



Throughfall and Stemflow: The Crowning Headwaters of the Aquatic Carbon Cycle

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Abstract

Dissolved organic matter (DOM) is a master variable that modulates the form and function of many ecosystems. Approximately, half of the mass of DOM is carbon. Fluxes of DOM transfer carbon and other vital elements between ecosystems and between organisms (e.g., trees to bacteria) and components (e.g., vegetation to soil) within ecosystems. The DOM flux out of trees and understory plants to the forest floor is a poorly studied component of the carbon and nutrient budgets of forest ecosystems. In freshwater systems, studies of DOM transport through terrestrial systems usually start at the stream. However, the interception of rainwater by vegetation marks the beginning of the terrestrial hydrological cycle making plant canopies the crowning headwaters of terrestrial aquatic carbon cycling. Rainwater interacts with canopies picking up DOM, which is then exported from the plant in stemflow and throughfall, where stemflow denotes water flowing down the plant stem and throughfall is the water that drips from and through the leaves, branches, and epiphytes of the canopy. As nearly all studies of vegetation-derived DOM to date report DOM derived from tree canopies (tree-DOM), in this chapter we discuss the quality, potential sources, and potential fates of tree-DOM. We then describe and discuss the drivers of variation of quantitative fluxes of tree-DOM and place these quantitative fluxes in biogeochemical and ecological contexts at scales ranging from the individual tree, forest, and watershed to global trends.

Keywords

Carbon • Dissolved organic matter (DOM) • CDOM • FDOM • Stemflow • Throughfall

8.1 Introduction

Dissolved organic matter (DOM) is a master variable in ecosystems. In soils, DOM affects the stabilization and distribution of soil carbon, soil microbial activity and function, and soil development processes (Jansen et al. 2014). In natural waters, DOM fuels microbial production and influences pollutant transport and bioavailability, and the colored fraction of DOM is the primary absorber of visible and ultraviolet sunlight and initiator of photoreactions (Mopper et al. 2015; Moran et al. 2016). Approximately half of the dry mass of DOM is carbon (DOC), the rest being comprised of hydrogen, oxygen, and other heteroatoms such as nitrogen and phosphorous (Dittmar and Stubbins 2014). From these few elements, a vast diversity

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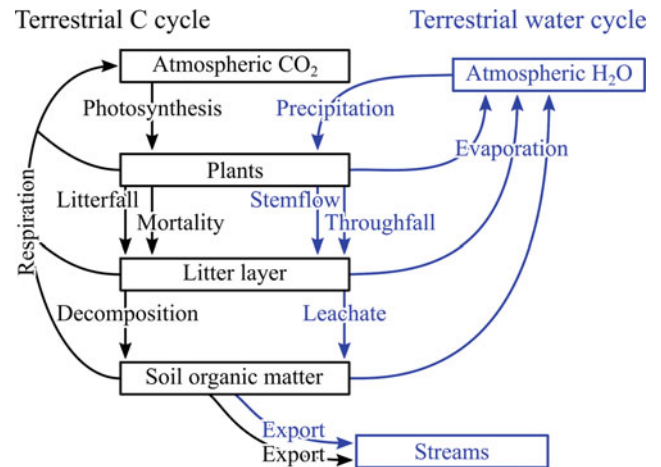
of chemical form and function are manifest within the DOM pool. Ultrahigh-resolution mass spectrometry (UHR-MS, e.g., Fourier transform ion cyclotron MS) has resolved thousands of molecular formulas within DOM (Mopper et al. 2007), including tree-DOM (Stubbins et al. 2017). Each of these molecular formulas represents the ratio of elemental building blocks (e.g., C, H, O, N, S, and P) that give rise to a certain mass observed by the mass spectrometer. However, for many of these molecular formulas, the theoretical number of ways in which the elements can be arranged (i.e., the number of potential isomers per formula) exceeds many millions (Hertkorn et al. 2007). Consequently, the DOM pool may contain billions of different molecules. Within this plethora of molecules are compounds of diverse source, chemistry, and reactivity. Aromatic compounds absorb light, making them the main component of the colored DOM (CDOM; Weishaar et al. 2003) that is the main initiator of photoreactions in natural waters (Mopper et al. 2015). In terrestrial systems, these aromatics are derived primarily from the structural compounds within vascular plants (Hedges 2002). Due to its color, CDOM can be easily quantified and characterized by absorbance and fluorescence spectrophotometry, while more advanced analytical approaches including nuclear magnetic resonance spectroscopy (NMR) and UHR-MS are required to characterize the entirety of DOM (Mopper et al. 2007).

In freshwater systems, DOM studies usually start at the stream, with some studies focusing on organic fluxes from leaf litter and soils (see Table 8.1). However, on vegetated landscapes, plants are the first interceptors of precipitation and the first potential source of DOM to the forest floor and the downstream aquatic carbon cycle (Fig. 8.1). Although vegetated ecosystems consist of a diverse array of plant types, few studies report DOM in net precipitation beneath the canopies of any

Table 8.1 Summary of annual areal carbon fluxes in tropical and subtropical, temperate, and boreal ecosystems

| | | Carbon Flux ($\text{g-C m}^{-2} \text{ yr}^{-1}$) | Combined TF+SF % | References |
|----------------------|-----------------------|---|------------------|------------------------------|
| Tropical/Subtropical | Stemflow DOC | 0.1–8.0 | – | Van Stan and Stubbins (2018) |
| | Throughfall DOC | 10–30 | – | Van Stan and Stubbins (2018) |
| | NPP | 1600–2200 | 0.5–2.4% | Stiling (1996) |
| | Soil respiration (SR) | 1092 | 0.9–3.5% | Raich and Schlesinger (1992) |
| | Heterotrophic SR | 764.4 | 1.3–5.0% | Raich and Schlesinger (1992) |
| | Litter leachate | 47–56 | 18–81% | Fujii et al. (2009) |
| | Organic soil horizons | 9 | 110–420% | McDowell et al. (1998) |
| | Mineral soil horizons | 4 | 250–950% | McDowell et al. (1998) |
| | Streams (1st order) | 3 | 330–1280% | McDowell et al. (1998) |
| Temperate | Stemflow DOC | 0.1–5.6 | – | Van Stan and Stubbins (2018) |
| | Throughfall DOC | 7–34 | – | Van Stan and Stubbins (2018) |
| | NPP | 1200–1300 | 0.5–3.3% | Stiling (1996) |
| | Soil respiration (SR) | 662 | 1.1–6.0% | Raich and Schlesinger (1992) |
| | Heterotrophic SR | 463.4 | 1.5–8.6% | Raich and Schlesinger (1992) |
| | Litter leachate | 5–20 | 36–800% | Park and Matzner (2003) |
| | Organic soil horizons | 7–40 | 18–570% | Michalzik et al. (2001) |
| | Mineral soil horizons | 2–19 | 37–2000% | Michalzik et al. (2001) |
| | Streams (first order) | 2 | 360–2000% | McDowell and Likens (1988) |
| Boreal | Stemflow DOC | 0.01–0.7 | – | Van Stan and Stubbins (2018) |
| | Throughfall DOC | 1.9–4.1 | – | Van Stan and Stubbins (2018) |
| | NPP | 800 | 0.3–0.6% | Stiling (1996) |
| | Soil respiration (SR) | 322 | 0.6–1.5% | Raich and Schlesinger (1992) |
| | Heterotrophic SR | 225.4 | 0.8–2.1% | Raich and Schlesinger (1992) |
| | Litter leachate | 20–48 | 4–24% | Koprivnjak and Moore (1992) |
| | Organic soil horizons | 22–60 | 3–22% | Koprivnjak and Moore (1992) |
| | Mineral soil horizons | 12–22 | 9–40% | Koprivnjak and Moore (1992) |
| | Streams (first order) | 3–7 | 27–160% | Eckhardt and Moore (1990) |

Fig. 8.1 Conceptual overview of the terrestrial carbon cycle and its interactions with the terrestrial water cycle. These carbon–water interactions along the precipitation-to-runoff pathway contribute, remove, and modify dissolved organic matter (DOM) in terrestrial waters



other plant besides trees (Gray 1997; Koprivnjak and Moore 1992). The earliest trees appear in the fossil record approximately 385 million years ago (Stein et al. 2007), since when they have fundamentally altered terrestrial (Algeo et al. 2001; Gensel and Edwards 2001) and wetland ecosystems (Greb et al. 2006). Forests are estimated to have covered close to 50 million km² of the planet 5000 years ago (Food and Agriculture Organization 2016) equivalent to approximately one-third of the earth’s land surface. Just as forests transformed the global ecosystem, humans now have a similarly profound influence upon global ecology and biogeochemistry. Deforestation during the Anthropocene (Crutzen 2002) or noosphere (Vernadsky 1945) has seen forest land cover reduced by approximately 50% to 31.7 million km² as of 2005 (Hansen et al. 2010) and deforestation was continuing at a rate of approximately 1.5 million km² yr⁻¹ between 2000 and 2012 (Hansen et al. 2013). Despite the vast and rapidly changing expanse of land covered by trees, forests still intercept most of the rainwater falling over land and account for 22% of global evapotranspiration (Porada et al. 2018). Once intercepted, ~90% of annual rainfall takes one of two hydrological flow paths to the forest floor: throughfall (water that drips from the canopy or falls directly through canopy gaps; 66–83% of precipitation) and stemflow (water funneled by the canopy to the stem; generally <3% of precipitation) (see Chap. 4 of this volume by Sadeghi et al. for a global review of throughfall and stemflow hydrology in forests and other vegetated ecosystems). Both stemflow (5–200 mg-C L⁻¹; Levia et al. 2011; Moore 2003; Tobón et al. 2004) and throughfall (1–100 mg-C L⁻¹; Inamdar et al. 2012; Le Mellec et al. 2010; Michalzik et al. 2001; Neff and Asner 2001) are enriched in DOM relative to rainwater (0.3–2 mg-C L⁻¹; Willey et al. 2000). Enrichment of throughfall and stemflow with tree-DOM is often enough to create visible changes in precipitation by absorbing light and “browning” the water (Fig. 8.2). In a recent manuscript, we reviewed much of the current literature on tree-DOM chemistry, concentrations, and fluxes (Van Stan and Stubbins 2018). In the current chapter, we summarize these topics and update or supplement them where appropriate. In particular, we have incorporated additional studies of tree-DOM fluxes and sought to further contextualize these fluxes at scales from the single tree to global trends.

8.2 Chemistry and Likely Sources of Tree-DOM

As noted above, stemflow and throughfall are enriched in DOC compared to the rainfall that is intercepted by trees. Thus, when rain falls on to trees it is picking up organics. However, it remains unclear if the organics in stemflow and throughfall are produced by trees, deposited upon trees, or generated by epiflora and epifauna. In all likelihood, each of these potential sources contributes a portion of the DOM washing from trees. The chemistry of tree-DOM can provide some insight as to its source.

Tree-DOM varies in its elemental stoichiometry both with flow path (stemflow versus throughfall) and species (Van Stan and Stubbins 2018). On average DOM C:N varies from 9:1 to 44:1 in throughfall (Goller et al. 2006; Michalzik et al. 2001; Schrumpf et al. 2006) and was 19:1 in the one study of stemflow we could find (Goller et al. 2006). These values are similar to those of vascular plant-derived sedimentary organic matter (C:N typically >20; Prah et al. 1994), within the range of C:N values reported for river waters (33±16:1; Sipler and Bronk 2015) and toward the lower end of values for plant leaf

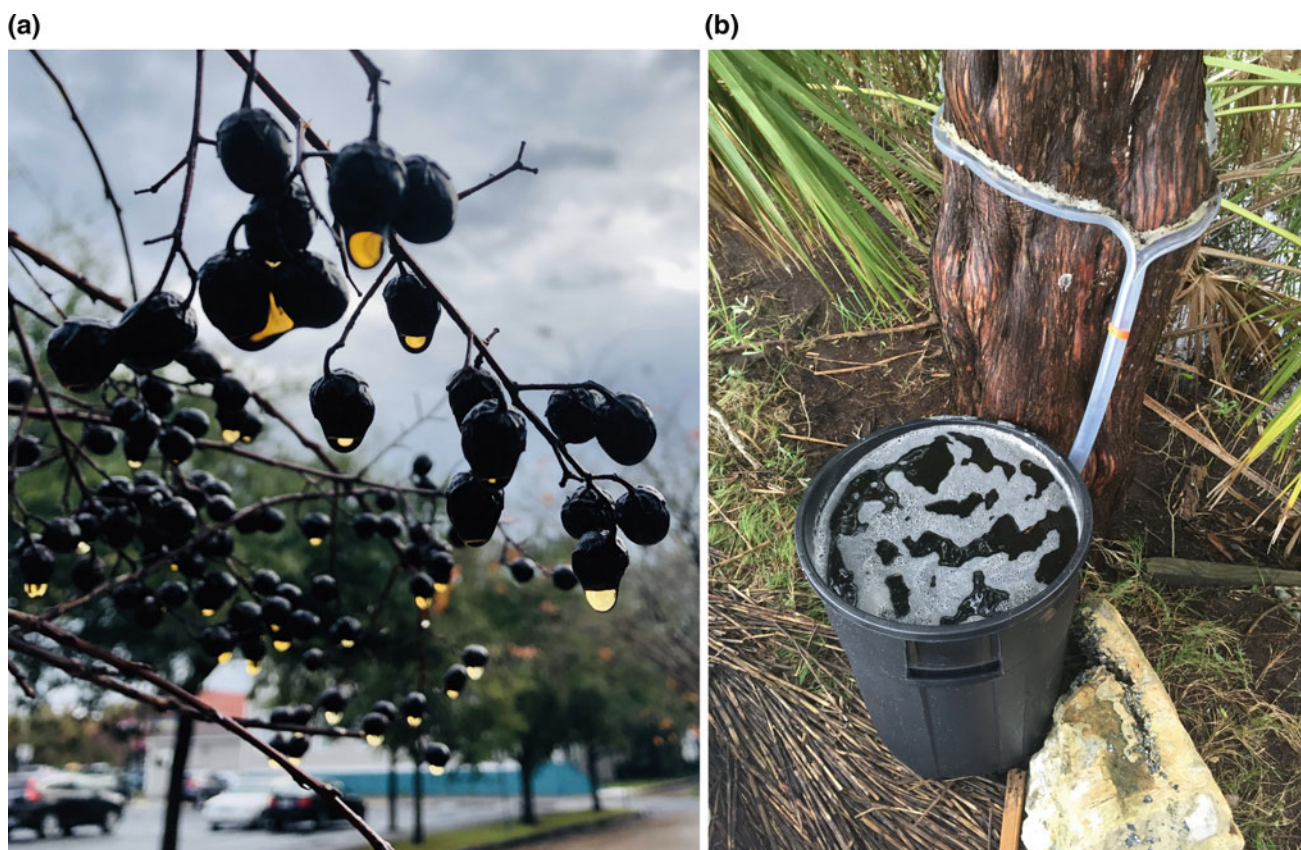


Fig. 8.2 Photographs showing **a** throughfall droplets enriched in CDOM prior to dropping to the surface and **b** stemflow being sampled during a large storm. Credit John T. Van Stan II

leachates (19 to 108:1; Fellman et al. 2013). Another ratio, between DOM color (i.e., absorbance at 254 nm) and DOC concentration, referred to as $SUVA_{254}$ ($L\ mg-C^{-1}\ m^{-1}$), provides an assessment of the relative aromatic content of DOM (Weishaar et al. 2003). $SUVA_{254}$ values for throughfall-DOM ($2.0\text{--}2.9\ L\ mg-C^{-1}\ m^{-1}$; Stubbins et al. 2017; Van Stan et al. 2017) and stemflow-DOM ($2.5\text{--}6.2\ L\ mg-C^{-1}\ m^{-1}$; Levia et al. 2012; Stubbins et al. 2017; Van Stan et al. 2017) are at the higher end or exceed the range in mean $SUVA_{254}$ values reported for US rivers ($1.3\text{--}4.6\ L\ mg-C^{-1}\ m^{-1}$; Spencer et al. 2012) indicating that throughfall and stemflow, in particular, are enriched in highly colored, aromatic-rich DOM compared to river DOM. Tree-DOM $SUVA_{254}$ values are similar to those for DOM leachates from freshly collected leaves ($2.7\text{--}3.4\ L\ mg-C^{-1}\ m^{-1}$; Fellman et al. 2013) and water-soluble organic carbon from atmospheric aerosols ($1.3\text{--}2.9\ L\ mg-C^{-1}\ m^{-1}$; Fan et al. 2016), but exceed the $SUVA_{254}$ values observed for rainwater when measured at the same site as tree-DOM $SUVA_{254}$ (e.g., $0.4\text{--}1.0\ L\ mg-C^{-1}\ m^{-1}$ for rainwater and $>2\ L\ mg-C^{-1}\ m^{-1}$ for all tree-DOM flow paths in Stubbins et al. (2017) and Van Stan et al. (2017)).

Few studies have used fluorescence spectroscopy to characterize tree-DOM. For throughfall fluorescent DOM (FDOM), 80–90% and 90–96% of total fluorescence in epiphyte-laden oak–cedar and broadleaved forests was humic-like in character (Inamdar et al. 2012; Van Stan et al. 2017). The only stemflow-DOM fluorescence study known to the authors reported a higher humic-like character (90–100% of total fluorescence) in stemflow compared to throughfall (80–90%; Van Stan et al. 2017). Protein-like fluorescence values for throughfall (4–20%) and stemflow (0–10%) are at the lower end of the range reported for leachates from fresh plant material (4–70%; Beggs and Summers 2011; Cuss and Guéguen 2013; Inamdar et al. 2012; Ohno and Bro 2006; Van Stan et al. 2015, 2017; Wickland et al. 2007), but exceed the concentrations found in streams ($<10\%$ although values up to $\sim 30\%$ have been reported at high discharge; Fellman et al. 2009) and in rainwater by more than four times on average (Van Stan et al. 2017). This suggests that, although tree-DOM is generally rich in humic-like fluorescence, throughfall and stemflow can contain relatively high levels of protein-like fluorescence (Howard et al. 2018; Qualls and Haines 1992), which can be exported to soils and streams.

Although it is unclear how features in fluorescence spectra for complex mixtures such as DOM relate to specific dissolved organic molecules, optical signatures similar to those observed in tree-DOM have been related to various moieties within DOM. For instance, the short-wavelength excitation:emission features have been related to aromatic amino acid structures (Tryptophan/Tyrosine; Fellman et al. 2010) and pools of more biolabile, and freshly produced or autochthonous DOM. Meanwhile, longer wavelength excitation:emission features are generally related to humic-like fluorescence of quinones (Cory and McKnight 2005), tannins (Maie et al. 2008), lignins (Hernes et al. 2009), and other polyphenolic structures consistent with tree-derived sources (Beggs and Summers 2011). The fluorescence signature of tree-DOM varies by tree species across a range of rainfall volumes and storm intensities (Cuss and Guéguen 2013; Van Stan et al. 2017). This suggests that trees and their associated biota impart species-specific and flow path-specific chemical and optical signatures to tree-DOM and that these signatures may be used to track tree-DOM from different flow paths and species into receiving ecosystems.

NMR data are scarce for tree-DOM. The data that exist indicate that aromatics (16–34%), carbohydrates (24–31%), and aliphatic carbon (14–25%) are the main structural components within tree-DOM (Bischoff et al. 2015). Trees and their epiphytes are direct sources of soluble carbohydrates (Coxson et al. 1992; Mahendrappa 1974), leaf waxes are readily eroded when leaf surfaces are abraded by rainfall (Baker and Hunt 1986), and aromatic lignin is a major structural component of vascular plants, the degradation products of which are washed from tree surfaces (Guggenberger and Zech 1994). Therefore, the enrichment of tree-DOM in carbohydrate, aliphatic, and aromatic carbon is consistent with tree-DOM being derived directly from modified foliar leachates and wash off (Guggenberger and Zech 1994; Kalbitz et al. 2007; Michalzik et al. 2001).

UHR-MS studies of tree-DOM are also rare. As of writing, a literature search turned up two studies (Ide et al. 2019; Stubbins et al. 2017). The molecular signatures of tree-DOM in throughfall and stemflow are broadly consistent with those of DOM in other aquatic ecosystems. Tree-DOM contained thousands of molecular formulas spanning the range of potential structural classes normally observed for DOM in natural waters via UHR-MS and included condensed aromatic, aromatic or alicyclic, and aliphatic compounds (Stubbins et al. 2017). Although tree-DOM was enriched in CHO-only formulas, nitrogen-, sulfur-, and phosphorous-containing formulas were also assigned. The molecular properties of tree-DOM are consistent with an autochthonous aromatic-rich source associated with the trees, their epiphytes, and the microhabitats they support. Elemental formulas enriched in oak stemflow were more diverse, enriched in aromatic formulas, and of higher molecular mass than for other tree-DOM classes, suggesting greater contributions from fresh and partially modified plant-derived organics (Stubbins et al. 2017). Oak throughfall was enriched in lower molecular weight, aliphatic and sugar formulas, suggesting greater contributions from foliar surfaces. While the optical properties and the majority of the elemental formulas within tree-DOM were consistent with vascular plant-derived organics, condensed aromatic formulas were also identified (Stubbins et al. 2017). As condensed aromatics are generally interpreted as deriving from partially combusted organics (Wagner et al. 2018), some of the tree-DOM may have derived from the atmospheric deposition of thermogenic and other windblown organics.

The above concentration and DOM quality data can inform, but not resolve questions about the source of organics in stemflow and throughfall. The high concentrations of DOC in stemflow and throughfall relative to rainfall clearly indicate that precipitation becomes enriched in organics as it interacts with vegetation. Furthermore, the C:N, optical and chemical character of tree-DOM is consistent with organic matter that is derived directly from the tree and its inhabitants. However, the tree-DOM quality data are also consistent with a depositional source that could accumulate on tree surfaces during dry spells and become mobilized during rainfall. In summary, the data suggest that trees are the predominant source of the DOM they export, but further studies are required to quantify the relevant contributions of trees, epibiota, and deposition to tree-DOM fluxes.

8.3 Tree-DOM Carbon Fluxes in Context

Fluxes of DOC from trees to the forest floor are a significant term compared to other forest and freshwater carbon fluxes. To allow comparisons between tree-DOM fluxes and other carbon fluxes, we report tree-DOM yields which have the units $\text{g-C m}^{-2} \text{yr}^{-1}$ and are calculated as the DOC load exported to the forest floor per projected canopy area (m^2) and, for a completely forested catchment, is directly comparable to classical DOC yields for fluvial systems that are normalized to the whole catchment area. These yields are also directly comparable to forest carbon cycle terms that are reported per area of forest.

An in-depth review of literature values and discussion of these calculations are provided in Van Stan and Stubbins (2018). In summary, stemflow DOC yields ranged from 0.01 to 8 $\text{g-C m}^{-2} \text{yr}^{-1}$ for tropical and subtropical forests, from 0.1 to

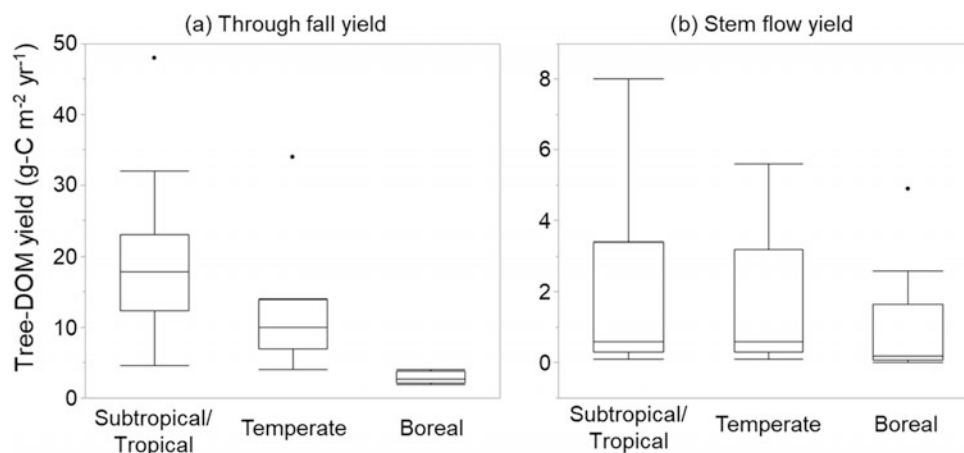


Fig. 8.3 Trends in tree-derived dissolved organic matter (tree-DOM) yield with latitude for **a** throughfall and **b** stemflow

5.6 $\text{g-C m}^{-2} \text{yr}^{-1}$ for temperate forests and from 0.01 to 0.7 $\text{g-C m}^{-2} \text{yr}^{-1}$ for boreal forests (Table 8.1 and Fig. 8.3). Throughfall DOC yields ranged from 4.6 to 48 $\text{g-C m}^{-2} \text{yr}^{-1}$ for tropical and subtropical forests, 7 to 34 $\text{g-C m}^{-2} \text{yr}^{-1}$ for temperate forests, and 1.9 to 4.1 $\text{g-C m}^{-2} \text{yr}^{-1}$ for boreal forests (Table 8.1; Fig. 8.3). Although throughfall contains lower concentrations of DOC than stemflow, throughfall DOC yields are higher than for stemflow due to the throughfall having far greater water yields (see Chap. 4).

Also apparent from these data is the trend in decreasing tree-DOM yield from the tropics toward the poles with yields of both stemflow and throughfall DOC being an order of magnitude lower in boreal systems than in the tropical, subtropical, and temperate forests (Table 8.1 and Fig. 8.3). This trend is consistent with, but stronger than, the latitudinal trend in forest net primary production (NPP) which falls by a factor of approximately 4 from tropical to boreal forests (Table 8.1; Stiling 1996). Consequently, combined tree-DOM yields (i.e., stemflow plus throughfall yields) constitute approximately 0.5–3% of total NPP in tropical, subtropical, and temperate forests, but only 0.3–0.6% of NPP in boreal forests (Table 8.1). Thus, the flux of carbon from trees to forest floor in stemflow and throughfall is a modest but significant fraction of forest carbon production.

Table 8.1 also compares combined tree-DOM yields to other fluxes of DOM in terrestrial flow paths from the litter on the forest floor to the streams draining forested catchments. Tree-DOM yields are similar in magnitude to the DOC fluxes from litter leachates into soils with litter-derived DOC fluxes usually exceeding tree-DOM yields. In the tropics and subtropics, tree-DOM yields exceed rates of DOC generated as water passes through organic and mineral soil horizons possibly by up to 9.5 times (Table 8.1). Tropical and subtropical tree-DOM yields also exceed DOC yields in streams draining forested catchments by 3–13 times. Moving to temperate systems, tree-DOM and soil leachate yields are similar in magnitude, but as in lower latitude systems, tree-DOM yields exceed stream DOC yields this time by a factor of 3.6–20 (Table 8.1). Finally, in boreal systems, tree-DOM yields are lower than DOC yields from soils but still remain similar to DOC yields in first-order streams. Though including significant uncertainty, this coarse comparison demonstrates that tree-DOM fluxes are of similar quantitative importance to other commonly studied aquatic carbon fluxes in forested catchments. Further, the broad latitudinal trends in tree-DOM and other yields suggest that the influence of tree-DOM in soil and stream organic matter biogeochemistry may be greatest in the tropics and diminish toward the poles. Comparing global distributions of soil and biomass organic carbon density reveals that the contribution of vegetation (i.e., biomass) to areal carbon stocks is greatest in tropical and subtropical forests, declining through temperate systems, and reaching global minima in boreal systems where soil organic carbon stores are generally greatly in excess of above-ground biomass carbon (Scharlemann et al. 2014). The influence of these global trends in the above- and below-ground distribution of organic carbon stocks likely drives the relative importance of soil- versus tree-derived fluxes of DOC at the global scale with tree-DOM dominating vegetation carbon-rich tropical and subtropical forests and soil-DOM dominating in soil carbon-rich boreal systems. That said, even in forested boreal systems, tree-DOM yields may still exceed DOC yields measured in the streams draining forested catchments.

As a major flux to the forest floor, tree-DOM may also contribute to carbon storage in soils. In mature temperate soils, carbon accumulation is relatively slow (1 to 12 $\text{g-C m}^{-2} \text{yr}^{-1}$), whereas rates in recently disturbed temperate soils can range from ~ 5 to 40 $\text{g-C m}^{-2} \text{yr}^{-1}$ (Schlesinger and Bernhardt 2013). Comparing these accumulation rates to the total amount of

tree-DOC (stemflow + throughfall) delivered to temperate forest soils (~ 7 to $40 \text{ g-C m}^{-2} \text{ yr}^{-1}$; Table 8.1), it is apparent that tree-DOC could provide a significant fraction of the carbon that accumulates in soils. Soil carbon is one of the largest organic carbon pools on Earth (Schlesinger and Bernhardt 2013). Thus, understanding how soil carbon will respond to land use, climate, and other environmental change is critical to predicting the future carbon budget and climate of the planet. The role of tree-DOM in soil carbon accumulation has been overlooked in both natural and urban settings to date. Future research is required to remedy this critical knowledge gap.

8.4 Biological Activity and Potential Impact and Fate of Tree-DOM

The above compared the quantitative fluxes of tree-DOM to other forest and aquatic carbon fluxes. Now we will consider the potential impact and fate of tree-DOM. There are a limited number of studies of tree-DOM biolability. Biolabile DOM is commonly defined as the fraction of DOM that can be readily consumed by microbes during relatively short-term bottle incubations (typically less than 1 month, e.g., Howard et al. 2018). These experiments are typically conducted under nutrient-replete conditions to try and ensure that DOC quality is the factor-limiting microbial activity and the percentage of DOC lost. These experiments are designed not to assess the rate of DOM loss in a natural system, but to assess a quality of the DOM—its biolability—quantified as the percentage of DOM lost during the incubation. The limited studies that have quantified tree-DOM biolability to date reveal that 30–73% of tree-DOM is biolabile (Howard et al. 2018; Qualls and Haines 1992). These results place tree-DOM among the most biolabile forms of DOM encountered in natural systems (e.g., DOM from phytoplankton cultures: 40–75% biolabile and DOM in permafrost thaw waters: $\sim 50\%$ biolabile; Bittar et al. 2015; Spencer et al. 2015). Qualls and Haines (1992) found tree-DOM (30–60% biolabile) to be more biolabile than DOM sampled from other points along the rainfall-to-runoff pathway (14–33% in litter leachates, soil solution, and stream water) but did not sample vegetation leachates. In studies where tree-DOM was not included, soil leachates have lower DOM biolability than tree-DOM (e.g., 7–15%; Wickland et al. 2007), whereas directly leaching vegetation can yield DOM that is similar to tree-DOM in that it is highly biolabile (11–93%; Wickland et al. 2007). DOM in blackwater rivers is generally of low biolability (e.g., $6 \pm 4\%$) compared to plant leachates in the same study ($38 \pm 17\%$; Textor et al. 2018). These results indicate that tree-DOM is among the most biolabile forms of DOM in natural systems and that this high biolability is consistent with the sourcing of tree-DOM from vegetation.

The highly biolabile nature of tree-DOM suggests that it supplies a carbon and energy subsidy to ecosystems downstream of the forest canopy, including soils and streams. It is clear that tree-DOM reaches the forest floor and soils. However, the extent to which tree-DOM fuels total and spatial patterns in forest soil respiration is unclear. A rough comparison with soil respiration rates (Table 8.1) indicates that tree-DOM could support from around 1 to 9% of heterotrophic respiration in tropical, subtropical, and temperate soils and only 1 to 2% in boreal soils. While there remains a lot of uncertainty in these estimates, tree-DOM could be a significant source of biolabile carbon to soil microbes. The supply of tree-DOM is accompanied by a supply of water and other nutrients that wash from trees. Thus, the regions where the flow paths of stemflow and throughfall intersect with the forest floor may represent temporally dynamic biogeochemical hotspots that flare into action during storm events. It remains unclear how the spatially and temporally patchy delivery of water, carbon, and other nutrients to the forest floor in stemflow and throughfall during storms factors into net biogeochemical fluxes at the forest scale. Furthermore, the role of these patchy flow paths in shaping forest ecology, forest structure, and soil carbon stores is unknown.

Tree-DOM fluxes may also directly, from overhanging limbs and focused stemflow paths, or indirectly, via surface and soil water flow, enter freshwater systems. In tropical, subtropical, and temperate systems, tree-DOM yields exceed stream DOC yields by 3 to 20 times (Table 8.1). Thus, the potential for tree-DOM to contribute to stream DOM export is clear (Fig. 8.1). However, what is less clear is how much of the tree-DOM flux actually makes it to the stream. As discussed above, tree-DOM is highly biolabile and rapidly removed by microbes in incubation studies. Consequently, a fraction of tree-DOM can be expected to be consumed by microbes as it makes its way along flow paths to the stream. Where these flow paths intersect with litter and soil microbes, the loss of biolabile tree-DOM can be expected to be significant. The organic signatures of tree-DOM (Stubbins et al. 2017) also contain features that may sorb to soils. These and other biotic and abiotic processes along the flow path from tree to stream will likely remove a fraction of tree-DOM completely, plus alter the optical and chemical signature of the remaining tree-DOM obscuring its detection in streams. Despite the potential loss and obfuscation of tree-DOM chemical signals, there are a wealth of optical, molecular, and isotopic geochemical techniques that should help resolve the fate and role of tree-DOM as a carbon flux through and energy and carbon source within soil and freshwater ecosystems.

| Month | <i>Tillandsia usneoides</i> | | | Oak (<i>Quercus virginiana</i>) | | | | Cedar (<i>Juniperus virginiana</i>) | | |
|-------|-----------------------------|----------|----------|-----------------------------------|----------|-----------|-----------|---------------------------------------|------|-----------|
| | Flowering | Fruiting | Dormancy | Flowering | Fruiting | Leaf shed | Full leaf | Pollen | Seed | Full leaf |
| 1 | | | | | | | | | | |
| 2 | | | | | | | | | | |
| 3 | | | | | | | | | | |
| 4 | | | | | | | | | | |
| 5 | | | | | | | | | | |
| 6 | | | | | | | | | | |
| 7 | | | | | | | | | | |
| 8 | | | | | | | | | | |
| 9 | | | | | | | | | | |
| 10 | | | | | | | | | | |
| 11 | | | | | | | | | | |
| 12 | | | | | | | | | | |

Fig. 8.4 Example monthly phenology calendar of the dominant arboreal epiphyte, Spanish moss (*T. usneoides*), and each of the dominant tree species, oak and cedar, based on literature (Barve et al. 2015; Cavender-Bares and Pahlich 2009; Lawson 1985; Mack 1995; Mopper and Simberloff 1995) and field observations at Skidaway Island (GA, USA)

8.5 Temporal Drivers of Tree-DOM

Sources of DOM on canopy surfaces available to throughfall and stemflow may vary temporally in response to seasonal and human drivers. The most visible signs of seasonal change include the annual cycle (i.e., phenological) of the plants themselves. Events such as flowering, leaf shedding, fruiting, and pollen/seed production are unlikely to occur simultaneously for each plant within the vegetated ecosystem. For example, a “simple” phenological calendar for a forest canopy dominated by two tree species and a single epiphyte (based on Van Stan et al. 2017) shows that dynamics in potential DOM sources (leaves, pollen, etc.) likely follow different temporal patterns (Fig. 8.4). Shifting canopy source materials may alter the tree-DOM composition with the seasons and species-by-species. An example is the production of glucose-rich nectar from extrafloral nectaries (Campbell et al. 2013). Figure 8.4 is illustrative, not comprehensive, as plant phenological dynamics vary markedly across ecosystems and by species within ecosystems. Epiphytic vegetation is ubiquitous across ecosystems (Van Stan and Pypker 2015), and their abundance and seasonal dynamics may alter the amount and quality of DOM in throughfall and stemflow (Van Stan et al. 2017). Seasonal changes also occur that alter the source regions and provenances of air masses and, thus, the materials in dry and wet deposition (Greene et al. 1999). Both of these shifts can cause seasonal changes in the microorganisms deposited and living on plant surfaces (Copeland et al. 2015; Jumpponen and Jones 2010) and change epifaunal interactions with the plant by initiating insect infestation, bird roosting, or attracting insectivores—all of which may contribute materials to throughfall and stemflow (Beard et al. 2002; Bittar et al. 2018; Gilmore et al. 1984; Stadler and Michalzik 1998). Human interactions may influence the timing and intensity of these events, see discussions on climate change and infestation (Kurz et al. 2008) or fire frequency (Abatzoglou and Williams 2016), or the canopy organic matter pool directly through air pollution or land use change (Chantigny 2003; Fang et al. 2007).

8.6 Conclusions

Plants are the first interceptors of precipitation and the first potential source of DOM to vegetated ecosystems and the downstream aquatic carbon cycle. Stemflow and throughfall are highly enriched in DOM compared to precipitation above plant canopies and other waters. Little is known about DOM in throughfall and stemflow for any other type of plant beyond trees. Tree DOM chemistry varies between flow paths and species. Quantifying the proportion of tree-DOM that is autochthonous (i.e. of tree origin) versus that derived from deposition to the tree requires further research. The few studies to have quantified tree-DOM biolability to date place tree-DOM among the most biolabile forms of DOM encountered in

natural systems. Tree-DOM flux is a significant term in forest ecosystem carbon budgets but constitutes a greater relative carbon flux in vegetation carbon-rich tropical and subtropical forests than in soil carbon-rich boreal systems. We recommend that the wealth of current optical, molecular, and isotopic geochemical techniques be applied to throughfall and stemflow waters to help resolve the source, fate, and role of tree-DOM in forest, soil, and freshwater ecosystems. We further recommend that studies of tree-DOM fluxes be expanded to other tree species and other forms of vegetation. Finally, additional studies are merited as tree-DOM is understudied with respect to its magnitude as carbon flux and its potential to shape terrestrial and aquatic ecosystems.

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