intact and have begun to settle into the forest floor. Five replicates of all litter and soils were sampled. An off-plot 6 m × 6 m area was selected that was adjacent to and similar to Control plots for O-horizon and A-horizon soil samples. From this established grid, five grid-cells were randomly selected for sampling and visible tree roots and decaying logs were avoided. A 10 cm × 10 cm square from each of the five grid cells was cut off of the soil surface and two 1.7 cm soil cores were taken from the 0–5 cm in the A-horizon beneath the collected O-horizon and homogenized. Freshly fallen needles from litter manipulation plots with screens were collected from multiple, evenly-spaced locations on plots. Wood samples included five replicates of the three different decomposition classes described above within 5 m of the off-plot area. Class 3 wood was sampled from partially-decayed logs that had retained fibrous structure and Class 5 wood was pulled from highly decomposed logs.

Litter and soils were sieved moist and visible roots and animals were removed. Moderately decomposed wood in Class 2 and fibrous wood in Class 3 was broken into pieces less than 2 cm in diameter. Subsamples were dried at 60°C to calculate field moist:dry soil ratios. Extraction was performed in 0.01 M K_2SO_4 1:100 dry w:v ratio for needles, Class 2, Class 3, Class 5, and O-horizon and 1:10 for A-horizon samples due to varying C contents of materials and targeting field-condition DOC concentrations (Kalbitz et al. 2003). Samples were shaken for 10 min, left in the refrigerator and stirred 3× in 24 h to allow for an equilibrium to be established between the solid and dissolved phase. Solutions were filtered through combusted GF/A and then through pre-rinsed 0.45 μm cellulose acetate syringe filters and analyzed for DOC concentration and spectroscopic properties.

Litter and soil extract biodegradation

Similar to previous research on BDOC in these soils, we define biodegradable DOC (BDOC) as the difference in DOC concentration before and after incubation (Yano et al. 2000). Accordingly, BDOC includes both DOC respired as CO_2 and DOC incorporated into microbial biomass.

Table 2 Description of litter and soils collected from areas nearby DIRT treatments for extraction and biodegradation experiment

Litter Type	Description
Needles	Needles; Fallen within 10 months of collection; primarily Doug-fir
Class 2	Woodchips that have undergone minimal decomposition; no bark
Class 3	Moderately decomposed wood; sloughed bark, structure maintained
Class 5	Highly decomposed; structure not intact; heartwood and sapwood decomposed
O-horizon	O-horizon soils
A-horizon	A-horizon soils (0–5 cm)

Inoculum was prepared according to methods of Fellman et al. (2008) in which 10 g of each litter and soil type was gently shaken in a 1:5 dry w:v ratio for 10 min with 0.01 M K_2SO_4, diluted 1:1 and filtered. 10 ml of inoculum was added to the corresponding litter or soil extract to ensure similar microbial communities exist in biodegradation experiment as in field conditions. Initial DOC concentrations of extracts were below 20 mg C L^{-1} and therefore did not require dilution to avoid microbial overgrowth during the incubation (Hongve et al. 2000). Extracts with inoculum were left in the dark at 25°C for 28 days with loosely placed caps to prevent evaporation. Incubation vessels were gently stirred every three days. DOC concentration measurements and all spectroscopic analyses were performed again after incubation.

Analytical measurements

UV-vis and fluorescence spectroscopy were used for C characterization of lysimeter solution DOC and extractable DOC. Absorbance measurements were made over wavelengths 240–560 nm using a Cary 300 Bio UV-vis spectrophotometer with a 1 cm quartz cuvette rinsed three times with MilliQ water and once with sample prior to measurements. Samples with absorbance greater than 0.2 cm^{-1} were diluted prior to fluorescence measurements to minimize inner filter effects. Specific ultraviolet (UV) absorbance at 254 nm (SUVA) is calculated as the UV absorbance at 254 nm normalized to sample DOC concentration and has been strongly correlated with aromaticity of DOC (Weishaar et al. 2003).

3-D fluorescence scans were run with a Fluorolog® spectrofluorometer (HORIBA Jobin Yvon, Inc.). Emission wavelengths and intensities are recorded during a scan of excitation wavelengths to create 3-D excitation-emission matrices (EEMs). Samples were placed in a 1 cm quartz cuvette and scans were run over an excitation range of 250–400 nm with 10 nm increments and an emission range of 350–550 nm with 2 nm increments. Subtraction of blank MilliQ water or K_2SO_4 solution spectra from sample spectra removed Raman scatter. Corrections also account for instrument-specific adjustments, first and second order Rayleigh scatter, and inner filter effects.

PARAFAC and fluorescence optical indices

The parallel factor analysis (PARAFAC) model developed by Cory and McKnight (2005) was used to unpack bulk EEMs into different components with unique excitation and emission spectra (Cory and Mcknight 2005). A component may be a single fluorophore or a group of similar fluorophores and therefore the knowledge of the chemical identity of each component varies by constituent (Table 3). The analysis resolves EEMs without making assumptions on the shapes of the spectra and a well-fit model explains greater than 99% of the fluorescence variation and errors should be less than 10%. The Cory and McKnight 13-component PARAFAC model was fit to collected fluorescence data (2005) with MATLAB® (ver. R2013b) and the model explained greater than 99% of DIRT soil DOC fluorescence and errors were less than 10%.

Ecologically relevant information can be extracted by calculating a variety of indices including a Redox Index (RI), Fluorescence Index (FI) (McKnight et al. 2001, modified by Cory et al. 2010) and Freshness Index (BIX) (Wilson and Xenopoulos 2009) (Table 4). While these indices were not created using soil DOC, they may still be relevant to soil solution chemistry. McKnight et al. (2001) developed the FI to gain information about the source of DOC using end members including Antarctic lakes with no nearby terrestrial inputs and catchments in the continental U.S. with abundant terrestrial inputs from partially broken down lignin and other terrestrial biomass. RI provides information about the redox conditions of DOC and was correlated using shifts in PARAFAC component loadings across an oxycline in an Antarctic lake and during ice cover in a subalpine lake in CO. RI is calculated as the ratio of reduced quinone-like fluorescence to oxidized quinone-like fluorescence (Cory and McKnight 2005). BIX was originally developed by Parlanti et al. (2000) through observations of degradation of macro-algae in marine waters and later updated by Wilson and Xenopoulos (2009).

Statistics

General linear mixed models were fit using the function 'lme' in the nlme package (Pinheiro et al. 2015) to DIRT soil extract data with soil depth fit as a repeated measure for each response variable. The best fit model was selected using BIC model selection criteria from four candidate models including a model without a correlation structure, a first-order autoregressive correlation structure, a compound symmetry correlation structure, and a general correlation structure. If appropriate, the assumption of equal variance among treatments was

Table 3 13 Cory and McKnight (2005) PARAFAC components with associated excitation maxima, minima and interpretations from various sources. Component descriptions are from Cory and McKnight (2005) unless otherwise noted. Q represents quinone-like fluorescence, SQ is semiquinone-like fluorescence, and HQ is hydroquinone-like fluorescence. Components without quinone-like fluorescence are designated with the letter C (component). For example, C11 is component 11 in the Cory and McKnight (2005) PARAFAC model

Cory and Mcknight (2005) Identifier	Cory and Mcknight (2005) Component	Excitation minima (nm)	Emission maxima (nm)	Description
Q1	C11	260	540	Oxidized quinone-like, terrestrial humic-like; photo-refractory (Nishimura et al. 2012)
Q2	C2	250	510	Oxidized quinone-like, terrestrial humic-like; photo-refractory (Nishimura et al. 2012)
Q3	C12	250	390	Oxidized; Correlated with percent aliphatic C. Higher aliphatic fraction has been correlated with microbial precursor material (Cory and McKnight 2005) Alternatively, relationship between aliphatic and Q3 could be due to quenching by nonaliphatic C
SQ1	C5	290	515	Terrestrial humic-like, humic acid-type; very sensitive to microbial and photochemical degradation (Nishimura et al. 2012); related to aromatic DOC and is identified as a reduced semiquinone
SQ2	C7	270 (380)	460	SQ2 has blue-shifted spectra relative to SQ1, suggesting SQ2 has a more conjugated system relative to SQ1 and is identified as a reduced semiquinone
SQ3	C9	345 (265)	410	Reduced semiquinone
HQ	C4	265	550	Correlated with percent ketone/aldehyde C; hydroquinone
Tryptophan-like	C8	270	360	Amino acid tryptophan; proteins or peptides that could be free amino acids or bound; could be less-degraded peptide material (Fellman et al. 2010)
Tyrosine-like	C13	280	350	Amino acid tryosine; proteins or peptides that could be free amino acids or bound; could be more-degraded peptide material (Fellman et al. 2010)
C3	C3	315	385	Indicates DOC of microbial or planktonic origin; listed as unknown component type in Cory and Mcknight (2005)
C6	C6	265–270	430	Listed as unknown component type in Cory and Mcknight (2005)
C10	C10	305	425	Terrestrial humic-like, fulvic acid-type (Nishimura et al. 2012); listed as unknown component type in Cory and Mcknight (2005)
C1	C1	335–340	450	May be a quinone derivative (a ketal) formed by reaction of a quinone with an alcohol. Also correlated with % anomeric, acetal, ketal C. Ubiquitous humic-like, associated with increased FI (Nishimura et al. 2012). Listed as unknown component type in Cory and Mcknight (2005)

Table 4 Absorbance and fluorescence DOC optical parameter calculations and interpretation

DOC Optical Parameter	Reference	Interpretation
Specific UV Absorbance (SUVA) (L mg C^{-1} m^{-1})	Weishaar et al. (2003)	UV absorbance of light at 254 nm normalized to sample DOC concentration. Values are strongly correlated with aromaticity of DOC.
Fluorescence Index (FI)	McKnight et al. (2001); Cory et al. (2010)	Ratio of emission intensities of 470 nm / 520 nm at excitation 370 nm.
Freshness Index (BIX)	Parlanti et al. (2000); Wilson and Xenopoulos (2009)	Ratio of emission intensities of 380 nm / max between 420 and 435 nm at excitation 310 nm. Indicates ratio of recently produced DOC to older, more decomposed DOC.
Redox Index (RI)	Cory and Mcknight (2005); Miller et al. (2006)	∑ loadings reduced quinones (SQ1 + SQ2 + SQ3 + HQ) / ∑ loadings oxidized quinones (Q11 + Q2 + Q3). Index is an indicator of oxidation state of DOC.
Proportion protein-like fluorescence	Cory and Mcknight (2005); Fellman et al. (2008); Fellman et al. (2010)	∑ % tyrosine (C13) + % tryptophan (C8) | Amino acids, suggestive of protein-like fluorophores in DOM.

relaxed for model fitting. The most suitable model for each response variables had no correlation structure. After ensuring assumptions of normality and equal variance among depths and treatments were met, *F*-tests were performed on the hypotheses that the interaction coefficient and main effect coefficients did not differ from zero.

A one-way ANOVA was used to test for differences in DOC optical parameters among DIRT treatment lysimeter samples or litter type extracts prior to incubation. Data was log-transformed if appropriate to meet assumptions for statistical tests. Once the main effects were determined to be significant, Tukey's post hoc Honest Significant Difference (HSD) test was used for pairwise comparisons at with a family-wise error rate of $\alpha = 0.05$ for lysimeter, litter and soil extracts used for biodegradation study. Tukey pairwise comparisons were performed using the package multcomp version 1.4–0 (Hothorn et al. 2008). Paired t-tests and 95% confidence intervals were constructed to test for differences in DOC optical parameters before and after incubation of litter and soil extracts. All statistical analyses were performed in R version 3.0.2 (R Core Team 2013).

Because EEM PARAFAC components can be complex to visualize and detect variation, principal component analysis (PCA) was applied to the correlation matrices of components to reduced dimensions that account for as much of the variation in the data as possible. Standardized data was shifted from original coordinate system to alternative orthogonal axes and values of principal component scores are projected onto these axes. The contribution to total fluorescence of components SQ3, SQ1 and C10 was less than 3% and therefore these three components were removed prior to analysis. PCA was applied to PARAFAC components of shallow soil and litter extracts before and after biodegradation and lysimeter and soil extracts from DIRT treatments.

Results

Off-plot litter and soil extract optical properties

Fluorescence components extracted from the EEM data have fluorescence signatures similar to model compounds and each been interpreted in an ecological context (Table 3.) HQ and Q2, a component with hydroquinone-like fluorescence and a component with quinone-like fluorescence, respectively, tended to make up the largest proportion of total fluorescence in lysimeters and litter and soil extracts (Fig. 1). The percent of total fluorescence from HQ of all samples was between 10 and 28% and the range of Q2 was 10–26%. SQ3, SQ1 and C10 generally contributed less than 3% of fluorescence. The small proportion of SQ1 and SQ3 that represent reduced quinone-like fluorescence could be indicative of relatively oxidized DOC. The average percent contribution of the oxidized quinone-like fluorescence from SQ2 was 4% across all samples, further suggestive of oxidized extractable DOC.

Needle and A-horizon extracts had significantly lower aromaticity (SUVA) than O-horizon and wood extracts (Table 5). Class 5 wood extracts had lower SUVA than O-horizon, Class 3 and Class 2 wood extracts. A-

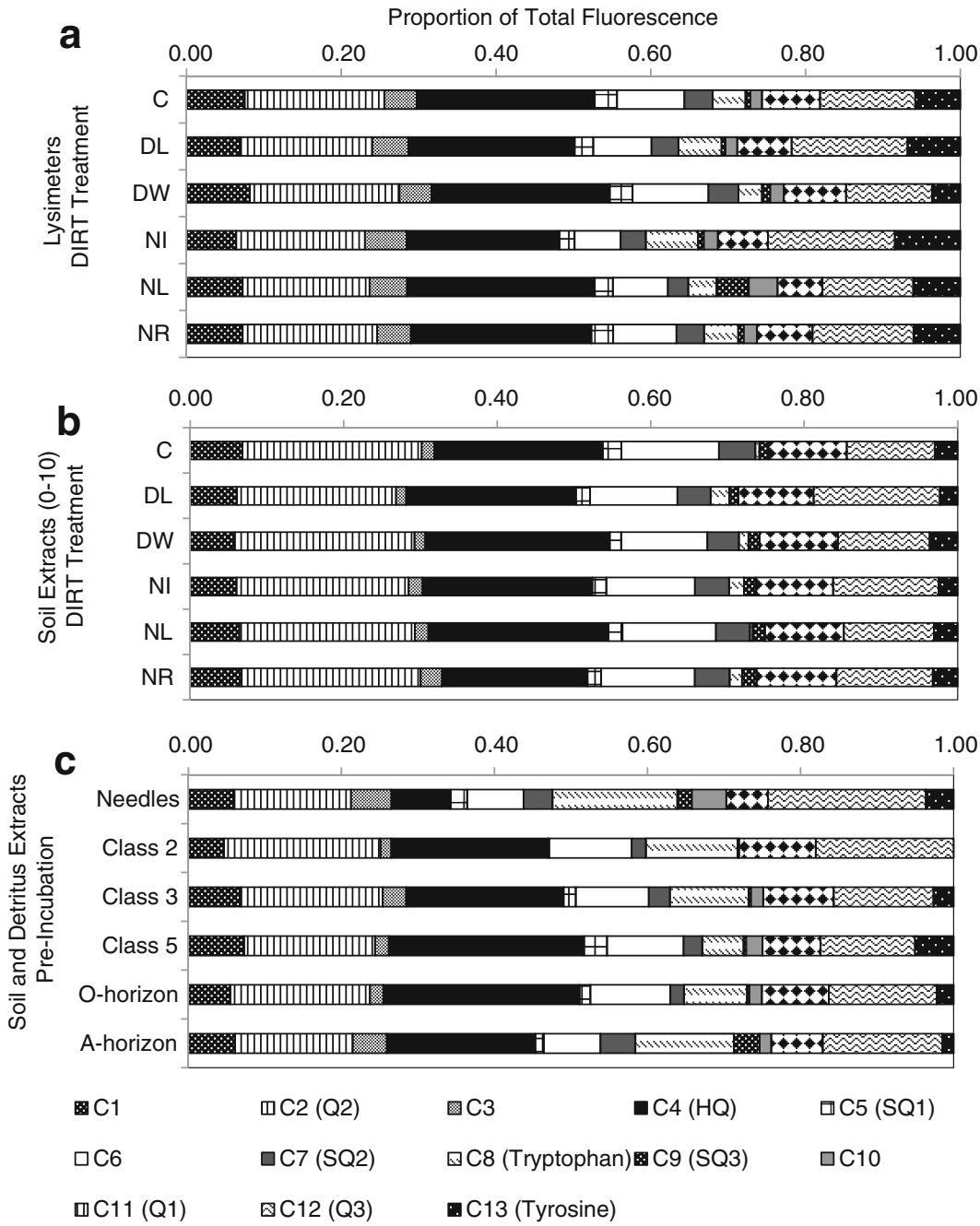

Fig. 1 PARAFAC components as a proportion of total fluorescence. **a** Lysimeter-collected (30 cm) soil solution DOC from DIRT treatments, **b** DOC extracted from soils in DIRT treatments sampled from 0 to 10 cm, **c** DOC extracted from off-plot soils and detritus

horizon and needle extracts had higher FI than O-horizon and wood extracts (Table 5). Needle extracts had the highest RI indices, suggesting DOC in these extracts has the most oxidized-like fluorescence. The proportion of reduced quinone-like fluorescence increased from Class 2, Class 3, Class 5, O-horizon and A-horizon extracts. Needle extracts had the highest proportion of protein-like fluorescence.

In the PCA of litter and soil extracts, PC1 explained 43.7% of variance and PC2 explained a further 24.3% of variance (Fig. 2). The dominant variables in determining PC1 scores included Q1, C6 and C3 and variables

Table 5 Mean and (SE) of DOC content and optical parameters of litter and soil extract DOC from fluorescence measurements. Pre and post columns represent measurements before and after 28-day incubation. Means with the same letter within each column are not significantly different (Tukey's honest significant difference). Asterisk after letter significance in post data columns represents significant difference between pre- and post-incubation data. One asterisk (*) indicates $P \leq 0.05$, two asterisks (**) indicate $P \leq 0.005$. No asterisk indicates an insignificant difference between pre- and post-incubation ($P > 0.05$). $n = 5$ for all values. Protein-like fluorescence is a proportion of total fluorescence

OM Extracted	Pre	Post	Pre	Post	Pre	Post
	DOC Content (mg C L^{-1} g^{-1})		SUVA (L mg C^{-1} m^{-1})		Redox Index (RI)	
Needles	4.47 (0.20)^{c}	2.75 (0.14)^{d,**}	1.59 (0.10)^{c}	1.56 (0.13)^{c}	0.27 (0.04)^{c}	0.29 (0.01)^{d}
O-horizon	21.35 (2.16)^{a}	12.83 (1.53)^{b,**}	3.23 (0.19)^{a}	3.81 (0.14)^{a,*}	0.41 (0.01)^{a}	0.42 (0.004)^{a}
A-horizon	0.62 (0.09)^{d}	0.38 (0.05)^{e,**}	1.56 (0.18)^{b}	1.43 (0.04)^{c}	0.43 (0.01)^{a}	0.45 (0.004)^{a}
Class 2	29.34 (0.85)^{a}	26.66 (1.04)^{a,**}	3.43 (0.07)^{a}	3.61 (0.23)^{a}	0.32 (0.01)^{b}	0.35 (0.02)^{c}
Class 3	7.75 (0.44)^{b}	5.33 (0.41)^{c,**}	3.08 (0.13)^{a}	3.24 (0.29)^{ab}	0.38 (0.01)^{a}	0.37 (0.01)^{b}
Class 5	4.10 (0.49)^{c}	2.88 (0.38)^{d,**}	2.63 (0.12)^{ab}	2.76 (0.19)^{b}	0.42 (0.01)^{a}	0.38 (0.02)^{b}
	Protein-like Fluorescence		Freshness Index (BIX)		Fluorescence Index (FI)	
Needles	0.20 (0.02)^{a}	0.16 (0.01)^{a,*}	0.76 (0.04)^{ab}	0.71 (0.03)^{b,*}	1.64 (0.05)^{a}	1.63 (0.02)^{b}
O-horizon	0.10 (0.01)^{b}	0.07 (0.003)^{c,*}	0.58 (0.02)^{d}	0.55 (0.01)^{e}	1.44 (0.01)^{b}	1.42 (0.02)^{de}
A-horizon	0.14 (0.03)^{ab}	0.07 (0.01)^{c,*}	0.78 (0.03)^{a}	0.85 (0.02)^{a,*}	1.67 (0.02)^{a}	1.69 (0.01)^{a}
Class 2	0.12 (0.01)^{b}	0.12 (0.01)^{ab}	0.67 (0.01)^{bc}	0.68 (0.01)^{bc}	1.50 (0.04)^{b}	1.51 (0.004)^{c}
Class 3	0.13 (0.002)^{ab}	0.11 (0.01)^{b}	0.62 (0.01)^{cd}	0.65 (0.01)^{cd,*}	1.46 (0.01)^{b}	1.46 (0.01)^{cd}
Class 5	0.10 (0.02)^{b}	0.10 (0.01)^{c}	0.55 (0.01)^{d}	0.61 (0.01)^{d,*}	1.38 (0.03)^{b}	1.38 (0.004)^{e}

largely determining PC2 scores were Q3, C1, Tyrosine, and Tryptophan. Extracts of the most decomposed and the least decomposed materials, A-horizon and needles, had more negative scores on the PC1 axis than all other groups. Extracts from the A-horizon are further distinguished from needle extracts by more positive PC2 scores, suggesting more influence of Q3, C1 and aromatic amino acid-like fluorescence in A-horizon DOC relative to needle-derived DOC. Class 2 wood extractable DOC was distinguished from all other groups with more negative PC2 scores.

DIRT treatment lysimeter and soil extract DOC chemistry

While DOC concentrations in Control and Double Litter treatment lysimeter solutions were slightly higher than in exclusion treatments, the difference was not statistically significant ($P = 0.80$) (Table 6). There were no significant differences in concentrations or optical parameters of DOC among DIRT soil extracts. In soil extracts, DIRT treatments had no impact on the values of SUVA, RI, BIX, and protein-like fluorescence (Appendix).

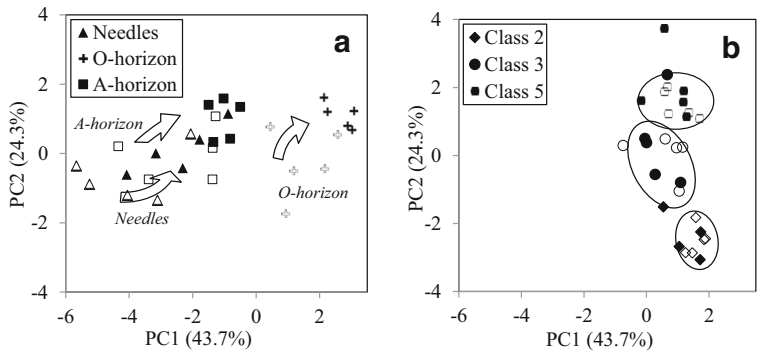

Fig. 2 Litter and soil extract PCA. Scores from pre and post biodegradation PARAFAC components. Pre biodegradation scores are shown with hollow shapes. **a** PCA of Needles, O-horizon, and 0–5 cm A-horizon extracts and shifts in scores as a result in biodegradation. **b** PCA of Class 2, Class 3 and Class 5 wood. Shift in scores as a result of biodegradation were inconsistent

Table 6 Mean DOC optical parameters of lysimeter-collected soil solutions in December 2014 from DIRT treatments and (SE). Lysimeters are installed at 30 cm depth. *C* Control, *DL* Double Litter, *DW* Double Wood, *NI* No Inputs, *NL* No Litter, *NR* No Roots. Analyses of variance demonstrated no significant differences in response variables among treatments. Protein-like fluorescence is a proportion of total fluorescence

Treatment	Count	DOC (mg C L^{-1})	SUVA (L mg C^{-1} m^{-1})	Redox Index (RI)	Protein-like Fluor.	Freshness Index (BIX)	Fluorescence Index (FI)
C	4	6.55 (2.11)	1.95 (0.36)	0.44 (0.01)	0.10 (0.02)	0.67 (0.05)	1.44 (0.03)
DL	6	6.31 (1.72)	1.95 (0.30)	0.41 (0.02)	0.12 (0.02)	0.71 (0.05)	1.50 (0.03)
DW	2	6.79 (1.38)	2.82 (0.23)	0.45 (0.02)	0.07 (0.01)	0.62 (0.005)	1.47 (0.02)
NI	3	3.99 (3.38)	2.23 (0.72)	0.39 (0.05)	0.15 (0.06)	0.64 (0.07)	1.49 (0.06)
NL	4	4.09 (1.46)	2.44 (0.56)	0.50 (0.06)	0.10 (0.01)	0.61 (0.03)	1.50 (0.06)
NR	6	4.60 (1.24)	1.95 (0.43)	0.45 (0.01)	0.10 (0.02)	0.74 (0.08)	1.48 (0.03)

PCA of lysimeter solution PARAFAC components showed that PC1 explained 68.2% of variance and PC2 explained 20.0% of variance (Fig. 3). Tryptophan, Q1, Q3, and C6 had the highest influence on scores on PC1. SQ2, C1, and C3 had the highest loadings for PC2. Lysimeter DOC scores did not show any clustering by treatment on the reduced-dimension PC axes.

Because soil extracts may capture a different pool of DOC than lysimeter-collected DOC, we expected that the soil extract PCA may uncover underlying DOC chemistry patterns that were not visible in the lysimeter PCA. PC1 explained 43.3% of variance and PC2 explained 20.2% of additional variance in the analysis of soil extracts from DIRT treatment soils from all depths (Fig. 3). C6, Q2 and C1 had the highest loadings in PC1 and Tryptophan, C3, HQ and Q3 were highest in PC2. Similar to lysimeter analysis, PCA scores for soil extracts did not appear to vary with DIRT treatments. Overall, PARAFAC components of lysimeter DOC and extractable DOC collected from DIRT treatment plots showed that fluorescence signatures did not differ among DIRT treatments.

There were significant differences in DOC content, SUVA, and RI observed with soil depth (Fig. 4). DOC content decreased rapidly from 0 to 10 cm and subsequently did not change significantly from 10 to 30 cm. SUVA in all treatments showed a distinct decrease in aromaticity from 10 to 20 cm relative to shallower and deeper soils and RI increased with soil depth, indicative of more reduced material in deep soils.

FI was the only optical index to have a significant interaction between litter manipulation treatment and soil depth, indicating that the difference in FI among soil depths varied among DIRT treatment ($P = 0.04$). FI tended to increase with soil depth in No Root, No Input and Control treatments (Fig. 4). Double Wood and No Litter treatments had slight increases in FI from 0 to 10 cm to 10–20 cm and then decreased in the 20–30 cm interval. However, treatment replicates had different patterns with soil depth and therefore the FI may be too variable to interpret for soil DOC characterization.

DOC composition differed between lysimeter DOC and soil extract DOC. SUVA values of extractable DOC had between 4.5% and 9.0% lower aromaticity than lysimeter solution DOC as calculated by the Weishaar et al. (2003) equation ($P = 0.005$). Percent aromaticity ranged from 9 to 27% in lysimeters and 7–23% in soil extracts (Weishaar et al. 2003). Lysimeter FI ranged between 1.36 and 1.66 which is significantly lower than the FI of soil extracts that had a range of 1.49–1.74 ($P < 0.005$) (Tables 5 and 6). The RI of DOC from lysimeters and extractable DOC was relatively oxidized. However, a larger RI in lysimeters indicates slightly more reduced quinone-like fluorescing DOC than in soil extracts ($P = 0.01$). The mean proportion of protein-like fluorescence in lysimeters is significantly larger than in soil extracts ($P < 0.005$). BIX did not differ significantly between lysimeter and soil extracts ($P = 0.49$).

Litter and soil extract DOC biodegradation

DOC content decreased in all extracts after incubation (Table 5). BDOC in all soil and litter extracts ranged from 4 to 39% of initial DOC (Table 7). Class 2 wood had the lowest percentage of BDOC with a range of 4–11%. Biodegradability did not seem to be related to initial extractable DOC optical properties.

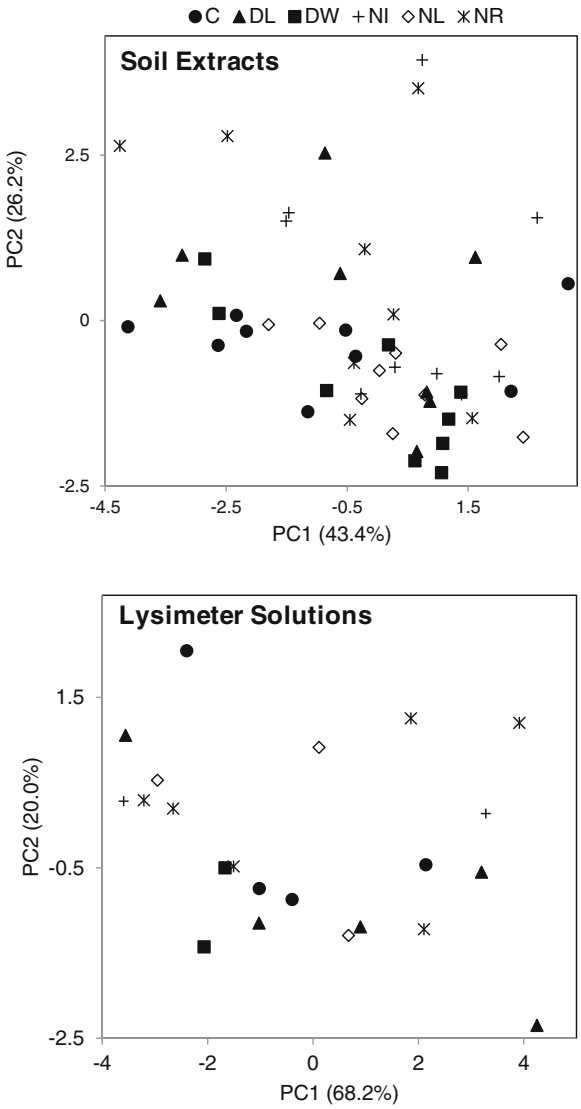

Fig. 3 DIRT soil extracts and lysimeter solution PCA. PCA on PARAFAC components from soil extracts from all soil depths (top) and lysimeter solutions (bottom). *C* Control, *DL* Double Litter, *DW* Double Wood, *NI* No Inputs, *NL* No Litter, *NR* No Roots

All confidence intervals on the difference in means pre and post incubation include a difference of zero for RI and FI (Table 5). Although not statistically significant, the estimated mean change in SUVA suggested a slight enrichment in aromaticity during degradation of all wood decomposition classes (Table 5). O-horizon extracts had the only DOC to show a significant increase in SUVA ($P = 0.04$). Protein-like fluorescence decreased during biodegradation in A-horizon, needles, and O-horizon extracts, but there was no statistically significant change in protein-like fluorescence in wood extracts of any decomposition class (Table 5).

PCA of PARAFAC components from soil and litter extracts before and after incubation showed that biodegradation resulted in movement on the PC axes (Fig. 2). Biodegradation of needles, A-horizon and O-horizon extracts increased the PC1 scores and slightly increased the scores on PC2. Decomposition of wood extracts increased the PC2 scores of Class 3, but replicates of Class 2 and Class 5 extracts shifted in various directions on the PC axes as a result of biodegradation.

Discussion

Total SOC in H.J. Andrews DIRT treatments has changed as a result of the litter manipulations (Lajtha et al. 2005). Because decomposition products of existing SOC contribute to the dissolved pool, we expected to find changes in the bulk SOC content reflected in the chemistry of DOC (Sanderman et al. 2008). We also expected to observe differences in DOC composition among DIRT treatments because fluorescence signatures of extractable DOC from different sources of detritus showed that extract chemistry varies by source. However, even after 17 years of litter additions and exclusions in DIRT treatments, DOC composition has not changed in either soil extracts or lysimeter solutions as assessed by UV-vis and fluorescence spectroscopic fingerprinting techniques.

Given this lack of detectable differences in DOC chemistry among DIRT treatments, we hypothesize that both biotic and abiotic processes regulate the chemistry of DOC that enters soil from fresh litter. Leachate from aboveground litter or root biomass and decomposition products from microbial processing enter the dissolved pool and undergo biodegradation (Bengtson and Bengtsson 2007; van Hees et al. 2005). Concurrently, inorganic-organic and organic-organic interactions can remove C from the dissolved pool either temporarily or to be retained in a long-term SOC store (Qualls 2000). Decomposition, incorporation, and transformations of DOC by preferential microbial consumption of more labile DOC and interaction of DOC with mineral surfaces may generate a pool in the mineral soil with a signature unlike that of DOC initially mobilized from fresh litter. Significantly higher SUVA in O-horizon extracts relative to A-horizon extracts indicates that DOC source materials in the O-horizon have a higher

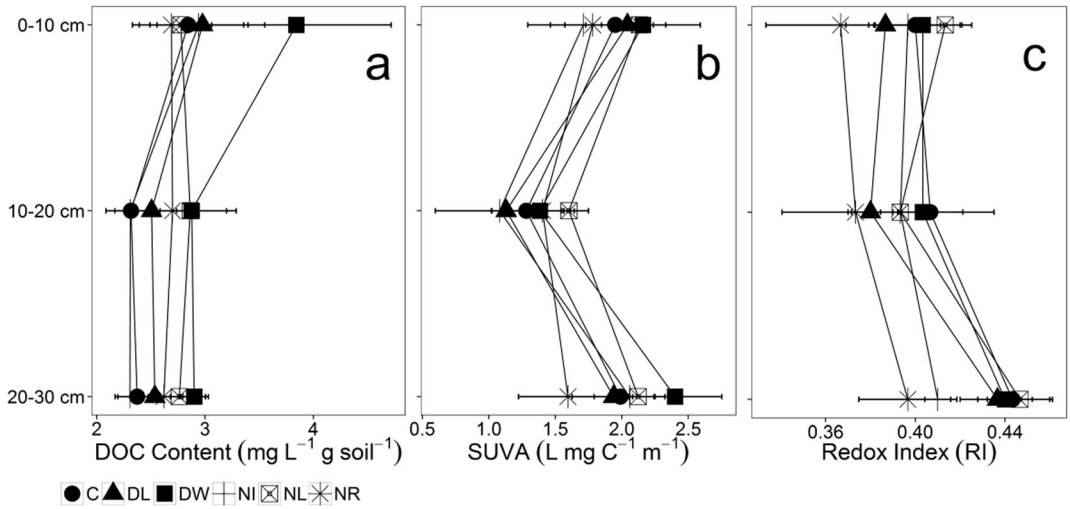

Fig. 4 Differences in optical parameters of DIRT soil extracts with soil depth. Soils were sampled in 10 cm increments. Error bars represent SE. Soils were sampled in March 2014. **a** DOC content, **b** Specific UV absorbance at 254 nm (SUVA) **c** Redox Index (RI)

proportion of potentially soluble aromatics. A high sorptive capacity of the mineral A-horizon in these soils with Andic properties could preferentially remove hydrophobic aromatic acids from solution, resulting in lower measured aromaticity in A-horizon DOC (Kramer et al. 2012). In addition to DOC derived from litter on the soil surface, breakdown of SOC within the profile continues to mobilize additional DOC that undergoes a similar combination of abiotic and biotic dynamic exchange reactions that moves C between the solid, liquid and gaseous phases (Sanderman et al. 2008). There is constant exchange between DOC and existing SOC at any position in a soil profile. For example, in a podzolized soil in Sweden, DOC in an Oe layer had ^{14}C signatures showing that the dissolved pool was produced within the Oe and that incoming Oi-derived DOC could either be sorbed within the Oe or lost through rapid biodegradation before reaching any deeper in the soil profile (Fröberg et al. 2003). Both biodegradation and abiotic interactions with soil mineral surfaces act to homogenize incoming DOC from diverse litter sources.

Table 7 Mean percent BDOC over 28 day laboratory incubation of extracted DOC from various source materials. BDOC was calculated as the difference in DOC concentration before and after incubation. $n = 5$

DOC Source Material	% BDOC
Needles	37.97 (3.36)[a]
A-horizon	38.95 (1.87)[a]
O-horizon	40.35 (3.84)[a]
Class 2	9.23 (1.27)[b]
Class 3	31.54 (2.60)[a]
Class 5	29.69 (1.30)[a]

Other research using litter manipulations over shorter durations has also demonstrated that leachate derived from plant detrital inputs does not significantly affect soil DOC chemistry. Yano et al. (2005) used resin fractionation of O-horizon leachate from detrital addition treatments (Double Litter, Double Wood) to show that there were minimal changes in soil DOC composition 3–4 years after DIRT treatment establishment. Kalbitz et al. (2007) identified no differences in fluorescence indices in O-horizon DOC as a result of 6 years of DIRT litter manipulations in sandy to loamy Haplic Cambisols. Sanderman and Kramer (2013) found ^{13}C NMR DOC chemistry converging from diverse source SOC across a 0.3 ky – 4.1 k.y. chronosequence in Hawaii. In other research, aboveground litter additions resulted in an increase in DOC concentration in leachate from the O-horizon but resulted in no change in UV absorbance (Fröberg et al. 2005). Expanding upon previous research, our work demonstrates that the lack of impact of litter leachates on soil DOC chemistry persists on decadal scales.

However, these small-scale results do not agree with many studies at the watershed scale that have shown that land use alters stream DOC chemistry (Williams et al. 2010; Wilson and Xenopoulos 2009). This discrepancy suggests that there are processes operating at the

watershed scale that we do not measure at the pedon scale. For example, soil extracts and lysimeters capture soil solution from the entire soil pore network. However, at the watershed scale, hydrologic transport primarily occurs through macropore flow or flowpaths that vary with conditions that result in water bypassing a portion of the soil pore network where DOC would experience both abiotic and biotic homogenization (Kirchner 2003; Weiler and McDonnell 2007).

The incubation experiment determined whether microbial biodegradation of extracts from different aboveground OM sources and O-horizon transformed the fluorescence signatures to be more similar to the DOC from the A-horizon. We expected that if microbial processing of DOC was responsible for homogenization of DOC among DIRT treatments, fluorescence signatures of degraded litter extracts would match that of DOC extracted from O- or A-horizon soils. The BDOC between 4 and 39% observed during the 28 day incubation is similar to that observed in other studies (Qualls and Haines 1992). Kalbitz et al. (2003) found a higher percentage of BDOC in extracts from fresher plant litter but in our data, there was no statistically significant difference in BDOC among soil horizons, needle, Class 3 and Class 5 extracts. There were changes in optical parameters of DOC from litter and soil extracts as a result of biodegradation, but the changes did not transform the chemistry to a signature closer to that observed in the O-horizon or A-horizon extracts. Hagedorn et al. (2015) also observed only a minor impact of biodegradation on a pool of ^{14}C-labelled DOC added to a chronosequence of soils. The similar direction of change of scores on the PC axes in replicates of needles, A-horizon, and O-horizon extracts demonstrated consistent change in PARAFAC components as a result of biodegradation. On the other hand, replicates of wood extracts exhibited inconsistent shifts, suggesting that patterns of decomposition in wood are different from that of needles and soils.

Adaptations of soil biotic communities to OM input chemistry may also explain why there are no differences in DOC composition among DIRT treatment plots. For example, Brant et al. (2006) observed a higher fungal:bacterial ratio in Double Wood soils associated with the breakdown of phenols. A shift in community and therefore a change in substrate use could control the incoming DOC chemistry and result in no change in fluorescence signatures between Double Wood and Control soils DOC. However, while changes in microbial community were demonstrated in Double Wood soils, Yarwood et al. (2013) found no differences in microbial biomass or community between Control and No Input treatments, so shifts in community composition appears to vary by DIRT treatment. Future research should address the capability of community composition to shape DOC chemistry.

Although we did not detect changes in DOC chemistry among litter manipulation treatments with fluorescence spectroscopy, changes could have occurred in non-fluorescing fractions of DOC such as carbohydrates. As an example, Yano et al. (2005) found that extracts of recently harvested roots had the highest DOC content relative to wood and needle extracts and therefore we expected to see an impact of roots on DOC chemistry. The major role of root litter contributions to DOC has also been suggested in a tree girdling experiment in a Scots pine forest on Entic Haplocryods. Soil extractable DOC concentrations were reduced by 40% by diminishing the flow of recent photosynthate to tree roots and associated mycorrhizal fungi (Giesler et al. 2007). Because major decreases were seen in the girdling experiment in compounds such as citrate, trehalose and monosaccharides that may not be captured in fluorescence techniques employed here, changes in chemistry as a result of root exclusion in No Root and No Input DIRT treatments may not be detectable with UV and fluorescence spectroscopy.

Optical indices reflected differences among litter and soil extract chemistries that coincide with existing knowledge of source material chemistry. Needle extracts had a higher proportion of protein-like fluorescence than soil and wood extracts although the difference was only statistically significantly relative to O-horizon, Class 5, and Class 2. Wood extracts had a high proportion of aromatics likely due to the high input of mobilized lignin decomposition products. The lack of mineral interaction with hydrophobic aromatics in the O-horizon may explain the high proportion of aromatics in O-horizon extracts relative to the A-horizon. While needle extracts were expected to release the least decomposed and most reduced DOC, RI of needle extracts showed the opposite. This may be reflective of the rapid decomposition of substrates such as needles that have not yet undergone significant loss of readily available C fractions. The A-horizon soil that likely contains the most processed SOC reflected the most reduced RI values.

Optical indices also showed differences among soil depths. In general, SUVA and δ^{13}C tend to decrease with soil depth with δ^{13}C decreasing due to additions

of processed DOC or because constituents already in solution are becoming increasingly altered (Sanderman et al. 2008). A distinctive pattern was observed in DIRT treatment soils in which SUVA decreased from 10 to 20 cm relative to the soil above and the soil below. The high SUVA values in 0–10 cm could be capturing DOC leaving the O-horizon that is particularly high in aromatics. Alternatively, the decrease in aromaticity from 10 to 20 cm might indicate a change in mineralogy and therefore a soil sorptivity shift that involves removal of aromatics from solution due to hydrophobic interactions. As expected, RI increased with soil depth, reflecting the more reducing conditions with increased soil depth. There were no distinct patterns of FI with soil depth and because the values of FI in the biodegradation experiment were also inconsistent, further adjustment of the FI calculation may be necessary before it can reliably be used in soil DOC characterization. Gabor et al. (2014) showed that a lower FI in 0–70 cm soils with higher plant inputs corresponded to a higher, more reduced RI in soil extracts from the Colorado Front Range. Similar to our observations of a greater change in optical indices with soil depth than among litter manipulation treatments, found that microbial communities and fluorescence indices varied more with soil depth than across landscape positions.

When patterns of each PARAFAC component with soil depth are observed individually, a few components show consistent trends but others have unsystematic variation such as tryptophan and tyrosine components. HQ, a component that corresponds to hydroquinone-like fluorescence, was relatively constant from 0 to 20 cm but a subsequent increase in the deeper 20–30 cm might signify a shift towards more reduced conditions. An oxidized quinone-like component, Q2, decreased from 20 to 30 cm and might reflect the increasing degree of decomposition with soil depth. The increase in Q2 during incubation in all extracts except Class 2 and Class 3 suggests that the fluorophore may be a decomposition product from microbial decomposition. Q3 is thought to be representative of relatively oxidized quinone-like fluorescence and was found to be abundant at all soil depths in the DIRT treatments with no statistically significant difference among depths. Cory and McKnight (2005) noted a relationship between the percent aliphatic C and proportion of Q3. The expected loss of relatively easily-degraded aliphatic C during biodegradation was confirmed by a decrease in Q3 during the incubation.

Evidence of the relatively oxidized conditions in H.J. Andrews DIRT soils were apparent in the components with reduced-like fluorescence contributing less than 5% of total fluorescence in most samples. HQ is a component thought to have fluorescence similar to quinones in intermediate redox states (Cory and Mcknight 2005). The slight increase in HQ at 20–30 cm reflects the higher degree of microbial processing with increasing soil depth.

Conclusions

It is critical that we gain a better understanding of the processes that control the links between litter chemistry, microbial decay, abiotic interactions, and soil C accumulation. The DIRT network provides a unique opportunity to study DOC response to long term changes in needles, wood and root inputs. Although there have been changes in SOC content among the H.J. Andrews Forest DIRT treatments (Lajtha et al. 2014; Lajtha et al. 2005), DOC concentrations and chemistry have not responded to 17 years of litter manipulations. A biotic and abiotic driven homogenization model explains the lack of differences among treatments whereby microbial biodegradation, inorganic-organic and organic-organic sorption interactions remove DOC constituents from solution. The combination of these processes effectively homogenizes DOC chemistry that enters the mineral soil from diverse detrital inputs.

These results differ from those observed at watershed scales that demonstrate land-use can significantly alter the chemistry of DOC in streams and rivers. The biochemistry of downstream waters can be resolved by decoupling smaller-scale soil processes from the macropore flow that controls the chemistry of stream DOC. As water is transported at watershed scales via preferential flowpaths, available sorption sites are bypassed and DOC may not experience the same degree of homogenization as DOC in a shallow soil. There are contrasting processes that regulate DOC chemistry during transport between shallow soils and broader landscapes.

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