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Interstorm Variability in the Biolability of Tree-Derived Dissolved Organic Matter (Tree-DOM) in Throughfall and Stemflow

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Abstract: Dissolved organic matter (DOM) drives carbon (C) cycling in soils. Current DOM work has paid little attention to interactions between rain and plant canopies (including their epiphytes), where rainfall is enriched with tree-derived DOM (tree-DOM) prior to reaching the soil. Tree-DOM during storms reaches soils as throughfall (drip through canopy gaps and from canopy surfaces) and stemflow (rainwater drained down the trunk). This study (1) assessed the susceptibility of tree-DOM to the consumption by microbes (biolability); (2) evaluated interstorm variability in the proportion and decay kinetics of biolabile tree-DOM (tree-BDOM), and (3) determined whether the presence of arboreal epiphytes affected tree-BDOM. Tree-BDOM from *Juniperus virginiana* L. was determined by subjecting throughfall and stemflow samples from five storms to 14-day microbial incubations. Tree-DOM was highly biolabile, decreasing in concentration by 36–73% within 1–4 days. Tree-BDOM yield was 3–63 mg-C m⁻² mm⁻¹ rainfall, which could represent 33–47% of annual net ecosystem exchange in Georgia (USA) forests. Amount and decay kinetics of tree-BDOM were not significantly different between throughfall versus stemflow, or epiphyte-covered versus bare canopy. However, epiphyte presence reduced water yields which reduced tree-BDOM yields. Interstorm proportions, rates and yields of tree-BDOM were highly variable, but throughfall and stemflow consistently contained high tree-BDOM proportions (>30%) compared to previously-published litter and soil leachate data (10–30%). The high biolability of tree-DOM indicates that tree-BDOM likely provides C subsidies to microbial communities at the forest floor, in soils and the rhizosphere.

Keywords: biolability; tree-DOM; dissolved organic matter (DOM); carbon; dissolved organic carbon (DOC); stemflow; throughfall

1. Introduction

Dissolved organic carbon (DOC) has long been known to exert significant influence over soil processes, from soil formation [1] to the preservation of soil organic matter [2] and pollutant transfer [3], as well as the cycling of other nutrients, e.g., nitrogen [4] and phosphorous [5]. Dissolved organic matter (DOM) is usually quantified as the concentration of DOC, which constitutes approximately 50% of DOM dry mass [6]. In vegetated landscapes, soils receive DOM during storms from multiple sources:

rain falling through canopy gaps and dripping from canopy surfaces (throughfall), droplets that drain down the stem (stemflow) and litter leachates. The fate and transport of these DOM sources in and through soils depends, in large part, on the portion that is degradable by microbial communities [7]. For litter leachates, this “biolability” has received decades of extensive research attention [8,9] compared to tree-derived DOM in throughfall and stemflow (tree-DOM) whose biolability has rarely been assessed [7].

The paucity of tree-DOM biolability research is surprising, because it is highly concentrated ($10\text{--}480\text{ mg-C L}^{-1}$), yields substantial C from canopies ($10\text{--}90\text{ g-C m}^{-2}\text{ year}^{-1}$), and its role in soils and downstream ecosystems is currently poorly understood [10]. In fact, total DOM yields (per unit canopy area), when converted to inputs per unit infiltration area, can exceed $300\text{ g-C m}^{-2}\text{ year}^{-1}$, for example [11], which, if processed in soils, can be approximately one-quarter of annual soil respiration, $1248\text{ g-C m}^{-2}\text{ year}^{-1}$ [12]. Arguably, a key endeavor to deciphering the role that tree-DOM plays in shaping the form and function of receiving ecosystems is the determination of how much may be consumed by soil microbial communities. Biolabile portions of tree-DOM (tree-BDOM) represent a mechanism preventing DOM loss from the ecosystem [7]. The remaining, non-biolabile tree-DOM may then be sequestered through mineral complexation deeper in the soil profile [13] or be flushed into streams and rivers along preferential pathways in the soil [14]. Thus, the first objective of this study was to quantify the biolabile portion and decay coefficient for tree-DOM at a subtropical cedar (*Juniperus virginiana* L.) forest site in southeast Georgia (USA) and compare these values for throughfall and stemflow. Forests cover 31% of the global land surface [15] and *Juniperus* vegetation can be found throughout forest types, from arid [16] to humid conditions [17].

Tree-BDOM has been found to vary significantly across a growing season (May through August) for weekly throughfall samples [7]. However, no work known to the authors has examined the interstorm variability of tree-BDOM. This minimal examination of temporal variability in tree-BDOM constrains our understanding of the respective relevance of decomposition versus adsorption in the removal of DOM from soils. To address this knowledge gap, our second objective was to evaluate the variability of throughfall and stemflow tree-BDOM quantities and decay coefficients between individual storm events.

Forest canopies can host substantial lichen, bryophyte and/or vascular epiphyte assemblages that trap detritus and aerosols [18], but the authors are unaware of any research on epiphyte influences over tree-BDOM. Epiphytes, although particularly concentrated in the tropics and subtropics, are found in all forests and warming of the temperate regions is expected to extend the range of vascular epiphytes poleward [19]. Thus, the role of epiphyte communities in forest biogeochemistry is gaining increased attention [18]. Epiphyte cover can increase mean DOC concentrations relative to bare canopies for cedar throughfall (54 ± 38 versus $20 \pm 13\text{ mg-C L}^{-1}$) and stemflow (63 ± 40 versus $36 \pm 29\text{ mg-C L}^{-1}$) at the study site [11]. However, the molecular signatures of tree-DOM derived from epiphyte-covered and bare cedar canopies were similar—containing over two-thirds carbohydrate formulas and being rich in highly unsaturated formulas [20]. These molecular signatures indicate the potential for high biolability whether epiphytes are present or not. However, an individual highly unsaturated molecular formula may represent many different structural isomers of correspondingly diverse biogeochemical functions, including biolability [21]. As a result, our third objective was to compare biolability of throughfall and stemflow from bare and epiphyte-covered cedar canopies. As tree-DOM represents the first, and in some cases the largest, enrichment of DOC in rainwater [10], and is large from cedar trees at our site: $5\text{--}48\text{ g-C m}^{-2}\text{ year}^{-1}$ [14], accomplishing these objectives advances our understanding of a key DOM supply to the forest floor, soil and other downstream ecosystems.

2. Materials and Methods

2.1. Study Site Description

The study was conducted in a forest on Skidaway Island, Georgia, USA, located at 31.9885° N, 81.0212° W (Figure 1a) along Georgia's coast. Climate is humid subtropical (Köppen *Cfa*). Thirty-year mean annual temperature and precipitation (exclusively rainfall) was 19.3 °C and 975 mm [22]. The forest site (Figure 1b) contained 162 stems ha⁻¹ of *Juniperus virginiana* L. (eastern red cedar, hereafter "cedar"). Cedars on site host substantial epiphyte biomass, *Tillandsia usneoides* L. (Spanish moss) (Figure 1c), yet some individual trees were bare. Further site information and a complete site inventory can be found in [11].

Figure 1. Location of (a) Skidaway Island in Chatham County (shaded area), Georgia, USA; and (b) the study site location on the Skidaway Institute of Oceanography campus; (c) Photograph provided showing an example cedar canopy hosting the epiphyte, *Tillandsia usneoides* L.

2.2. Rainfall, Throughfall and Stemflow Sampling

Sampling of rainfall, throughfall and stemflow was performed for five storms during the 2017 growing season: 14 May, 3 June, 30 July, 28 August and 23 October following published methods [11]. Three bulk rainfall and twenty throughfall samplers consisting of 0.18 m² high density polyethylene (HDPE) bins were deployed immediately before each storm. Rainfall was collected in an open area immediately beside the forest site and throughfall samplers were evenly split between bare ($n = 10$) and epiphyte-covered ($n = 10$) cedar canopies. Ten individual cedar trees were selected for stemflow sampling, five each with bare and epiphyte-covered canopies (individual tree characteristics provided in Table S1). Stemflow samplers consisted of collars made from polyethylene tubing cut longitudinally, wrapped around the stem at 1.4 m height, fixed to the stem with aluminum nails, sealed to the bark with silicone, and connected to a 120 L HDPE bin. All samplers were pre-cleaned with pH 2 (using trace clean 6 N HCl) ultrapurified water (Milli-Q), then triple-rinsed with ultrapure water, air dried, and covered until the start of a storm. Sample volumes were measured manually with graduated cylinders. Samples for DOC quantification were collected within hours after a storm, filtered to 0.2 µm through hydrophilic polypropylene syringe filters (Acrodisc) into precombusted glass vials, acidified, then stored at 4 °C in the dark until quantification of DOC concentration (hold period no longer than one month). All sampling materials were precleaned with acidified ultrapure water, triple-rinsed with ultrapure water, then triple-rinsed with sample water.

2.3. Bioincubations

Bioincubations lasting 14 days and based on a modified protocol [7,23] were performed to estimate the biolabile portion and decay coefficients for tree-DOM in throughfall and stemflow for each

storm. Immediately after each storm, in addition to the sample taken for DOC analysis in Section 2.2, four 20 mL samples per stemflow sampler and from a composite sample of every two throughfall samplers were filtered to 0.2 µm and placed into precombusted glass vials. A bacterial inoculum was added (2 mL) to each vial along with 2 mL of Nitrogen-Phosphorous-Potassium (NPK) nutrient solution (10:10:10) to prevent nutrient limitation from constraining biodegradation. As throughfall and stemflow at this site contain 10^4 – 10^6 bacteria mL^{−1} [24], the inoculum was prepared for each storm from a volume-weighted composite of freshly collected throughfall and stemflow samples filtered through a 50 µm mesh to remove microbial grazers and coarse particulates. Caps were placed loosely on the bottles to allow air movement, then samples were incubated for 1, 2, 4, and 14 days at 25 °C in the dark on a shaker table (60 rpm). After bioincubation, each sample was filtered to 0.2 µm into a new precombusted glass vial, acidified, then stored at 4 °C in the dark until quantification of DOC concentration (hold period no longer than one month).

2.4. Dissolved Organic Carbon Concentrations

Concentrations of DOC were determined as nonpurgable organic C using a total organic carbon (TOC)-VCPH analyzer with an ASI-V autosampler (Shimadzu, Columbia, MD, USA). Calibration curves were made with potassium hydrogen phthalate stock solution. Instrument reproducibility was checked against deep seawater reference material from the Consensus Reference Material (CRM) Project. CRM analyses were <5% from reported (<http://yyy.rsmas.miami.edu/groups/biogeochem/Table1.htm>). This configuration has a minimum DOC detection limit of 0.034 ± 0.004 mg L^{−1} with typical standard errors for DOC concentration being $1.7 \pm 0.5\%$ [25].

2.5. Data Analysis

First-order decay curves were fit to the DOC concentrations quantified after bioincubations:

$$\%DOC_{remaining} = be^{-kt} + c \quad (1)$$

where b is the biolabile proportion, k is the decay coefficient, and c is the recalcitrant proportion of tree-DOM that would theoretically resist biodegradation indefinitely under these experimental conditions. First-order decay curves were only fit to sample data where DOC concentrations stopped decreasing between two consecutive measurements. Tree-BDOM yield (mg-C m^{−2} mm^{−1} rainfall) for each storm from each flux/cover type was computed as the product of b and total tree-DOM yield. Total tree-DOM yield was calculated as DOC concentration (mg-C L^{−1}) × water volume (L)/canopy area (m²) and rainfall amount (mm). Two-way Analysis of Variance (ANOVA) with a Tukey's Honest Significant Differences (HSD) test was performed to compare initial DOC concentrations between fluxes with and without epiphyte cover using Statistica 13.2 (Statsoft, Tulsa, OK, USA). The threshold for significance was $p < 0.05$ unless otherwise noted and variability about the mean is expressed in the text as standard deviation.

3. Results

3.1. Hydrometeorology for Sampled Storms

Sampled storms ranged in magnitude from 8 mm to almost 50 mm, while storm duration ranged from 8.5 to 59.3 h (Table 1). Rainfall intensity for sampled storms varied from 0.7 to 1.8 mm h^{−1} (Table 1). Throughfall volumes were generally larger beneath bare compared to epiphyte-covered cedar canopies, except for the largest storm (14 May 2017; Table 1). Stemflow volumes from the sampled bare cedar trees were 2–5 times greater than observed beneath the epiphyte-covered cedars (Table 1). The sum of throughfall and stemflow exceeded total rainfall for the 30 July storm (9.2 mm net rainfall versus 8.9 mm gross rainfall), which is a common artifact observed when throughfall drip points

are oversampled [26], rainfall is undersampled, or wind conditions permit greater three-dimensional rainfall capture area than represented by two-dimensional projected canopy areas [27].

Table 1. Rainfall conditions and throughfall and stemflow (mm across canopy area) for the five storms sampled for biolability testing. Throughfall and stemflow as percent rainfall provided in parentheses.

Condition	14 May 2017	3 June 2017	30 July 2017	28 August 2017	23 October 2017
Magnitude, mm	48.3	8	8.9	26.1	30.8
Duration, h	59.3	11.5	8.5	30	17.3
Intensity, mm h ^{−1}	0.8	0.7	1.0	0.9	1.8
Throughfall					
Bare, mm (%)	26.4 (55%)	4.7 (58%)	7.5 (84%)	19.0 (73%)	25 (81%)
Epiphyte, mm (%)	28.0 (58%)	2.1 (26%)	2.9 (33%)	13.8 (53%)	20.0 (65%)
Stemflow					
Bare, mm (%)	8.0 (17%)	1.0 (12%)	1.7 (19%)	3.9 (15%)	4.4 (14%)
Epiphyte, mm (%)	4.0 (8%)	0.2 (3%)	0.4 (4%)	0.9 (4%)	1.6 (5%)

3.2. Initial DOM Concentrations

DOC concentrations in rainwater (<7 mg-C L^{−1}) were always significantly lower than in throughfall and stemflow (entire dataset provided in Table S2). The highest mean concentration across sample types was found in stemflow from epiphyte-covered canopies, 85 ± 38 mg-C L^{−1}, followed by epiphyte-covered throughfall, 64 ± 34 mg-C L^{−1}, then bare-canopy stemflow, 55 ± 34 mg-C L^{−1}, and bare-canopy throughfall, 35 ± 19 mg-C L^{−1} (Table S2). The maximum initial tree-DOM concentration observed was 143 mg-C L^{−1} from epiphyte-covered stemflow (Table S2). Significant differences between sample types were found for bare-canopy throughfall versus epiphyte-covered throughfall, bare-canopy stemflow versus epiphyte-covered stemflow, and bare-canopy throughfall versus epiphyte-covered stemflow ($p < 0.001$).

3.3. Interstorm Tree-DOM Biolability

Tree-DOM concentrations declined over the bioincubation experiments, conforming to first-order decay models (Figure S1 and Table S3). Greater tree-BDOM proportions generally related to larger decay coefficients (Figure 2). Mean tree-BDOM proportion was greatest during the smallest magnitude storm (3 June, 8.0 mm) for all sample types except bare-canopy throughfall, 70 ± 20% (Figure 2). Eighty-eight percent of tree-DOM, on average, in stemflow from bare and epiphyte-covered canopies and epiphyte-covered throughfall was biolabile for the 3 June storm (Figure 2). The 3 June storm also had the largest range in mean decay coefficients across sample types, 2.4–6.7 day^{−1} for bare-canopy versus epiphyte-covered throughfall, respectively (Figure 2). The proceeding storm, 30 July, had the largest range in mean tree-BDOM across sample types, 34 ± 12% for epiphyte-covered stemflow versus 73 ± 9% for bare-canopy throughfall, but the mean decay coefficient was generally similar (Figure 2). For the 28 August storm, all sample types had similar mean tree-BDOM proportions, 49–55%, but decay coefficients were as low as 1.4 day^{−1} for epiphyte-covered stemflow and over double this value, 3.7 day^{−1} for bare-canopy throughfall (Figure 2). The 23 October and 14 May storms were both large magnitude storms (30.8 and 48.3 mm, respectively), and tree-BDOM proportions were generally the lowest on average, barring epiphyte-covered throughfall on 23 October (Figure 2). Tree-BDOM regardless of epiphyte cover or flux type produced the lowest decay coefficients, 0.2–0.8 day^{−1}, for the largest, 14 May, storm (Figure 2).

Figure 2. Mean, standard error, and standard deviation for biolabile proportion (black) and the decay coefficient (red) across the five sampled storms during 2017 arranged by increasing storm magnitude for bare-canopy throughfall (TF-B), epiphyte-covered throughfall (TF-E), bare-canopy stemflow (SF-B), and epiphyte-covered stemflow (SF-E).

3.4. Tree-BDOM Yield

For individual storms, mean tree-BDOM yield from any cover ranged over an order of magnitude, from 3.1 to 62.6 mg-C m⁻² mm⁻¹ of rainfall (Table 2). Greater water yields of throughfall from bare canopies (Table S2) compared to all other fluxes resulted in generally larger tree-BDOM yields for smaller storms (3 June, 30 July: Table 1) compared to throughfall from epiphyte-covered canopies (Table 2). Under rain events large enough to saturate the epiphyte-covered canopy areas (14 May, 28 August, 23 October), throughfall yielded greater tree-BDOM beneath epiphyte-covered canopy than bare canopy (Table 2). For stemflow, tree-BDOM yields were consistently greater from bare compared to epiphyte-covered canopies for all storms (Table 2) regardless of storm conditions (Table 1) and despite higher initial DOM concentrations from epiphyte-covered canopies (Table S2).

Table 2. Mean and standard deviation of biolabile tree-DOM (tree-BDOM) yields for throughfall (TF) and stemflow (SF) samples in each storm.

	Biolabile Yield (mg-C m ⁻² mm ⁻¹ Rainfall)				
	14 May 2017	3 June 2017	30 July 2017	28 August 2017	23 October 2017
TF, bare	10.3 ± 2.0	33.3 ± 15.2	62.6 ± 32.5	18.9 ± 6.1	16.3 ± 3.5
TF, epiphyte	12.2 ± 1.5	32.8 ± 18.8	25.5 ± 10.1	45.0 ± 17.1	28.6 ± 6.6
SF, bare	5.6 ± 1.8	10.6 ± 5.5	16.1 ± 8.7	7.4 ± 2.5	4.9 ± 1.1
SF, epiphyte	3.9 ± 2.2	3.7 ± 1.9	5.4 ± 3.0	3.3 ± 1.7	3.1 ± 0.6

4. Discussion

4.1. Hydrometeorology

A previous, more comprehensive sampling of storms at the study site, but for fewer cedar trees indicates that the sampled storms (Table 1) nearly represent the full range of typical rain event magnitudes and durations (7–74 mm [11]). However, rain event intensities for sampled storms (0.7–1.8 mm h⁻¹) were low compared to previous studies at the site (1–31 mm h⁻¹ [11]). Throughfall water yields for these storms were comparable to previous work on the same cedar species [11,28,29]. Stemflow water yields from epiphyte-covered cedar trees were similar to past studies; however, bare stemflow volumes were higher, >10% for all storms (Table 1), than reported elsewhere,

5–7% of rainfall [28,29], and for two previously-monitored cedar trees at this site, 4.2% of rainfall [11]. Epiphytes intercepting rainwater and disrupting stemflow pathways on the epiphyte-covered trees likely diminished stemflow yield compared to the bare canopies. Elevated stemflow yield from bare cedar trees at the study site compared to other studies on the same species, however, may be a function of meteorological variables not measured (i.e., wind conditions [27]) or neighborhood conditions along the forest edge that improved individual trees' ability to entrain rainfall as stemflow [30].

4.2. Tree-DOM Concentration and Biolability

Concentrations of tree-DOM measured immediately after storm sampling were within the range reported by past throughfall and stemflow research, 10–480 mg-C L⁻¹ [10]. Epiphyte presence enriched both stemflow and throughfall with tree-DOM compared to samples collected from bare canopies. The tangled, pendulous morphology of *T. usneoides* may account for increased tree-DOM concentrations, because it (1) can capture greater aerosols [31] and (2) trap and decompose materials (litter, insect frass, etc.) [32]. For stemflow and throughfall, regardless of the presence of epiphytes, tree-DOM concentrations varied between storms where increasing rainfall amount appears to dilute the limited store of tree-DOM along flowpaths through the canopy (Table S2), as reported previously at this site [11].

Tree-DOM in throughfall and stemflow was highly and rapidly biolabile, with an interquartile range of 36–73% biodegradation over 1–4 days (Figure S1), compared to other fluxes along the rainfall-to-runoff pathway: 14–33% in litter leachates, soil solution and stream water over several days [7]. Throughfall samples from Qualls and Haines [7] decayed less rapidly than observed in this study, exhausting the BDOM proportion after 1–2 weeks. The range of tree-BDOM percentages in cedar throughfall and stemflow agrees with values observed in broadleaved throughfall, ~60% [7]. Results agree with the optical character and molecular signatures of cedar tree-DOM from previous work at the site [20]. Thus, tree-DOM delivered to soils via throughfall or stemflow may be susceptible to significant biological alterations. When water yields are prodigious and highly localized (i.e., stemflow yields over 10% of rainfall for bare cedars), tree-DOM may rapidly infiltrate along root channels [33,34] to bypass biodegradation processes in the immediate soil. Throughfall, which is generally an area-diffuse flux, likely supplies a subsidy of tree-BDOM to the soil, up to 0.5 g-C m⁻² in a single storm (i.e., on 14 May), that prevents DOM loss from the ecosystems and contributes to respiration when consumed.

There was a substantial range in tree-BDOM percentage, 2–96%, rate, 0.1–11.0 days⁻¹, and yield, 3–63 mg-C m⁻² mm⁻¹ of rainfall between the sampled storms (Figure 2; Table 2), that exceeded previously-reported ranges for throughfall tree-BDOM, 30–60% [7]. As indicated by the similar molecular formulas of epiphyte versus bare canopy tree-DOM [20], the presence or absence of epiphyte cover did not appear to influence the tree-BDOM percentage or rate (Figure 2). There was, however, a marked effect on tree-BDOM storm yields due to the epiphytes' reduction of water yields (Table 2). Interstorm variability in tree-BDOM characteristics was high and not significantly correlated to any storm data available in this study (rainfall amount, intensity, duration) (Table S2). This prevents the use of discrete storm data to estimate annual yields of tree-BDOM from throughfall and stemflow. Therefore, it is recommended that future work examine what controls may drive the high interstorm variability in tree-BDOM observed in this study. Canopy structural variability across phenological events was not measured during this study, thus we suggest future work assess the connection between canopy structure and tree-BDOM. Further information is also needed to scale spatially, including data on the interstorm variability in tree-BDOM in other forest types and whether the temporal drivers vary geographically. Perhaps optical metrics, many of which are now able to be automatically collected in the field [35], can progress large-scale data collection efforts on tree-DOM and its biolability.

5. Conclusions

Little information has been reported on the proportion, rate and yield of tree-BDOM in throughfall and stemflow. In this study, bioincubation experiments on tree-DOM from epiphyte-covered and bare *Juniperus virginiana* (cedar) at Skidaway Island (Georgia, USA) found throughfall and stemflow to be largely biolabile, 36–73% (interquartile range). Cedar tree-BDOM was consumed rapidly (within 1–4 days) and yielded 3–63 mg-C m⁻² mm⁻¹ of rainfall. A simple estimate of tree-BDOM annual yield using the mean biolability proportion for each hydrologic flux and total tree-DOM annual yields previously computed at this site [14] equates to 21.3–30.2 g-C m⁻² year⁻¹ of tree-BDOM, which is 33–47% of the 65 g-C m⁻² year⁻¹ of net ecosystem exchange estimated for Georgia (USA) forests [31]. Tree-BDOM proportions and biodegradation rates were not significantly different between throughfall and stemflow, or under epiphyte versus bare canopy conditions. However, differences in water yield between fluxes, and due to epiphyte presence, influenced tree-BDOM yields per storm. The proportion, rate and yield of tree-BDOM varied markedly between storms and was not explained by storm amount, duration, or intensity. It is recommended that future work seek to characterize drivers of interstorm variability in tree-BDOM across forest types. This will enhance understanding of a key DOM supply to soil ecosystems by enabling temporal and spatial scaling of the first, and potentially most biolabile, enrichment of rainwater with DOM along the rainfall-to-runoff pathway.

Supplementary Materials: The following are available online at <http://www.mdpi.com/1999-4907/9/5/236/s1>, Figure S1: Example tree-DOM decomposition curves, Table S1: Structural characteristics of stemflow trees, Table S2: Raw dataset, Table S3: First order decay kinetics.

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