

Linking LiDAR with streamwater biogeochemistry in coastal temperate rainforest watersheds

Jason B. Fellman, Brian Buma, Eran Hood, Richard T. Edwards, and David V. D'Amore

Abstract: The goal of this study was to use watershed characteristics derived from light detection and ranging (LiDAR) data to predict stream biogeochemistry in Perhumid Coastal Temperate Rainforest (PCTR) watersheds. Over a 2-day period, we sampled 37 streams for concentrations of dissolved C, N, P, major cations, and measures of dissolved organic matter quality (specific ultraviolet absorbance, $SUVA_{254}$) and bioavailability. Random forest – classification and regression tree analysis showed that aboveground biomass and structure and watershed characteristics, inclusive of mean watershed slope and elevation, watershed size, and topographic wetness, explained more than 60% of the variation in concentration for most measured constituents. These results indicate this approach may be particularly useful for predicting stream biogeochemistry in small forested watersheds where fine resolution is needed to resolve subtle differences in forest biomass, structure, and topography. Overall, we suggest that the use of LiDAR in many of the small and remote watersheds across the Southeast Alaskan PCTR as well as other forested regions could help inform land management decisions that have the potential to alter ecosystems services related to watershed biogeochemical fluxes.

Résumé : L'étude avait pour but d'utiliser des caractéristiques des bassins versants tirées de données de lidar pour prédire la biogéochimie de cours d'eau dans des bassins versants de la forêt pluviale tempérée du littoral du Pacifique (FPTLP). Sur une période de 2 jours, nous avons échantillonné 37 cours d'eau pour en déterminer les concentrations de C, N et P dissous et des cations majeurs, et mesurer la qualité (absorbance UV spécifique, $SUVA_{254}$) de la matière organique dissoute et la biodisponibilité. L'analyse de forêt aléatoire – d'arbre de classification montre que la biomasse et la structure en surface et les caractéristiques du bassin versant, y compris la pente moyenne, l'élévation moyenne, la taille et l'humidité topographique, expliquent plus de 60% des variations des concentrations pour la plupart des paramètres mesurés. Ces résultats indiquent que cette approche pourrait s'avérer particulièrement utile pour prédire la biogéochimie des cours d'eau dans les petits bassins versants forestiers où une haute résolution est nécessaire pour distinguer des variations subtiles de la biomasse forestière, de la structure et de la topographie. En général, nous postulons que l'utilisation du lidar dans bon nombre des petits bassins versants isolés de la FPTLP du sud-est de l'Alaska, ainsi que dans d'autres régions forestières, pourrait éclairer des décisions d'aménagement du territoire qui ont le potentiel de modifier des services écosystémiques associés aux flux biogéochimiques dans les bassins versants. [Traduit par la Rédaction]

Introduction

Stream export of terrestrial-derived dissolved organic matter (DOM) is increasingly being recognized as an important component of watershed-scale carbon cycling because of impacts to the carbon balance of terrestrial ecosystems, especially over decadal time scales (Cole et al. 2007). Riverine DOM also acts as a vector for nitrogen (N), phosphorus (P), trace metals, and contaminants (Qualls and Richardson 2003; Pellerin et al. 2004; Lidman et al. 2014), making the terrestrial-aquatic flux of DOM an important control on the ecology (e.g., heterotrophic metabolism) and chemical properties (e.g., pH) of aquatic ecosystems (Dallzell et al. 2005; Wiegner et al. 2005). These ecological qualities of DOM vary with its chemical quality and bioavailability. Hence, DOM derived from different watershed sources (e.g., urban runoff, wetland and forest soils) may have different impacts on aquatic ecosystem processes (Kaplan and Bott 1985; Williams et al. 2010).

Streamwater DOM, measured as dissolved organic carbon (DOC), and nutrient concentrations (N and P) are controlled by multiple watershed characteristics, including landscape–soil type, land-use history, watershed size, and vegetation (Clark et al. 2004; Kaplan

et al. 2006; Tank et al. 2012). Wetlands are a well-recognized source of DOM and nutrients to streams, and many studies have used watershed wetland coverage as a first-order approximation of DOC concentrations (Dillon and Molot 1997; Gergel et al. 1999; D'Amore et al. 2015). However, wetland coverage alone cannot predict the spatial and temporal variability in streamwater DOM (Ågren et al. 2007). This is particularly true as watersheds increase in size and complexity and as varying ecological factors (e.g., species composition, cover type) influence the availability of soluble DOM for export to streams. Moreover, streamwater DOM and nutrient fluxes are being altered in many regions as a result of forest conversion (Stanley and Maxted 2008; Moore et al. 2013; Regnier et al. 2013) urban development (Pellerin et al. 2004; Petrone 2010), and hydrologic modification (Miller 2012). Thus, quantifying DOM and nutrient export from varied landscape types helps elucidate how topography, biological factors (e.g., aboveground biomass), and land use change impact stream carbon export.

There has been much research over the last several decades attempting to relate landscape characteristics to stream biogeochemistry (Dillon and Molot 1997; Mattsson et al. 2005; Stanley

Received 18 March 2016. Accepted 23 August 2016.

J.B. Fellman. Environmental Science Program and Alaska Coastal Rainforest Center, University of Alaska Southeast, Juneau, AK 99801, USA.

B. Buma and E. Hood. Environmental Science Program, University of Alaska Southeast, Juneau, AK 99801, USA.

R.T. Edwards and D.V. D'Amore. USDA Forest Service, Pacific Northwest Research Station, Juneau, AK 99801, USA.

Corresponding author: Jason Fellman (email: jbfellman@alaska.edu).

Copyright remains with the author(s) or their institution(s). Permission for reuse (free in most cases) can be obtained from [RightsLink](http://RightsLink.com).

and Maxted 2008). Yet, many of these landscape analyses have had mixed success in predicting stream biogeochemical concentrations (Frost et al. 2006; Cuevas et al. 2006). Thus, new tools for predicting streamwater biogeochemistry at the watershed scale are necessary, particularly for improving land management as it pertains to biogeochemical cycling. LiDAR (light detection and ranging) is a remote sensing technology commonly used to acquire topography of the ground surface (bare earth) and vegetation structure (surface model) at fine spatial resolution over large scales. Recent research has highlighted the ability of LiDAR to model forest biomass, structure, and composition (Hudak et al. 2012). LiDAR has also been useful for estimating DOC concentrations in boreal forest streams using contributing landscape components because it provides a robust level of detail for watershed characteristics such as slope and watershed surface area (Creed et al. 2008; Ågren et al. 2014). Being able to use LiDAR as a predictive tool would be especially beneficial in heterogeneous landscapes such as the Perhumid Coastal Temperate Rainforest (PCTR) of Southeast Alaska where small headwater streams are abundant, poorly accessible for sampling, and estimated to contain some of the highest areal DOC fluxes in the world (D'Amore et al. 2015).

The goal of this study was to use watershed landcover characteristics derived from LiDAR data, such as biomass, watershed morphology, and relative disturbance exposure, to predict stream biogeochemistry in PCTR watersheds. Over a 2-day period, we sampled 37 streams draining small subwatersheds and analyzed the surface water for N, P, major cations, DOM concentration, quality (as measured by the specific ultraviolet absorbance, $SUVA_{254}$) and bioavailability. Linking high-resolution forest structural information with stream biogeochemical concentrations is a relatively novel application of LiDAR, which could provide an improved method for estimating the land-to-ocean flux of DOM and nutrients in this region. We also measured stable isotopes of water ($\delta^{18}O$) in all study streams to help identify watershed sources of streamwater and their potential influence on stream biogeochemistry.

Methods

Site description and field methods

Streamwater was collected from the Cowee Creek watershed located on the western margin of the 3800 km² Juneau Icefield. The research watershed is part of the USDA Forest Service Héén Latinee Experimental Forest, near Juneau, Alaska (Fig. 1). Juneau has a moderate maritime climate with persistent cloud cover and a mean monthly temperature at sea level ranging from -2 to 14 °C. Numerous glacial epochs have sculpted the Coast Mountains of Southeast Alaska leaving steep-sloping watersheds with serrated ridges creating an orographic barrier that results in a mean annual precipitation at sea level in Juneau of ~2100 mm but is estimated to be as high as 5000 mm at higher elevations. Most of this precipitation falls as rain during large frontal storms in autumn (August–November) or as snow at high elevations during the winter. Southeast Alaska also contains extensive lowlands containing carbon-rich peatlands mixed with coniferous forest resulting in some of the densest terrestrial carbon stocks (>300 Mg C·ha⁻¹) in the world (Heath et al. 2011). Soil carbon densities in the region's abundant wetlands can be as high as 600 Mg C·ha⁻¹ (Johnson et al. 2011).

The 118 km² Cowee Creek watershed contains three hanging glaciers, with 13% of the watershed covered by glacier ice, 57% covered by forest, and 5% covered by wetlands (Fellman et al. 2014b). The remainder of the watershed consists of alpine landscapes. Mean watershed elevation is 638 m, with a mean slope of 23°. The upper reaches of the watershed are characterized by recently deglaciated terrain with high alpine tundra, exposed bedrock, poorly developed soils, and little vascular vegetation. At mid to lower elevations, the landscape is older, consisting of mixed coniferous forest dominated by *Picea sitchensis* and *Tsuga heterophylla* with an understory of blueberry (*Vaccinium* spp.) on moderate slopes and

well-drained flat lands and *Alnus* spp. along avalanche–landslide paths and riparian areas. In low-gradient areas that are poorly drained, forested and unforest wetlands develop: forested dominated by *P. sitchensis* and *T. heterophylla* with an understory of skunk cabbage (*Lysichiton americanus*) and *Vaccinium* spp., and unforest dominated by ericaceous shrubs, sedges (*Carex* spp.), shore pine (*Pinus contorta*), and *Sphagnum* spp.

Streamwater was collected from 37 subwatersheds within the Cowee Creek watershed over a 2-day period in July of 2014 (Fig. 1). The 37 subwatersheds range in area from <1.0 to 16.7 km² with a mean slope of 23.7° (Table 1). Although the lower reaches of Cowee Creek contain anadromous salmon, the small and steeply sloping study streams do not support salmon. Streams were sampled during midsummer baseflow conditions before the onset of the late summer – early fall wet season in the region. All streamwater samples were field-filtered through precombusted (450 °C for 4 h) Whatman glass fiber filters (nominal pore size 0.7 µm) and placed in acid-washed polyethylene bottles for nutrient and cation analyses and in precombusted (450 °C for 4 h) glass vials for DOM analyses. Stream temperature and specific conductivity were measured at the study reach using a hand-held YSI (model 556) meter.

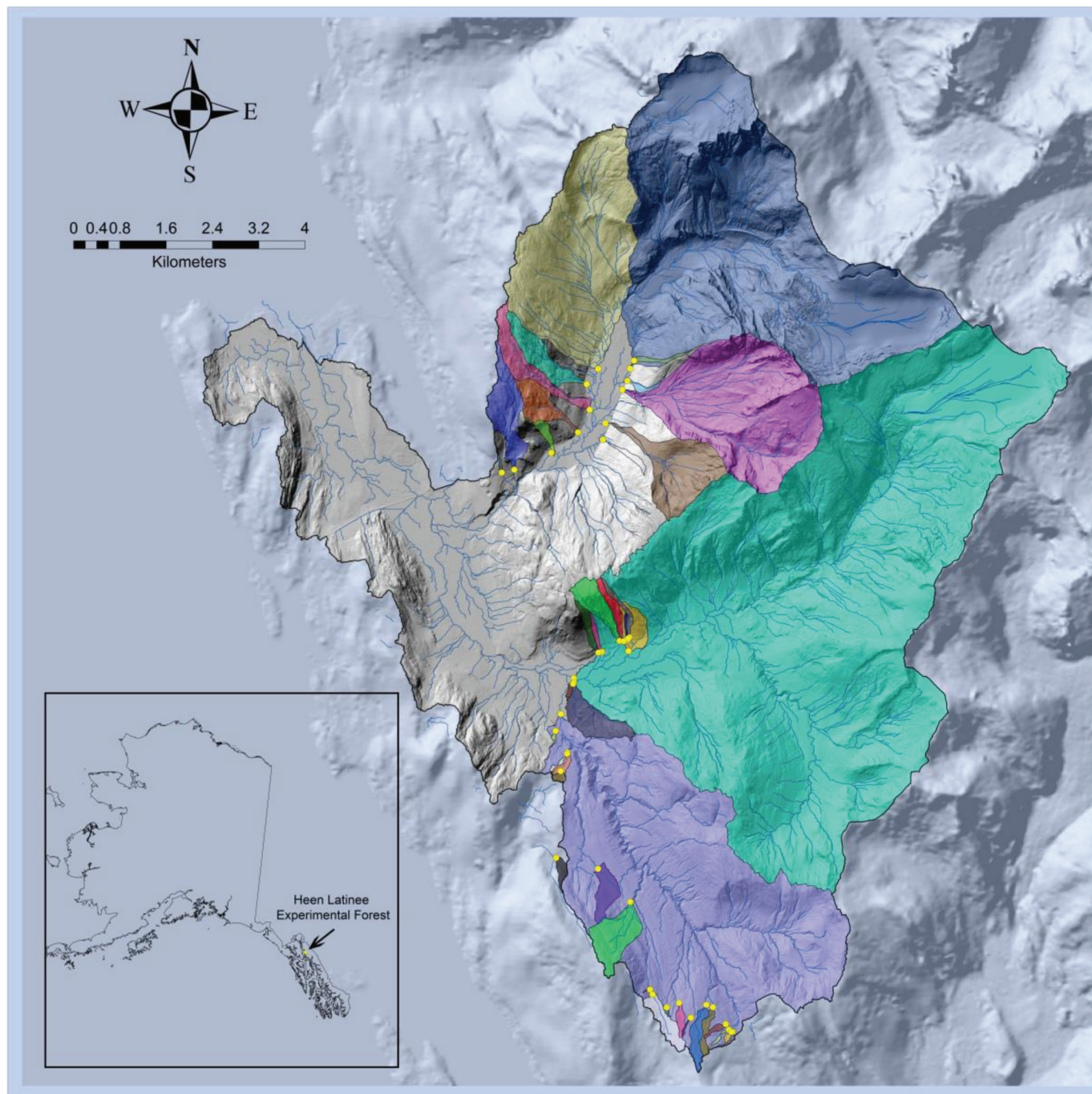
Landscape components and LiDAR analysis

LiDAR measurements of Cowee Creek watershed were obtained at a mean point density of about eight measurements per square metre. These data were used to produce a high-resolution 1 m² digital elevation model (DEM) of the watershed, from which subwatersheds for each of the 37 stream sampling sites were delineated. Mean aboveground biomass, canopy cover percentage, and tree height were extracted from the LiDAR map (details below). The mean slope, percentage of the area less than 10° slope, mean watershed elevation, watershed area, watershed surface area, and topographic wetness index (indicator of soil moisture conditions and calculated using the upslope contributing area and slope; Sørensen et al. 2006) were extracted from the LiDAR DEM. Finally, mean wind exposure (calculated based on topographic sheltering from predominant storm tracks in the region) and slide suitability (susceptibility to landslide initiation and based on topographic drivers such as slope and topographic position) were calculated from LiDAR data following Buma and Johnson (2015). The end result is a suite of vegetative, topographic, and disturbance-relevant variables describing each subwatershed.

Determination of aboveground biomass

Aboveground biomass was mapped using high-resolution LiDAR. Extensive field biomass measurements were completed to calibrate the watershed biomass map. Briefly, 47 plots (400 m²) were established throughout the study area, stratified according to observed canopy height (utilizing a preliminary 5 m × 5 m LiDAR map) so the entire range of aboveground biomass was sampled. At each point, all trees were measured for species, diameter at breast height, canopy condition, breakage, and live–dead status. Total standing aboveground biomass was then tallied using equations from Ter-Mikaelian and Korzukhin (1997) and Standish et al. (1985). For broken trees, actual height was estimated using Keyser (2008), and then tapering equations from Kozak et al. (1969) were applied to generate accurate biomass estimates. Foliage mass was removed from dead trees; if tree species could not be determined, it was assumed to be *P. sitchensis* for biomass calculations. Standing biomass was assumed to be 50% carbon. For downed material, the standard line-intercept method of Brown (1974) was used. Two 20 m perpendicular lines were measured for each plot. A specific gravity of 0.39 and 0.19 for sound and rotten wood, respectively, was assumed for carbon calculations (Harmon et al. 2011). The total carbon at each point was then modeled from the LiDAR data using standard methods (e.g., Hudak et al. 2012). Briefly, using a multivariate adaptive regression splines technique (Friedman 1991; Güneralp et al. 2014), 61 statistical descriptions of the LiDAR

Fig. 1. Map of the study watersheds and stream sampling sites (yellow circles) near Juneau, Southeast Alaska.



point cloud (e.g., median height of all returns, 20 m resolution), and five additional spatial data sets (forest type, land cover, precipitation, wind exposure, and landslide susceptibility), observed biomass was fit to the LiDAR data and then extrapolated over the entire watershed. The final model was a good fit to the observed data without overfitting ($r^2 = 0.76$, mean error $2.03 \text{ Mg}\cdot\text{ha}^{-1}$). The result is a 20 m resolution biomass map of the entire study area (see Buma et al. 2016 for full details on methods).

Biogeochemical and stable water isotope analyses

A 25 mL water sample was also collected for $\delta^{18}\text{O}$ analysis of streamwater to assist in identification of the different water sources (e.g., rainwater versus snowmelt) contributing to streamflow. Snow and glacier ice are often depleted in $\delta^{18}\text{O}$ relative to

rainfall and groundwater because low temperatures and increasing elevation typically result in natural fractionation (Dansgaard 1964; Dietermann and Weiler 2013). Thus, comparison of $\delta^{18}\text{O}$ in precipitation and surface water can be used for flow path analysis and runoff generation (Vitvar and Balderer 1997) and as an indicator of the origin of surface water in watersheds where glacier ice and snowmelt contribute to streamflow (Fellman et al. 2014a). Water isotope samples were stored in glass bottles with zero headspace at room temperature until analysis on a Picarro L2120-i analyzer. Values for $\delta^{18}\text{O}$ are reported in per mil (‰) after normalization to Vienna standard mean ocean water (Paul et al. 2007).

Concentrations of DOC and total dissolved N were analyzed by high temperature combustion (nonpurgeable organic carbon) on

Table 1. Mean watershed characteristics and biogeochemical concentrations for our 37 study streams.

	Min.	Max.	Mean	SD
Size (ha)	0.75	597.2	49.3	127.8
Slope (°)	9.5	35.3	23.7	7.1
Elevation (m)	119.0	1008.8	439.6	215.3
Aboveground biomass (Mg·ha ⁻¹)	71.7	652.8	367.3	186.9
TWI	7.9	9.5	8.7	0.4
Stream temperature (°C)	3.2	84.2	15.8	19.0
Specific conductivity (μS·cm ⁻¹)	5.1	13.8	9.7	1.6
δ ¹⁸ O (‰)	-10.2	-14.4	-12.5	0.8
DOC (mg C·L ⁻¹)	0.41	30.48	5.73	6.09
DON (mg N·L ⁻¹)	<0.01	0.42	0.11	0.10
SUVA ₂₅₄ (L·mg C ⁻¹ ·m ⁻¹)	2.95	4.69	3.94	0.54
BDOC (mg C·L ⁻¹)	0.07	4.98	0.87	1.13
DIN (mg N·L ⁻¹)	BD	0.19	0.02	0.04
SRP (μg P·L ⁻¹)	BD	17.41	1.86	2.87
TP (μg P·L ⁻¹)	11.74	33.27	19.74	4.74
Ca ²⁺ (mg·L ⁻¹)	BD	14.43	3.97	3.49
Mg ²⁺ (mg·L ⁻¹)	BD	1.46	0.41	0.35
K ⁺ (mg·L ⁻¹)	BD	0.59	0.12	0.13

Note: TWI, topographic wetness index; DOC, dissolved organic carbon; DON, dissolved organic nitrogen; SUVA₂₅₄, specific ultraviolet absorbance; BDOC, bioavailable DOC; DIN, dissolved inorganic nitrogen; SRP, soluble reactive phosphorus; TP, total phosphorus. BD corresponds to below detection limit.

a Shimadzu TOC-V-CSH analyzer using a high-sensitivity catalyst to enable low detection limits for DOC. Analytical precision for DOC ranged from 0.02 to 0.04 mg C·L⁻¹ for concentrations less than 5 mg C·L⁻¹ and from 0.1 to 0.2 mg C·L⁻¹ for samples greater than 5 mg C·L⁻¹. Major anions (NO₃⁻-N) were measured using a Dionex DX600 ion chromatograph with an AS18A anion column, and cations (Ca²⁺, K⁺, Mg²⁺, and NH₄⁺-N) were measured using a Dionex ICS-1500 with a CS16C cation column. Dissolved organic nitrogen (DON) was calculated as the difference between total dissolved N and dissolved inorganic N (DIN = NH₄⁺-N + NO₃⁻-N). Soluble reactive phosphorus (SRP) was measured using the ascorbic acid method (Murphy and Riley 1962) with a 5 cm quartz cell to enable the detection of low SRP concentrations (lower detection limit of ~1 μg P·L⁻¹). Total phosphorus (TP) was measured by persulfate digestion combined with the ascorbic acid method (Valderrama 1981).

We used SUVA₂₅₄ to assess DOM quality (Weishaar et al. 2003). The SUVA₂₅₄ of DOM, which is an indicator of aromatic carbon content, was measured at 254 nm on a Genesys 5 Spectrophotometer. In forested and wetland streams, SUVA₂₅₄ typically ranges from 3 to 5 L·mg C⁻¹·m⁻¹ corresponding to an aromatic C content of 15%–35% (Weishaar et al. 2003). Bioavailable DOC (BDOC) was measured for each stream using laboratory incubations following the methods of Fellman et al. (2008). Streamwater was initially filtered through a 0.2 μm filter, a microbial inoculum was added, DOC was analyzed, and samples were incubated in the dark at room temperature. After 30 days, the solution was refiltered through a 0.2 μm filter, DOC was remeasured, and BDOC was calculated as the difference in sample DOC before and after the 30-day incubation. The microbial inoculum was prepared by leaching stream sediments followed by filtration through a Whatman GF/D filter (2.7 μm).

Statistical methods

For each chemical species considered, an identical statistical procedure was followed for analysis. A random forest – classification and regression tree (CART) technique was used. CART models are useful when complex interactions and autocorrelation between variables are expected (Breiman et al. 1984), data are often non-normally distributed, and interpretable results are needed (as opposed to simply a predictive model). However, it is susceptible to nonoptimal solutions, and as a result, variable selection prior is often practiced (e.g., Cutler et al. 2007). In this case, the five most

important variables (as measured by total reduction in deviance) were determined using random forest (Breiman 2001). While this method is robust to the nonoptimal solutions, interpreting interactions between the variables is difficult. To investigate specific interactions between those variables, traditional CART methods using the rpart package from R were utilized. Optimal tree size was determined by minimizing the 10-fold cross-validated error. Linear regressions in R were calculated where appropriate, and if necessary, data were log-transformed to meet normality and equal variance assumptions.

Results

Water δ¹⁸O analysis

Streamwater δ¹⁸O values ranged from -10.2‰ to -14.4‰, with a mean of -12.5‰ (Table 1; Fig. 2). These values were slightly more depleted than the mean value for historical rainfall (-11.7‰; Fellman et al. 2014) collected in Juneau (~60 km southeast of Cowee Creek), likely indicating isotopically depleted water from snowmelt contributed to streamflow in a number of our study streams. Regression analyses showed that as watershed size ($r^2 = 0.27$, $P < 0.01$, log₁₀-transformed), maximum elevation ($r^2 = 0.23$, $P < 0.01$, log₁₀-transformed), and mean watershed slope increased ($r^2 = 0.48$, $P < 0.01$, log₁₀-transformed), streamwater δ¹⁸O values become more depleted. The random forest – CART analysis (model $r^2 = 0.81$) identified mean watershed slope followed by the percentage of the watershed <10° as the most useful in explaining streamwater δ¹⁸O values (Fig. 2).

DOM concentration, quality, and bioavailability

Concentrations of DOC ranged from 0.6 to 30.5 mg C·L⁻¹ across the study streams, but only four streams had concentrations >10.0 mg C·L⁻¹ (Table 1; Fig. 3a). Random forest – CART analysis identified four landscape components that explained the greatest variation in stream DOC concentration (model $r^2 = 0.89$), with mean watershed slope (negative relationship) the strongest predictor of DOC (Fig. 3a). In watersheds with a mean slope > 13.75° ($n = 34$), aboveground biomass (negative relationship) and to a lesser extent topographic wetness and percentage of low-slope area (<10°) best explained stream DOC concentration (Fig. 3a). Similar to DOC, mean watershed slope (negative relationship) was the strongest predictor of streamwater DON concentration (model $r^2 = 0.80$; Fig. 3b). Mean tree height (negative relationship) was also associated with low streamwater DON concentration in high-gradient watersheds (slope ≥ 15.25°). Overall, concentrations of DOC and DON were positively related for all streams together ($r^2 = 0.81$, $P < 0.01$, log₁₀-transformed) and negatively related to streamwater δ¹⁸O values (DOC: $r^2 = 0.47$, $P < 0.01$; DON: $r^2 = 0.47$, $P < 0.01$).

Streamwater SUVA₂₅₄ values varied from 3.0 to 4.7 L·mg C⁻¹·m⁻¹ across the study streams (Table 1), corresponding to a range in aromaticity of 23% to 34% (Weishaar et al. 2003). Random forest – CART analysis showed that landslide susceptibility (negative relationship) was the strongest predictor of SUVA₂₅₄ values (model $r^2 = 0.77$; Fig. 4a). In watersheds with low landslide susceptibility, mean slope (negative relationship) was the strongest predictor of SUVA₂₅₄ values followed by landslide susceptibility (on that subset of plots) and aboveground biomass (Fig. 4a). Overall, SUVA₂₅₄ values were negatively related to landslide susceptibility ($r^2 = 0.35$, $P < 0.01$) and positively related to streamwater δ¹⁸O values ($r^2 = 0.34$, $P < 0.01$) across all streams.

Percent BDOC varied from 3% to 28% (0.1 to 5.0 mg C·L⁻¹) across the study streams. Random forest – CART analysis identified four predictor variables that best explained streamwater BDOC concentration (model $r^2 = 0.93$; Fig. 4b), with mean watershed slope (negative relationship) the strongest predictor of concentrations ($r^2 = 0.28$, $P < 0.01$, log₁₀-transformed). Topographic wetness (positive relationship) was also important in controlling BDOC concentration in low-gradient watersheds, whereas aboveground

Fig. 2. Random forest – classification and regression tree (CART) tree and box-and-whisker plots for $\delta^{18}\text{O}$ values (‰) across the 37 study streams.

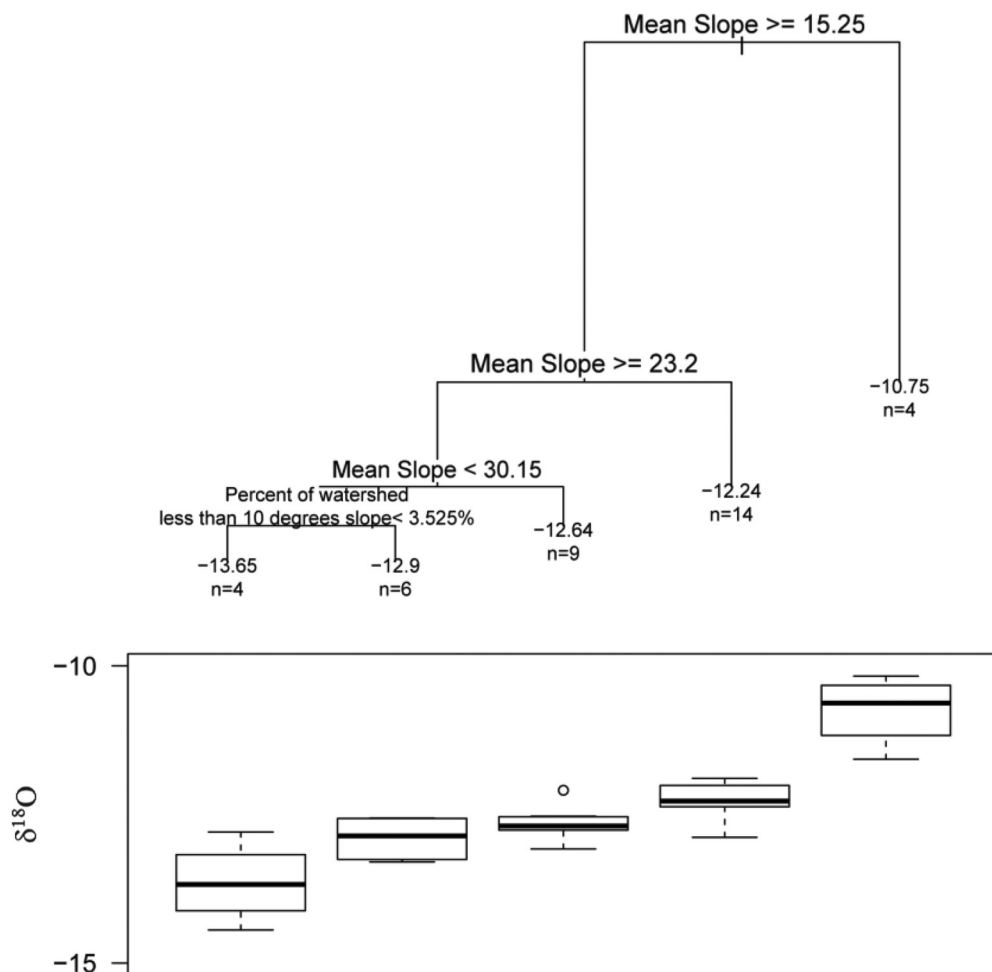


Fig. 3. Random forest – CART tree and box-and-whisker plots for concentrations of (a) dissolved organic carbon (DOC; mg C·L⁻¹) and (b) dissolved organic nitrogen (DON; mg N·L⁻¹) across the 37 study streams.

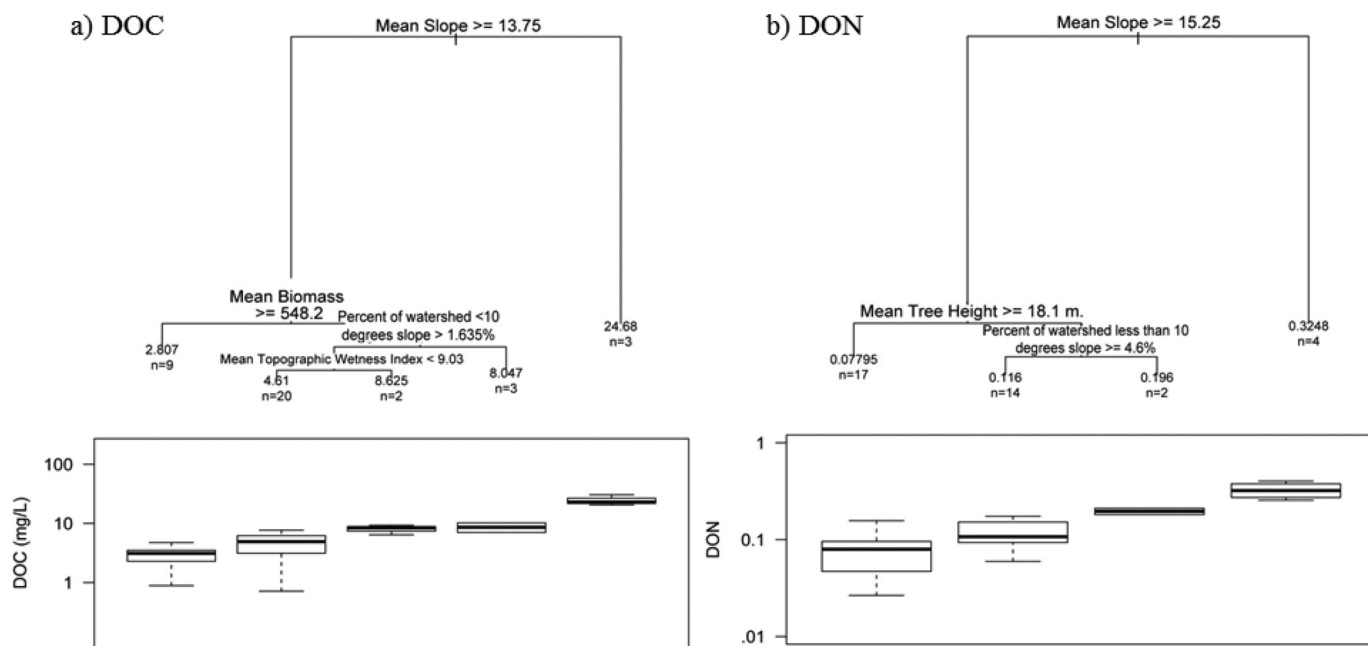


Fig. 4. Random forest – CART tree and box-and-whisker plots for (a) specific ultraviolet absorbance (SUVA_{254}) values ($\text{L}\cdot\text{mg}^{-1}\cdot\text{m}^{-1}$) and (b) bioavailable DOC (BDOC) concentrations ($\text{mg C}\cdot\text{L}^{-1}$) across the 37 study streams.

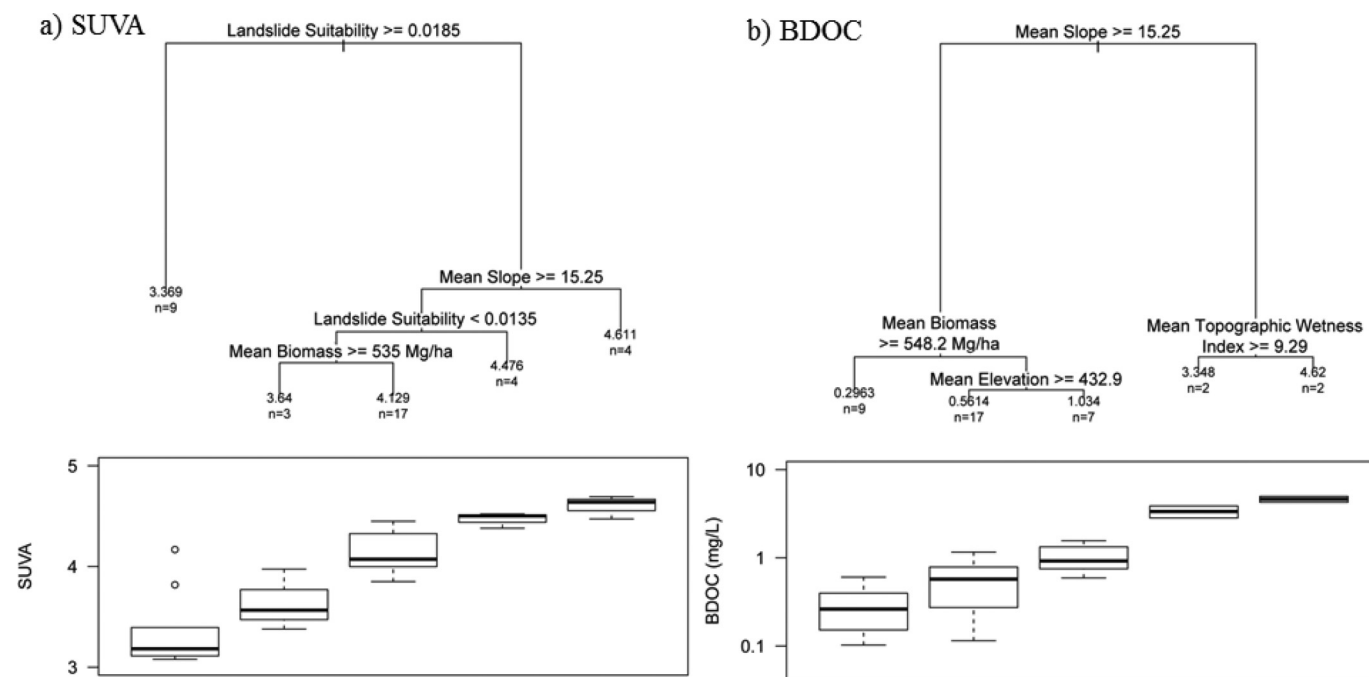
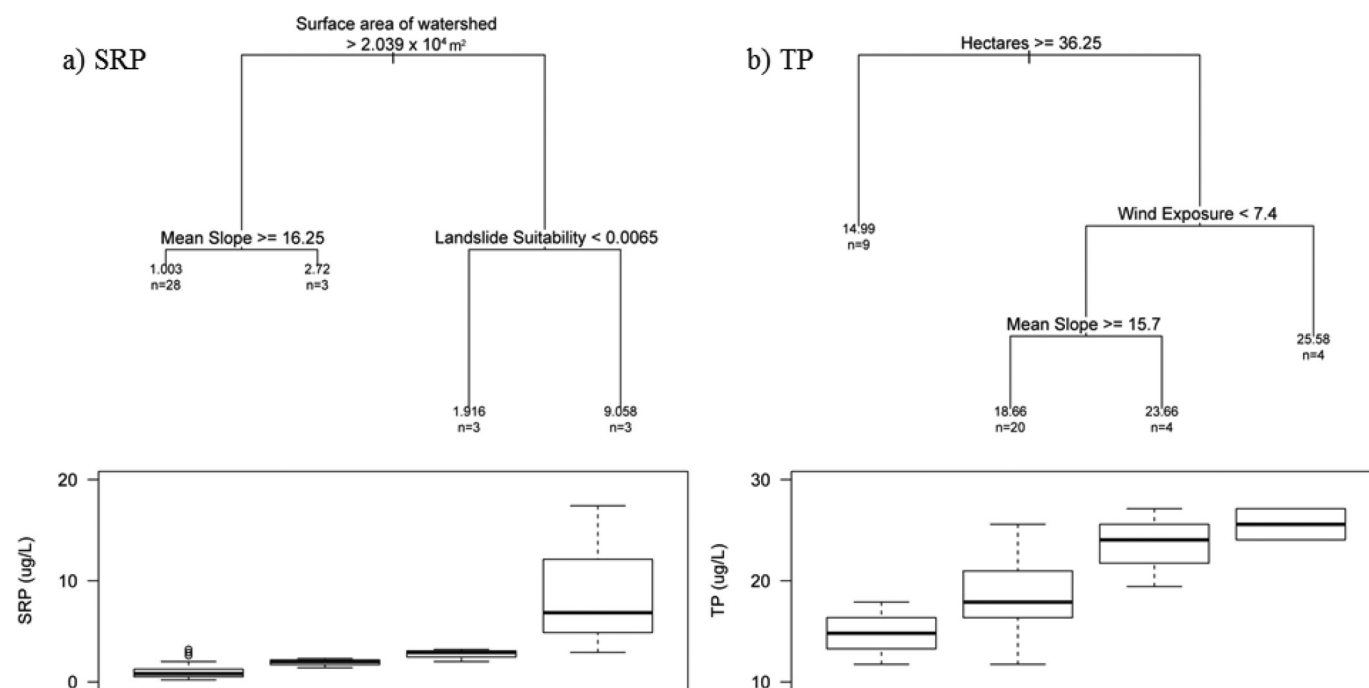


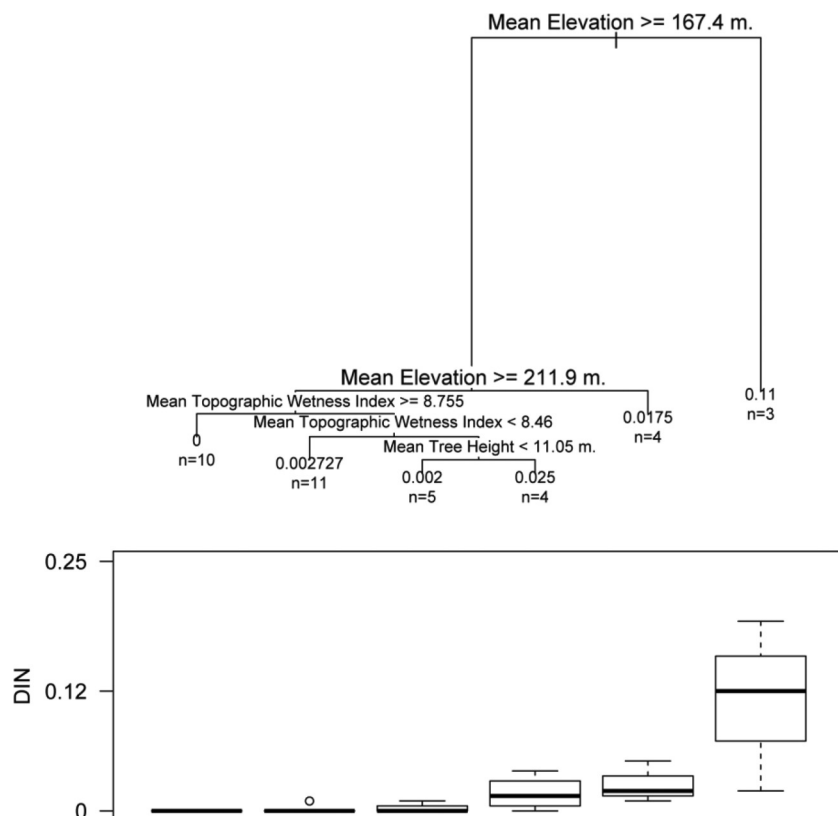
Fig. 5. Random forest – CART tree and box-and-whisker plots for concentrations ($\mu\text{g P}\cdot\text{L}^{-1}$) of (a) soluble reactive P (SRP) and (b) total P (TP) across the 37 study streams.



biomass and mean watershed elevation were important in steeply sloping watersheds. Concentrations of BDOC were positively related to SUVA_{254} values ($r^2 = 0.43$, $P < 0.01$, $\log_{10}$ -transformed) and SRP concentrations ($r^2 = 0.18$, $P < 0.01$, $\log_{10}$ -transformed), providing evidence of a link among DOM quality, nutrient availability, and DOC bioavailability to stream microbial communities. Similar to DOM concentration, $\delta^{18}\text{O}$ values were positively related to SUVA_{254} ($r^2 = 0.34$, $P < 0.01$) and BDOC concentrations ($r^2 = 0.55$, $P < 0.01$, $\log_{10}$ -transformed).

Inorganic nutrient concentrations

Concentrations of SRP ranged from below detection to $17.4 \mu\text{g P}\cdot\text{L}^{-1}$ (mean of $1.9 \mu\text{g P}\cdot\text{L}^{-1}$), although there were only two streams with concentrations $> 5 \mu\text{g P}\cdot\text{L}^{-1}$ (Table 1; Fig. 5a). Watershed surface area (positive relationship) was the strongest control on stream-water SRP concentration and to a lesser extent slope and landslide exposure (model $r^2 = 0.57$; Fig. 5a). However, cross-validation of the model was poor due to the large number of streams with concentrations at or below the lower detection limit ($\sim 1 \mu\text{g P}\cdot\text{L}^{-1}$).

Fig. 6. Random forest – CART tree and box-and-whisker plots for concentrations (mg N·L⁻¹) of dissolved inorganic N (DIN) across the 37 study streams.

Mean TP concentrations were $19.7 \mu\text{g P}\cdot\text{L}^{-1}$, suggesting inorganic P contributes very little to streamwater P in most of our study streams. Watershed size (positive relationship) explained the most variation in TP concentration (model $r^2 = 0.61$; Fig. 5b), with wind storm exposure and to a lesser extent watershed slope influential in small watersheds ($<0.36 \text{ km}^2$). Streamwater DIN concentrations ($\text{NO}_3\text{-N}$ is $\sim 70\%$ of DIN) were controlled by both landscape and vegetative factors, with mean watershed elevation (negative relationship) the most influential followed by topographic wetness and mean tree height (model $r^2 = 0.66$; Fig. 6). Similar to SRP, DIN concentrations were typically at or near the lower detection limit resulting in poor cross-validation of the model.

Random forest – CART analysis of streamwater base nutrient cations (Ca^{2+} , Mg^{2+} , and K^+) showed that watershed morphology (watershed size and topographic wetness) was the strongest predictor of Ca^{2+} concentration (model $r^2 = 0.57$; Fig. 7). Forest biomass and structure were the most influential controls on K^+ and Mg^{2+} concentrations. In particular, canopy coverage (positive relationship) controlled K^+ concentration (model $r^2 = 0.74$; Fig. 8a), and aboveground biomass (positive relationship) was surprisingly the most important driver of Mg^{2+} concentration (model $r^2 = 0.32$; Fig. 8b). Although aboveground biomass was excluded by the CART analysis in favor of mean canopy cover, these two variables were positively related ($r^2 = 0.93$, $P < 0.01$). Together, these results provide more evidence of a tight vegetative control on streamwater K^+ concentration.

Discussion

Our initial goal of evaluating whether LiDAR generated data on forest biomass, structure, and watershed morphology would be a strong predictor of stream biogeochemistry was supported for most of the biogeochemical species examined in this study. Small, steep streams in the PCTR generally have short water residence times and demonstrate tight hydrobiogeochemical connectivity

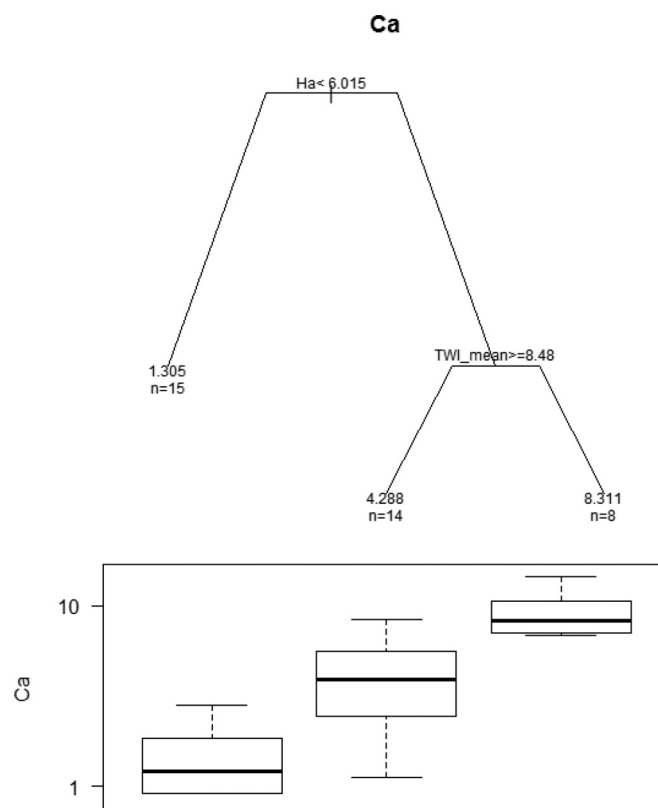
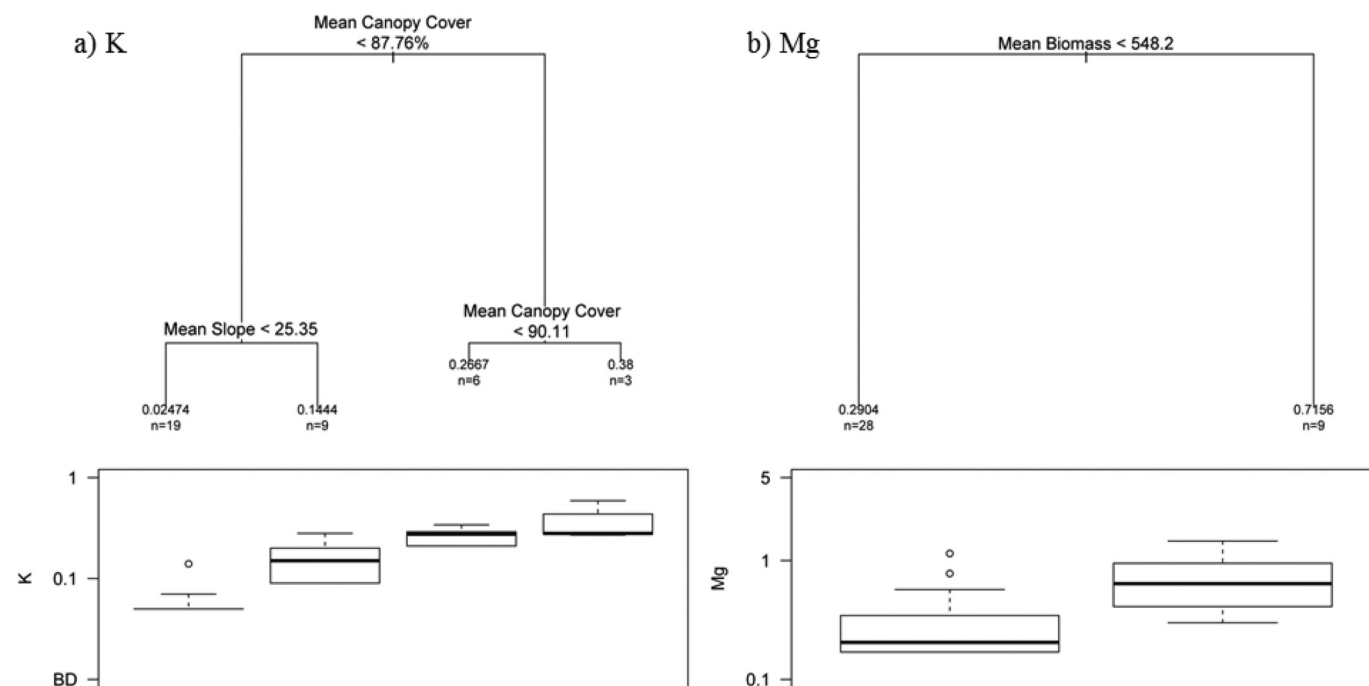
Fig. 7. Random forest – CART tree and box-and-whisker plots for concentrations (mg·L⁻¹) of Ca^{2+} across the 37 study streams.

Fig. 8. Random forest – CART tree and box-and-whisker plots for concentrations ($\text{mg}\cdot\text{L}^{-1}$) of (a) K^+ and (b) Mg^{2+} across the 37 study streams.



with terrestrial ecosystems (Fellman et al. 2009; D'Amore et al. 2010). Thus, our approach of sampling numerous small watersheds (mean size $<0.5 \text{ km}^2$) minimizes some potential confounding factors, such as the instream uptake and (or) production of DOM and nutrients along the stream network (Brookshire et al. 2005; del Giorgio and Pace 2008). We also recognize that sampling streams only once limited our interpretation to the measurement period, and this snapshot may miss seasonal changes in underlying drivers of stream biogeochemistry. With these limitations in mind, our findings demonstrate that landscape and vegetative predictors generated from high-resolution LiDAR data have clear potential to enhance our understanding of how changes in management regime impact stream biogeochemistry in small to mid-sized forested watersheds.

Our finding that mean watershed slope was the strongest predictor of DOC and DON concentration is consistent with studies in Southeast Alaska (D'Amore et al. 2015) and other forested regions (Rasmussen et al. 1989; Frost et al. 2006; Jankowski et al. 2014). This relationship reflects the rapid movement of water and the existence of shallow, organic-rich soils in steeper-sloped watersheds as opposed to the presence of carbon-rich wetlands in low-gradient watersheds that contribute abundant DOM to streams (Fellman et al. 2009; D'Amore et al. 2010). Wetlands are most common in flatter areas of the watershed, although they can occur on benches in otherwise steeply sloping watersheds or on slopes as steep as 15° in Southeast Alaska (D'Amore et al. 2015). Moreover, our finding that in addition to slope, aboveground biomass and to a lesser extent topographic wetness (wetter areas are more likely to contain carbon-rich soils) explained 88% of the variation in stream DOC concentration suggests that LiDAR-generated data on forest biomass and watershed morphology is a robust technique for estimating stream DOC. This approach may be particularly useful for predicting stream DOC in small forested watersheds where fine resolution is needed to resolve subtle differences in forest biomass, structure, and topography.

Watershed morphology appears to be an important control on stream DOM biogeochemistry, with DOM bioavailability best explained by watershed slope and DOM quality (estimated by SUVA_{254}) controlled by landslide susceptibility and watershed

slope. The highest BDOC concentrations were associated with low-gradient watersheds, thus confirming the importance of wetlands and (or) organic carbon-rich soils as a potential source of bioavailable DOM to stream ecosystems (Kaplan et al. 2006; Fellman et al. 2008). Similarly, DOM derived from wetlands or from forest floors with deep organic soils is enriched in aromatic carbon content (typically SUVA_{254} values 4 to $4.6 \text{ L}\cdot\text{mg C}^{-1}\cdot\text{m}^{-1}$) and typically dominates the DOM pool in low-gradient watersheds (Fellman et al. 2009; Hanley et al. 2013). On the other hand, we hypothesize that in steeply sloping watersheds with high potential for landslide initiation, shallow, organic, carbon-rich soils combined with DOM adsorption on mineral soils (Qualls and Haines 1992; Qualls 2000) reduces aromatic carbon inputs to streams resulting in SUVA_{254} values generally $<4.0 \text{ L}\cdot\text{mg C}^{-1}\cdot\text{m}^{-1}$.

Our findings that streamwater SRP and TP concentrations were best explained by watershed surface area-size, slope, elevation, and windstorm exposure was not surprising given landscape erosion can substantially increase the supply of available P to ecosystems (Vitousek et al. 2003; Porder et al. 2005). This combination of predictive variables also suggests exposure to ecological disturbance (i.e., windthrow), which can mix soils and expose material for more rapid weathering, influences streamwater P concentrations. Despite this evidence for weathering of P (mean TP = $19.7 \mu\text{g P}\cdot\text{L}^{-1}$), streamwater SRP concentrations were at or near lower detection (mean = $1.9 \mu\text{g P}\cdot\text{L}^{-1}$) in most of study streams. This suggests efficient retention of available P through biological uptake (Cleveland et al. 2002; Simon et al. 2005; Olander and Vitousek 2005) and sorption of P (Giesler et al. 2004; Olander and Vitousek 2005) in either soils or streams.

The variation in streamwater DIN and base cation concentrations (Mg^{2+} , Ca^{2+} , and K^+) were best explained by a combination of vegetative and landscape controls across our study watersheds. In particular, streamwater DIN concentrations were elevated in mid-to high-elevation watersheds with a low to moderate topographic wetness index. This pattern likely results from the leaching of NO_3^- from alder (*Alnus* spp.)-influenced soils that typically dominate riparian areas and avalanche-landslide paths common to steeply sloping watersheds (Compton et al. 2003). The essential plant nutrients Mg^{2+} , K^+ , and Ca^{2+} are derived from rock weather-

ing, and our finding that streamwater Mg^{2+} and K^+ were best explained by aboveground biomass, canopy coverage, and tree height is consistent with the idea that forest productivity (Vitousek 1982) and foliar leaching (Oyarzún et al. 2005) are strong controls on soluble base cation concentrations. However, Ca^{2+} concentrations were mostly strongly related to watershed characteristics (watershed size), suggesting plant uptake and retention was minimal relative to the supply of Ca^{2+} through rock weathering (Vitousek 1977). Although our findings provide evidence of a vegetative and landscape control on stream Mg^{2+} , Ca^{2+} , and K^+ , marine aerosols have been shown to influence anion-cation concentrations in coastal streams (Wigington et al. 1998) and therefore provide an additional source of variability not included in our analysis.

Streamwater $\delta^{18}\text{O}$ values were significantly related to several watershed characteristics (slope, elevation) and stream DOM concentration, bioavailability, and SUVA_{254} values. These results are consistent with previous research in the Alaskan PCTR showing that streamwater $\delta^{18}\text{O}$ can be used to estimate stream DOM concentration in watersheds where landscape source pools have unique isotopic signatures (Fellman et al. 2014a). Streams with high mean watershed slopes and elevations had the most depleted $\delta^{18}\text{O}$ values and lowest DOM concentrations (both DOC and DON) and SUVA_{254} values, reflecting the low contribution of organic matter in snowmelt to streamflow. Alternatively, streams with the greatest DOM concentration and most enriched $\delta^{18}\text{O}$ values were associated with low-gradient watersheds dominated by wetlands. Moreover, $\delta^{18}\text{O}$ values in low-gradient streams were enriched as much as 1.5‰ relative to typical values for historical rainfall in Juneau, suggesting water residence time in these watersheds was long enough to allow for evaporative water loss to occur, thus enriching streamwater $\delta^{18}\text{O}$ values (Hamilton et al. 2005; Dogramaci et al. 2012). These findings differ from studies of northern forested watersheds (Striegl et al. 2005; Frost et al. 2006), which showed that increased water residence allows for enhanced removal of DOM due to photo- and (or) biodegradation processes (Lapierre et al. 2013; Kothawala et al. 2014), likely because of the much smaller watershed sizes and lower overall water residence times in our study watersheds.

This study demonstrates the usefulness of combining stable isotopes of water and high-resolution LiDAR analyses to better understand the dynamics of the streamwater DOM pool. For instance, long-term changes in stream DOM export are driven not only by watershed morphology but by interacting ecosystem processes such as net ecosystem production, soil carbon and nutrient cycling, and watershed hydrology (Evans et al. 2005; Räike et al. 2015; Butman et al. 2016). Understanding the role of varying sources of streamwater in driving watershed DOM export is critical for predicting how changes in hydrologic forcing, such as increasing amounts of precipitation falling as rain rather than snow, will impact future watershed carbon fluxes. In this context, shifts in streamwater $\delta^{18}\text{O}$ will allow its use as a proxy for hydrological and linked ecosystem effects that can be expected to occur under projected climate change in the region (Shanley et al. 2015).

There are thousands of streams in the Alaskan PCTR that drain into nearshore marine ecosystems; many of them are poorly accessible for direct measurement, and each has a different mosaic of landscape features and contributing soils. Describing the linkages among landscape cover, biomass, and stream biogeochemistry is a critical step in understanding how changes in climate and forest management may influence terrestrial and linked aquatic ecosystem processes. Our finding that LiDAR-generated data on watershed morphology and vegetation explained more than 57% of the variation in concentration for all measured constituents except Mg^{2+} demonstrates the potential for this high-resolution landscape analysis to generate first-order estimates of stream DOM and nutrient export across the region. These findings provide evidence for a biogeochemical division that exists within the

Cowee Creek watershed where streams can be organized by their dominant watershed characteristics (i.e., aboveground biomass, slope). We suggest the use of LiDAR or other biomass quantification methodologies in many of the small and remote watersheds across the Alaskan PCTR could help calibrate regional biogeochemical flux models to predict the potential impacts of forest change and management activities on future carbon and nutrient export to the Gulf of Alaska. With proper field calibration, this approach could also be applied to other forested regions with high landscape heterogeneity and relatively small watersheds, such as the Pacific Northwest of the USA and southern Patagonia. This information could inform land management decisions that have the potential to alter ecosystem services related to watershed biogeochemical fluxes.

Acknowledgements

We thank John Krapek at University of Alaska Fairbanks for field assistance and Durelle Scott at Virginia Tech for laboratory analysis. This study was supported by an Alaska NASA EPSCoR grant to B.B. and the USDA Forest Service Pacific Northwest Research Station.

References

- Ågren, A., Buffam, I., Jansson, M., and Laudon, H. 2007. Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export. *J. Geophys. Res.* **112**(G3). doi:10.1029/2006JG000381.
- Ågren, A.M., Buffam, I., Cooper, D.M., Tiwari, T., Evans, C.D., and Laudon, H. 2014. Can the heterogeneity in stream dissolved organic carbon be explained by contributing landscape elements? *Biogeosciences*, **11**(4): 1199–1213. doi:10.5194/bg-11-1199-2014.
- Breiman, L. 2001. Random forest. *Machine Learning*, **45**(1): 5–32. doi:10.1023/A:1010933404324.
- Breiman, L., Friedman, J., Olshen, R., and Stone, C. 1984. *Classification and regression trees*. Wadsworth, Belmont, Calif.
- Brookshire, E.N.J., Valett, H.M., Thomas, S.A., and Webster, J.R. 2005. Coupled cycling of dissolved organic nitrogen and carbon in a forest stream. *Ecology*, **86**(9): 2487–2496. doi:10.1890/04-1184.
- Brown, J.K. 1974. Handbook for inventorying downed woody material. In USDA Forest Service Gen. Tech. Rep. INT-16. USDA Forest Service, Ogden, Utah.
- Buma, B., and Johnson, A.C. 2015. The role of windstorm exposure and yellow cedar decline on landslide susceptibility in southeast Alaskan temperate rainforests. *Geomorphology*, **228**: 504–511. doi:10.1016/j.geomorph.2014.10.014.
- Buma, B., Krapek, J., and Edwards, R.T. 2016. Watershed-scale forest biomass distribution in a perhumid temperate rainforest as driven by topographic, soil, and disturbance variables. *Can. J. For. Res.* **46**(6): 844–854. doi:10.1139/cjfr-2016-0041.
- Butman, D., Stackpoole, S., Stets, E., McDonald, C.P., Clow, D.W., and Striegl, R.G. 2016. Aquatic carbon cycling in the conterminous United States and implications for terrestrial carbon accounting. *Proc. Natl. Acad. Sci.* **113**(1): 58–63. doi:10.1073/pnas.1512651112. PMID:26699473.
- Clark, M.J., Cresser, M.S., Smart, R., Chapman, P.J., and Edwards, A.C. 2004. The influence of catchment characteristics on the seasonality of carbon and nitrogen species concentrations in upland rivers of Northern Scotland. *Biogeochemistry*, **68**(1): 1–19. doi:10.1023/B:BIOG.0000025733.07568.11.
- Cleveland, C.C., Townsend, A.R., and Schmidt, S.K. 2002. Phosphorus limitation of microbial processes in moist tropical forests: evidence from short-term laboratory incubations and field studies. *Ecosystems*, **5**(7): 0680–0691. doi:10.1007/s10021-002-0202-9.
- Cole, J.J., Prairie, Y.T., Caraco, N.F., McDowell, W.H., Tranvik, L.J., Striegl, R.G., Duarte, C.M., Kortelainen, P., Downing, J.A., Middelburg, J.J., and Melack, J. 2007. Plumbing the Global Carbon Cycle: integrating inland waters into the terrestrial carbon budget. *Ecosystems*, **10**(1): 172–185. doi:10.1007/s10021-006-9013-8.
- Compton, J.E., Church, M.R., Larned, S.T., and Hogsett, W.E. 2003. Nitrogen export from forested watersheds in the Oregon Coast Range: the role of N_2 -fixing red alder. *Ecosystems*, **6**(8): 773–785. doi:10.1007/s10021-002-0207-4.
- Creed, I.F., Beall, F.D., Clair, T.A., Dillon, P.J., and Hesslein, R.H. 2008. Predicting export of dissolved organic carbon from forested catchments in glaciated landscapes with shallow soils: a simple but robust DOC export model. *Global Biogeochem. Cycles*, **22**(4). doi:10.1029/2008GB003294.
- Cuevas, J.G., Soto, D., Arismendi, I., Pino, M., Lara, A., and Oyarzún, C. 2006. Relating land cover to stream properties in southern Chilean watersheds: trade-off between geographic scale, sample size, and explicative power. *Biogeochemistry*, **81**(3): 313–329. doi:10.1007/s10533-006-9043-5.
- Cutler, D.R., Edwards, T.C., Beard, K.H., Cutler, A., Hess, K.T., Gibson, J., and Lawler, J.J. 2007. Random forests for classification in ecology. *Ecology*, **88**(11): 2783–2792. doi:10.1890/07-0539.1. PMID:18051647.

- Dalzell, B.J., Filley, T.R., and Harbor, J.M. 2005. Flood pulse influences on terrestrial organic matter export from an agricultural watershed. *J. Geophys. Res.* **110**(G2). doi:10.1029/2005JG000043.
- D'Amore, D.V., Fellman, J.B., Edwards, R.T., and Hood, E. 2010. Controls on dissolved organic matter concentrations in soils and streams from a forested wetland and sloping bog in southeast Alaska. *Ecology*, **91**(3): 249–261. doi:10.1002/eco.101.
- D'Amore, D.V., Edwards, R.T., Herendeen, P.A., Hood, E., and Fellman, J.B. 2015. Dissolved organic carbon fluxes from hydrogeologic units in Alaskan coastal temperate rainforest watersheds. *Soil Sci. Soc. Am. J.* **79**(2): 378. doi:10.2136/sssaj2014.09.0380.
- Dansgaard, W. 1964. Stable isotopes in precipitation. *Tellus*, **16**(4): 436–468. doi:10.1111/j.2153-3490.1964.tb00181.x.
- Del Giorgio, P.A., and Pace, M.L. 2008. Relative independence of organic carbon transport and processing in a large temperate river: the Hudson River as both pipe and reactor. *Limnol. Oceanogr.* **53**(1): 185–197. doi:10.4319/lo.2008.53.1.0185.
- Dietermann, N., and Weiler, M. 2013. Spatial distribution of stable water isotopes in alpine snow cover. *Hydrol. Earth Syst. Sci.* **17**(7): 2657–2668. doi:10.5194/hess-17-2657-2013.
- Dillon, P.J., and Molot, L.A. 1997. Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments. *Water Resour. Res.* **33**(11): 2591–2600. doi:10.1029/97WR01921.
- Dogramaci, S., Skrzypek, G., Dodson, W., and Grierson, P.F. 2012. Stable isotope and hydrochemical evolution of groundwater in the semi-arid Hamersley Basin of subtropical northwest Australia. *J. Hydrol.* **475**: 281–293. doi:10.1016/j.jhydrol.2012.10.004.
- Evans, C.D., Monteith, D.T., and Cooper, D.M. 2005. Long-term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. *Environ. Pollut.* **137**(1): 55–71. doi:10.1016/j.envpol.2004.12.031. PMID:15944040.
- Fellman, J.B., D'Amore, D.V., Hood, E., and Boone, R.D. 2008. Fluorescence characteristics and biodegradability of dissolved organic matter in forest and wetland soils from coastal temperate watersheds in southeast Alaska. *Biogeochemistry*, **88**(2): 169–184. doi:10.1007/s10533-008-9203-x.
- Fellman, J.B., Hood, E., Edwards, R.T., and D'Amore, D.V. 2009. Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds. *J. Geophys. Res.* **114**(G1). doi:10.1029/2008JG000790.
- Fellman, J.B., Hood, E., Spencer, R.G.M., Stubbins, A., and Raymond, P.A. 2014a. Watershed glacier coverage influences dissolved organic matter biogeochemistry in coastal watersheds of southeast Alaska. *Ecosystems*, **17**(6): 1014–1025. doi:10.1007/s10021-014-9777-1.
- Fellman, J.B., Nagorski, S., Pyare, S., Vermilyea, A.W., Scott, D., and Hood, E. 2014b. Stream temperature response to variable glacier coverage in coastal watersheds of southeast Alaska. *Hydrol. Process.* **28**(4): 2062–2073. doi:10.1002/hyp.9742.
- Friedman, J. 1991. Multivariate adaptive regression splines. *Ann. Stat.* **19**(1): 1–67. doi:10.1214/aos/1176347963.
- Frost, P.C., Larson, J.H., Johnston, C.A., Young, K.C., Maurice, P.A., Lamberti, G.A., and Bridgman, S.D. 2006. Landscape predictors of stream dissolved organic matter concentration and physicochemistry in a Lake Superior river watershed. *Aquat. Sci.* **68**(1): 40–51. doi:10.1007/s00027-005-0802-5.
- Gergel, S.E., Turner, M.G., and Kratz, T.K. 1999. Dissolved organic carbon as an indicator of the scale of watershed influence on lakes and rivers. *Ecol. Appl.* **9**(4): 1377–1390. doi:10.1890/1051-0761(1999)009[1377:DOCAAI]2.0.CO;2.
- Giesler, R., Satoh, F., Istedt, U., and Nordgren, A. 2004. Microbially available phosphorus in boreal forests: effects of aluminum and iron accumulation in the humus layer. *Ecosystems*, **7**(2). doi:10.1007/s10021-003-0223-z.
- Güneralp, İ., Filippi, A.M., and Randall, J. 2014. Estimation of floodplain above-ground biomass using multispectral remote sensing and nonparametric modeling. *Int. J. Appl. Earth Observ. Geoinform.* **33**: 119–126. doi:10.1016/j.jag.2014.05.004.
- Hamilton, S.K., Bunn, S.E., Thoms, M.C., and Marshall, J.C. 2005. Persistence of aquatic refugia between flow pulses in a dryland river system (Cooper Creek, Australia). *Limnol. Oceanogr.* **50**(3): 743–754. doi:10.4319/lo.2005.50.3.0743.
- Hanley, K.W., Wollheim, W.M., Salisbury, J., Huntington, T., and Aiken, G. 2013. Controls on dissolved organic carbon quantity and chemical character in temperate rivers of North America: controls on DOC in North American rivers. *Global Biogeochem. Cycles*, **27**(2): 492–504. doi:10.1002/gbc.20044.
- Harmon, M., Woodall, C., Fasth, B., Sexton, J., and Yatkov, M. 2011. Differences between standing and downed dead tree wood density reduction factors: a comparison across decay classes and tree species. USDA Forest Service Research Paper NRS-15.
- Heath, L.S., Smith, J.E., Woodall, C.W., Azuma, D.L., and Waddell, K.L. 2011. Carbon stocks on forestland of the United States, with emphasis on USDA Forest Service ownership. *Ecosphere*, **2**(1): art6. doi:10.1890/ES10-00126.1.
- Hudak, A.T., Strand, E.K., Vierling, L.A., Byrne, J.C., Eitel, J.U.H., Martinuzzi, S., and Falkowski, M.J. 2012. Quantifying aboveground forest carbon pools and fluxes from repeat LiDAR surveys. *Remote Sens. Environ.* **123**: 25–40. doi:10.1016/j.rse.2012.02.023.
- Jankowski, K., Schindler, D.E., and Lisi, P.J. 2014. Temperature sensitivity of community respiration rates in streams is associated with watershed geomorphic features. *Ecology*, **95**(10): 2707–2714. doi:10.1890/14-0608.1.
- Johnson, K.D., Harden, J., McGuire, A.D., Bliss, N.B., Bockheim, J.G., Clark, M., Nettleton-Hollingsworth, T., Jorgenson, M.T., Kane, E.S., Mack, M., O'Donnell, J., Ping, C.-L., Schuur, E.A.G., Turetsky, M.R., and Valentine, D.W. 2011. Soil carbon distribution in Alaska in relation to soil-forming factors. *Geoderma*, **167–168**: 71–84. doi:10.1016/j.geoderma.2011.10.006.
- Kaplan, L.A., and Bott, T.L. 1985. Acclimation of stream-bed heterotrophic microflora: metabolic responses to dissolved organic matter. *Freshw. Biol.* **15**(4): 479–492. doi:10.1111/j.1365-2427.1985.tb00218.x.
- Kaplan, L.A., Newbold, J.D., Horn, D.J.V., Dow, C.L., Aufdenkampe, A.K., and Jackson, J.K. 2006. Organic matter transport in New York City drinking-water-supply watersheds. *J. N. Am. Benthol. Soc.* **25**(4): 912–927. doi:10.1899/0887-3593(2006)025[0912:OMTINY]2.0.CO;2.
- Keyser, C.E. 2008. Southeast Alaska and coastal British Columbia (AK) variant overview — forest vegetation simulator. Internal Rep. US Department of Agriculture, Forest Service, Forest Management Service Center, Fort Collins, Colo.
- Kothawala, D.N., Stedmon, C.A., Müller, R.A., Weyhenmeyer, G.A., Köhler, S.J., and Tranvik, L.J. 2014. Controls of dissolved organic matter quality: evidence from a large-scale boreal lake survey. *Global Change Biol.* **20**(4): 1101–1114. doi:10.1111/gcb.12488.
- Kozak, A., Munro, D.D., and Smith, J.H.G. 1969. Taper functions and their application in forest inventory. *For. Chron.* **45**(4): 278–283. doi:10.5558/tfc45278-4.
- Lapierre, J.-F., Guillemette, F., Berggren, M., and del Giorgio, P.A. 2013. Increases in terrestrially derived carbon stimulate organic carbon processing and CO₂ emissions in boreal aquatic ecosystems. *Nat. Commun.* **4**: 2972. doi:10.1038/ncomms3972. PMID:24336188.
- Lidman, F., Köhler, S.J., Mörtz, C.-M., and Laudon, H. 2014. Metal transport in the boreal landscape — the role of wetlands and the affinity for organic matter. *Environ. Sci. Technol.* **48**(7): 3783–3790. doi:10.1021/es4045506. PMID:24576080.
- Mattsson, T., Kortelainen, P., and Räike, A. 2005. Export of DOM from boreal catchments: impacts of land use cover and climate. *Biogeochemistry*, **76**(2): 373–394. doi:10.1007/s10533-005-6897-x.
- Miller, M.P. 2012. The influence of reservoirs, climate, land use and hydrologic conditions on loads and chemical quality of dissolved organic carbon in the Colorado River. *Water Resour. Res.* **48**(12): n/a–n/a. doi:10.1029/2012WR012312.
- Moore, S., Evans, C.D., Page, S.E., Garnett, M.H., Jones, T.G., Freeman, C., Hooijer, A., Wiltshire, A.J., Limin, S.H., and Gauci, V. 2013. Deep instability of deforested tropical peatlands revealed by fluvial organic carbon fluxes. *Nature*, **493**(7434): 660–663. doi:10.1038/nature11818. PMID:23364745.
- Murphy, J., and Riley, J.P. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta*, **27**: 31–36. doi:10.1016/S0003-2670(00)88444-5.
- Olander, L., and Vitousek, P. 2005. Short-term controls over inorganic phosphorus during soil and ecosystem development. *Soil Biol. Biochem.* **37**(4): 651–659. doi:10.1016/j.soilbio.2004.08.022.
- Oyarzún, C.E., Godoy, R., De Schrijver, A., Staelens, J., and Lust, N. 2005. Water chemistry and nutrient budgets in an undisturbed evergreen rainforest of southern Chile. *Biogeochemistry*, **71**(1): 107–123. doi:10.1007/s10533-005-4107-5.
- Paul, D., Skrzypek, G., and Fórizs, I. 2007. Normalization of measured stable isotopic compositions to isotope reference scales — a review. *Rapid Commun. Mass Spectrom.* **21**(18): 3006–3014. doi:10.1002/rcm.3185. PMID:17705258.
- Pellerin, B.A., Wollheim, W.M., Hopkinson, C.S., McDowell, W.H., Williams, M.R., Vörösmarty, C.J., and Daley, M.L. 2004. Role of wetlands and developed land use on dissolved organic nitrogen concentrations and DON/TDN in northeastern U.S. rivers and streams. *Limnol. Oceanogr.* **49**(4): 910–918. doi:10.4319/lo.2004.49.4.0910.
- Petrone, K.C. 2010. Catchment export of carbon, nitrogen, and phosphorus across an agro-urban land use gradient, Swan–Canning River system, southwestern Australia. *J. Geophys. Res.* **115**(G1). doi:10.1029/2009JG001051.
- Porder, S., Paytan, A., and Vitousek, P.M. 2005. Erosion and landscape development affect plant nutrient status in the Hawaiian Islands. *Oecologia*, **142**(3): 440–449. doi:10.1007/s00442-004-1743-8. PMID:15538635.
- Qualls, R.G. 2000. Comparison of the behavior of soluble organic and inorganic nutrients in forest soils. *For. Ecol. Manage.* **138**(1–3): 29–50. doi:10.1016/S0378-1127(00)00410-2.
- Qualls, R.G., and Haines, B.L. 1992. Biodegradability of dissolved organic matter in forest throughfall, soil solution, and stream water. *Soil Sci. Soc. Am. J.* **56**(2): 578. doi:10.2136/sssaj1992.03615995005600020038x.
- Qualls, R.G., and Richardson, C.J. 2003. Factors controlling concentration, export, and decomposition of dissolved organic nutrients in the Everglades of Florida. *Biogeochemistry*, **62**(2): 197–229. doi:10.1023/A:1021150503664.
- Räike, A., Kortelainen, P., Mattsson, T., and Thomas, D.N. 2015. Long-term trends (1975–2014) in the concentrations and export of carbon from Finnish rivers to the Baltic Sea: organic and inorganic components compared. *Aquat. Sci.* doi:10.1007/s00027-015-0451-2.
- Rasmussen, J.B., Godbout, L., and Schallenberg, M. 1989. The humic content of lake water and its relationship to watershed and lake morphometry. *Limnol. Oceanogr.* **34**(7): 1336–1343. doi:10.4319/lo.1989.34.7.1336.
- Regnier, P., Friedlstein, P., Ciais, P., Mackenzie, F.T., Gruber, N., Janssens, I.A., Laruelle, G.G., Lauerwald, R., Luyssaert, S., Andersson, A.J., Arndt, S., Arnosti, C., Borges, A.V., Dale, A.W., Gallego-Sala, A., Goddard, Y., Goossens, N., Hartmann, J., Heinze, C., Ilyina, T., Joos, F., LaRoue, D.E., Leifeld, J., Meysman, F.J.R., Munhoven, G., Raymond, P.A., Spahni, R., Suntharalingam, P., and Thullner, M. 2013. Anthropo-

- genic perturbation of the carbon fluxes from land to ocean. *Nat. Geosci.* **6**(8): 597–607. doi:10.1038/ngeo1830.
- Shanley, C.S., Pyare, S., Goldstein, M.I., Alaback, P.B., Albert, D.M., Beier, C.M., Brinkman, T.J., Edwards, R.T., Hood, E., MacKinnon, A., McPhee, M.V., Patterson, T.M., Suring, L.H., Tallmon, D.A., and Wipfli, M.S. 2015. Climate change implications in the northern coastal temperate rainforest of North America. *Clim. Change*, **130**: 155–170. doi:10.1007/s10584-015-1355-9.
- Simon, K.S., Townsend, C.R., Biggs, B.J.F., and Bowden, W.B. 2005. Temporal variation of N and P uptake in 2 New Zealand streams. *J. N. Am. Benthol. Soc.* **24**(1): 1–18. doi:10.1899/0887-3593(2005)024<0001:TVONAP>2.0.CO;2.
- Sørensen, R., Zinko, U., and Seibert, J. 2006. On the calculation of the topographic wetness index: evaluation of different methods based on field observations. *Hydrol. Earth Syst. Sci.* **10**(1): 101–112. doi:10.5194/hess-10-101-2006.
- Standish, J., Manning, G., and Demaerschalk, J. 1985. Development of biomass equations for British Columbia tree species. Agriculture Canada, Ministry of State for Forestry, Pacific Forest Research Centre, Victoria, B.C. Inf. Rep. No. BC-X-264.
- Stanley, E.H., and Maxted, J.T. 2008. Changes in the dissolved nitrogen pool across land cover gradients in Wisconsin streams. *Ecol. Appl.* **18**(7): 1579–1590. doi:10.1890/07-1379.1. PMID:18839755.
- Striegl, R.G., Aiken, G.R., Dornblaser, M.M., Raymond, P.A., and Wickland, K.P. 2005. A decrease in discharge-normalized DOC export by the Yukon River during summer through autumn. *Geophys. Res. Lett.* **32**(21). doi:10.1029/2005GL024413.
- Tank, S.E., Raymond, P.A., Striegl, R.G., McClelland, J.W., Holmes, R.M., Fiske, G.J., and Peterson, B.J. 2012. A land-to-ocean perspective on the magnitude, source and implication of DIC flux from major Arctic rivers to the Arctic Ocean: Arctic river DIC. *Global Biogeochem. Cycles*, **26**(4). doi:10.1029/2011GB004192.
- Ter-Mikaelian, M.T., and Korzukhin, M.D. 1997. Biomass equations for sixty-five North American tree species. *For. Ecol. Manage.* **97**(1): 1–24. doi:10.1016/S0378-1127(97)00019-4.
- Valderrama, J.C. 1981. The simultaneous analysis of total nitrogen and total phosphorus in natural waters. *Mar. Chem.* **10**(2): 109–122. doi:10.1016/0304-4203(81)90027-X.
- Vitousek, P.M. 1977. The regulation of element concentrations in mountain streams in the northeastern United States. *Ecol. Monogr.* **47**(1): 65. doi:10.2307/1942224.
- Vitousek, P.M. 1982. Nutrient cycling and nutrient use efficiency. *Am. Nat.* **119**(4): 553–572. doi:10.1086/283931.
- Vitousek, P., Chadwick, O., Matson, P., Allison, S., Derry, L., Kettley, L., Luers, A., Mecking, E., Monastera, V., and Porder, S. 2003. Erosion and the rejuvenation of weathering-derived nutrient supply in an old tropical landscape. *Ecosystems*, **6**(8): 762–772. doi:10.1007/s10021-003-0199-8.
- Vitvar, T., and Balderer, W. 1997. Estimation of mean water residence times and runoff generation by 180 measurements in a pre-Alpine catchment (Rietlochzbach, Eastern Switzerland). *Appl. Geochem.* **12**(6): 787–796. doi:10.1016/S0883-2927(97)00045-0.
- Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., and Mopper, K. 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environ. Sci. Technol.* **37**(20): 4702–4708. doi:10.1021/es030360x. PMID:14594381.
- Wiegner, T.N., Kaplan, L.A., Newbold, J.D., and Ostrom, P.H. 2005. Contribution of dissolved organic C to stream metabolism: a mesocosm study using ¹³C-enriched tree-tissue leachate. *J. N. Am. Benthol. Soc.* **24**(1): 48–67. doi:10.1899/0887-3593(2005)024<0048:CODOCT>2.0.CO;2.
- Wigington, P.J., Church, M.R., Strickland, T.C., Eshleman, K.N., and Sickie, J.V. 1998. Autumn chemistry of Oregon coast range streams. *J. Am. Water Resour. Assoc.* **34**(5): 1035–1049. doi:10.1111/j.1752-1688.1998.tb04152.x.
- Williams, C.J., Yamashita, Y., Wilson, H.F., Jaffé, R., and Xenopoulos, M.A. 2010. Unraveling the role of land use and microbial activity in shaping dissolved organic matter characteristics in stream ecosystems. *Limnol. Oceanogr.* **55**(3): 1159–1171. doi:10.4319/lo.2010.55.3.1159.