Tree-DOM: Dissolved organic matter in throughfall and stemflow

John T. Van Stan, Aron Stubbins

1Department of Geology & Geography, Georgia Southern University, Statesboro, Georgia; 2Departments of Marine & Environmental Sciences, Chemistry & Chemical Biology, and Civil & Environmental Engineering, Northeastern University, Nahant, Massachusetts, USA

Abstract

Rainfall onto trees entrains dissolved organic matter (tree-DOM). Tree-DOM is then exported down stems in stemflow and through leaves, branches, and gaps as throughfall. We synthesize tree-DOM literature, presenting trends in and controls of tree-DOM concentrations, fluxes, and chemistry. Tree-DOM concentrations are higher in stemflow (7–482 mg-C L\(^{-1}\)) than throughfall (1–61 mg-C L\(^{-1}\)) with both being enriched in DOM compared to rainwater. Per unit area of landscape, trees often generate as much DOM as is exported by rivers, suggesting tree-derived DOM (tree-DOM) is a quantitatively significant component of the inland water-carbon cycle. At the local scale, the patchy and pulsed delivery of tree-DOM to downstream ecosystems creates potential biogeochemical and ecological hot-spots and hot-moments. Here, we synthesize the tree-DOM literature highlighting areas for continued research into the potential importance of tree-DOM in shaping aquatic ecosystems at local through regional scales.

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, 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...
the hydrogen, oxygen and other heteroatoms that constitute dissolved organic molecules (Dittmar and Stubbins 2012). Consequently, the fluvial export of DOM links carbon stores and production sites on land to those in the ocean.

Traditionally, small streams are treated as the headwaters of fluvial systems. In vegetated catchments, the first modifications to precipitation by flora and, thus, the first source of terrigenous DOM, is combined into the overall stream response (Raymond et al. 2016). DOM processes at the intersection of precipitation and vegetation have received little attention compared to DOM derived from other hydrological fluxes. Although all types of vegetation intercept rainfall and generate vegetation-derived DOM, this synthesis focuses on tree-derived DOM (tree-DOM) as forest cover is not only a dominant vegetation type, but is the primary interceptor of rainfall globally (Angelini et al. 2011).

The earliest trees appear in the fossil record approximately 385 million years ago, since then they have fundamentally altered terrestrial (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 yr ago (FAO 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 (Hansen et al. 2010). For example, deforestation during the Anthropocene has seen forest land cover reduced by approximately 50% to 32 million km² as of 2005 (Hansen et al. 2010). Despite this loss of forest, most rain over the land surface falls on forests and ~ 90% of this flux makes it to the forest floor (Murray 2014) as throughfall (rain from canopy drips and through gaps) and stemflow (droplets funneled by the canopy to the stem).

Throughfall and stemflow are enriched in DOM relative to rainfall. Forest canopies create patterns of DOM-enriched precipitation flux controlled by interactions between biotic (e.g., canopy phenology) and abiotic (e.g., meteorological conditions) factors (Fig. 1a). Localized areas of high throughfall and especially stemflow flux (due to significantly greater rainfall capture area compared to the input area: Fig. 1b) can initiate preferential flow paths through soils affecting a host of watershed features including: soil moisture replenishment, shallow groundwater recharge, and soil microbial community structure and function (Levia and Germer 2015; Moore et al. 2016). The spatial and temporal heterogeneity of water and material fluxes delivered by vegetation drives hot spots and hot moments of biogeochemical activity wherever stemflow and throughfall flow pathways intercept with downstream ecosystems (McClain et al. 2003). Despite the potential for DOM delivery from trees to downstream ecosystems, few studies have measured tree-DOM and even fewer have contextualized it within the broader DOM and biogeochemical cycles of inland waters (Michalzik et al. 2001; Neff and Asner 2001; Kolka et al. 2008).

This article (1) reviews current knowledge of the processes that influence tree-DOM concentration, yield, flux and chemical character to conceptualize how biotic and abiotic factors control tree-DOM, (2) compares tree-DOM components (throughfall and stemflow) to rainfall, litter leachates, soil leachates and stream discharge, (3) summarizes documented and hypothesized tree-DOM interactions with inland waters, and (4) critically evaluates our current knowledge to identify major gaps.

**Tree-DOM concentration**

Interest in DOM losses from plant canopies during storms began just before the turn of the 20th century when Wehmer (1892) posited that “plant food” (a term that was used for both salts and carbohydrates) was removed from leaves by precipitation (LeClerc and Breazeale 1908). The first observations of throughfall (Dalbro 1955) and stemflow (Mahendrappa 1974) DOM came several decades later. Historically, more studies examine throughfall DOM than stemflow DOM, but stemflow shows a greater variability in DOC concentration across forest types than throughfall, 7–332 mg-C L⁻¹ vs. 5–57 mg-C L⁻¹ for volume-weighted means, respectively (Table 1). Throughfall DOC concentration had the greatest range for forests with pronounced differences in seasonal leaf states (temperate oceanic and continental) and rain conditions (tropical dry) (Table 1). Studies on evergreen forest types (tropical moist, tropical rain, and boreal forests) found the least variability in throughfall DOC concentration (Table 1); whereas, seasonally dry tropical forests generated the greatest range in stemflow DOC concentrations (Table 1). Similar to throughfall, stemflow DOC concentration ranges were large for most temperate forests and small for evergreen forests (Table 1).

The boreal tundra forest had the greatest reported mean throughfall (57 mg-C L⁻¹) and one of the highest stemflow (155 mg L⁻¹) concentrations (Table 1). Mean concentrations

---

**Fig. 1.** (a) Stemflow (SF) and throughfall (TF) dissolved organic matter (DOM) is a product of interacting biotic and abiotic factors that control the washoff of wet and dry deposition (WD and DD, respectively) as well as how canopy exchange (CE) regulates uptake and leaching. (b) When estimating DOM yields and loads for SF, one must consider that SF is produced from a “funneling” of rainfall captured by the projected canopy area and drained to the basal area.
Table 1. UN-FAO secondary forest ecological zones’ (without arid zones) annual volume-weighted mean concentrations of throughfall (TF) and stemflow (SF) dissolved organic carbon (DOC). Due to the paucity of data on tree DOC, montane forest ecological zones for each climate were placed in the closest climate classification (i.e., temperate montane forest situated within a temperate continental climate was grouped into the temperate continental forest ecological zone).

| Forest type                          | TF (mg-C L\(^{-1}\)) Mean (SD) | SF (mg-C L\(^{-1}\)) Mean (SD) | Studies                      |
|--------------------------------------|---------------------------------|---------------------------------|------------------------------|
|                                      |                                 |                                 |                              |
| Tropical rain                        |                                 |                                 |                              |
| Tropical rain                        | 6 (3)                           | -                               | McDowell (1998)              |
|                                      | 12 (6)                          | 11 (12)                         | Tobón et al. (2004)          |
|                                      | 13 (12)                         | 11 (16)                         | Sedimentary plain            |
|                                      | 11 (8)                          | 10 (14)                         | High Terrace                 |
|                                      | 8 (7)                           | 19 (32)                         | Low Terrace                  |
|                                      | 12 (-)                          | 15 (-)                          | Floodplain                   |
|                                      | 11 (-)                          | 14 (-)                          | Microcatchment 1             |
|                                      | 12 (-)                          | -                               | Microcatchment 2.1           |
|                                      | 15 (-)                          | -                               | Microcatchment 2.2           |
|                                      | 17 (-)                          | 19 (-)                          | Microcatchment 2.3           |
|                                      | 11 (4)                          | 16 (12)                         | Fringe Rhizophora mangle     |
|                                      | 6 (2)                           | 11 (11)                         | Dwarf R. mangle              |
|                                     |                                 |                                 |                              |
| Tropical moist                       |                                 |                                 |                              |
| Tropical moist                       | 5 (1)                           | -                               | Möller et al. (2005)         |
|                                      | 9 (3)                           | -                               | Fujii et al. (2009)          |
|                                      | 5 (1)                           | -                               | Soeharto                      |
|                                      | -                               | 40 (16)                         | Bankirai                     |
|                                      | -                               | 16 (6)                          | Hofhansl et al. (2012)       |
|                                      | -                               | 26 (7)                          | Secondary ravine             |
|                                     |                                 |                                 |                              |
| Tropical dry and seasonally dry      |                                 |                                 |                              |
| Tropical dry and seasonally dry      | 9 (42)                          | 54 (270)                        | Eucalypt                     |
|                                      | 10 (8)                          | -                               | Savanna                      |
|                                      | 9 (2)                           | -                               | Schrumpf et al. (2006)       |
|                                      | 12 (2)                          | -                               | Mature forest                |
|                                      | 7 (5)                           | -                               | Secondary forest             |
|                                      | 10 (4)                          | 10 (5)                          | Secondary hardwood           |
|                                      | 8 (3)                           | 7 (4)                           | Natural hardwood             |
|                                      | 5 (1)                           | 43 (28)                         | Wang et al. (2004)           |
|                                      | 7 (3)                           | 8 (5)                           | Secondary hardwood           |
|                                      | 6 (2)                           | 6 (2)                           | Natural hardwood             |
|                                    | 11 (8)                          | 18 (14)                         | Guo et al. (2005)            |
|                                      | 10 (7)                          | 19 (17)                         | Schima superba               |
|                                      | 6 (24)                          | -                               | Cunninghamia lanceolata      |
|                                      |                                 |                                 |                              |
| Subtropical humid                    |                                 |                                 |                              |
| Subtropical humid                    | 10 (4)                          | 10 (5)                          | Secondary hardwood           |
| Subtropical humid                    | 8 (3)                           | 7 (4)                           | Natural hardwood             |
| Subtropical humid                    | 5 (1)                           | 43 (28)                         | Wang et al. (2004)           |
| Subtropical humid                    | 7 (3)                           | 8 (5)                           | Secondary hardwood           |
| Subtropical humid                    | 6 (2)                           | 6 (2)                           | Natural hardwood             |
| Subtropical humid                    | 11 (8)                          | 18 (14)                         | Guo et al. (2005)            |
| Subtropical humid                    | 10 (7)                          | 19 (17)                         | Schima superba               |
| Subtropical humid                    | 6 (24)                          | -                               | Cunninghamia lanceolata      |
| Subtropical dry                      |                                 |                                 |                              |
| Subtropical dry                      | 5 (1)                           | 22 (9)                          | Cerrado                      |
| Subtropical steppe                   | 11 (4)                          | 53 (42)                         | Pinus caribaea               |
of tree-DOM from forest types that have extended dry periods (tropical seasonally dry and temperate steppe) were also comparatively elevated (Table 1). The lowest mean throughfall DOC concentration, and second-lowest mean stemflow DOC concentration, for any forest type was found for tropical rainforests (Table 1). Other humid forest types (tropical moist and subtropical humid) produced similarly low tree-DOM concentrations compared to those reported for tropical rainforests (Table 1). For stemflow, the ability of tree species-specific canopy structures to funnel rainfall to their stem is a factor in controlling DOC concentrations (Fig. 2). A combination of drooping branching architecture, low branch-to-stem angle and higher epiphyte cover generally diminished the proportion of rainfall drained to the stem leading to smaller stemflow volumes, but less dilute/higher tree-DOM concentrations (Fig. 2). Although increasing rainfall amount has been similarly shown to dilute throughfall DOC concentrations (Levia et al. 2012), no clear species-specific structural influences over throughfall DOC concentrations have been identified.

Seasonal-to-intrastorm variability in tree-DOM concentrations can be significant. The first study to examine temporal dynamics of throughfall DOC found concentrations beneath summer fully leafed canopy were >20 times greater than during winter leafless conditions (Comiskey 1978). In a German deciduous forest, changes in throughfall DOC concentrations over several orders of magnitude were also observed and significantly correlated to mean seasonal air temperature (Solinger et al. 2001). Concentrations of stemflow DOC also diminished by 50–60% under leafless canopy conditions compared to fully leafed conditions, likely due to dilution by the enhanced stemflow generation of leafless canopies (Levia et al. 2012), but possibly due to the decrease in leaf surface area and biological activity associated with winter senescence.

Storm conditions often change with season, and have been found to alter tree-DOM concentration. Throughfall and stemflow-DOC concentrations are inversely related to storm-scale rainfall amount and intensity, indicating that large or intense storms are able to wash tree surfaces clean.
and dilute tree-DOM (Goller et al. 2006; Levia et al. 2012). The mesoscale synoptic conditions that develop and steer storm systems affect throughfall and stemflow-DOC concentrations by controlling the intensity and duration of discrete rainfall events (Siegert et al. 2017).

Variability of throughfall and stemflow-DOC concentration within individual storms has been rarely examined. Within a storm, throughfall DOC concentrations decreased exponentially as surfaces wash clean, until reaching a steady leaching concentration (Germer et al. 2007). The within-storm DOC concentrations of stemflow depended on the tree species’ canopy structure. Branching architectures promoting stemflow yield, like that of Fagus grandifolia (Ehrh. American beech) decreased concentrations of DOC as the storm progresses as found for throughfall, but intermediate stemflow producers, like Liriodendron tulipifera (L. tulip poplar) generated relatively constant DOC concentrations throughout a storm (Levia et al. 2012). Recently, it was observed that for low stemflow generators, like epiphyte-laden Quercus virginiana, stemflow DOC concentrations increased linearly with rainfall amount up to the maximum observed storm size of 74 mm (Van Stan et al. in press).

Disturbances between storms can also alter the concentration of tree-DOM. Concentrations of tree-DOM varied between wet and dry seasons, with throughfall and stemflow DOC concentrations being approximately 10 times higher at the start of the rainy season due to the buildup of materials over the dry season (Laclau et al. 2003; Ciglasch et al. 2004). Insect infestation of forest canopies can increase tree-DOM concentration by up to 240 times, per observations of afflicted Picea abies trees (Stadler and Michalzik 1998). Other disturbances that have been found to influence tree-DOM concentrations include drought, volcanic activity (Heartsill-Scalley et al. 2007) and fire (Germer et al. 2007; White 2015).

**Tree-DOM chemistry**

As noted above, when rain interacts with trees, the throughfall and stemflow generated becomes greatly enriched in DOM relative to rainwater. Given the potential for tree species, canopy type, epiphyte cover, season and many other factors to influence the types of molecules entrained by rainwater as it interacts with vegetation, tree-DOM chemistry may vary widely dependent upon its source. The potential diversity of tree-DOM is evident in the variability in the C : N of throughfall-DOM, which has been reported to range from 9 : 1 to 44 : 1 within temperate forests (Michalzik et al. 2001), from 16 : 1 to 21 : 1 within

---

**Fig. 2.** Mean event-based stemflow dissolved organic carbon (DOC) concentrations (ranges provided where reported) indirectly relate to stemflow production for low stemflow producers. High stemflow producers generally dilute canopy DOC sources, resulting in low concentrations. Species were selected from past literature to represent the common range of canopy structures and stemflow production reported, including: Q. pyrenaica (Moreno et al. 2001), L. laricina, P. rubens and Betula (Mahendrappa 1974), P. tremuloides (Kolka et al. 1999), Fagus (Levia et al. 2012), Lauro-Fagaceae forest (Liu and Sheu 2003), and P. montana (Frangi and Lugo 1985).
rainforests (Schrumpf et al. 2006), and to be 19 ± 1 : 1 for a single montane forest (Goller et al. 2006). Stemflow-DOM C : N for the same montane forest was statistically indistinguishable from throughfall-DOM C : N (19 ± 1 : 1; Goller et al. 2006). These values are within the range of C : N values reported for river waters (33 ± 16 : 1; Sipler and Bronk 2015). Data for tree-DOM sulfur and phosphorous content is scarce. Throughfall-DOM C : S ranged from 123 : 1 to 136 : 1 under rainforest, was 58 : 1 for shrubs (Schrumpf et al. 2006), and was 73 ± 19 : 1 below a montane forest (Goller et al. 2006). Stemflow-DOM C : S was 42 ± 13 : 1, and throughfall and stemflow-DOM C : P were 100 ± 42 : 1 and 64 ± 39 : 1, respectively below the same montane forest (Goller et al. 2006). Thus, at the fundamental level of elemental stoichiometry, tree-DOM chemistry varies with flow path and for a given flow path within the same forest.

Optical characterization of the colored fraction of DOM (CDOM) provides information about DOM quality. Ultraviolet-visible absorption spectra for tree-CDOM are broadly consistent with those for CDOM in natural waters, decreasing approximately exponentially with increasing wavelength (Stubbins et al. 2017). The range in mean spectral slope values (5275–295 nm; Helms et al. 2008) for stemflow (0.0144 nm–1) and throughfall (0.0157–0.0165 nm–1; Stubbins et al. 2017) are consistent with values for U.S. rivers (0.012–0.023 nm–1; Spencer et al. 2012). In other natural waters 5275–295 becomes shallower with increasing molecular weight and biodegradation (Helms et al. 2008), suggesting stemflow is more biologically processed and/or of greater molecular weight than throughfall. However, the use of spectral slope and its derivatives (e.g., the spectral slope ratio; Helms et al. 2008) as proxies for tree-DOM quality should be made with caution. These spectral indices were developed for aquatic systems quite different from stemflow and throughfall, and, even within the original systems for which the indices were defined the indices vary with a number of factors, including degree of microbial degradation, photodegradation, and molecular weight (Helms et al. 2008).

Another optical property of DOM, the specific ultraviolet absorbance at 254 nm (SUVA254: L mg C–1 m–1), defined as the decadic absorption coefficient at 254 nm (m–1) normalized to DOC (mg C L–1), provides an assessment of the relative aromatic content of DOM (Weishaar et al. 2003). Sometimes SUVA254 values are calculated using the non-conventional Napierian absorption coefficient (i.e., decadic absorption coefficient × 2.303). Values reported in this manner (e.g., Levia et al. 2012) were corrected for consistency here. SUVA254 values for throughfall-DOM (2.2–2.9 L mg C–1 m–1; Stubbins et al. 2017) and stemflow-DOM (2.5–6.2 L mg C–1 m–1; Levia et al. 2012; Stubbins et al. 2017) are at the higher end or exceed the range in mean SUVA254 values reported for U.S. rivers (1.3–4.6 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. Ultrahigh resolution Fourier transform ion cyclotron mass spectrometry (FT-ICR/MS) data also revealed tree-DOM to be enriched in aromatic molecular signatures compared to riverine samples analyzed under near-identical conditions (Stubbins et al. 2017), corroborating the interpretation of the SUVA254 data.

Quantitative measurements of aromatic carbon in tree-DOM are rare. Throughfall and stemflow-DOM from a spruce and two beech forests were freeze dried and analyzed by solid state cross polarization 13C nuclear magnetic resonance spectroscopy (NMR; Bischoff et al. 2015). Spruce throughfall- and stemflow-DOM were 19.6% and 19.0% aromatic carbon, while beech throughfall and stemflow-DOM ranged from 29.1% to 33.9% and from 16.1% to 16.9%, respectively (Bischoff et al. 2015). Assuming SUVA254 provides a robust indication of relative aromatic content, consideration of the NMR data and SUVA254 data indicates the potential variability that exists for tree-DOM chemistry. The NMR data indicate that for the trees studied, spruce stemflow and throughfall-DOM contain similar levels of aromatic carbon (~19%), beech throughfall-DOM is enriched in aromatic carbon (~30%) relative to beech stemflow-DOM (~16%; all from Bischoff et al. 2015), and optical data indicate oak and cedar throughfall-DOM is depleted in aromatic carbon (SUVA254 2.2–2.9 mg C–1 m–1) compared to oak and cedar stemflow (SUVA254 3.0–5.1 mg C–1 m–1; both from Stubbins et al. 2017). Thus, the relative aromatic content of both stemflow and throughfall can vary with tree species and between stemflow and throughfall for the same species.

The photoreactivity of DOM increases with DOM absorbance and aromatic content (Stubbins et al. 2008). Given the relatively high levels of CDOM in throughfall and stemflow, tree-CDOM has the potential to initiate a suite of photoreactions, including the photo-mineralization and photo-modification of tree-DOM itself. CDOM-initiated photoreactions in natural waters can also increase or decrease the biodegradability of DOM, dependent upon the initial DOM chemistry (Bittar et al. 2015; Mopper et al. 2015), and lead to production of reactive transients, including reactive oxygen species (Mopper et al. 2015), that may impact leaf and leaf microbiome health. While the optical and chemical signatures of tree-DOM suggest it will be highly photoreactive, the degree to which this photoreactivity is realized will depend upon the level of sunlight exposure experienced by tree-DOM within the canopy and receiving waters.

The NMR data mentioned above provides clues as to the sources of tree-DOM. This NMR data indicates that carbohydrates (24–31% of signal intensity) and aliphatic carbon (14–25% of signal intensity) are the other main structural components within tree-DOM (Bischoff et al. 2015). Trees and their epiphytes are direct sources of soluble carbohydrates (Mahendrappa 1974; Coxson et al. 1992), 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 washoff (Guggenberger and Zech 1994; Michalzik et al. 2001; Kalbitz et al. 2007).

The relatively high bio-lability (percentage loss due to microbial degradation) of tree-DOM (50–75%; Qualls and Haines 1992) also suggests that a significant fraction of the dissolved organic molecules within stemflow and throughfall have undergone minimal biodegradation prior to export from the tree. However, the high molecular diversity of tree-DOM and lack of defined features in ultraviolet-visible absorbance spectra (Stubbins et al. 2017) is suggestive of some reworking of simple, primary biomolecules prior to leaching and/or export from the tree. Consistent with tree-DOM being composed primarily of a gradient of freshly released to partially degraded plant-derived organics, the fluorescence signatures of tree-DOM are generally enriched in freshly produced protein-like fluorescence, but also contain some more processed humic-like fluorescence signals (Johnson et al. 2011; Inamdar et al. 2012; Van Stan et al. in press).

How DOM sorbs to, and extracts from, solid phase extraction columns of varying chemistry provides further information about DOM chemistry and mobility in the environment. About half to two thirds of tree-DOM can be operationally defined as hydrophobic organic acids, which can be sorbed to the resin XAD-8 at pH 2 (Ciglasch et al. 2004). This is within the range (19–90%) and close to the mean (54%) reported for DOM in inland waters (Mopper et al. 2007). As a large percentage of tree-DOM is biolabile and a large percentage is hydrophobic, during small rainfall events when overland flow is minimal, significant fractions of tree-DOM will likely be biodegraded and/or sorbed in local soils. However, during the large rainfall events that are increasingly recognized as being important in annual fluvial DOC export (Raymond et al. 2016) it is likely that overland flow delivers tree-DOM efficiently to inland waters.

The chemical data summarized above is all consistent with the majority of tree-DOM being derived directly from the tree and its associated biota. However, FT-ICR/MS molecular signatures of tree-DOM contain some molecular formulas consistent with dissolved black carbon (Stubbins et al. 2017), a suite of condensed aromatic molecules thought to be derived only from combustion sources (Wagner et al. this issue). These compounds could have been deposited to the trees from local and distal combustion sources prior to the rain events sampled suggesting deposited aerosol carbon may form a significant fraction of tree-DOM. However, the molecular, optical and structural character of tree-DOM taken together with the high concentrations washing off trees, indicate that tree-DOM is likely primarily derived directly from the tree itself, including its proto-soils, epiphytes and epifauna, with minimal inputs from heterochthonous sources.

Tree-DOM load and yield

For consistency with fluvial terminology, tree-DOM load (g-C yr⁻¹) is expressed here as the quantity of DOC (g) delivered to the forest floor over a given timeframe (e.g., per year, per storm) by a single tree. Tree-DOM yield (g-C m⁻² yr⁻¹) is the DOC load exported to the forest floor per projected canopy area (m²) and, for a completely forested catchment, is directly comparable to classical DOC yields for fluvial systems that are normalized to the whole catchment area. Throughfall yield is easily computed as it is a diffuse load across the forest floor (anywhere there is canopy cover), but stemflow is a spatially concentrated load at the base of tree stems produced from some canopy drainage area (Fig. 1b)—just as river discharge is a concentrated load at the base of a watershed produced from some catchment drainage area. Therefore, stemflow DOC yields are computed as the load, at the stem base, divided by the drainage area, represented by projected canopy area (Fig. 1b). Stemflow DOC yields ranged from 0.01 g-C m⁻² yr⁻¹ to 8 g-C m⁻² yr⁻¹ (Table 2) and varied in response to species-specific canopy structure (Fig. 3). Although canopy structures that favor stemflow generation result in lower DOC concentrations (Fig. 2), the greater stemflow water yield of these tree species translates to greater DOC yield per canopy area (Fig. 3).

The first estimates of throughfall DOC yield ranged from ~9 g-C m⁻² yr⁻¹ beneath a Quercus petraea (sessile oak) forest (Carlisle et al. 1966) to 90 g-C m⁻² yr⁻¹ over a single growing season for an apple orchard (Dalbro 1955). Throughfall DOC yields reported from natural forests did not exceed 48 g-C m⁻² yr⁻¹ (Table 2). Low-latitude subtropical and tropical forests produced the greatest mean and maximum throughfall DOC yield (Table 2). Mean throughfall DOC yield for higher-latitude subtropical and temperate forests were similar (Table 2), but it is possible that the fewer studies in the subtropics have missed significant stemflow producing species. There was a latitudinal trend in the mean throughfall DOC load for primary forest ecological zones: throughfall DOC yields decreased poleward from the tropics (Table 2). The difference in mean throughfall DOC load between the tropics and the boreal forests was over 80% (Table 2). Range in reported throughfall DOC load was greatest for the tropical forests and least for the boreal forests (Table 2).

When thinking of the forest floor, the largest tree-DOM loads are experienced as stemflow delivers concentrated DOC around the stem base of a tree (Table 2). Arithmetic mean stemflow DOC loads followed a similar latitudinal pattern as throughfall (Table 2). Figure 3 demonstrates the importance of species-specific canopy structure and stand structure in stemflow DOC yield, and this is directly transferable to stemflow DOC load. Indeed, the range in stemflow DOC load spans an order of magnitude for most primary forest ecological zones (Table 2). Although often overlooked in
Table 2. Annual throughfall (TF) and stemflow (SF) dissolved organic carbon (DOC) loads (g-C m⁻² yr⁻¹) and yields (g-C m⁻² yr⁻¹) for individual trees in UN-FAO primary forest ecological zones. Yields are normalized to tree projected canopy area. Primary forest ecological zones were used due to few studies reporting tree-DOM loads, particularly stemflow. Arid zones excluded.

| Forest type     | TF DOC Load/yield | SF DOC Load/yield | Study                                      |
|-----------------|-------------------|-------------------|--------------------------------------------|
| Tropical        |                   | 101/8.0           | Frangi and Lugo (1985)                     |
|                 | 453/15.1          |                   | Schrumpfl et al. (2006)                    |
|                 | 601/20.0          |                   | Mature forest                              |
|                 | 141/14.8          | 3/0.3             | Sedimentary plain                          |
|                 | 338/19.0          | 5/0.3             | High terrace                               |
|                 | 172/17.5          | 5/0.5             | Low terrace                                |
|                 | 213/17.6          | 7/0.6             | Floodplain                                 |
|                 | 453/30.2          | -                 | Germer et al. (2007)                       |
|                 | 546/18.2          | -                 | Fujii et al. (2009)                        |
|                 | 291/9.7           | -                 | Soehartian                                  |
|                 | 285/9.5           | 3/0.1             | Tobón et al. (2004)                        |
| Subtropical     | 139/4.6           | 15/0.5            | Laclau et al. (2003)                       |
|                 | 143/4.8           | 3/0.1             | Eucalypt                                   |
|                 | 463/23.1          | 31/1.5            | Liu and Shu (2003)                         |
|                 | 378/18.9          | 13/0.7            | secondary hardwood                         |
|                 | 396/13.2          | -                 | Natural hardwood                           |
|                 | 811/23.0          | 24/0.7            | Heartsill-Scalley et al. (2007)            |
|                 | 746/48.0          | 83/5.3            | Van Stan et al. (in press)                 |
|                 | 413/32.0          | 98/7.5            | Oak with epiphytes                         |
| Temperate       | 123/4.1           | -                 | McDowell and Likens (1988)                 |
|                 | 144/34.0          | 24/5.6            | Moore and Jackson (1989)                   |
|                 | 262/13.1          | -                 | Qualls and Haines (1992)                   |
|                 | 167/13.9          | -                 | Currie et al. (1996)                       |
|                 | 164/11.7          | -                 | Pine forest                                |
|                 | 88/6.8            | 11/0.8            | Kolka et al. (1999)                        |
|                 | 252/14.0          | 10/0.5            | P. tremuloides                             |
|                 | 85/7.7            | 6/0.6             | B. papyrifera-A. rubrum                    |
|                 | 92/8.4            | 1/0.1             | A. balsamea                                |
|                 | 161/7.0           | -                 | P. mariana                                 |
|                 | -                 | 44/4.9            | Solinger et al. (2001)                     |
|                 | -                 | 18/2.6            | Levia et al. (2012)                        |
| Boreal          | 37/1.9            | 2/0.1             | Dalva and Moore (1991)                     |
|                 | 45/2.2            | 1/0.05            | Broadleaved upland forest                  |
|                 | 41/2.1            | 3/0.2             | Swamp forest                               |
|                 | 45/4.1            | 0.1/0.01          | Needleleaved upland forest                 |
|                 |                   |                   | Koprivnjak and Moore (1992)                |
|                 |                   |                   | Woodland                                   |
Several interacting cross-scale factors control the yield and load of tree-DOM (Fig. 4). At the microscale, the phyllosphere microbial community generates, competes for, and even eventually becomes DOM (Vorholt 2012) available for throughfall and stemflow (Fig. 4). Some of these microbes may even be gut microbes in organic excretions from infestation (Stadler et al. 2001). Bark surface microrelief and physico-chemical properties can affect the branchflow and branchflow chemistry (Guggenberger and Zech 1994; Van Stan et al. 2016) that supports throughfall drip points and stemflow (Fig. 4). The presence, structure and abundance of arboreal epiphyte communities can diminish tree-DOM load and yield by obstructing canopy flow paths, but they have also been found to contribute greater amounts of DOC to throughfall and stemflow concentrations (Van Stan and Pypker 2015; Stubbins et al. 2017).

Both throughfall and stemflow have marked seasonality in their DOC yield and load. Throughfall DOC loads tend to diminish with leaf fall due to the increased, but dilute “free” throughfall fraction (Comiskey 1978). Stemflow DOC yields diminish too, possibly because of less canopy area to receive dry deposited or organism-derived DOM (Levia et al. 2012) and the decrease in tree-DOM production while the tree and its ectosymbionts are in senescence. The impact of phenology on tree-DOM load and yield beyond the leaf and leafless stages has not been deeply investigated, but studies on inorganics in throughfall and stemflow show significant shifts in canopy exchange of solutes with season (Van Stan et al. 2012). Wind conditions and canopy exposure (Fig. 4) not only alter the amount of dry deposition (Heartsill-Scalley et al. 2007), but alter the amount of rainfall intercepted and drained as throughfall and stemflow by individual trees (Herwitz and Slye 1995). Storm volume and intensity conditions can alter DOC concentrations (Goller et al. 2006; Levia et al. 2012), which are linked to air mass source regions, movements and associated mesoscale meteorological conditions (Siegert et al. 2017).

**Tree-DOM in context of the terrestrial hydrologic flow paths**

Throughfall and stemflow not only initiate the terrestrial hydrologic flow path in forested catchments, they can be
significantly enriched in DOC (especially stemflow) compared to other hydrological fluxes along the rainfall-to-discharge pathway (Tables 1, 3). Mean annual stemflow DOC concentrations are often twice those of throughfall (Table 1) and can be greater than observed in litter leachates, soil leachates, and rivers from catchments under similar climate conditions (Table 3). A caveat is that high stemflow-generating forests can produce DOC concentrations equivalent to throughfall and rainfall (Fig. 2; Table 1). Total tree-DOM yields, 2.0–53.3 g-C m\(^{-2}\) yr\(^{-1}\) (Table 2) also compare favorably to other yields throughout the catchment (Table 3). As the first source of terrigenous DOC to the hydrological flow path, tree-DOM also contributes DOC to the fluxes estimated to occur from downstream sources (Fig. 5). For instance, throughfall and stemflow are the precipitation waters supplied to the subcanopy litter and organic soil horizons, and tree-DOM is presumably a component of the DOC quantified as leaving these layers (Fig. 5). While it must be remembered that tree-DOM yields reported here assume continuous forest cover, this simple comparison demonstrates that tree-DOM yields are of the same order of magnitude as fluvial DOM yields (Tables 1, 3). To ascertain the fate of tree-DOM and the proportion that reaches inland waters is a challenge that needs to be addressed.

The hydrological nature of each tree-DOM flux—typically throughfall is diffuse, while stemflow is concentrated at the stem—leads to different interactions with the inland water component of the C cycle. More than half of tree-DOM appears to be composed of compounds likely to be rapidly biodegraded in the litter layer and soil and/or to be sorbed onto mineral soils (Qualls and Haines 1992; Ciglasch et al. 2004). Therefore, under low to moderate rainfall, throughfall DOC likely slowly percolates through the litter layer and soil matrix where much of it may be consumed or sorbed, diminishing the likelihood that it can infiltrate into the soil profile (Michalzik et al. 2001) or reach inland waters unchanged. However, much of the fluvial export of DOM from inland waters occurs during flood events triggered by heavy rainfall (Raymond et al. 2016). During these short-lived but biogeochemically important pulse-shunt events, overland flow is promoted, making the rapid transfer of tree-DOM to inland waters more likely (Fig. 5). Inorganic geochemical and isotopic data used with hydrograph separation techniques demonstrate that throughfall and stemflow can be delivered to streams (Hagedorn et al. 2000; Inamdar et al. 2013) and throughfall contributions during storms can be significant (30–80%), particularly during peak stream discharge (Katsumaya et al. 2001; Inamdar and Mitchell 2007). Under these high discharge conditions it is likely that tree-DOM is also shunted from its point of entrainment in the canopy, through the hydrological networks of the tree, across the land and into flooding rivers where it can be rapidly swept.

---

**Fig. 4.** Conceptual schematic illustrating our current understanding of the biotic and abiotic factors influence tree-derived dissolved organic matter (tree-DOM) flux. Controls exist across scales, from the microscale where the microbial phyllosphere uptakes volatile organic compounds (VOCs), competes for organic nutrients on the surface (C), produces compounds for antibiosis and signal interference (A) as well as plant hormones (H)—panel adapted from Vorholt (2012)—to the macroscale synoptic meteorological conditions controlling wet and dry deposition processes.
downstream forming part of the pulse-shunt hypothesized to translocate fluvial biogeochemical hotspots to higher order streams as storm size increases (Fig. 5). Tree-DOM compounds from the first interaction between terrestrial surfaces and precipitation may, thus, contribute to ecological processes much further down the rainfall-to-discharge path than previously hypothesized or evaluated.

In addition to the potential for temporal patchiness to influence the efficiency of tree-DOM delivery to inland waters, spatial patterns are at play. Throughfall can be focused spatially to drip points (Keim et al. 2005), potentially allowing tree-DOM to be more effectively transported deeper into soil horizons or nearby waterways. Tree-DOM transported by stemflow may also bypass sinks in the litter and mineral topsoils through preferential flow along roots (Levia and Germer 2015). Deep infiltration of tree-DOM by stemflow could result in mineral complexation (Aitkenhead-Peterson et al. 2003) or tree-DOM may access subsurface flow paths to near-stream saturated zones and variable source areas where DOM supports denitrification (Korom 1992).

The shared ability of throughfall and stemflow to entrain and transport solutes along hydrologic flow paths is linked to the spatiotemporal heterogeneity of their input patterns at the surface (Keim et al. 2005; Johnson and Lehmann 2006). McClain et al. (2003) used DOC as an exemplary solute to highlight the importance of hydrological flow paths to the heterogeneity of biogeochemical processes that influence solute exchange at the terrestrial–aquatic interface. In this context, substantial tree-DOM supplies delivered via preferential flow paths over the duration of a single storm may represent transport-type biogeochemical hot moments

### Table 3. Selected estimates of dissolved organic carbon (DOC) volume-weighted mean annual concentrations and annual yields from litter leachates through organic and mineral soil horizons and into 1st to higher order streams across climate zones.

| Forest type | Hydrologic flux | Concentration (mg-C L⁻¹) | Yield (g-C m⁻² yr⁻¹) | Study |
|-------------|-----------------|--------------------------|----------------------|-------|
| Tropical    | Litter leachate | 25–35                    | 47–56                | Fujii et al. (2009) |
|             | Organic soil horizons | 5                     | 9                    | McDowell (1998)       |
|             | Mineral soil horizons | 2                     | 4                    | McDowell (1998)       |
|             | Stream (1st order) | 2                       | 3                    | McDowell (1998)       |
| Subtropical | Litter leachate | 17–53                    | 32–47                | Ciglasch et al. (2004) |
|             | Organic soil horizons | 34                    | 2.5                  | Richter and Markewitz (1996) |
|             | Mineral soil horizons | 1.5                    | 0.1                  | Richter and Markewitz (1996) |
|             | Stream (1st order) | 3–7                     | 3.4                  | Spencer et al. (2012), Little Wekiva |
| Temperate   | Litter leachate | 21–30                    | 5–20                 | Park and Matzner (2003) |
|             | Organic soil horizons | 10–49                 | 7–40                 | Michalzik et al. (2001) |
|             | Mineral soil horizons | 1–7                    | 2–19                 | Michalzik et al. (2001) |
|             | Stream (1st order) | 1–3                     | 2                    | McDowell and Likens (1988) |
| Boreal      | Litter leachate | 20–48                    | 1–6                  | Koprivnjak and Moore (1992) |
|             | Organic soil horizons | 22–60                | 2–3                  | Koprivnjak and Moore (1992) |
|             | Mineral soil horizons | 12–22                | 1                    | Koprivnjak and Moore (1992) |
|             | Stream (1st order) | 3–7                     | 1–18                 | Eckhardt and Moore (1990) |
| All         | Large rivers    | 1–12*                   | 1–9                  | *Spencer et al. (2012) |
|             |                 |                         |                      | Raymond and Spencer (2015) |

**Fig. 5.** Integration of tree-derived dissolved organic matter (tree-DOM) as the first source of terrigenous DOM into the overall watershed response, with new upstream tree-DOM fluxes (in red) connected to current head-watershed processes (in black) contributing DOM to the river drainage network during storm events.
Conclusions and future directions

Although tree-DOM is a quantitatively significant flux of carbon, similar in magnitude to DOM yields for fluvial systems, tree-DOM remains poorly integrated into models, budgets, and conceptualizations of terrestrial and aquatic ecosystem biogeochemistry. The delivery of highly biolabile tree-DOM to downstream ecosystems via temporally and spatially patchy hydrological flow paths likely plays a significant role in shaping the form and function of these receiving ecosystems. There is a lot to learn about what controls the amount and quality of tree-DOM exported to soils and inland waters, and the ecological and biogeochemical influence tree-DOM exerts in these downstream ecosystem once it arrives. Below we note some future directions for research.

The drivers that modulate tree-DOM entrainment into throughfall and stemflow are diverse, including rainwater chemistry, precipitation intensity and frequency, tree taxonomy and related morphology, phenoseason, epiphytes and epifauna, tree infestation, the presence of proto-soils in trees, and preceding atmospheric deposition. The rate of tree-DOM entrainment into stemflow and throughfall likely controls the amount of tree-DOM exported from a tree, although given the highly biolabile and potentially photochemically labile nature of tree-DOM, both the quantity and quality of tree-DOM may be modified as it flows from its point of generation in the tree toward the forest floor. Any modification of tree-DOM during export from the tree will be dependent upon the flow path taken to the forest floor, as well as tree-DOM chemistry, tree light field, and the community of symbionts on the tree surface.

To determine tree-DOM export from a single tree requires significant effort as variability with season, storm size, storm frequency, etc. must be determined. Moving beyond single trees to the scale of forest, catchments or continents requires scaling laws to be developed. As we seek to develop these scaling laws, it is first critical to determine how much variability exists and then to seek the primary modulators of variability with a focus upon drivers that can be scaled based upon available or achievable datasets. Current evidence suggests that rainfall frequency, rainfall amount, and rainfall partitioning into stemflow, throughfall and interception all influence tree-DOM yields. These variables are good drivers to assess as they are also relatively easy to scale. Patterns of rainfall are available from local to global scales. Laws that govern rainfall partitioning have been developed (Muzylo et al. 2009), but require further model training and validation to generate reliable estimates of throughfall and stemflow hydrological fluxes. In addition to these hydrological drivers, biological drivers, such as tree taxa, presence and type of epiflora and epifauna, phenoseason and diurnal variation in plant activity, should be assessed. In time, these assessments should allow better understanding and prediction of the quantity and the quality of tree-DOM generation and export.

In tandem with developing a systematic understanding of the factors controlling tree-DOM export, the potential influence of tree-DOM in receiving soil and aquatic ecosystems should be assessed. The synchronous delivery of water, nutrients, and biolabile DOC likely results in hotspots and hot moments of biological activity that could be important to regional biogeochemical fluxes and the structuring of receiving ecosystems. When trying to assess the role of tree-DOM in inland waters, we first need to know how much tree-DOM makes it to aquatic ecosystems and under what conditions. To assess the presence of tree-DOM in inland waters, current chemical analytical techniques should be coupled to endmember mixing models and in-depth hydrological studies. Focusing on ecosystems and hydrological events when connectivity between trees and streams is likely to be highest would allow the greatest chance of finding tree-DOM in streams. We know that the inorganic chemical imprint of throughfall is discernible in streams as a major fraction of the overland or surface flow (Evans and Davies 1998). Coupling inorganic and organic analyses of throughfall and stemflow endmember chemistry with assessments of the same analytical suite within streams across hydrological events should allow the contribution of tree-DOM to streams to be better constrained. In addition to being of interest in its own right, tree-DOM’s diverse chemical constituents represent an information-rich set of tracers that should find increasing use as tracers of the hydrological paths of both stemflow and throughfall in receiving ecosystems.

In forests, tree canopies are the sites of first contact between precipitation and terrestrial ecosystems. It is imperative we understand the current interactions at the head of the terrestrial hydrological cycle, as evidence from this review indicates they may shape the hydrology, ecology, and biogeochemistry of what follows downstream. Looking to the future, climate change and shifting land use will continue to alter patterns of precipitation and forest cover. To predict the consequences of these changes for terrestrial and aquatic ecosystems, we will need to understand the interactions of precipitation and vegetation, including generation and export of tree-DOM.
References

Aitkenhead-Peterson, J., W. McDowell, J. Neff, E. Stuart, and L. Robert. 2003. Sources, production, and regulation of allochthonous dissolved organic matter inputs to surface waters, p. 26–70. In E. G. Findlay and R. L. Sinsabaugh [eds.], Aquatic ecosystems: Interactivity of dissolved organic matter. Academic Press.

Angelini, I. M., and others. 2011. On the coupling between vegetation and the atmosphere. Theor. Appl. Climatol. 105: 243–261. doi:10.1007/s00704-010-0377-5

Backnäs, S., J. Laine-Kaulio, and B. Kløve. 2012. Phosphorous forms and related soil chemistry in preferential flowpaths and the soil matrix of a forested podzolic till soil profile. Geoderma 189–190: 50–64. doi:10.1016/j.geoderma.2012.04.016

Baker, E. A., and G. M. Hunt. 1986. Erosion of waxes from leaf surfaces by simulated rain. New Phytol. 102: 161–173. doi:10.1111/j.1469-8137.1986.tb00807.x

Bischoff, S., M. T. Schwarz, J. Siemens, L. Thieme, W. Wilcke, and B. Michalzik. 2015. Properties of dissolved and total organic matter in throughfall, stemflow and forest floor leachate of central European forests. Biogeoosciences 12: 2695–2706. doi:10.5194/bg-12-2695-2015

Bittar, T. B., A. A. H. Vieira, A. Stubbins, and K. Mopper. 2015. Competition between photochemical and biological degradation of dissolved organic matter from the cyanobacterium Microcystis aeruginosa. Limnol. Oceanogr. 60: 1172–1194. doi:10.1002/lno.10090

Carlisle, A., A. H. F. Brown, and E. J. White. 1966. The organic matter and nutrient elements in the precipitation beneath a sessile oak (Quercus petraea) canopy. J. Ecol. 54: 87–98. doi:10.2307/2257660

Ciglasch, H., J. Lilienfein, K. Kaiser, and W. Wilcke. 2004. Dissolved organic matter under native Cerrado and Pinus caribaea plantations in the Brazilian savanna. Biogeochemistry 67: 157–182. doi:10.1023/B:BIOG.0000015281.74705.f8

Comiskey, J. C. 1978. Aspects of the organic carbon cycle on Walker Branch Watershed: A study in land/water interaction, p. 509. Doctoral dissertation. Univ. of Tennessee.

Currie, W. S., J. D. Aber, W. H. McDowell, R. D. Boone, and A. H. Magill. 1996. Vertical transport of dissolved organic C and N under long-term N amendments in pine and hardwood forests. Biogeochemistry 35: 471–505. doi:10.1007/BF02183037

Dalbro, S. 1955. Leaching of apple foliage by rain. In 14th International Horticultural Congress, Scheveningen, Holland, 29 August–06 September, 1955.

Dalva, T., and T. R. Moore. 1991. Sources and sinks of dissolved organic carbon in a forested swamp catchment. Biogeochemistry 15: 1–19. doi:10.1007/BF00002806

Dematte, M. E. S. P. 1999. Information on Brazilian palms for ornamental use, p. 41–46. In Second International Symposium on ornamental palms and other monocots from the tropics. Acta Horticulturae, v. 486.

Dittmar, T., and A. Stubbins. 2012. Dissolved organic matter in aquatic systems, p. 125–156. In H. Holland and K. Turekian [eds.], Treatise on geochemistry, 2nd ed. V. 12. Elsevier.

Eckhardt, B. W., and T. R. Moore. 1990. Controls on dissolved organic carbon concentrations in streams, southern Québec. Can. J. Fish. Aquat. Sci. 47: 1537–1544. doi:10.1139/f90-173

Evans, C., and T. D. Davies. 1998. Causes of concentration/discharge hysteresis and its potential as a tool for analysis of episode hydrochemistry. Water Resour. Res. 34: 129–137. doi:10.1029/97WR01881

FAO. 2016. State of the world’s forests 2016. Forests and agriculture: Land-use challenges and opportunities; [accessed 2017 December 29]. Available from http://www.fao.org/3/a-i5588e.pdf

Frangi, J. L., and A. E. Lugo. 1985. Ecosystem dynamics of a subtropical floodplain forest. Ecol. Monogr. 55: 351–369. doi:10.1139/f95-213

Gensel, P. G., and D. Edwards. 2001. Plants invade the land: Evolutionary and environmental perspectives. Columbia Univ. Press.

Germer, S., C. Neill, A. V. Krusche, S. C. G. Neto, and H. Elenbeer. 2007. Seasonal and within-event dynamics of rainfall and throughfall chemistry in an open tropical rainforest in Rondonia, Brazil. Biogeochemistry 86: 155–174. doi:10.1007/s10533-007-9152-9

Goller, R., W. Wilcke, K. Fleischbein, C. Valarezo, and W. Zech. 2006. Dissolved nitrogen, phosphorous, and sulfur forms in the ecosystem fluxes of a montane forest in Ecuador. Biogeochemistry 77: 57–89. doi:10.1007/s10533-005-1061-1

Greb, S. F., W. A. DiMichele, and R. A. Gastaldo. 2006. Evolution and importance of wetlands in earth history, p. 1–40. In W. A. DiMichele and S. Greb [eds.], Wetlands through time. Geological Society of America.

Guggenberger, G., and W. Zech. 1994. Composition and dynamics of dissolved carbohydrates and lignin-degradation products in two coniferous forests, NE Bavaria, Germany. Soil Biol. Biochem. 26: 19–27. doi:10.1016/0038-0717(94)90191-0
Guo, J.-F., Y.-S. Yang, G.-S. Chen, and P. Lin. 2005. Dissolved organic carbon and nitrogen in precipitation, throughfall and stemflow from Schima superba and Cunninghamia lanceolate plantations in subtropical China. J. For. Res. 16: 19–22. doi:10.1007/s10533-011-9595-x

Kalbitz, K., A. Meyer, R. Yang, and P. Gerstberger. 2007. Response of dissolved organic matter in the forest floor to long-term manipulation of litter and throughfall inputs. Biogeochemistry 86: 301–318. doi:10.1007/s10533-007-9161-8

Katsuyama, M., N. Ohte, and S. Kobashi. 2001. A three-component end-member analysis of streamwater hydrochemistry in a small Japanese forested headwater catchment. Hydrol. Process. 15: 249–260. doi:10.1002/hyp.155

Keim, R. F., A. E. Skaugset, and M. Weiler. 2005. Temporal persistence of spatial patterns in throughfall. J. Hydrol. 314: 263–274. doi:10.1016/j.jhydrol.2005.03.021

Kolka, R., P. Weishampel, and M. Fröberg. 2008. Measurement and importance of dissolved organic carbon, p. 171–176. In C. M. Hoover [ed.], Field measurements for forest carbon monitoring. Springer.

Kolka, R. K., E. A. Nater, D. F. Grigal, and E. S. Verry. 1999. Atmospheric inputs of mercury and organic carbon in to a forested upland/bog watershed. Water Air Soil Pollut. 113: 273–294. doi:10.1023/A:1005020326683

Koprivnjak, J.-F., and T. R. Moore. 1992. Sources, sinks, and fluxes of dissolved organic carbon in subarctic fen catchments. Arct. Alp. Res. 24: 204–210. doi:10.2307/1551658

Korom, S. F. 1992. Natural denitrification in the saturated zone: A review. Water Resour. Res. 28: 1637–1668. doi:10.1029/92WR00252

Laclau, J.-P., J. Ranger, J.-P. Bouillet, J. de Dieu Nzila, and P. Deleporte. 2003. Nutrient cycling in a clonal stand of Eucalyptus and an adjacent savanna ecosystem in Congo 1. Chemical composition of rainfall, throughfall and stemflow solutions. For. Ecol. Manag. 176: 105–119. doi:10.1016/S0378-1127(02)00280-3

Le Clerc, J. A., and J. F. Breazeale. 1908. Plant food removed from growing plants by rain or dew, p. 389. United States Department of Agriculture Yearbook of Agriculture.

Levia, D. F., J. T. Van Stan, S. P. Inamdar, M. J. Jarvis, M. J. Mitchell, S. M. Mage, C. E. Scheick, and P. J. McHale. 2012. Stemflow and dissolved organic carbon cycling: Temporal variability in concentration, flux, and UV-vis spectral metrics in a temperate broadleaf deciduous forest in the eastern United States. Can. J. For. Res. 42: 207–216. doi:10.1139/x11-173

Levia, D. F., and S. Germer. 2015. A review of stemflow generation dynamics and stemflow-environment interactions in forests and shrublands. Rev. Geophys. 53: 673–714. doi:10.1002/2015RG000479

Liu, C. P., and B. H. Sheu. 2003. Dissolved organic carbon in precipitation, throughfall, stemflow, soil solution, and stream water at the Guandaushi subtropical forest in Taiwan. For Ecol Manage 172: 315–325. doi:10.1016/S0378-1127(01)00793-9

Mahendrappa, M. K. 1974. Chemical composition of stemflow from some eastern Canadian tree species. Can. J. For. Res. 4: 1–7. doi:10.1139/x74-001
McClain, M. E., and others. 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems 6: 301–312. doi:10.1007/s10021-003-0161-9

McDowell, W. H. 1998. Internal nutrient fluxes in a Puerto Rican rain forest. J. Trop. Ecol. 14: 521–536. doi:10.1017/S0266474898000376

McDowell, W. H., and G. E. Likens. 1988. Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. Ecol. Monogr. 58: 177–195. doi:10.2307/2937024

McKee, A. J., and C. E. Carlyle-Moses. 2017. Modelling stemflow production by juvenile lodgepole pine (Pinus contorta var. latifolia) trees. J. For. Res. 28: 565–576. doi:10.1007/s11676-016-0336-9

Michalzik, B., K. Kaiser, and G. Guggenberger. 2005. Dissolved organic carbon and nitrogen – a synthesis for temperate forests. Biogeochemistry 52: 173–205. doi:10.1023/A:1006441620810

Möller, A., K. Kaiser, and G. Guggenberger. 2005. Dissolved organic carbon and nitrogen in precipitation, throughfall, soil solution, and stream water of the tropical highlands in northern Thailand. J. Plant Nutr. Soil Sci. 168: 649–659. doi:10.1002/jpln.200521804

Moore, L. D., J. T. Van Stan, T. E. Gay, C. Rosier, and T. Wu. 2016. Alteration of soil chitinolytic bacterial and ammonia oxidizing archaeal community diversity by rainwater redistribution in an epiphyte-laden Quercus virginiana canopy. Soil Biol. Biochem. 100: 33–41. doi:10.1016/j.soilbio.2016.05.016

Moore, T. R. 1987. An assessment of a simple spectrophotometric method for the determination of dissolved organic carbon in freshwaters. N. Z. J. Mar. Freshw. Res. 21: 585–589. doi:10.1080/00288330.1987.9516262

Moore, T. R. 2003. Dissolved organic carbon in a northern boreal landscape. Global Biogeochem. Cycles 17: 1109. doi:10.1109/2003GB002050

Moore, T. R., and R. J. Jackson. 1989. Dynamics of dissolved organic carbon in forested and disturbed catchments, Westland, New Zealand 2. Larry River. Water Resour. Res. 25: 1331–1339. doi:10.1029/WR025i006p01331

Mopper, K., A. Stubbins, J. D. Ritchie, H. M. Bialk, and P. G. Hatcher. 2007. Advanced instrumental approaches for characterization of marine dissolved organic matter: Mass spectrometry and nuclear magnetic resonance spectroscopy. Chem. Rev. 107: 419–442. doi:10.1021/cr050359b

Mopper, K., D. Kiefer, and A. Stubbins. 2015. Marine photochemistry of organic matter: Processes and impacts, p. 389–450. In D. A. Hansell and C. A. Carlson [eds.], Biogeochemistry of marine dissolved organic matter, 2nd ed. Academic Press.

Moran, M. A., and others. 2016. Deciphering ocean carbon in a changing world. Proc. Natl. Acad. Sci. USA 113: 3143–3151. doi:10.1073/pnas.1514645113

Moreno, G., J. F. Gallardo, and F. Bussotti. 2001. Canopy modification of atmospheric deposition in oligotrophic Quercus pyrenaica forests of an unpolluted region (central-western Spain). For. Ecol. Manag. 149: 47–60. doi:10.1016/S0378-1127(00)00544-2

Murray, S. J. 2014. Trends in 20th century global rainfall interception as simulated by a dynamic global vegetation model: Implications for global water resources. Ecohydrology 7: 102–114. doi:10.1002/eco.1325

Muzylo, A., P. Llorens, F. Valente, J. J. Keizer, F. Domingo, and J. H. C. Gash. 2009. A review of rainfall interception modelling. J. Hydrol. 370: 191–206. doi:10.1016/j.jhydrol.2009.02.058

Neff, J. C., and G. P. Asner. 2001. Dissolved organic carbon in terrestrial ecosystems: Synthesis and a model. Ecosystems 4: 29–48. doi:10.1007/s100210000058

Park, J.-H., and E. Matzner. 2003. Controls on the release of dissolved organic carbon and nitrogen from a deciduous forest floor investigated by manipulations of aboveground litter inputs and water flux. Biogeochemistry 66: 265–286. doi:10.1023/B:BIOG.0000005341.19412.7b

Pretzsch, H., and others. 2015. Crown size and growing space requirement of common tree species in urban centres, parks, and forests. Urban For. Urban Green. 14: 466–479. doi:10.1016/j.ufug.2015.04.006

Qualls, R. G., B. L. Haines, and W. T. Swank. 1991. Fluxes of dissolved organic nutrients and humic substances in a deciduous forest. Ecology 72: 254–266. doi:10.2307/1938919

Qualls, R. G., and B. L. Haines. 1992. Biodegradability of dissolved organic nutrients and humic substances in a deciduous forest. Soil Sci. Soc. Am. J. 56: 578–586. doi:10.2136/sssaj1992.03615995005600020038x

Raymond, P. A., and R. G. M. Spencer. 2015. Rivirine DOM, p. 509–533. In D. A. Hansell and C. A. Carlson [eds.], Biogeochemistry of marine dissolved organic matter, 2nd ed. Elsevier.

Raymond, P. A., J. E. Saiers, and W. V. Sobczak. 2016. Hydrological and biogeochemical controls on watershed dissolved organic matter transport: Pulse-shunt concept. Ecology 97: 5–16. doi:10.1890/14-1684.1

Richter, D. D., and D. Markewitz. 1996. Carbon changes during the growth of loblolly pine on formerly cultivated soil. The Calhoun Experimental Forest, USA, p. 397–407. In D. S. Powell, P. Smith, and J. U. Smith [eds.], Evaluation of soil organic matter models. NATO Advances Studies Institute series, v. 138. Springer.

Schrumpf, M., W. Zech, J. Lehmann, and H. V. C. Lyaruu. 2006. TOC, TON, TOS and TOP in rainfall, throughfall, litter percolate and soil solution of a montane rainforest succession at Mt. Kilimanjaro, Tanzania. Biogeochemistry 78: 361–387. doi:10.1007/s10533-005-4428-4

Schwarzl, K., S. Ebermann, and N. Schalling. 2012. Evidence of double-funneling effect of beech trees by visualization of flow pathways using dye tracer. J. Hydrol. 470–471: 184–192. doi:10.1016/j.jhydrol.2012.08.048
Siegert, C. M., D. F. Levia, D. J. Leathers, J. T. Van Stan, and M. J. Mitchell. 2017. Do storm synoptic patterns affect biogeochemical fluxes from temperate deciduous forest canopies? Biogeochemistry 132: 273–292. doi:10.1007/s10533-017-0300-6

Sipler, R. E., and D. A. Bronk. 2015. Dynamics of dissolved organic nitrogen, p. 127–232. In D. A. Hansell and C. A. Carlson [eds.], Biogeochemistry of marine dissolved organic matter, 2nd ed. Academic Press.

Stubbins, A., L. M. Silva, T. Dittmar, and J. T. Van Stan. 2017. Molecular and optical properties of tree-derived dissolved organic matter in throughfall and stemflow from live oaks and eastern red cedar. Front. Earth Sci. 5: 22. doi:10.3389/feart.2017.00022

Stubbins, A., V. Hubbard, G. Uher, G. Aiken, C. S. Law, R. C. Upstill-Goddard, and K. Mopper. 2008. Relating carbon monoxide photoproduction to dissolved organic matter functionality. Environ. Sci. Technol. 42: 3271–3276. doi:10.1021/es703014q

Stubbins, A., L. M. Silva, T. Dittmar, and J. T. Van Stan. 2017. Molecular and optical properties of tree-derived dissolved organic matter in throughfall and stemflow from live oaks and eastern red cedar. Front. Earth Sci. 5: 22. doi:10.3389/feart.2017.00022

Tobón, C., J. Sevink, and J. M. Verstraten. 2004. Solute fluxes in throughfall and stemflow in four forest ecosystems in northwest Amazonia. Biogeochemistry 70: 1–25. doi:10.1023/B:BIOG.0000049334.10381.f8

Turgeon, J. M. L., and F. Courchesne. 2008. Hydrochemical behavior of dissolved nitrogen and carbon in a headwater stream of the Canadian Shield: Relevance of antecedent soil moisture conditions. Hydrol. Process. 22: 327–339. doi:10.1002/hyp.6613

Van Stan, J. T., D. F. Levia, S. P. Inamdar, M. Lepori-Bui, and M. J. Mitchell. 2012. The effects of phenoseason and storm characteristics on throughfall solute washoff and leaching dynamics from a temperate deciduous forest canopy. Sci. Total Environ. 430: 48–58. doi:10.1016/j.scitotenv.2012.04.060

Van Stan, J. T., and T. G. Pypker. 2015. A review and evaluation of forest canopy epiphyte roles in the partitioning and chemical alteration of precipitation. Sci. Total Environ. 536: 813–824. doi:10.1016/j.scitotenv.2015.07.134

Van Stan, J. T., E. S. Lewis, A. Hildebrandt, C. Rebmann, and J. Friesen. 2016. Impact of interacting bark structure and rainfall conditions on stemflow variability in a temperate beech-oak forest, central Germany. Hydrol. Sci. J. 61: 2071–2083. doi:10.1080/02626667.2015.1083104

Wagner, S., R. Jaffé, and A. Stubbins. Dissolved black carbon in aquatic ecosystems. Limnol. Oceanogr. Lett. 3: 168–185. doi:10.1002/lo2.10076

Weishaar, J. L., G. R. Aiken, B. A. Bergamaschi, M. S. Fram, R. Fujii, and K. Mopper. 2003. Evaluation of specific ultra-violet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ. Sci. Technol. 37: 4702–4708. doi:10.1021/es030360x

White, A. 2015. Examining the impacts of wildfire on throughfall and stemflow chemistry and flux at plot and catchment scales, p. 52. Masters thesis. The Univ. of Arizona.

Wehmer, C. 1892. Zur frage nach der Entleerung absterbender Organe, insbesondere der Laubblätter. Landw. Jb. 21: 513–569.

Weishaar, J. L., G. R. Aiken, B. A. Bergamaschi, M. S. Fram, R. Fujii, and K. Mopper. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. Environ. Sci. Technol. 37: 4702–4708. doi:10.1021/es030360x

White, A. 2015. Examining the impacts of wildfire on throughfall and stemflow chemistry and flux at plot and catchment scales, p. 52. Masters thesis. The Univ. of Arizona.

Acknowledgments

We thank the reviewers. JTVS acknowledges support from US-NSF (1518726).