Biogeochemistry (2019) 146:191–207
https://doi.org/10.1007/s10533-019-00620-2

Dissolved black carbon in throughfall and stemflow in a fire-managed longleaf pine woodland

Sasha Wagner · Steven Brantley · Stribling Stuber · John Van Stan · Ansley Whitetree · Aron Stubbins

Received: 18 June 2019 / Accepted: 9 November 2019 / Published online: 21 November 2019

Abstract The interception of rainfall by trees enriches rainwater with tree-derived dissolved organic matter (tree-DOM), which represents the first terrigenous source of DOM during storm events. The tree-DOM is then exported from the canopy via rainfall that drips from leaves and branches (throughfall) or is funneled down the tree trunk (stemflow) to the forest floor. Here, we evaluate contributions of dissolved black carbon (DBC) to tree-DOM in fire-managed longleaf pine woodlands (*Pinus palustris*). These are the first quantitative measurements of throughfall and stemflow DBC for any type of forest or tree species. The inter-storm variability of tree-DOM concentrations, composition, and optical properties in throughfall and stemflow were also examined. Tree-DOM was enriched in dissolved organic carbon (DOC) and DBC compared to rainfall, and concentrations did not vary with storm size. Therefore, longleaf and slash pines contain a large repository of leachable organic matter that was not significantly diminished, even during large storm events. The aromaticity of stemflow DOM increased with amount of rainfall, suggesting bark may need to undergo a certain degree of saturation for the solubilization of DBC and other aromatic components. In tree-DOM, DBC comprised ~ 2% of DOC. A simple mass balance suggested annual yields of DBC in throughfall and stemflow (50–350 kg-DBC and 19 kg-DBC km^{-2} $year^{-1}$, respectively). Therefore, atmospheric deposition would be enough to sustain a continual source of tree-derived DBC in longleaf pine ecosystems regularly maintained by fire.

Responsible Editor: John Harrison.

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10533-019-00620-2) contains supplementary material, which is available to authorized users.

S. Wagner (✉)
Department of Earth and Environmental Sciences, Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY 12180, USA
e-mail: wagnes3@rpi.edu

S. Brantley · S. Stuber
Jones Center at Ichauway, Newton, GA, USA

J. Van Stan · A. Whitetree
Department of Geology and Geography, Georgia Southern University, Statesboro, GA, USA

J. Van Stan
Applied Coastal Research Laboratory, Georgia Southern University, Savannah, GA, USA

A. Stubbins
Departments of Marine and Environmental Sciences, Civil and Environmental Engineering, and Chemistry and Chemical Biology, Northeastern University, Boston, MA, USA

Keywords Dissolved black carbon · Throughfall · Stemflow · Longleaf pine · Tree-DOM · Prescribed fire

Introduction

Vegetation fires burn over 460 Mha of the Earth's land surface each year (Randerson et al. 2012), resulting in the emission of large amounts of CO_2 to the atmosphere (van der Werf et al. 2010) and the production of black carbon (BC) during incomplete combustion of biomass (Schmidt and Noack 2000). BC is a heterogeneous mixture of thermally altered molecules, ranging from slightly charred biomass to soot particles (Masiello 2004). BC is carbon-enriched and differs in how it is biogeochemically processed compared to its unburned precursor material, which has major implications for local and global carbon cycles (Wagner et al. 2018). In the current study, we focus on quantifying the condensed aromatic fraction of BC formed at higher charring temperatures (from 250 up to ~ 700 °C; Schneider et al. 2010). Condensed aromatic BC is refractory and largely retained in soils (Kuzyakov et al. 2014; Reisser et al. 2016). However, soil BC does not accumulate indefinitely. A portion is solubilized and removed from the landscape in the form of dissolved BC (DBC), serving as a continual source of fire-derived carbon to inland waters (Wagner et al. 2018). Hydrological events enhance the mobilization of DBC in river catchments, where DBC concentrations have been shown to increase with increasing discharge (Dittmar et al. 2012; Wagner et al. 2015; Stubbins et al. 2015).

Small streams are traditionally considered the headwaters of river systems. In forested catchments however, the chemical composition of rainfall is altered prior to entering headwaters, when precipitation interacts with trees. Throughfall (rain that passes through canopy gaps or drips from aboveground biomass) and stemflow (rain intercepted by the canopy is funneled to the stem) are enriched in DOM compared to rainfall (Van Stan and Stubbins 2018). Therefore, the interception of rainfall by forest canopies produces the first source of terrigenous DOM during rainfall events. In forested catchments, annual tree-DOM yields can equal or exceed riverine DOM yields (Van Stan et al. 2017; Van Stan and Stubbins 2018), spotlighting the importance of tree-derived DOM (tree-DOM) in terrestrial carbon cycles. Several factors control the amount and composition of tree-DOM, including canopy phenology, microbial activity, and meteorological conditions (Guggenberger and Zech 1994; Van Stan et al. 2012; Vorholt 2012). These dynamic factors contribute to the high degree of inter-storm variability observed for tree-DOM quality and quantity (Van Stan et al. 2017). Based upon optical measurements, throughfall and stemflow, in particular, are enriched in aromatic, highly colored DOM (Levia et al. 2012; Inamdar et al. 2012; Stubbins et al. 2017). Taken together, the optical and structural features of throughfall and stemflow indicate tree-DOM is largely autochthonous, derived from the tree itself (Van Stan and Stubbins 2018). However, molecular formulas consistent with condensed aromatic DBC, have been identified in the molecular signatures of tree-DOM (Stubbins et al. 2017), which indicates atmospheric BC deposited to the canopy and stem could also contribute to tree-DOM.

In the current study, we evaluate contributions of DBC to tree-DOM in longleaf pine woodlands managed by frequent (~ 2-year return interval) prescribed fire. The longleaf pine ecosystem is characterized by a widely spaced canopy, scant midstory vegetation, and continuous groundcover dominated by grasses (Kirkman and Jack 2017). Frequent fires are necessary to maintain the structure and function of this open, savanna-like, and biologically diverse woodland (Kirkman and Jack 2017). Since only a small portion of available biomass is exposed to thermal degradation during prescribed fires, the production of BC under controlled burn conditions is generally low (Schmidt and Noack 2000). For example, prescribed burning resulted in the conversion of 4–6% of fire-affected biomass to BC in a subtropical scrub oak ecosystem compared to much larger atmospheric carbon losses, which averaged 68% of fire-affected biomass (Alexis et al. 2007). The land-air partitioning of BC during a specific burn event varies with fire behavior, fuel type, and environmental conditions (Santín et al. 2016). However, it is estimated that > 80% of BC produced during fire remains on-site and < 20% is emitted to the air as atmospheric BC (Kuhlbusch and Crutzen 1995). Therefore, we postulated that atmospheric BC would be a source of tree-derived DBC, particularly in fire-maintained longleaf pine ecosystems. Here, we examine the inter-storm variability of tree-DOM concentrations, optical properties, and DBC content in longleaf pine throughfall and stemflow. Data reported below includes the first quantitative measurements of throughfall and stemflow DBC for any type of forest or tree species. Annual yields of tree-DOM and tree-DBC were estimated from inter-storm trends and discussed within the context of terrestrial carbon fluxes typically observed for river catchments.

Methods

Site description

Our study was located at the Jones Center at Ichauway, a ~ 11,400 ha private preserve and research center in Baker County, Georgia (31.22N, 84.48W). Climate at the site is classified as humid subtropical (Peel et al. 2007) with a long growing season (~ 250 days) and short, mild winters. Mean annual temperature is 19 °C and mean annual rainfall is 1310 mm, which is evenly distributed throughout the year. The site is dominated by mature (80–100-year-old), second-growth longleaf pine woodland and is generally burned on a 2-year fire-return interval (i.e. the time between fires in a defined area). The current fire-return interval for the majority of the preserve has been in place since 1992. Prior to that, some areas were often burned annually, but prescribed fires were inconsistent and longer periods without fire were likely. The frequent fire at these sites has resulted in a sparse-to-non-existent mid-story/shrub layer and near-continuous ground-cover layer dominated by *Aristida stricta* var. *beyrichiana* Trin. & Rupr. (wiregrass, Poaceae). Approximately 4500 ha are characterized by native groundcover, indicating little or no interruption in the long-term fire regime from land cover alteration since European settlement. Basal area across longleaf pine woodlands on Ichauway ranges from 6 to 20 m^2 ha^{-1}, with sites selected for the current study representing the higher end of that range. The canopy is dominated by *Pinus palustris* Mill. (longleaf pine, Pinaceae), which accounts for 60 to > 90% of canopy basal area in most sites. On wetter sites, like our stemflow sampling site, *Pinus elliottii* Engelm. (slash pine), a pine very similar to longleaf in phenology and morphology, co-occurs with longleaf pine. The pines shed pollen in February through April (Boyer 1972) and though they are never leafless, they do shed needles from the previous year, primarily from May to November (Sheffield et al. 2003).

Sample collection

Throughfall samples were collected between February and June 2016 during ten discrete rain events ranging in size from 0.6 to 86 mm of bulk precipitation. Samples were collected at fifteen points in an annually burned stand of longleaf pine, stratified across areas with low, medium, and high canopy cover (n = 5 for each cover class). Low, medium, and high canopy cover classes were characterized structurally as canopy gaps, a single layer of canopy branches, and multiple layers of canopy branches, respectively. To quantify canopy cover, the canopy leaf area index was estimated for each cover class using a LI-COR Inc. LI-2200 Plant Canopy Analyzer. Leaf area indices (mean ± 1 SD) within a ~ 10 m radius of the sampling points were determined to be 0.59 ± 0.28, 1.04 ± 0.19, and 1.4 ± 0.19 for low, medium, and high cover classes, respectively. Bulk precipitation (rainfall) samples (n = 3) were collected from an open field adjacent to the throughfall monitoring site. Stemflow was collected from 18 pines (12 longleaf pines, 6 slash pines) at three sites during 10 discrete rain events ranging in size from 0.4 to 109 mm of bulk precipitation. Two stemflow sites were directly burned every 2 years and the other site, though unburned, was embedded within a larger matrix of longleaf pine woodlands burned biennially. Trees ranged in size from 14.4 to 34.4 cm diameter at breast height. Stemflow was captured and collected by coiling longitudinally-split 3.81 cm (inner diameter) polyvinyl chloride hose completely around target trees, attaching the hose with nails, and sealing the hose to the tree with silicone caulk. The hose drained into sealed 18.9 L (5 gallon) buckets.

Throughfall and bulk rainfall samples were collected in 0.18 m^2 high-density polyethylene (HDPE) rectangular bins. Stemflow buckets were also HDPE. Prior to deploying sample collectors before an expected rain event, all bins and buckets were rinsed with deionized (DI) water filtered to 20 MΩ, washed with DI water acidified to a pH of 2 and soaked overnight, and then triple rinsed with filtered DI water and allowed to air-dry upside-down to prevent contamination. Stemflow collection hoses were permanently attached to trees, thus they were not acid-washed or rinsed in between rain events. Nalgene bottles (1 L) were used to collect subsamples of throughfall and stemflow after a rain event and were washed and rinsed in the same manner as the bins and dried in a drying oven covered with pre-ashed foil. Samples were collected within 12–16 h following a rain event. During subsample collection in the field, bottles were rinsed with sample at least once, depending on sample volume. Field blanks and lab blanks were collected to assess possible contamination of DOM from collection process or from HDPE containers themselves.

After collection, samples were immediately stored at 3 °C. Within 24 h of collection, samples were filtered using a vacuum flask and pump with ashed glass fiber filters (0.7 µm porosity). Lab blanks were similarly processed to assess possible contamination. All glassware used to process samples were rinsed, washed, and dried in the same manner described above. Samples were again stored at 3 °C and subsequently shipped on ice, overnight for further analysis.

Dissolved organic carbon concentrations

Concentrations of DOM were quantified as dissolved organic carbon (DOC). Filtered samples were acidified to pH 2 using HCl, then DOC was measured as nonpurgable organic carbon using a Shimadzu TOC-V CPH analyzer equipped with an ASI-V autosampler. Sample DOC was quantified using a calibration curve made with a potassium hydrogen phthalate stock solution. Measurement accuracy and reproducibility was assessed by analyzing deep seawater and low carbon water reference materials obtained from the Consensus Reference Material (CRM) project (https://hansell-lab.rsmas.miami.edu/consensus-reference-material/index.html). Analyses of CRM were within 5% of reported values. This configuration has a DOC detection limit of 0.034 ± 0.004 mg C L^{-1} with standard errors for DOC concentration being $1.7 \pm 0.5\%$ (Stubbins and Dittmar 2012). Procedural blanks exhibited DOC concentrations that were 0.3 mg C L^{-1}, on average. Thus, carbon contamination from sample collection and processing was negligible.

Optical measurements

Absorbance spectra were collected (200–800 nm) using a Horiba Aqualog-UV-800-C spectrophotometer and a quartz cuvette with a 1 cm path length. Sample spectra were blank corrected using spectra collected from ultrapure water (MilliQ, Millipore). If sample optical density at 250 nm exceeded a value of 2 (dimensionless), the sample was diluted with ultrapure water and reanalyzed. Optical density at 254 nm was converted to Naperian absorbance coefficients ($a254$; m^{-1}; Hu et al. 2002) and used to quantify chromophoric DOM (CDOM) signals. For each sample, the decadic absorption coefficient at 254 nm (m^{-1}) was divided by its DOC concentration (mg-C L^{-1}) to determine the specific UV absorbance at 254 nm ($SUVA_{254}$; L mg-C^{-1} m^{-1}), a metric of relative DOM aromaticity (Weishaar et al. 2003).

Solid phase extraction of dissolved organic matter

DOM was isolated from samples via solid phase extraction (SPE; Varian Bond Elut PPL cartridges, 1 g, 6 mL; Dittmar et al. 2008) prior to DBC analysis. Briefly, SPE cartridges were conditioned with methanol, ultrapure water, and acidified water. Filtered and acidified samples were passed through the SPE cartridges by gravity. Isolated DOM was then eluted from the SPE cartridges with methanol and stored at − 20 °C until DBC analysis.

Dissolved black carbon analysis

Sample DBC was quantified on a subset of samples using the benzenepolycarboxylic acid (BPCA) method, which chemically degrades condensed aromatic compounds into benzenehexacarboxylic acid (B6CA) and benzenepentacarboxylic acid (B5CA) molecular markers (Dittmar 2008). The BPCA method has been cited as a robust approach for measuring condensed aromatics in environmental matrices, particularly DOM (Hammes et al. 2007; Roth et al. 2012). BPCAs were oxidized and quantified following previously described methods (Dittmar 2008; Wagner et al. 2017). Briefly, aliquots of SPE-isolated DOM (~ 0.5 mg-C equivalents) were transferred to 2 mL glass ampules and dried under a stream of argon until complete evaporation of methanol. Concentrated HNO_3 (0.5 mL) was added to each ampule, then ampules were flame-sealed and heated to 160 °C for 6 h. After oxidation, ampules were opened and HNO_3 was dried at 60 °C under a stream of argon. The BPCA-containing residue was redissolved in dilute H_3PO_4 for subsequent analysis by high performance liquid chromatography (HPLC). Quantification of BPCAs was performed using a Shimadzu HPLC system equipped with an autosampler, pump, and UV absorbance detector. B6CA and B5CA were separated on an Agilent Poroshell 120 phenyl-hexyl column (4.6 × 150 mm, 2.7 µm) using an aqueous gradient of H_3PO_4 (0.6 M; pH 1) and sodium phosphate (20 mM; pH 6) buffers (Wagner et al. 2017). BPCAs were quantified using calibration curves for commercially available B6CA and B5CA (Tokyo Chemical Industry; Tokyo, Japan) using a 5 mM BPCA-C stock solution. The average coefficients of variation for replicate measurements of B6CA and B5CA were < 5%. Sample DBC concentrations were calculated using the established power relationship between DBC (µM-C) and the sum of B6CA and B5CA (nM-BPCA) in the following equation ($n = 352$, $R = 998$, $p < 0.0001$; Stubbins et al. 2015): $DBC = 0.0891 \times (B6CA + B5CA)^{0.9175}$. DBC concentrations calculated using this equation are directly comparable to those measured in previous studies (Dittmar et al. 2012; Jaffé et al. 2013; Wagner et al. 2018). Here, DBC refers to the concentration of condensed aromatic carbon ascribed to a pyrogenic source.

Results

Rainfall partitioning

Rainfall partitioning of longleaf pine trees was calculated as the percentage of total rainfall that transits the canopy (throughfall) or is funneled to and down the tree trunk (stemflow). Recovered sample volumes for throughfall and stemflow were linearly correlated with rainfall ($p < 0.0001$; Fig. 1). The proportion of rainfall recovered as throughfall was 94%, 91%, and 86% in areas of low, medium, and high canopy cover, respectively (Fig. 1). Only 0.75% of rainfall was recovered as stemflow (Fig. 1) which typically corresponded to < 10 L of stemflow volume per tree per storm event. However, stemflow volumes exceeding 15 L were observed for some trees during the largest captured storm event. Here, we normalized stemflow to canopy area so calculated stemflow volumes (mm) could be directly compared to rainfall and other hydrological fluxes (water yields) at regional scale (Friesen et al. 2015).

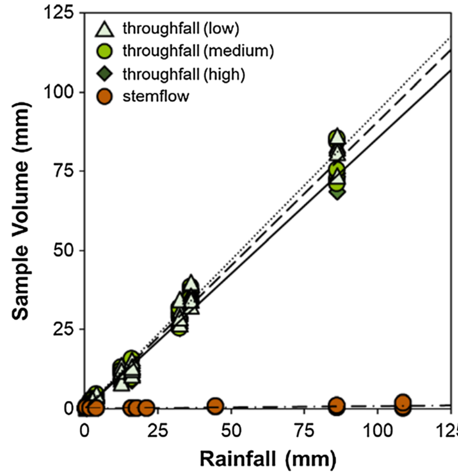

Fig. 1 Rainfall partitioning for throughfall in areas of low (light green triangles), medium (green circles), and high (dark green diamonds) canopy cover and stemflow (brown circles). Intercepts were not statistically different from zero, therefore regression lines were forced through the origin. Slopes and standard errors for throughfall in areas of low (dotted line), medium (dashed line), and high (solid line) canopy cover were 0.94 ± 0.01, 0.91 ± 0.01, and 0.86 ± 0.01, respectively. The slope and standard error for stemflow (dash dot line) was 0.0075 ± 0.0004. (Color figure online)

Tree-DOM concentrations

Throughfall and stemflow were significantly enriched in DOC, DBC, and CDOM compared to rainfall (Fig. 2a–c). DOC concentrations were lowest in rainfall (2.5 ± 2.5 mg-C L^{-1}), and significantly increased in throughfall with degree of canopy cover (low canopy cover, 5.5 ± 4.3 mg-C L^{-1}; high canopy cover, 16 ± 9.3 mg-C L^{-1}; Fig. 2a). Stemflow was significantly enriched in DOC compared to throughfall (Fig. 2a) and yielded the highest DOC sample overall (200 mg-C L^{-1}). Throughfall DBC concentrations were lowest in areas of low canopy cover (0.085 ± 0.075 mg-C L^{-1}) and highest in areas of high canopy cover (0.39 ± 0.19 mg-C L^{-1}) and significantly enriched compared to rainfall (0.024 ± 0.019 mg-C L^{-1}; Fig. 2b). Compared to both rainfall and throughfall, stemflow was

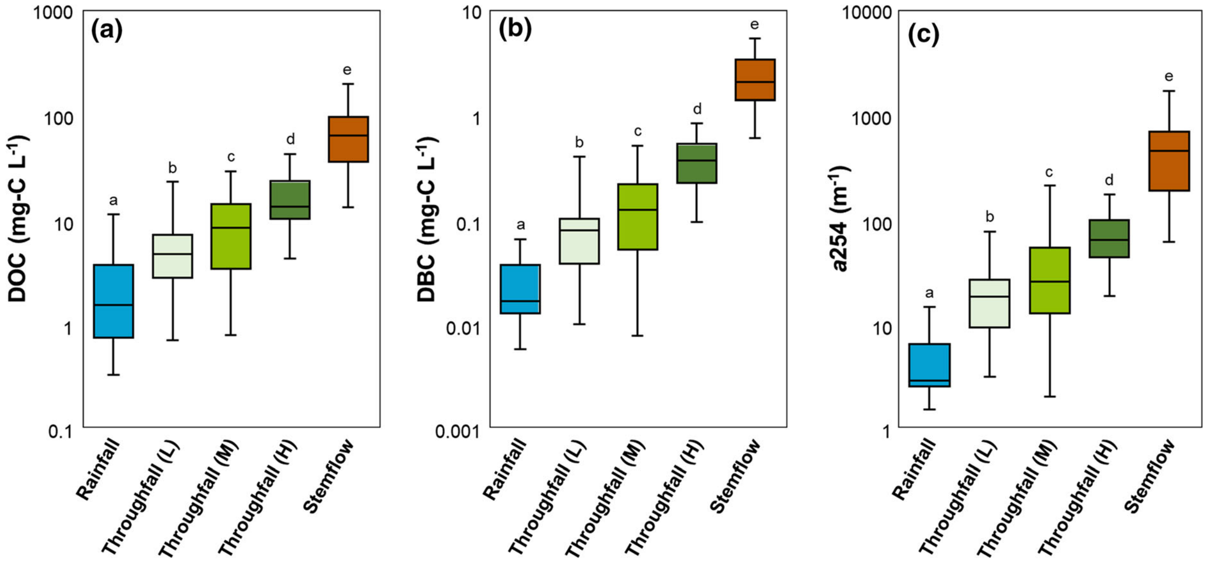

Fig. 2 Box plots show the maximum value, minimum value, median value, and interquartile range for dissolved organic carbon (DOC), dissolved black carbon (DBC), and chromophoric dissolved organic matter (Napierian absorption coefficient at 254 nm; *a*254) for all collected rainfall, throughfall, and stemflow samples. Outliers are not shown. Boxes with different letters indicate significant differences among sample types (Mann–Whitney test for nonparametric distributions; $p < 0.05$)

significantly enriched in DBC (2.3 ± 1.2 mg-C L^{-1}) and yielded the highest DBC sample overall (5.5 mg-C L^{-1}; Fig. 2b). CDOM was significantly enriched in throughfall (low canopy cover, 19 ± 14 m^{-1}; high canopy cover, 71 ± 38 m^{-1}) compared to rainfall (5 ± 7 m^{-1}; Fig. 2c). Stemflow yielded the highest CDOM on average (507 ± 379 m^{-1}), and the highest CDOM measurement overall (1720 m^{-1}; Fig. 2c).

Tree-DOM composition

$SUVA_{254}$ is strongly correlated with the aromatic content of DOM (Weishaar et al. 2003). Mean $SUVA_{254}$ values in throughfall and stemflow were significantly higher than in rainfall (1.2 ± 0.7 L mg-C^{-1} m^{-1}; Fig. 3a). Stemflow had significantly higher $SUVA_{254}$ (2.8 ± 1.0 L mg-C^{-1} m^{-1}) than throughfall, which varied with degree of canopy cover (low canopy cover, 1.7 ± 0.7 L mg-C^{-1} m^{-1}; high canopy cover, 2.2 ± 0.8 L mg-C^{-1} m^{-1}; Fig. 3a). The DBC:DOC ratio is used to describe the contribution of DBC to bulk DOC and varies across diverse aquatic environments (Wagner et al. 2018). Mean ratios of DBC:DOC were significantly higher in both high cover throughfall (2.4 ± 0.6%) and stemflow (3.0 ± 0.8%) compared to rainfall (1.6 ± 1.1%; Fig. 3b). The ratios of individually quantified BPCAs (B6CA:B5CA) describe the degree of condensed aromaticity of the measured DBC pool (Abiven et al. 2011) and have been used to infer how DBC is mobilized in river catchments (Stubbins et al. 2015; Wagner et al. 2015). Mean B6CA:B5CA values for rainfall (0.30 ± 0.05) were lower than for throughfall (low cover, 0.33 ± 0.05; high cover, 0.41 ± 0.05) and stemflow (0.43 ± 0.06; Fig. 3c).

Effect of storm size on tree-DOM

Throughfall data were plotted as individual points to show how tree-DOM varied with storm size (Fig. 4a–c). Throughfall data were then pooled (low, medium, and high canopy cover) and binned according to amount of rainfall (< 10, 10–20, 20–40, > 40 mm) to statistically determine how DOM concentrations varied with storm size (Figs. 4a–c, S1a–c). Throughfall DOC concentrations were significantly higher, on average, during small storm events (< 10 mm rainfall; Figs. 4a, S1a). However, there was no difference in throughfall DOC concentration among larger storms (> 10 mm rainfall; Figs. 4a, S1a). While there was some variation in throughfall DBC with storm size, no overall trend was observed (Fig. 4b, S1b). Similarly,

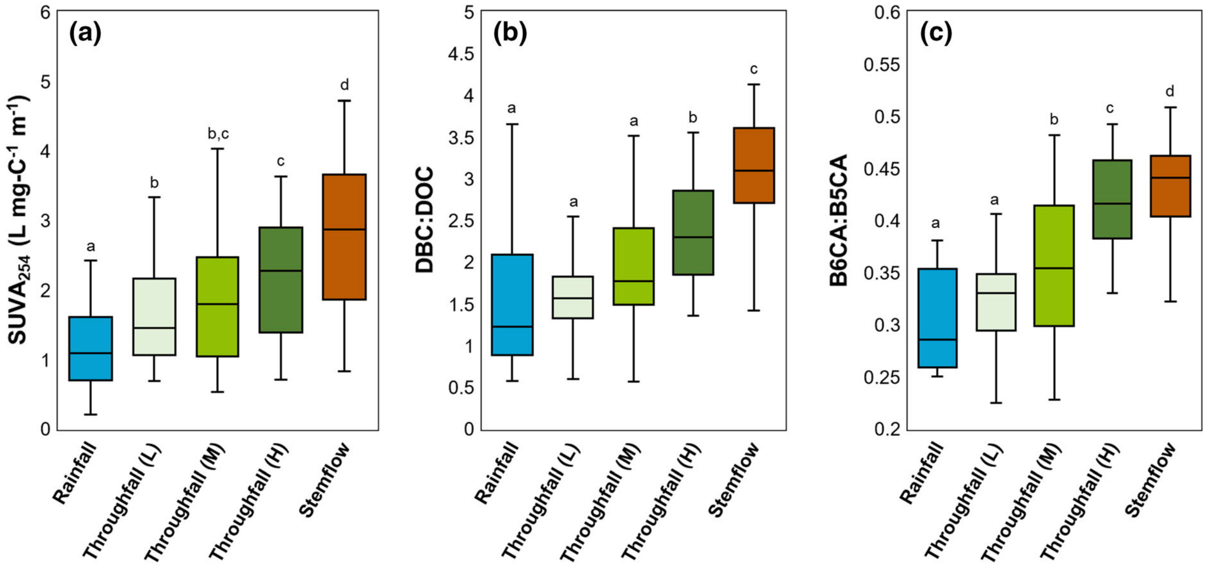

Fig. 3 Box plots show the maximum value, minimum value, median value, and interquartile range for carbon-normalized absorbance at 254 nm ($SUVA_{254}$), the ratio of dissolved black carbon to dissolved organic carbon (DBC:DOC), and BPCA ratio (B6CA:B5CA) for all collected rainfall, throughfall, and stemflow samples. Outliers are not shown. Boxes with different letters indicate significant differences in mean values among sample types (Student's t-test; $p < 0.05$)

throughfall CDOM did not vary significantly with amount of rainfall (Figs. 4c, S1c). Stemflow data were plotted as individual points (Fig. 4d–f) and also binned by amount of rainfall (< 10, 10–20, 20–50, > 50 mm) to assess variability in DOM concentrations versus storm size (Fig. S1d–f). Due to study site access and/or volume limitations, not all throughfall and stemflow samples were captured simultaneously during the same storm events (see Table S1 for individual sample details). Therefore, throughfall and stemflow data were binned according to storm size based upon the distribution of data collected for each parameter. Storm size had no effect on stemflow DOC concentrations (Figs. 4d, S1d). Stemflow DBC and CDOM varied widely among individual pines per storm event and the amount of rainfall had no apparent effect overall on their concentrations (Figs. 4e, f, S1e, f). Qualitative DOM characteristics ($SUVA_{254}$, DBC:DOC, B6CA:B5CA) for throughfall did not vary significantly with storm size (Figs. 5a–c, S2a–c). However, stemflow became enriched in CDOM and DBC relative to bulk DOC with increased rainfall amounts (Figs. 5d, e, S2d, e). More highly condensed aromatic compounds were also mobilized during heavier rain events, as evidenced by the significant increase in stemflow B6CA:B5CA for storms > 50 mm (Figs. 5f, S2f).

Per storm and annual yields of tree-derived DOC and DBC

Tree-derived DOC and DBC yields were calculated as the concentration of DOC or DBC (mg-C L^{-1}) multiplied by sample volume (L) divided by container area (for throughfall; 0.18 m^2) or mean canopy area (for stemflow; 12 m^2). Given the relative consistency of their concentrations in throughfall and stemflow, DOC and DBC yields increased linearly with increasing amounts of rainfall, despite high variability among trees (Fig. 6a, b). Stemflow DOC and DBC yields were roughly an order of magnitude less than throughfall yields (Fig. 6c–d). Low sample volumes (i.e. typically < 1% of rainfall; Fig. 1) and normalization to canopy area both contribute to low yields observed for stemflow, which initially seemed to contradict extremely high DOC and DBC concentrations (Fig. 2a, b).

Linear relationships between rainfall (mm) and carbon yields were used to estimate total annual yields for DOC and DBC (kg-C km^{-2} $year^{-1}$) using local rainfall data from Ichawaynochaway Creek (GA, USA; USGS #02355350; years 2009–2011 and 2014–2016). Linear relationships were forced through zero, as intercepts were insignificantly different from zero (i.e. at zero rainfall, there was zero throughfall or

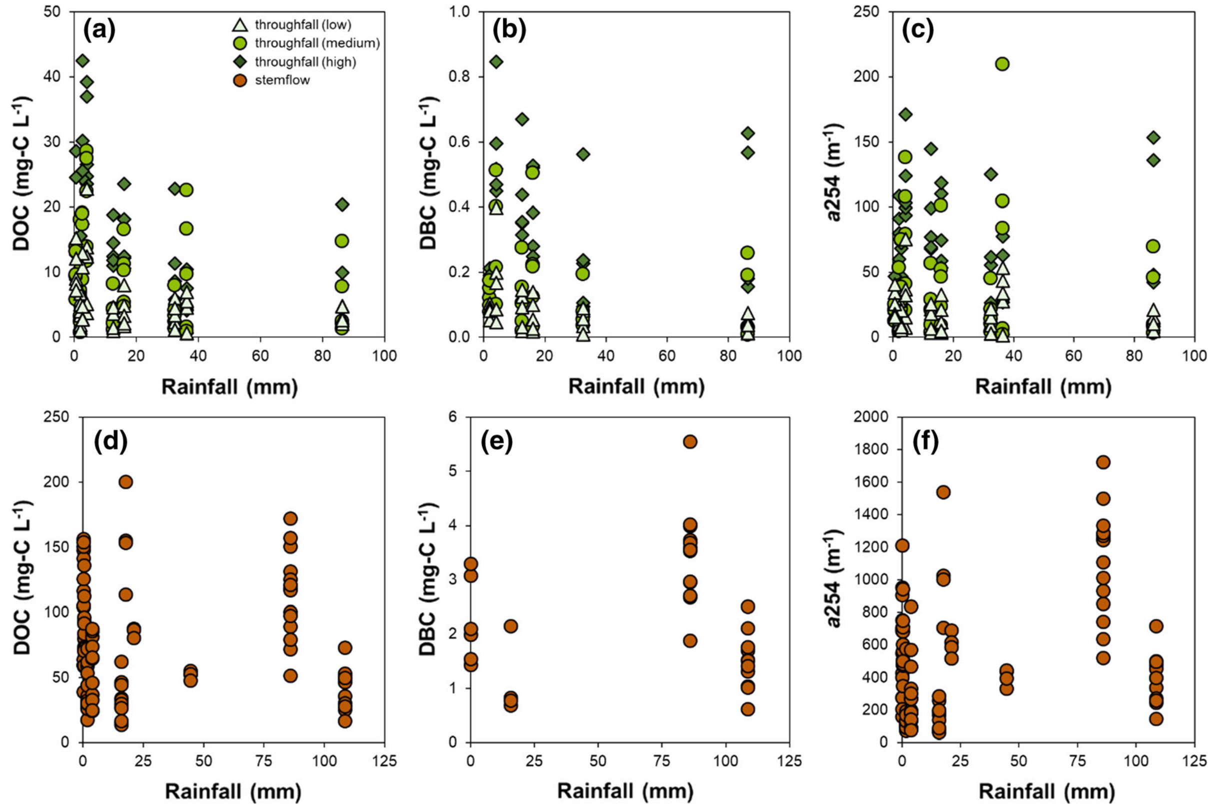

Fig. 4 Concentrations of dissolved organic carbon (DOC), dissolved black carbon (DBC), and chromophoric dissolved organic matter (Napierian absorption coefficient at 254 nm; *a*254) versus rainfall in throughfall (low canopy cover, light green triangles; medium canopy cover; green circles; high canopy cover; dark green diamonds) and stemflow (brown circles). (Color figure online)

stemflow). The slopes of the regressions (Fig. 6a–d) were used to generate annual yields of tree-derived DOC and DBC. Throughfall (under low and high cover) and stemflow yields were calculated per event, summed for each year, then yearly yields averaged to obtain annual fluxes. Errors associated with interannual rainfall variability were greater than regression-derived errors, and are included with the following flux estimates. Annual fluxes for throughfall were calculated using regressions for samples collected under low and high canopy cover, respectively (4 ± 1 to 13 ± 3 mg-DOC km^2 $year^{-1}$ and 50 ± 12 to 350 ± 80 kg-DBC km^2 $year^{-1}$). Annual fluxes for stemflow were roughly an order of magnitude less than for throughfall, totaling 0.6 ± 0.1 mg-DOC km^2 $year^{-1}$ and 19 ± 4 kg-DBC km^2 $year^{-1}$.

Discussion

Factors controlling bulk tree-DOM mobility and export

The interception and diversion of rainfall by tree canopies is controlled by a variety of environmental factors and forest characteristics including, leaf area, storage capacity, and meteorological conditions (Crockford and Richardson 2000). The observed partitioning of rainfall volume (Fig. 1) is consistent with those previously determined for throughfall and stemflow in a managed longleaf pine plantation (80% and 2%, respectively; Bryant et al. 2005) and falls within the range of rainfall partitioning values reported for a variety of forest types (throughfall, 60–90%; stemflow, 0.1–22%; Johnson and Lehmann 2006; Levia et al. 2011). Throughfall and stemflow recoveries indicate < 14% of rainfall is intercepted by

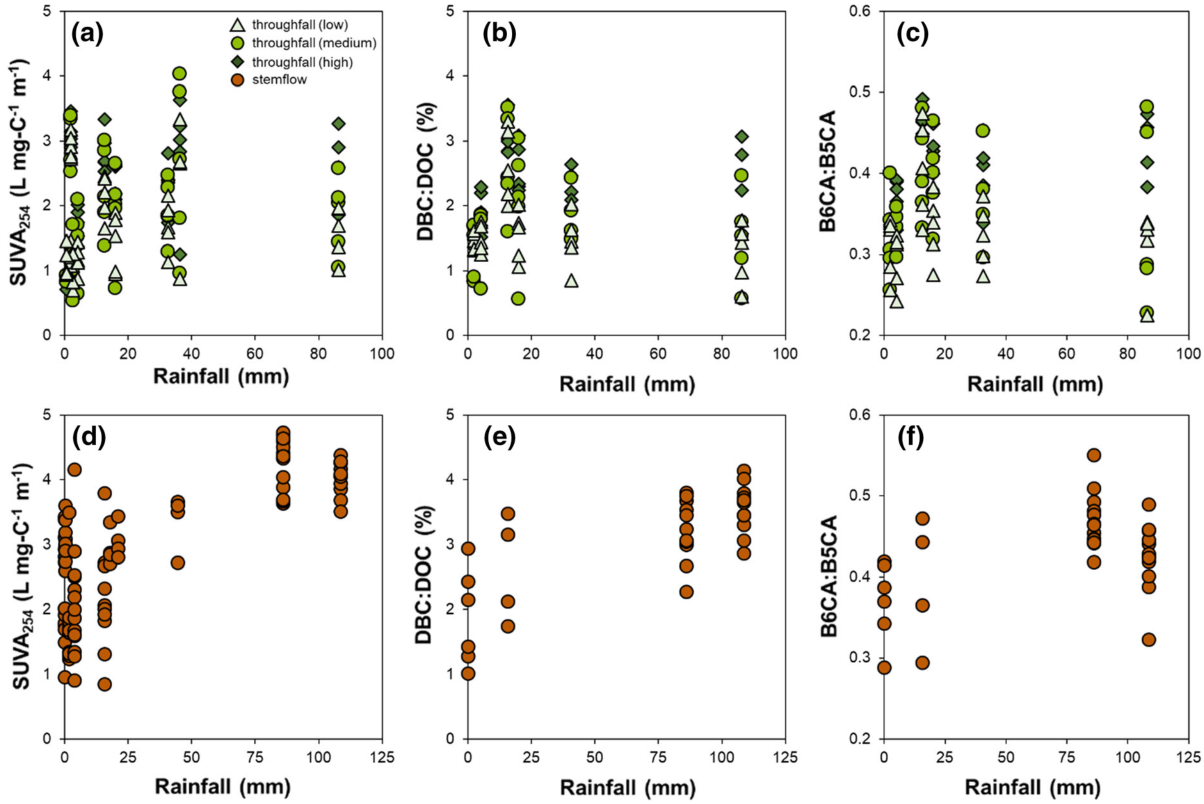

Fig. 5 Carbon-normalized absorbance at 254 nm ($SUVA_{254}$), the ratio of dissolved black carbon to dissolved organic carbon (DBC:DOC), and BPCA ratio (B6CA:B5CA) versus rainfall in throughfall (low canopy cover, light green triangles; medium canopy cover; green circles; high canopy cover; dark green diamonds) and stemflow (brown circles). (Color figure online)

longleaf and slash pines and stemflow represents a small hydrological flux for these woodland ecosystems. Stemflow DOC concentrations (73 ± 42 mg-C L^{-1}; Fig. 2a) generally exceeded those reported for other subtropical forest types (~ 24 mg-C L^{-1}; Van Stan and Stubbins 2018), spotlighting an important pathway for the delivery of tree-DOM to the basal area of longleaf and slash pines. Enrichments in throughfall DOM with increasing canopy cover (Fig. 2a–c) were likely due to the increased opportunity for rainfall to interact with long, needle-like leaves in areas of greater canopy cover. Low rainfall interception and rapid rinsing of DOM from coniferous canopies has been shown to result in high throughfall DOC concentrations in other subtropical pine forests (Bhat et al. 2011). Correspondingly, throughfall DOC concentrations observed here (Fig. 2a) are generally higher than those previously reported for subtropical forest types (~ 8 mg-C L^{-1}; Van Stan and Stubbins 2018).

Annual throughfall and stemflow DOC yields are within the range of those previously determined for a variety of tree species (Van Stan and Stubbins 2018), including DOC yields observed for other subtropical tree species (0.8–46 mg-DOC km^2 $year^{-1}$; Van Stan et al. 2017). Several biotic and abiotic factors influence the magnitude of tree-DOM yields. At the microscale, the texture of bark surfaces control flow paths of intercepted rainwater though the tree "catchment" and physico-chemical properties control the amount of DOM rinsed and leached from the tree (Guggenberger and Zech 1994; Van Stan et al. 2016). Local microbial communities participate in the degradation, uptake, and excretion of organic compounds (Vorholt 2012), which contribute to DOM in throughfall and stemflow. Tree phenology (e.g., leaf-on versus leaf-off in deciduous forests) can have a large impact on the seasonality of tree-DOM quality and quantity (Van Stan et al. 2012). Concentrations of throughfall and stemflow DOC remained relatively constant

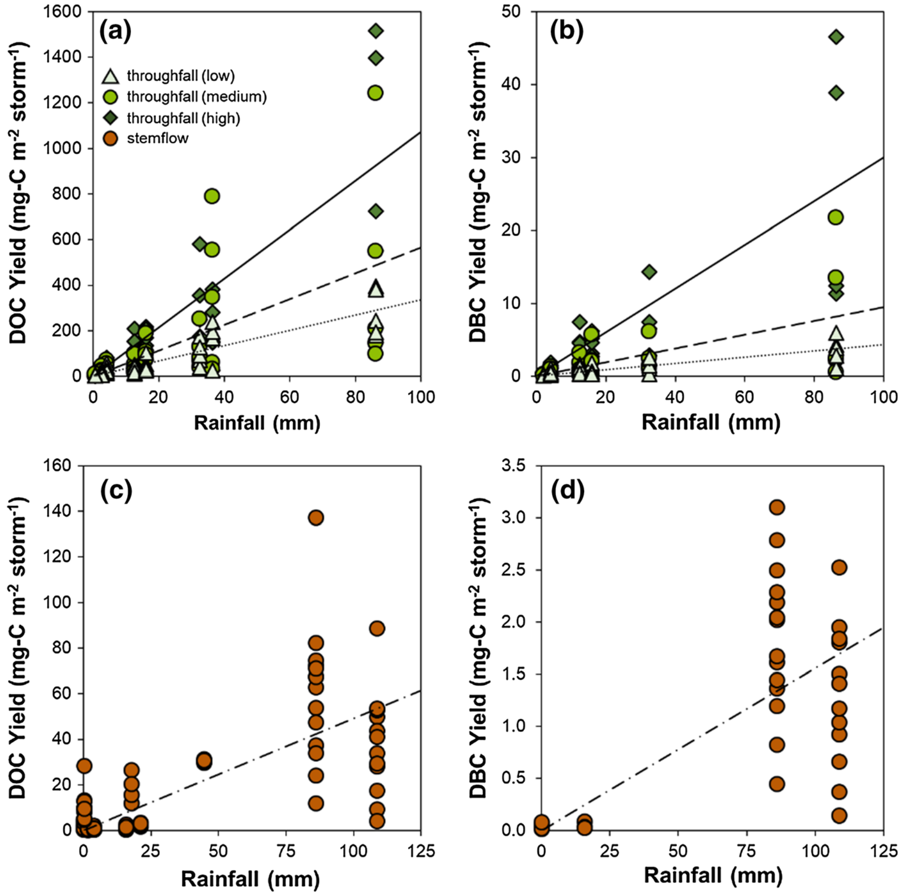

Fig. 6 Per storm event yields of dissolved organic carbon (DOC) and dissolved black carbon (DBC) versus rainfall in throughfall (low canopy cover, light green triangles; medium canopy cover; green circles; high canopy cover; dark green diamonds) and stemflow (brown circles). Intercepts were not statistically different from zero, therefore regression lines were forced through the origin. Linear relationships were significant ($p < 0.0001$) and used to extrapolate annual yields for tree-derived DBC and DOC. Slopes and standard errors for throughfall DOC yields in areas of low, medium, and high canopy cover were 3.4 ± 0.2, 5.7 ± 0.8, and 10.7 ± 0.8 mg-C m^{-2} mm^{-1}, respectively. The slope and standard error for stemflow DOC yields was 0.49 ± 0.03 mg-C m^{-2} mm^{-1}. Slopes and standard errors for throughfall DBC yields in areas of low (dotted line), medium (dashed line), and high (solid line) canopy cover were 0.043 ± 0.004, 0.095 ± 0.018, and 0.300 ± 0.035 mg-C m^{-2} mm^{-1}, respectively. The slope and standard error for stemflow DBC yields (dash dot line) was 0.016 ± 0.001 mg-C m^{-2} mm^{-1}. (Color figure online)

despite varying amounts of rainfall (Fig. 4a, d). As longleaf and slash pines retain needles year-round (Sheffield et al. 2003), phenologically driven differences in tree-DOM concentrations and quality are likely to be minimal compared to deciduous trees. The current study captured storms from February to July and included pollen shed (Boyer 1972), however pollen-driven variations in tree-DOM were not observed here. Additional sampling is needed to fully assess year-round, seasonally driven tree-DOM variations. However, storm size (rainfall depth) was shown to be the primary modulator of tree-DOM yields in longleaf pine woodlands (Fig. 6a–d). Since rainfall at the study site is evenly distributed throughout the year, and storm events captured in the current study span the range of storm event sizes typically observed for this area, then we would expect annual tree-DOM yields estimated for longleaf pine woodlands to remain within the range of what is reported here, even if additional storms were included.

Previous research examining variations in throughfall and stemflow DOC as a function of rainfall amount is limited to one study, in which DOC concentrations typically decreased exponentially with increasing storm size until a consistent concentration was reached for large storm events (Van Stan et al. 2017). The only exception was for epiphyte-covered live oak trees, where stemflow DOC concentrations increased linearly with storm size (Van Stan et al. 2017). Decreases in DOC concentration with increasing rainfall amounts were not observed for throughfall or stemflow in longleaf pine woodlands (Fig. 4a, d). Exponential decreases in throughfall and stemflow DOC with increasing storm size has been interpreted as trees containing a finite amount of leachable organic material that is depleted during a large storm event (Van Stan et al. 2017). However, the consistently high tree-DOM concentrations in throughfall and stemflow across a range of storm sizes observed here indicates longleaf pines contain a large repository of leachable organic matter that is not significantly diminished, even during storm events exceeding 80 mm of rainfall (Fig. 4a–f). This suggests that the hydrology and DOM biogeochemistry of longleaf pines and epiphyte-covered live oaks are similarly complex (Van Stan et al. 2017), behaving more like small river catchments containing a diversity of carbon stores and hydrological flow paths where increased water fluxes result in elevated amounts of DOM (Raymond and Saiers 2010; Yoon and Raymond 2012).

Aromatic quality of tree-DOM

$SUVA_{254}$ values observed for throughfall and stemflow (1.7–2.8 mg-C^{-1} m^{-1}; Fig. 3a) fall within the range of mean $SUVA_{254}$ values reported for U.S. rivers (1.3–4.6 mg-C^{-1} m^{-1}; Spencer et al. 2012), indicating longleaf pine tree-DOM is similarly enriched in aromatic carbon. Tree-DOM is comprised of a diverse population of molecular formulas consistent with vascular plant-derived organics (Stubbins et al. 2017). Lignin, a major structural component of vascular plants, and its degradation products are suggested to be one of the major aromatic components of tree-DOM (Guggenberger and Zech 1994). The degradation products of lignin can be enriched in bark-derived DOM (Guggenberger et al. 1994), providing one explanation for higher $SUVA_{254}$ values observed in stemflow than throughfall (Fig. 3a). Throughfall and stemflow $SUVA_{254}$ for longleaf pines were within the range of DOM leached from fresh vegetation (Van Stan et al. 2015; Wickland et al. 2007) and values reported previously for other forest types (Stubbins et al. 2017; Van Stan et al. 2017; Hernes et al. 2017; Inamdar et al. 2012). However, the wide range of $SUVA_{254}$ values for throughfall and stemflow (Fig. 3a) suggests hydrological flow paths for rainwater and how it interacts with canopy architecture and other tree surfaces is not consistent among storm events, and is supported by previous high-resolution spatiotemporal water isotope monitoring work (Hsueh et al. 2016).

The $SUVA_{254}$ of throughfall DOM did not vary significantly with amount of rainfall (Fig. 5a, S2a), suggesting sources and flow paths of DOM in longleaf pine canopies are similar among different storm events. However, stemflow $SUVA_{254}$ increased significantly with storm size (Fig. 5d, S2d), indicating different physico-chemical processes govern the dissolution and mobility of tree-DOM in stemflow. This enrichment in CDOM relative to bulk DOC is inconsistent with trends previously observed for subtropical oak and cedar species, in which $SUVA_{254}$ remained constant with increasing rainfall amounts (Van Stan et al. 2017). The dimensions, canopy structure, and bark texture of longleaf pine trees are quite different than oak and cedar, therefore we would expect relationships between DOM composition and rainfall amounts for each of these tree "catchments" to also differ. Higher stemflow $SUVA_{254}$ with increased storm size (Fig. 5d) indicate longleaf pine surfaces may need to undergo a certain degree of saturation by rainfall for the solubilization of aromatic DOM components. Longleaf pine bark is thick and scaly, and increased contributions of CDOM to DOC during large rain events suggests it takes a significant amount of rain ($>$ 75 mm) to sufficiently wet the trunk and rinse or leach tree-derived aromatic compounds (Fig. 5d–f). Therefore, we suggest that the composition of tree-DOM, particularly in stemflow, is primarily driven by meteorological conditions and storm intensity in longleaf pine woodlands. Similar relationships are observed between $SUVA_{254}$ and discharge in rivers, where these trends have been interpreted as indicating the enhanced mobilization of highly colored DOM from organic-rich surface soils that become saturated during periods of high flow (Schuster et al. 2008; Sanderman et al. 2009).

Sources of black carbon in tree-DOM

Higher DBC:DOC ratios in throughfall and stemflow compared to rainfall indicates dissolution and rinsing of charred organic material from tree surfaces (Fig. 3b). One might expect throughfall and stemflow DBC to be derived from charred areas of the tree itself. However, prescribed fires are low-intensity and near-ground (Certini 2005), unlike high-intensity fires which consume more biomass and can result in crown scorching (Van Wagner 1977). The charring of longleaf pine canopies was not observed, and direct charring of bark surfaces was restricted to low areas of the trunk. To facilitate sample collection, stemflow was diverted near breast-height, above much of the highly charred portion of the trunk. Therefore, we assume the majority of DBC measured in tree-DOM to be primarily derived from atmospheric deposition of thermally altered organics to the canopy and stem, rather than from the leaching of charred tree surfaces. Fine BC particles (< 2 µm) have long atmospheric lifetimes and can be deposited in regions far from the immediate burn area (Bond et al. 2004; Jurado et al. 2008). Coarse BC particles (> 150 µm) can become airborne, but do not travel far and are generally deposited to the immediate burn area (Oris et al. 2014). Coniferous trees efficiently remove atmospheric particulates (Yang et al. 2015) and BC aerosols have been shown to stick to tree needles (Yamane et al. 2012). A recent study also shows urban trees to be sinks for atmospheric soot, where the majority of BC captured accumulates on leaf surfaces (Rindy et al. 2019). Therefore, we would expect the needled canopies and roughed bark trunks characteristic of longleaf and slash pine trees to be effective filters of atmospheric particulates generated during regular prescribed burning. Aerosolized BC retained on the trunk and canopy would then be a source of tree-derived DBC upon interaction with rainwater during a storm event. The molecular components of tree-DOM are derived not only autochthonously from the tree itself, but also from allochthonous organics atmospherically deposited to leaf and bark surfaces (Guggenberger and Zech 1994). The identification of condensed aromatic molecular formulas in DOM sampled from unburned tree stands provides further evidence for contributions of atmospherically derived DBC to throughfall and stemflow (Stubbins et al. 2017).

If we assume the hydrology and biogeochemistry of trees are analogous to small river catchments, particularly those located in areas where prescribed burning is frequent, then we would also expect the accumulation of atmospherically deposited BC to serve as a continual source of DBC to throughfall and stemflow, consistent with observations for fire-affected watersheds (Dittmar et al. 2012; Wagner et al. 2015). The proportion of DBC in DOC and BPCA ratios may also be indicators of post-depositional biogeochemical processes that would enhance contributions of DBC to tree-DOM. Ratios of DBC:DOC and B6CA:B5CA are lower in rainfall than in throughfall and stemflow (Fig. 3a, b). Depletions in DBC and B6CA in rainfall is consistent with signatures of solubilized pyrogenic aerosols (Ding et al. 2015) having undergone some degree of photodegradation during atmospheric transit (Khan et al. 2017). Exposure to sunlight and other oxidative conditions have been shown to enhance the dissolution of charcoal and soot in water (Decesari et al. 2002; Roebuck et al. 2017). Similarly, the aging and oxidation of charcoal in soils has been shown to increase the proportion and degree of condensed aromaticity of leached DBC (Abiven et al. 2011; Wagner et al. 2017). Therefore, the photo-oxidation and/or aging of BC atmospherically deposited to tree surfaces may promote the solubilization of B6CA-enriched DBC observed in throughfall and stemflow (Fig. 3b, c). While ratios of DBC:DOC and B6CA:B5CA for throughfall did not vary with storm size (Fig. 5a–c), stemflow became enriched in DBC and B6CA with increased amounts of rainfall (Fig. 5d, e). The importance of tree hydrology in the mobilization of highly condensed aromatic compounds in stemflow was further evidenced by the significant increase in B6CA:B5CA for large storm events (> 50 mm; Fig. 5f, S2f). Similar enrichments in DBC and B6CA are observed during periods of high discharge and overland flow in river catchments (Stubbins et al. 2015; Wagner et al. 2015).

Contributions of throughfall and stemflow DBC to local pyrogenic carbon cycles

Frequent burning of managed longleaf pine woodlands is utilized to maintain the health and biodiversity of the ecosystem (Mitchell et al. 2014). The amount of charcoal produced during prescribed burning is small compared to atmospheric carbon losses (Alexis et al.

2007; Starr et al. 2015; Fig. 7), but results in frequent "pulses" of BC to soils where it accumulates to represent 5 to 7% of bulk soil organic carbon in longleaf pine woodlands (Butnor et al. 2017; Fig. 7). The atmospheric deposition of BC to terrestrial environments (Wozniak et al. 2011) is roughly an order of magnitude higher than to oceanic surface waters (Jurado et al. 2008). In areas of active fire, BC emissions to the atmosphere are expected to be elevated compared to globally averaged deposition to terrestrial environments, although these data remain poorly constrained (Santín et al. 2016). Based upon estimates for temperate watersheds, annual deposition of atmospheric BC (Wozniak et al. 2011) was on the same order of magnitude as the removal of DBC via throughfall and stemflow (Fig. 7). As pine woodland sites are frequently burned, it is likely that BC deposition to our study site is further elevated due to the generation of an additional aerosol BC load during prescribed burns. Therefore, we suggest that the atmospheric deposition of charred material from regional and local combustion processes would be enough to sustain a continual source of tree-derived DBC in longleaf pine ecosystems regularly maintained by fire. Annual throughfall plus stemflow DOC and DBC yields were small in comparison to aboveground net primary production (150–500 mg-C km^{-2} year^{-1}; Mitchell et al. 1999), but within the range of net ecosystem exchange in longleaf pine woodlands, which range from being carbon neutral (6 ± 33 mg-C km^{-2} year^{-1}) to a moderate net sink of carbon (− 160 ± 25 mg-C km^{-2} year^{-1}; Starr et al. 2015). Carbon stocks and annual carbon fluxes, including throughfall and stemflow DOC and DBC, for longleaf pine woodlands are summarized in Fig. 7. The aerial extent of longleaf pine woodlands is 17,400 km^2 (McIntyre et al. 2018). About 6000 km^2 of this total woodland area is mature and frequently burned (McIntyre et al. 2018), like the study site we describe here. Thus, annual tree-DOM yields estimated here are relevant to over one third of the remaining longleaf pine woodlands in the southeastern United States.

Tree-DOM within the context of river catchments

If a catchment is entirely forested by longleaf pine, annual throughfall plus stemflow DOC yields could be sufficient to account for DOC yields typical of major global rivers (0.4–9 mg-DOC km^{-2} year^{-1}; Raymond and Spencer 2015). Given low carbon yields, it is unlikely that throughfall and stemflow would significantly contribute to DOM in inland waters during small storm events (Fig. 6a–d). However, carbon yields increase during large storm events, when runoff could also provide a pathway for the rapid delivery of fresh, minimally degraded tree-DOM to inland waters. Annual yields of throughfall plus stemflow DBC in

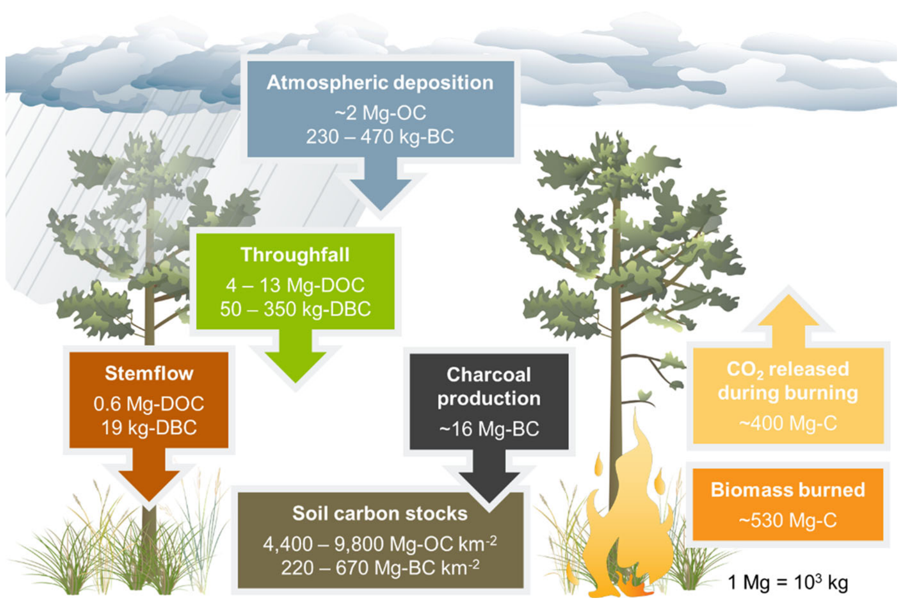

Fig. 7 Stocks and annual fluxes of carbon in longleaf pine woodlands (flux units are km^{-2} year^{-1}; stock units are km^{-2}). Throughfall and stemflow were determined in this study. Terrestrial atmospheric deposition rates from Wozniak et al. (2011). Soil carbon stocks from Butnor et al. (2017). Amount of CO_2 produced during burning from Starr et al. (2015). Biomass burned and amount converted to charcoal were estimated from Alexis et al. (2007)

fire-managed longleaf pine woodlands are similar to those of the Paraíba do Sul, a Brazilian river which drains a landscape cleared by intense slash-and-burn (50 kg-DBC km^{-2} year^{-1}; Dittmar et al. 2012), but low in comparison to riverine DBC yields quantified globally (Jaffé et al. 2013; Raymond and Spencer 2015). Low tree-DBC yields result from DBC comprising less than 4% of bulk DOC in throughfall and stemflow (Fig. 3b). These proportions are consistent with that of glacier-fed rivers, in which DBC is primarily sourced from atmospheric deposition (Ding et al. 2015), but low in comparison to rivers globally, where DBC comprises 10% of DOC on average (Jaffé et al. 2013).

The apparent coupling between DBC, DOC, and CDOM in throughfall and stemflow (Fig. S3a–d) is consistent with covariance observed in rivers (Jaffé et al. 2013; Stubbins et al. 2015). Linear regressions indicate that DBC only comprises about 2% of tree-derived DOC on average (Fig. S3a–b). Low DBC:DOC in throughfall and stemflow compared to rivers can be explained by (1) large inputs of non-DBC tree-DOC, (2) contrasting labilities of DBC and bulk tree-DOC, and/or (3) overwhelming soil DOM signatures in-stream. Atmospherically deposited DBC that is rinsed from canopy or trunk surfaces is quickly diluted by overwhelming inputs of fresh DOC leached from the tree itself, as seen from low DBC:DOC in smaller storm events (Fig. 5e). Bulk tree-DOC is highly biolabile, where up to 70% of DOC is mineralized within just a few days (Howard et al. 2018). The high biolability of tree-DOC is in stark contrast with the apparent long-term recalcitrance of condensed aromatics in soil (Kuzyakov et al. 2014) and the deep ocean (Coppola and Druffel 2016). Therefore, while bulk tree-DOM would provide a carbon subsidy to local microbial communities at the forest floor (Howard et al. 2018), preferential biodegradation of non-DBC components would result in an enrichment of tree-DBC relative to tree-DOC in soils. Bio-refractory DBC comprises ~ 2% of bulk DOC (Fig. S3a, b). If 70% of the non-DBC tree-DOC is removed via biodegradation (Howard et al. 2018), bio-refractory DBC would then comprise a larger portion (~ 7%) of the 31% of bulk DOC that remains after processing. The resulting ~ 7% DBC:DOC ratio is similar to what is observed for some rivers (Jaffé et al. 2013). During storm events, throughfall and stemflow contribute to in-stream discharge (Inamdar et al. 2013). However, in-stream tree-DBC inputs are likely to be overwhelmed by inputs from soils, where accumulated BC is mobilized to inland waters at much greater loads (Wagner et al. 2018).

Conclusions

Throughfall and stemflow were enriched in DOM, representing a local source of carbon to longleaf pine woodland soils. Tree-DOM was enriched in CDOM, however condensed aromatic DBC comprised only 2% of bulk DOC on average, a much smaller proportion than is typically observed for DOM in other freshwater environments. Stemflow DOC became enriched in DBC and CDOM with increased rainfall amounts, indicating solubilization of highly aromatic DOM components increased as tree surfaces became more saturated with water. Concentrations of tree-derived DOC and DBC did not vary with storm size, suggesting longleaf pines contain a large repository of leachable organic material that is not significantly diminished, even during heavy rain events. Carbon yields increased significantly with storm size, enabling annual flux estimates for throughfall and stemflow (4 mg-DOC km^{-2} year^{-1} under low canopy cover to 13 mg-DOC km^{-2} year^{-1} under dense canopy cover and 0.6 mg-DOC km^{-2} year^{-1}, respectively). Annual yields of DBC in throughfall and stemflow (50–350 kg-DBC km^{-2} year^{-1} and 19 kg-DBC km^{-2} year^{-1}, respectively) were less than for DOC, and on the same order of magnitude as fluxes estimated for the atmospheric deposition of BC to terrestrial environments. The hydrology and biogeochemistry of trees are analogous to small river catchments in how tree-DOM, including DBC, is mobilized by rainfall. Therefore, we would expect the accumulation of atmospherically deposited charcoal, particularly in longleaf pine woodlands where prescribed burning is frequent, to be a continual source of DBC in throughfall and stemflow, consistent with what is observed in fire-affected watersheds.

Acknowledgements This work is supported by National Science Foundation Grants DEB #1824613 and EAR #1518726 and the Jones Center at Ichauway. M. Belovitch, D. Cross, M. Hederman, and R. Ritger are thanked for their hard work on sample prep, collection, and processing, and we especially appreciate E. Rea's efforts on coordinating all of the above and ensuring prompt deliveries of samples. We thank J.

Brandes at the University of Georgia, Skidaway Institute of Oceanography for the use of his HPLC instrument for analyses.

References

Abiven S, Hengartner P, Schneider MPW, Singh N, Schmidt MWI (2011) Pyrogenic carbon soluble fraction is larger and more aromatic in aged charcoal than in fresh charcoal. Soil Biol Biochem 43:1615–1617

Alexis MA, Rasse DP, Rumpel C, Bardoux G, Pechot N, Schmalzer P, Drake B, Mariotti A (2007) Fire impact on C and N losses and charcoal production in a scrub oak ecosystem. Biogeochem 82:201–216. https://doi.org/10.1007/s10533-006-9063-1

Bhat S, Jacobs JM, Bryant ML (2011) The chemical composition of rainfall and throughfall in five forest communities: a case study in Fort Benning, Georgia. Water Air Soil Pollut 218:323–332. https://doi.org/10.1007/s11270-010-0644-1

Bond TC, Streets DG, Yarber KF, Nelson SM, Woo JH, Klimont Z (2004) A technology-based global inventory of black and organic carbon emissions from combustion. J Geophys Res. https://doi.org/10.1029/2003JD003697

Boyer WD (1972) Air temperature, heat sums, and pollen shedding phenology of longleaf pine. Ecology 54:420–426

Bryant ML, Bhat S, Jacobs JM (2005) Measurements and modeling of throughfall variability for five forest communities in the southeastern US. J Hydrol 312:95–108

Butnor JR, Samuelson LJ, Johnsen KH, Anderson PH, Benecke CAG, Boot CM, Cotrufo MF, Heckman KA, Jackson JA, Stokes TA, Zarnoch SJ (2017) Vertical distribution and persistence of soil organic carbon in fire-adapted longleaf pine forests. Forest Ecol Manag 390:15–26

Certini G (2005) Effects of fire on properties of forest soils: a review. Oecologia 143:1–10

Coppola AI, Druffel ERM (2016) Cycling of black carbon in the ocean. Geophys Res Lett 43:4477–4482. https://doi.org/10.1002/2016GL068574

Crockford RH, Richardson DP (2000) Partitioning of rainfall into throughfall, stemflow and interception: effect of forest type, ground cover and climate. Hydrol Process 14:2903–2920

Decesari S, Facchini MC, Matta E, Mircea M, Fuzzi S, Chughtai AR, Smith DM (2002) Water soluble organic compounds formed by oxidation of soot. Atmos Environ 36:1827–1832

Ding Y, Yamashita Y, Jones J, Jaffé R (2015) Dissolved black carbon in boreal forest and glacial rivers of central Alaska: assessment of biomass burning versus anthropogenic sources. Biogeochem 123:15–25. https://doi.org/10.1007/s10533-014-0050-7

Dittmar T (2008) The molecular level determination of black carbon in marine dissolved organic matter. Org Geochem 39:396–407

Dittmar T, Koch B, Hertkorn N, Kattner G (2008) A simple and efficient method for the solid-phase extraction of dissolved organic matter (SPE-DOM) from seawater. Limnol Oceanogr- Methods 6:230–235

Dittmar T, de Rezende CE, Manecki M, Niggemann J, Ovalle ARC, Stubbins A, Bernardes MC (2012) Continuous flux of dissolved organic carbon from a vanished tropical forest biome. Nat Geosci 5:618–622

Friesen J, Lundquist J, Van Stan JT (2015) Evolution of forest precipitation water storage measurement methods. Hydrol Process 29:2504–2520. https://doi.org/10.1002/hyp.10376

Guggenberger G, Zech W (1994) Composition and dynamics of dissolved carbohydrates and lignin-degradation products in two coniferous forests, N.E. Bavaria, Germany. Soil Biol Biochem 26:19–27. https://doi.org/10.1016/0038-0717(94)90191-0

Guggenberger G, Zech W, Schulten HR (1994) Formation and mobilization pathways of dissolved organic matter: Evidence from chemical structural studies of organic matter fractions in acid forest floor solutions. Org Geochem 21:51–66. https://doi.org/10.1016/0146-6380(94)90087-6

Hammes K et al (2007) Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. Global Biogeochem Cy. https://doi.org/10.1029/2006GB002914

Hernes PJ, Spencer RGM, Dyda RY, O'Geen AT, Dahlgren RA (2017) The genesis and exodus of vascular plant DOM from an oak woodland landscape. Front Earth Sci. https://doi.org/10.3389/feart.2017.00009

Howard DH, Van Stan JT, Whitetree A, Zhu L, Stubbins A (2018) Interstorm variability in the biolability of tree-derived dissolved organic matter (tree-DOM) in throughfall and stemflow. Forests 9:236. https://doi.org/10.3390/f9050236

Hsueh YH, Allen ST, Keim RF (2016) Fine-scale spatial variability of throughfall amount and isotopic composition under a hardwood forest canopy. Hydrol Process 30:1796–1803

Hu C, Muller-Karger FE, Zepp RG (2002) Absorbance, absorption coefficient, and apparent quantum yield: a comment on common ambiguity in the use of these optical concepts. Limnol Oceanogr 47:1261–1267

Inamdar S, Finger N, Singh S, Mitchell M, Levia D, Bais H, Scott D, McHale P (2012) Dissolved organic matter (DOM) concentration and quality in a forested mid-Atlantic watershed, USA. Biogeochem 108:55–76. https://doi.org/10.1007/s10533-011-9572-4

Inamdar S, Dhillon G, Singh S, Dutta S, Levia DF, Mitchell MJ, Van Stan J, McHale P (2013) Temporal variation in end-member chemistry and its influence on runoff mixing patterns in a forested, Piedmont catchment. Water Resour Res 49:1828–1844. https://doi.org/10.1002/wrcr.20158

Jaffé R, Ding Y, Niggeman J, Vähätalo AV, Stubbins A, Spencer RGM, Campbell J, Dittmar T (2013) Global charcoal mobilization via dissolution and riverine transport to the oceans. Science 340:345–347

Johnson MS, Lehmann J (2006) Double-funneling of trees: stemflow and root-induced preferential flow. Ecoscience 13:324–333. https://doi.org/10.2980/i1195-6860-13-3-324.1

Jurado E, Dachs J, Duarte CM, Simo R (2008) Atmospheric deposition of organic and black carbon in the global oceans. Atmos Environ 42:7931–7939

Khan AL, Wagner S, Jaffé R, Xian P, Williams M, Armstrong R, McKnight D (2017) Dissolved black carbon in the global cryosphere: concentrations and chemical signatures.

Geophys Res Lett 44:6226–6234. https://doi.org/10.1002/2017GL073485
Kirkman LK, Jack SB (2017) Ecological restoration and management of longleaf pine forests, 1st edn. CRC Press, Boca Raton
Kuhlbusch TA, Crutzen PJ (1995) Toward a global estimate of black carbon in residues of vegetation fires representing a sink of atmospheric CO_2 and a source of O_2. Global Biogeochem Cy 9:491–501
Kuzyakov Y, Bogomolova I, Glaser B (2014) Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific ^{14}C analysis. Soil Biol Biochem 70:229–236
Levia DF, Keim RF, Carlyle-Moses DE, Frost EE (2011) Throughfall and stemflow in wooded ecosystems. In: Levia DF, Carlyle-Moses DE, Tanaka T (eds) Forest hydrology and biogeochemistry: synthesis of past research and future directions. Springer, Heidelberg, pp 425–443
Levia DF, Van Stan JT, Inamdar SP, Jarvis MT, Mitchell MJ, Mage SM, Scheik CE, McHale PJ (2012) Stemflow and dissolved organic carbon cycling: temporal variability in concentration, flux, and UV-Vis spectral metrics in a temperate broadleaved deciduous forest in the eastern United States. Can J Forest Res 42:207–216. https://doi.org/10.1139/x11-173
Masiello CA (2004) New directions in black carbon organic geochemistry. Mar Chem 92:201–213
McIntyre RK, Guldin JM, Ettel T, Ware C, Jones K (2018) Restoration of longleaf pine in the southern United States: a status report. In: Kirschman JE (comp) Proceedings of the 19th Biennial Southern Silvicultural Research Conference, General Technical Report SRS-234, USDA, Forest Service, Southern Research Station, Asheville, North Carolina, pp 297–302
Mitchell RJ, Kirkman LK, Pecot SD, Wilson CA, Palik BJ, Boring LR (1999) Patterns and controls of ecosystem function in longleaf pine-wiregrass savannas. I. Aboveground net primary productivity. Can J For Res 29:743–751
Mitchell RJ, Liu Y, O'Brien JJ, Elliott KJ, Starr G, Miniat CF, Hiers JK (2014) Future climate and fire interactions in the southeastern region of the United States. Forest Ecol Manag 327:316–326
Oris F, Ali AA, Asselin H, Paradis L, Bergeron Y, Finsinger W (2014) Charcoal dispersion and deposition in boreal lakes from 3 years of monitoring: differences between local and regional fires. Geophys Res Lett 41:6743–6752. https://doi.org/10.1002/2014GL060984
Peel MC, Finlayson BL, McMahon TA (2007) Updated world map of the Koppen-Geiger climate classification. Hydrol Earth Syst Sc 11:1633–1644
Randerson JT, Chen Y, van der Werf GR, Rogers BM, Morton DC (2012) Global burned area and biomass burning emissions from small fires. J Geophyis Res. https://doi.org/10.1029/2012JG002128
Raymond PA, Saiers JE (2010) Event controlled DOC export from forested watersheds. Biogeochem 100:197–209. https://doi.org/10.1007/s10533-010-9416-7
Raymond PA, Spencer RGM (2015) Riverine DOM. In: Hansell DA, Carlson CA (eds) Biogeochemistry of marine dissolved organic matter, 2nd edn. Elsevier, Oxford, pp 509–533
Reisser M, Purves RS, Schmidt MWI, Abiven S (2016) Pyrogenic carbon in soils: a literature-based inventory and a global estimation of its content in soil organic carbon and stocks. Front Earth Sci 4:80. https://doi.org/10.3389/feart.2016.00080
Rindy JE, Ponette-Gonzalez AG, Barrett TE, Sheesley RJ, Weathers KC (2019) Urban trees are sinks for soot: elemental carbon accumulation by two widespread oak species. Environ Sci Technol 53:10092–10101. https://doi.org/10.1021/acs.est.9b02844
Roebuck JA, Podgorski DC, Wagner S, Jaffé R (2017) Photodissolution of charcoal and fire-impacted soil as a potential source of dissolved black carbon in aquatic environments. Org Geochem 112:16–21. https://doi.org/10.1016/j.orggeochem.2017.06.018
Roth PJ, Lehndorff E, Brodowski S, Bornemann L, Sánchez-García L, Gustafsson O, Amelung W (2012) Differentiation of charcoal, soot and diagenetic carbon in soil: method comparison and perspectives. Org Geochem 46:66–75
Sanderman J, Lohse KA, Baldock JA, Amundson R (2009) Linking soils and streams: sources and chemistry of dissolved organic matter in a small coastal watershed. Water Resour Res. https://doi.org/10.1029/2008WR006977
Santín C, Doerr SH, Kane ES, Masiello CA, Ohlson M, De La Rosa JM, Preston CM, Dittmar T (2016) Towards a global assessment of pyrogenic carbon from vegetation fires. Glob Change Biol 22:67–91. https://doi.org/10.1111/gcb.12985
Schmidt MWI, Noack AG (2000) Black carbon in soils and sediments: analysis, distribution, implications, and current challenges. Global Biogeochem Cy 14:777–793. https://doi.org/10.1029/1999GB001208
Schneider MPW, Hilf M, Vogt UF, Schmidt MWI (2010) The benzene polycarboxylic acid (BPCA) pattern of wood pyrolyzed between 200°C and 1000°C. Org Geochem 41:1082–1088
Schuster PF, Shanley JB, Marvin-Dipasquale M, Reddy MM, Aiken GR, Roth DA, Taylor HE, Krabbenhoft DP, DeWild JF (2008) Mercury and organic carbon dynamics during runoff episodes from a northeastern USA watershed. Water Air Soil Pollut 187:89–108
Sheffield MCP, Gagnon JL, Jack SB, McConville DJ (2003) Phenological patterns of mature longleaf pine (*Pinus palustris* Miller) under two different soil moisture regimes. Forest Ecol Manag 179:157–167
Spencer RGM, Butler KD, Aiken GR (2012) Dissolved organic carbon and chromophoric dissolved organic matter properties of rivers in the USA. J Geophys Res. https://doi.org/10.1029/2011JG001928
Starr G, Staudhammer CL, Loescher HW, Mitchell R, Whelan A, Hiers JK, O'Brien JJ (2015) Time series analysis of forest carbon dynamics: recovery of Pinus palustris physiology following a prescribed fire. New Forest 46:63–90
Stubbins A, Dittmar T (2012) Low volume quantification of dissolved organic carbon and dissolved nitrogen. Limnol Oceanogr-Meth 10:347–352. https://doi.org/10.4319/lom.2012.10.347
Stubbins A, Spencer RGM, Mann PJ, Holmes RM, McClelland JW, Niggemann J, Dittmar T (2015) Utilizing colored dissolved organic matter to derive dissolved black carbon

export by arctic rivers. Front Earth Sci 3:63. https://doi.org/10.3389/feart.2015.00063

Stubbins A, Silva LM, Dittmar T, Van Stan JT (2017) Molecular and optical properties of tree-derived dissolved organic matter in throughfall and stemflow from live oak and eastern red cedar. Front Earth Sci. https://doi.org/10.3389/feart.2017.00022

van der Werf GR, Randerson JT, Giglio L, Collatz GJ, Mu M, Kasibhatla PS, Morton DC, DeFries RS, Jin Y, van Leeuwen TT (2010) Global fire emissions and the contribution of deforestation, savanna, forest, agricultural, and peat fires (1997–2009). Atmos Chem Phys 10:11707–11735. https://doi.org/10.5194/acp-10-11707-2010

Van Wagner CE (1977) Conditions for the start and spread of crown fire. Can J For Res 7:23–34

Van Stan JT, Stubbins A (2018) Tree-DOM: Dissolved organic matter in throughfall and stemflow. Limnol Oceanogr-Lett 3:199–214

Van Stan JT, Levia DF, Inamdar SP, Lepori-Bui M, Mitchell MJ (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. https://doi.org/10.1016/j.scitotenv.2012.04.060

Van Stan JT, Stubbins A, Bittar T, Reichard JS, Wright KA, Jenkins RB (2015) Tillandsia usneoides (L.) L. (Spanish moss) water storage and leachate characteristics from two maritime oak forest settings. Ecohydrology 8:988–1004. https://doi.org/10.1002/eco.1549

Van Stan JT, Lewis ES, Hildebrandt A, Rebmann C, Friesen J (2016) Impact of interacting bark and rainfall conditions on stemflow variability in a temperate beech-oak forest, Central Germany. Hydrolog Sci J 61:2071–2083. https://doi.org/10.1080/02626667.2015.1083104

Van Stan JT, Wagner S, Guillemette F, Whitetree A, Lewis J, Silva L, Stubbins A (2017) Temporal dynamics in the concentration, flux, and optical properties of tree-derived dissolved organic matter (tree-DOM) in an epiphyte-laden oak-cedar forest. J Geophys Res Biogeosci. https://doi.org/10.1002/2017JG004111

Vorholt JA (2012) Microbial life in the phyllosphere. Nat Rev Microbiol 10:828–840. https://doi.org/10.1038/nrmicro2910

Wagner S, Cawley KM, Rosario-Ortiz F, Jaffé R (2015) In-stream sources and links between particulate and dissolved black carbon following a wildfire. Biogeochem 124:145–161

Wagner S, Brandes J, Goranov AI, Drake TW, Spencer RGM, Stubbins A (2017) Online quantification and compound-specific stable isotopic analysis of black carbon in environmental matrices via liquid chromatography-isotope ratio mass spectrometry. Limnol Oceanogr-Meth 15:995–1006. https://doi.org/10.1002/lom3.10219

Wagner S, Jaffé R, Stubbins A (2018) Dissolved black carbon in aquatic ecosystems. Limnol Oceanogr Lett 3:168–185. https://doi.org/10.1002/lol2.10076

Weishaar JL, Aiken GR, Bergamaschi BA, Fram MS, Fugii R, Mopper K (2003) Evaluation of specific ultraviolet absorbance as an indicator of chemical composition and reactivity of dissolved organic carbon. Environ Sci Technol 37:4702–4708. https://doi.org/10.1021/es030360x

Wickland KP, Neff JC, Aiken GR (2007) Dissolved organic carbon in Alaskan boreal forests: Sources, chemical characteristics, and biodegradability. Ecosystems 10:1323–1340. https://doi.org/10.1007/s10021-007-9101-4

Wozniak AS, Bauer JE, Dickhut RM (2011) Fossil and contemporary aerosol particulate organic carbon in the eastern United States: Implications for deposition and inputs to watersheds. Global Biogeochem Cy. https://doi.org/10.1029/2010GB003855

Yamane K, Nakaba S, Yamaguchi M, Kuroda K, Sano Y, Lenggoro IW, Izuta T, Funada R (2012) Visualization of artificially deposited submicron-sized aerosol particles on the surfaces of leaves and needles. Asian J Atmos Environ 6–4:275–280. https://doi.org/10.5572/ajae.2012.6.4.275

Yang J, Chang Y, Yan P (2015) Ranking the suitability of common urban tree species for controlling $PM_{2.5}$ pollution. Atmos Pollut Res 6:267–277

Yoon B, Raymond PA (2012) Dissolved organic matter export from a forested watershed during Hurricane Irene. Geophys Res Lett. https://doi.org/10.1029/2012GL052785