A global hotspot for dissolved organic carbon in hypermaritime watersheds of coastal British Columbia.

Allison A. Oliver[1,2], Suzanne E. Tank[1,2], Ian Giesbrecht[2,7], Maartje C. Korver[2], William C. Floyd[3,4,2], Paul Sanborn[5,2], Chuck Bulmer[6], Ken P. Lertzman[7,2]

[1]University of Alberta, Department of Biological Sciences, CW 405, Biological Sciences Bldg., University of Alberta, Edmonton, Alberta, T6G 2E9, Canada
[2]Hakai Institute, Tula Foundation, Box 309, Heriot Bay, British Columbia, V0P 1H0, Canada
[3]Ministry of Forests, Lands and Natural Resource Operations, 2100 Labieux Rd, Nanaimo, BC, V9T 6E9, Canada
[4]Vancouver Island University, 900 Fifth Street, Nanaimo, BC, V9R 5S5, Canada
[5]Ecosystem Science and Management Program, University of Northern British Columbia, 3333 University Way, Prince George, BC, V2N 4Z9, Canada
[6]BC Ministry of Forests Lands and Natural Resource Operations, 3401 Reservoir Rd, Vernon, BC, V1B 2C7, Canada
[7]School of Resource and Environmental Management, Simon Fraser University, TASC 1- Room 8405, 8888 University Drive, Burnaby, BC, V5A 1S6, Canada

Correspondence to: Allison A. Oliver (aaoliver@ualberta.ca)

Abstract.

The perhumid region of the coastal temperate rainforest (CTR) of Pacific North America is one of the wettest places on Earth and contains numerous small catchments that discharge freshwater and high concentrations of dissolved organic carbon (DOC) directly to the coastal ocean. However, empirical data on the flux and composition of DOC exported from these watersheds is scarce. We established monitoring stations at the outlets of seven catchments on Calvert and Hecate Islands, British Columbia, which represent the rain dominated hypermaritime region of the perhumid CTR. Over several years, we measured stream discharge, stream water DOC concentration, and stream water dissolved organic matter (DOM) composition. Discharge and DOC concentrations were used to calculate DOC fluxes and yields, and DOM composition was characterized using absorbance and fluorescence spectroscopy with parallel factor analysis (PARAFAC). The areal estimate of annual DOC yield in water year 2015 was 33.3 Mg C km^{-2} yr^{-1}, with individual watersheds ranging from an average of 24.1-37.7 Mg C km^{-2} yr^{-1}. This represents some of the highest DOC yields to be measured at the coastal margin. We observed seasonality in the quantity and composition of exports, with the majority of DOC export occurring during the extended wet period (September-April). Stream flow from catchments reacted quickly to rain inputs, resulting in rapid export of relatively fresh, highly terrestrial-like DOM. DOC concentration and measures of DOM composition were related to stream discharge and stream temperature, and correlated with watershed attributes, including the extent of lakes and wetlands, and thickness of organic and mineral soil horizons. Our discovery of high DOC yields from these small catchments in the CTR is especially compelling as they deliver relatively fresh, highly terrestrial organic matter directly to the coastal ocean. Hypermaritime landscapes are common on the British Columbia coast, suggesting that this coastal margin may play an important role in the regional processing of carbon and in linking terrestrial carbon to marine ecosystems.

1 Introduction

Freshwater aquatic ecosystems process and transport a significant amount of carbon (Cole et al., 2007; Aufdenkampe et al., 2011; Dai et al., 2012). Globally, riverine export is estimated to deliver around 0.9 Pg C yr^{-1} from land to the coastal ocean (Cole et al., 2007), with typically >50% quantified as dissolved organic carbon (DOC)(Meybeck, 1982; Ludwig et al.,

1996; Alvarez-Cobelas et al., 2012; Mayorga et al., 2010). Rivers draining coastal watersheds serve as conduits of DOC from terrestrial and freshwater sources to marine environments (Mulholland and Watts, 1982; Bauer et al., 2013; McClelland et al., 2014) and can have important implications for coastal carbon cycling, biogeochemical interactions, ecosystem productivity, and food webs (Hopkinson et al., 1998; Tallis, 2009; Tank et al., 2012; Regnier et al., 2013). In addition, because the transfer of water and organic matter from watersheds to the coastal ocean represents an important pathway for carbon cycling and ecological subsidies between ecosystems, better understanding of these linkages is needed for constraining predictions of ecosystem productivity in response to perturbations such as climate change. In regions where empirical data are currently scarce, quantifying land-to-ocean DOC export is therefore a priority for improving the accuracy of watershed and coastal carbon models (Bauer et al., 2013).

While quantifying DOC flux within and across systems is required for understanding the magnitude of carbon exchange, the composition of DOC (as dissolved organic matter, or DOM) is also important for determining the ecological significance of carbon exported from coastal watersheds. The aquatic DOM pool is a complex mixture that reflects both source material and processing along the watershed terrestrial-aquatic continuum, and as a result can show significant spatial and temporal variation (Hudson et al., 2007; Graeber et al., 2012; Wallin et al., 2015). Both DOC concentration and DOM composition can serve as indicators of watershed characteristics (Koehler et al., 2009), hydrologic flow paths (Johnson et al., 2011; Helton et al., 2015), and watershed biogeochemical processes (Emili and Price, 2013). DOM composition can also influence its role in downstream processing and ecological function, such as susceptibility to biological (Judd et al., 2006) and physiochemical interactions (Yamashita and Jaffé, 2008).

The coastal temperate rainforests (CTR) of Pacific North America extend from the Gulf of Alaska, through British Columbia, to Northern California and span a wide range of precipitation and climate regimes. Within this rainforest region, the “perhumid” zone has cool summers and summer precipitation is common (>10% of annual precipitation) (Alaback, 1996)(Fig. 1). The perhumid CTR extends from southeast Alaska through the outer coast of central British Columbia and contains forests and soils that have accumulated large amounts of organic carbon above and below ground (Leighty et al., 2006; Gorham et al., 2012). Due to high

amounts of precipitation and close proximity to the coast, this area represents a potential hotspot for the transport and metabolism of carbon across the land-to-ocean continuum, and quantifying these fluxes is pertinent for understanding global carbon cycling.

Within the large perhumid CTR, there is substantial spatial variation in climate and landscape characteristics that create uncertainty about carbon cycling and pattern. In Alaska, for example, riverine DOC concentrations vary with wetland cover (D'Amore et al. 2015a) and glacial cover (Fellman et al. 2014). Previous studies have shown that streams in southeast Alaska can contain high DOC concentrations (Fellman et al., 2009a; D'Amore et al., 2015a) and produce high DOC yields (D'Amore et al., 2015b; D'Amore et al., 2016, Stackpoole et al., 2016), but no known field estimates have been generated for the perhumid CTR of British Columbia, an area of approximately 97,824 km^2 (adapted from Wolf et al., 1995). Within the perhumid CTR of British Columbia, terrestrial ecologists have defined a large (29,935 km^2) *hypermaritime* sub-region where rainfall dominates over snow, seasonality is moderated by the ocean, and wetlands are extensive (Pojar et al., 1991; area estimated using British Columbia Biogeoclimatic Ecosystem Classification Subzone/Variant mapping Version 10, August 31, 2016, available at: https://catalogue.data.gov.bc.ca/dataset/f358a53b-ffde-4830-a325-a5a03ff672c3). Previous work in the hypermaritime CTR showed that DOC concentrations are high in small streams and tend to increase during rain events (Gibson et al., 2000; Fitzgerald et al., 2003; Emili and Price, 2013). Taken together, these conditions should be expected to generate high yields and fluxes of DOC from hypermaritime watersheds to the coastal ocean.

The objectives of this study were to provide the first field-based estimates of DOC exports from watersheds in the extensive hypermaritime region of British Columbia's perhumid CTR, to describe the temporal and spatial dynamics of exported DOC concentration and DOM composition, and to identify relationships between DOC concentration, DOM composition, and watershed characteristics.

2 Methods

2.1 Study Sites

Study sites are located on northern Calvert Island and adjacent Hecate Island on the central coast of British Columbia, Canada (Lat 51.650, Long -128.035; Fig. 1). Average annual precipitation and air temperature at sea level from 1981-2010 was 3356 mm yr^{-1} and 8.4 °C

(average annual min= 0.9°C, average annual max= 17.9°C) (available online at http://www.climatewna.com/; Wang et al., 2012), with precipitation dominated by rain, and winter snowpack persisting only at higher elevations. Sites are located within the hypermaritime region of the CTR on the outer coast of British Columbia. Soils overlying the granodiorite bedrock (Roddick, 1996) are usually < 1 m thick, and have formed in sandy colluvium and patchy morainal deposits, with limited areas of coarse glacial outwash. Chemical weathering and organic matter accumulation in the cool, moist climate have produced soils dominated by Podzols and Folic Histosols, with Hemists up to 2 m thick in depressional sites (IUSS Working Group WRB, 2015). The landscape is comprised of a mosaic of ecosystem types, including exposed bedrock, extensive wetlands, bog forests and woodlands, with organic rich soils (Green, 2014; Thompson et al., 2016). Forest stands are generally short with open canopies reflecting the lower productivity of the hypermaritime forests compared to the rest of the perhumid CTR (Banner et al., 2005). Dominant trees are western redcedar, yellow-cedar, shore pine and western hemlock with composition varying across topographic and edaphic gradients. Widespread understory plants include bryophytes, salal, deer fern, and tufted clubrush. Wetland plants are locally abundant including diverse *Sphagnum* mosses and sedges. Although the watersheds have no history of mining or industrial logging, archaeological evidence suggests that humans have occupied this landscape for at least 13,000 years (McLaren et al., 2014). This occupation has had a local effect on forest productivity near habitation sites (Trant et al., 2016) and on fire regimes (Hoffman et al., 2016). We selected seven watersheds with streams draining directly into the ocean (Fig. 1). These numbered watersheds (626, 693, 703, 708, 819 844, and 1015) range in size (3.2 to 12.8 km^2) and topography (maximum elevation 160 m to 1012 m), are variably affected by lakes (0.3 – 9.1% lake coverage), and – as is characteristic of the perhumid CTR– have a high degree of wetland coverage (24– 50%) (Table 1).

2.2 Soils and watershed characteristics

Watersheds and streams were delineated using a 3 m resolution digital elevation model (DEM) derived from airborne laser scanning (LiDAR) and flow accumulation analysis using geographic information systems (GIS) to summarize watershed characteristics for each watershed polygon and for all watersheds combined (Gonzalez Arriola et al., 2015; Table 1). Topographic measures were estimated from the DEM, and lake and wetland cover estimated

153 from Province of British Columbia Terrestrial Ecosystem Mapping (TEM) (Green, 2014), and
154 soil material thickness estimated from unpublished digital soil maps (Supplemental S1). We
155 recorded thickness of organic soil material, thickness of mineral soil material, and total soil depth
156 to bedrock at a total of 353 field sites. Mineral soil horizons have ≤ 17% organic C, while
157 organic soil horizons have > 17% organic C, per the Canadian System of Soil Classification (Soil
158 Classification Working Group, 1998). In addition to field-sampled sites, 40 sites with exposed
159 bedrock (0 cm soil depth) were located using aerial photography. Soil thicknesses were
160 combined with a suite of topographic, vegetation, and remote sensing (LiDAR and RapidEye
161 satellite imagery) data for each sampling point and used to train a random forest model
162 (randomForest package in R; Liaw and Wiener, 2002) that was used to predict soil depth values.
163 Soil material thicknesses were then averaged for each watershed (Table 1). For additional details
164 on field site selection and methods used for predictions of soil thickness, see Supplemental S1.1.

165 **2.3 Sample Collection and Analysis**

166 From May 2013 to July 2016, we collected stream water grab samples from each
167 watershed stream outlet every 2-3 weeks (n_{total}= 402), with less frequent sampling (~ monthly)
168 during winter (Fig. 1). All samples were filtered in the field (Millipore Millex-HP Hydrophilic
169 PES 0.45μm) and kept in the dark, on ice until analysis. DOC samples were filtered into 60 mL
170 amber glass bottles and preserved with 7.5M H_3PO_4. Fe samples were filtered into 125 mL
171 HDPE bottles and preserved with 8M HNO_3. DOC and Fe samples were analyzed at the BC
172 Ministry of the Environment Technical Services Laboratory (Victoria, BC, Canada). DOC
173 concentrations were determined on a TOC analyzer (Aurora 1030; OI-Analytical) using wet
174 chemical oxidation with persulfate followed by infrared detection of CO_2. Fe concentrations
175 were determined on a dual-view ICP-OES spectrophotometer (Prodigy; Teledyne Leeman Labs)
176 using a Seaspray pneumatic nebulizer.

177 In May 2014, we began collecting stream samples for stable isotopic composition of $\delta^{13}C$
178 in DOC ($\delta^{13}C$-DOC; n= 173) and optical characterization of DOM using absorbance
179 spectroscopy (n= 259). Beginning in January 2016, we also analyzed samples using fluorescence
180 spectroscopy (see section 2.6). Samples collected for $\delta^{13}C$-DOC were filtered into 40 mL EPA
181 glass vials and preserved with H_3PO_4. $\delta^{13}C$-DOC samples were analyzed at GG Hatch Stable
182 Isotope Laboratory (Ottawa, ON, Canada) using high temperature combustion (TIC-TOC

Combustion Analyser Model 1030; OI Analytical) coupled to a continuous flow isotope ratio mass spectrometry (Finnigan Mat DeltaPlusXP; Thermo Fischer Scientific)(Lalonde et al. 2014). Samples analyzed for optical characterization using absorbance and fluorescence were filtered into 125 mL amber HDPE bottles and analyzed at the Hakai Institute (Calvert Island, BC, Canada) within 24 hours of collection.

2.4 Hydrology: Precipitation and Stream Discharge

We measured precipitation using a TB4-L tipping bucket rain gauge with a 0.2 mm resolution (Campbell Scientific Ltd.) located in watershed 708 (elevation= 16 m a.s.l). The rain gauge was calibrated twice per year using a Field Calibration Device, model 653 (HYQUEST Solutions Ltd).

We determined continuous stream discharge for each watershed by developing stage discharge rating curves at fixed hydrometric stations situated in close proximity to each stream outlet. Sites were located above tidewater influence and were selected based on favourable conditions (i.e., channel stability and stable hydraulic conditions) for the installation and operation of pressure transducers to measure stream stage. From August 2014 to May 2016 (21 months), we measured stage every 5 minutes using an OTT PLS –L (OTT Hydromet, Colorado, USA) pressure transducer (0-4 m range SDI-12) connected to a CR1000 (Campbell Scientific, Edmonton, Canada) data logger. Stream discharge was measured over various intervals using either the velocity area method (for flows < 0.5 m^3s^{-1}; ISO Standard 9196:1992, ISO Standard 748:2007) or salt dilution (for flows > 0.5 m^3s^{-1}; Moore, 2005). Rating curves were developed using the relationship between stream stage height and stream discharge (Supplemental S2).

2.5 DOC flux

From October 1, 2014 to April 30, 2016, we estimated DOC flux for each watershed using measured DOC concentrations (n= 224) and continuous discharge recorded at 15-minute intervals. The watersheds in this region respond rapidly to rain inputs and as a result DOC concentrations are highly variable. To address this variability, routine DOC concentration data (as described in section 2.2) were supplemented with additional grab samples (n= 21) collected around the peak of the hydrograph during several high flow events throughout the year. We performed watershed-specific estimates of DOC flux using the "rloadest" package (Lorenz et al., 2015) in R (version 3.2.5, R Core Team, 2016), which replicates functions developed in the U.S.

Geological Survey load-estimator program, LOADEST (Runkel et al., 2004). LOADEST is a multiple-regression adjusted maximum likelihood estimation model that calibrates a regression between measured constituent values and stream flow across seasons and time and then fits it to combinations of coefficients representing nine predetermined models of constituent flux. To account for potentially small sample size, the best model was selected using the second order Akaike Information Criterion (AICc) (Akaike, 1981; Hurvich and Tsai, 1989). Input data were log-transformed to avoid bias and centered to reduce multicollinearity. For additional details on model selection, see Supplemental Table S3.1.

2.6 Optical characterization of DOM

Prior to May 2014, absorbance measures of water samples (n= 99) were conducted on a Varian Cary-50 (Varian, Inc.) spectrophotometer at the BC Ministry of the Environment Technical Services Laboratory (Victoria, BC, Canada) to determine specific UV absorption at 254 nm ($SUVA_{254}$). After May 2014, we conducted optical characterization of DOM by absorbance and fluorescence spectroscopy at the Hakai Institute field station (Calvert Island, BC, Canada) using an Aqualog fluorometer (Horiba Scientific, Edison, New Jersey, USA). Strongly absorbing samples (absorbance units > 0.2 at 250 nm) were diluted prior to analysis to avoid excessive inner filter effects (Lakowicz, 1999). Samples were run in 1 cm quartz cells and scanned from 220-800 nm at 2 nm intervals to determine $SUVA_{254}$ as well as the spectral slope ratio (S_R). $SUVA_{254}$ has been shown to positively correlate with increasing molecular aromaticity associated with the fulvic acid fraction of DOM (Weishaar et al., 2003), and is calculated by dividing the Decadic absorption coefficient at 254 nm by DOC concentration (mg C L^{-1}). To account for potential Fe interference with absorbance values, we corrected $SUVA_{254}$ values by Fe concentration according the method described in Poulin et al., (2014). S_R has been shown to negatively correlate with molecular weight (Helms et al., 2008), and is calculated as the ratio of the spectral slope from 275 nm to 295 nm ($S_{275\text{-}295}$) to the spectral slope from 350 nm to 400 nm ($S_{350\text{-}400}$).

We measured excitation and emission spectra (as excitation emission matrices, EEMs) on samples every three weeks from January to July 2016 (n= 63). Samples were run in 1 cm quartz cells and scanned from excitation wavelengths of 230-550 nm at 5nm increments, and emission wavelengths of 210-620 nm at 2 nm increments. The Horiba Aqualog applied the appropriate

instrument corrections for excitation and emission, inner filter effects, and Raman signal calibration. We calculated the Fluorescence Index and Freshness Index for each EEM. The Fluorescence Index is often used to indicate DOM source, where higher values are more indicative of microbial-derived sources of DOM and lower values indicate more terrestrial-derived sources (McKnight et al., 2001), and is calculated as the ratio of emission intensity at 450 nm to 500 nm, at an excitation of 370 nm. The Freshness Index is used to indicate the contribution of authochthonous or recently microbial-produced DOM, with higher values suggesting greater autochthony (i.e., microbial inputs), and is calculated as the ratio of emission intensity at 380 nm to the maximum emission intensity between 420 nm and 435 nm, at excitation 310 nm (Wilson and Xenopoulos, 2009).

To further characterize features of DOM composition, we performed parallel factor analysis (PARAFAC) using EEM data within the drEEM toolbox for Matlab (Mathworks, MA, USA) (Murphy et al., 2013). PARAFAC is a statistical technique used to decompose the complex mixture of the fluorescing DOM pool into quantifiable, individual components (Stedmon et al., 2003). We detected a total of six unique components, and validated the model using core consistency and split-half analysis (Murphy et al., 2013; Stedmon and Bro, 2008). Components with similar spectra from previous studies were identified using the online fluorescence repository, OpenFluor (Murphy et al., 2014), and additional components with similar peaks were identified through literature review. Since the actual chemical structure of fluorophores is unknown, we used the concentration of each fluorophore as maximum fluorescence of excitation and emission in Raman Units (F_{max}) to derive the percent contribution of each fluorophore component to total fluorescence. Relationships between PARAFAC components were also evaluated using Pearson correlation coefficients in the R package "Hmisc" (Harrell et al., 2016).

2.7 Evaluating relationships in DOC concentration and DOM composition with stream discharge and temperature

We used linear mixed effects models to assess the relationship between DOC concentration or DOM composition (δ^{13}C-DOC, S_R, $SUVA_{254}$, Fluorescence Index, Freshness Index, PARAFAC components), stream discharge, and stream temperature. Analysis was performed in R using the nlme package (Pinheiro et al., 2016). Watershed was included as a

random intercept to account for repeat measures on each watershed. For some parameters, a random slope of either discharge or temperature was also included based on data assessment and model selection. Model selection was performed using AIC to compare models fit using Maximum Likelihood (ML) (Burnham and Anderson, 2002; Symonds and Moussalli, 2010). The final model was fit using Restricted Maximum Likelihood (REML). Marginal R^2, which represents an approximation of the proportion of the variance explained by the fixed factors alone, and conditional R^2, which represents an approximation of the proportion of the variance explained by both the fixed and random factors, were calculated based on the methods described in Nakagawa and Schielzeth (2013) and Johnson (2014).

2.8 Redundancy analysis: Relationships between DOC concentration, DOM composition, and watershed characteristics

We evaluated relationships between stream water DOC and watershed characteristics by relating DOC concentration and measures of DOM composition to catchment attributes using redundancy analysis (RDA; type 2 scaling) in the package rdaTest (Legendre and Durand, 2014) in R (version 3.2.2, R Core Team, 2015). To maximize the amount of information available, we performed RDA analysis on samples collected from January to July 2016, and therefore included all parameters of optical characterization (i.e., all PARAFAC components and spectral indices). We assessed the collinearity of DOM compositional variables using a variance inflation factor (VIF) criteria of > 10, which resulted in the removal of PARAFAC components C2, C3, and C5 prior to RDA analysis. Catchment attributes for each watershed included average slope, percent area of lakes, percent area of wetlands, average depth of mineral soil, and average depth of organic soil. Relationships between variables were linear, so no transformations were necessary and variables were standardized prior to analysis. To account for repeat monthly measures per watershed and potential temporal correlation associated with monthly sampling, we included sample month as a covariable ("partial-RDA"). To test whether the RDA axes significantly explained variation in the dataset, we compared permutations of residuals using ANOVA (9,999 iterations; test.axes function of rdaTest).

3 Results

3.1 Hydrology

We present work for water year 2015 (WY2015; October 1, 2014 – September 30, 2015) and water year 2016 (WY2016; October 1, 2015 – September, 30, 2016). Annual precipitation for both water years was lower than historical mean annual precipitation (WY2015= 2661 mm; WY2016= 2587 mm). It is worth noting that mean annual precipitation at our rain gauge location (2890 mm yr^{-1}, elevation = 16 m) is substantially lower than the average amount received at higher elevations, which from 1981-2010 was approximately 5027 mm yr^{-1} at an elevation of 1000m within our study area. This area receives a very high amount of annual rainfall but also experiences seasonal variation, with an extended wet period from fall through spring, and a much shorter, typically drier period during summer. In WY2015 and WY2016, 86-88% of the annual precipitation on Calvert Island occurred during the 8-months of wetter and cooler weather between September and April (~ 75% of the year), designated the "wet period" (WY2015 wet= 2388 mm, average air temp= 7.97°C; WY2016 wet= 2235 mm; average air temp= 7.38°C). The remaining annual precipitation occurred during the drier and warmer summer months of May – August, designated the "dry period" (WY2015 dry= 314 mm, average air temp= 13.4°C; WY2016 dry= 352 mm, average air temp= 13.1°C). Overall, although WY2015 was slightly wetter than WY2016, the two years were comparable in relative precipitation during the wet versus dry periods.

Stream discharge (Q) responded rapidly to rain events and as a result, closely tracked patterns in total precipitation (Fig. 2). Total Q for all watersheds was on average 22% greater for the wet period of WY2015 (total Q= 223.02 * 10^6; range= 5.13 * 10^6 – 111.51 * 10^6 m^3) compared to the wet period of WY2016 (total Q= 182.89 * 10^6; range= 4.17 * 10^6 – 91.45 * 10^6 m^3). Stream discharge and stream temperature were significantly different for wet versus dry periods (Mann-Whitney tests, $p < 0.0001$).

3.2 Temporal and spatial patterns in DOC concentration, yield and flux

Stream waters were high in DOC concentration relative to the global average for freshwater discharged directly to the ocean (average DOC for Calvert and Hecate Islands = 10.4 mg L^{-1}, std= 3.8; average global DOC= ~ 6 mg L^{-1}) (Meybeck, 1982; Harrison et al., 2005) (Table 1; Fig. 3). Q-weighted average DOC concentrations were higher than average measured DOC concentrations (11.1 mg L^{-1}, Table 1), and also resulted in slightly different ranking of the watersheds for highest to lowest DOC concentration. Within watersheds, Q-weighted DOC

concentrations ranged from a low of 8.4 mg L^{-1} (watershed 693) to a high of 19.3 mg L^{-1} (watershed 819), and concentrations were significantly different between watersheds (Kruskal-Wallis test, $p < 0.0001$). Seasonal variability tended to be higher in watersheds where DOC concentration was also high (watersheds 626, 819, and 844) and lower in watersheds with greater lake area (watersheds 1015 and 708) (Table 1; box plots, Figure 3). On an annual basis, DOC concentrations generally decreased through the wet period, and increased through the dry period, and concentrations were significantly lower during the wet period compared to the dry period (Mann-Whitney test, $p = 0.0123$). Results of our linear mixed effects (LME) model (Supplemental Table S6.1) indicate that DOC concentration was positively related to both discharge ($b = 0.613$, $p < 0.001$) and temperature ($b = 0.162$, $p = 0.011$) (model conditional $R^2 = 0.57$, marginal $R^2 = 0.09$).

Annual and monthly DOC yields are presented in Table 1. For the total period of available Q (October 1, 2014 - April 30, 2016; 19 months), areal (all watersheds) DOC yield was 52.3 Mg C km^{-2} (95% CI= 45.7 to 68.2 Mg C km^{-2}) and individual watershed yields ranged from 24.1 to 43.6 Mg C km^{-2}. For WY2015, areal annual DOC yield was 33.3 Mg C km^{-2} yr^{-1} (95% CI= 28.9 to 38.1 Mg C km^{-2} yr^{-1}). Total monthly rainfall was strongly correlated with monthly DOC yield (Fig. 4), and average monthly yield for the wet period (3.35 Mg C km^{-2} mo^{-1}; 95% CI= 2.94 to 4.40 Mg C km^{-2} mo^{-1}) was significantly greater than average monthly yield during the dry period (0.50 Mg C km^{-2} mo^{-1}; 95% CI= 0.41 to 0.62 Mg C km^{-2} mo^{-1}) (Mann-Whitney test, $p < 0.0001$).

Across our study watersheds, DOC flux generally increased with increasing watershed area (Fig. 5). In WY2015, total DOC flux for all watersheds included in our study was 1562 Mg C (95% CI= 1355 to 1787 Mg C), and individual watershed flux ranged from ranged from 82 to 276 Mg C. DOC flux was significantly different in wet versus dry periods (Mann-Whitney test, $p < 0.0001$). Overall, 94% of the export in WY2015 occurred during the wet period, and export for the wet period of WY2015 was lower than export for the wet period of WY2016 (Fig. 5).

3.3 Temporal and spatial patterns in DOM composition

The stable isotopic composition of dissolved organic carbon (δ^{13}C-DOC) was relatively tightly constrained over space and time (average δ^{13}C-DOC= -26.53‰, std= 0.36; range= -27.67‰ to -24.89‰). Values of S_R were low compared to the range typically observed in surface

waters (average S_R = 0.78, std= 0.04; range= 0.71 to 0.89) and Fe-corrected $SUVA_{254}$ values were at the high end of the range compared to most surface waters (average $SUVA_{254}$ for Calvert and Hecate Islands= 4.42 L mg^{-1} m^{-1}, std= 0.46; range of $SUVA_{254}$ in surface waters = 1.0 to 5.0 L mg^{-1} m^{-1}) (Spencer et al., 2012). Values for both Fluorescence Index (average Fluorescence Index= 1.36, std= 0.04; range= 1.30 to 1.44) and Freshness Index (average Freshness Index= 0.46, std= 0.02; range= 0.41 to 0.49) were relatively low compared to the typical range found in surface waters (Fellman et al., 2010; Hansen et al., 2016). Differences between watersheds were observed for δ^{13}C-DOC (Kruskal-Wallis test, p= 0.0043), S_R (Kruskal-Wallis test, p= 0.0001), Fluorescence Index (Kruskal-Wallis test, p= 0.0030), and Freshness Index (Kruskal-Wallis test, p= 0.0099), but watersheds did not differ in $SUVA_{254}$ (Kruskal-Wallis test, p= 0.4837).

We observed seasonal variability in δ^{13}C-DOC throughout the period of sample (Fig. 3 and our LME model (Supplemental Table S6.1) indicate that δ^{13}C-DOC declined with increasing discharge (b= -0.049, p= 0.014) and stream temperature (b= -0.024, p< 0.001) (model conditional R^2= 0.35, marginal R^2= 0.10). In contrast, although $SUVA_{254}$ appeared to exhibit a general seasonal trend of values increasing over the wet period and decreasing over the dry period, $SUVA_{254}$ was not significantly related to either discharge or stream temperature in the LME model results. S_R also appeared to fluctuate seasonally, with lower values during the wet season and higher values during the dry season. S_R was negatively related to discharge (b= -0.026, p< 0.001) and positively related to the interaction between discharge and stream temperature (b= 0.0015, p< 0.001) (model conditional R^2= 0.62, marginal R^2= 0.28). Freshness Index was negatively related to stream temperature (b= -0.003, p= 0.008) (model conditional R^2= 0.59, marginal R^2= 0.23), while Fluorescence Index was not significantly related to either discharge or stream temperature.

3.4 PARAFAC characterization of DOM

Six fluorescence components were identified through PARAFAC ("C1" through "C6") (Table 2). Additional details on PARAFAC model results are provided in Supplemental Table S4.1, Fig. S4.2, and Fig. S4.3. Of the six components, four were found to have close spectral matches in the OpenFluor database (C1, C3, C5, C6; minimum similarity score > 0.95), while the remaining two (C2 and C4) were found to have similar peaks represented in the literature. The first four components (C1 through C4) are described as terrestrial-derived, whereas

components C5 and C6 are described as autochthonous or microbially-derived (Table 2). In general, the rank order of each components' percent contribution to total fluorescence was maintained over time, with C1 comprising the majority of total fluorescence across all watersheds (Fig. 6).

Across watersheds, components fluctuated synchronously over time and variation between watersheds was relatively low, although slightly more variation between watersheds was observed during the beginning of the dry period relative to other times of the year (Fig 6). The percent contributions of components C1, C3, C5 and C6 to total fluorescence were not significantly different across watersheds (for all components Kruskal-Wallis test, $p > 0.05$), however percent composition of both C2 and C4 were different (Kruskal-Wallis test, $p = 0.0306$ and $p= 0.0307$, respectively) and higher for watersheds 819 and 844 relative to the other watersheds (Supplemental Fig. S4.4).

PARAFAC components exhibited significant relationships with stream discharge and stream temperature, although predicted changes (beta, or *b*) in fluorescence components with discharge and/or stream temperature were small (Supplemental Table S6.2). C3 increased with discharge ($b= 0.006$, $p= 0.003$), whereas C2, C4, and C5 decreased with discharge (C2: $b= -0.005$, $p= 0.022$; C4: $b= -0.008$, $p= 0.002$; C5: $b= -0.008$, $p= 0.002$). C1, C4, and C6 increased with temperature (C1: $b= 0.001$, $p= 0.050$; C4: $b= 0.003$, $p< 0.001$; C6: $b= 0.005$, $p= 0.005$), while both C3 and C5 decreased with temperature (C3: $b= -0.003$, $p= 0.003$; C5: $b= -0.003$, $p= 0.027$). Conditional R^2 values for the models ranged from 0.28 to 0.69, while marginal R^2 ranged from 0.20 to 0.46. Overall, greater changes in component contribution to total fluorescence were observed with changes in discharge relative to changes in stream temperature.

3.5 Relationships between watershed characteristics, DOC concentrations, and DOM composition

Results of the partial-RDA (type 2 scaling) were significant in explaining variability in DOM concentration and composition (semi-partial $R^2= 0.33$, $F= 7.90$, $p< 0.0001$) (Fig. 7). Axes 1 through 3 were statistically significant at $p< 0.001$, and the relative contribution of each axis to the total explained variance was 47%, 30%, and 22%, respectively. Additional details on the RDA test are provided in Supplemental Figs. S5.1-S5.2 and Tables S5.3 – S5.5. Axis 1 described a gradient of watershed coverage by water-inundated ecosystem types, ranging from more

wetland coverage to more lake coverage. Total lake coverage (area) and mean mineral soil material thickness showed a strong positive contribution, and wetland coverage (area) showed a strong negative contribution to this axis. Freshness Index, Fluorescence Index, S_R and fluorescence component C6 were positively correlated with Axis 1, while component C4 showed a clear negative correlation. Axis 2 described a subtler gradient of soil material thickness ranging from greater mean organic soil material thickness to greater mean mineral soil material thickness. DOC concentration, δ^{13}C-DOC, $SUVA_{254}$, and fluorescence component C1 all showed a strong, positive correlation with Axis 2. Axis 3 described a gradient of watershed steepness, from lower gradient slopes with more wetland area and thicker organic soil material to steeper slopes with less developed organic horizons. Average slope contributed negatively to Axis 3 (see Supplemental Table S5.5), followed by positive contributions from both wetland area and thickness of organic soil material. δ^{13}C-DOC showed the most positive correlation with Axis 3, whereas fluorescence components C1 and C4 showed the most negative.

4 Discussion

4.1 DOC export from small catchments to the coastal ocean

In comparison to global models of DOC export (Mayorga et al., 2010) and DOC exports quantified for southeastern Alaska (D'Amore et al., 2015a; D'Amore et al., 2016; Stackpoole et al., 2017), our estimates of freshwater DOC yield from Calvert and Hecate Island watersheds are in the upper range predicted for the perhumid rainforest region. When compared to watersheds of similar size, DOC yields from Calvert and Hecate Island watersheds are some of the highest observed (see reviews in Hope et al., 1994; Alvarez-Cobelas et al., 2012), including DOC yields from many tropical rivers, despite the fact that tropical rivers have been shown to export very high DOC (e.g., Autuna River, Venezuela, DOC yield= 56,946 kg C km^{-2} yr^{-1}; Castillo et al., 2004), and are often regarded as having disproportionately high carbon export compared to temperate and Arctic rivers (Aitkenhead and McDowell, 2000; Borges et al., 2015). Our estimates of DOC yield are comparable to, or higher than, previous estimates from high-latitude catchments of similar size that receive high amounts of precipitation and contain extensive organic soils and wetlands (e.g. Naiman, 1982 (DOC yield= 48,380 kg C km^{-2} yr^{-1}); Brooks et al., 1999 (DOC yield= 20,300 kg C km^{-2} yr^{-1}); Ågren et al., 2007 (DOC yield= 32,043 kg C km^{-2} yr^{-1})). However, many of these catchments represent low (first or second) order headwater

streams that drain to higher order stream reaches, rather than directly to the ocean. Although headwater streams have been shown to export up to 90% of the total annual carbon in stream systems (Leach et al., 2016), significant processing and loss typically occurs during downstream transit (Battin et al., 2008).

Over much of the incised outer coast of the CTR, small rainfall-dominated catchments contribute high amounts of freshwater runoff to the coastal ocean (Royer, 1982; Morrison et al., 2012; Carmack et al., 2015). Small mountainous watersheds that discharge directly to the ocean can exhibit disproportionately high fluxes of carbon relative to watershed size, and in aggregate may deliver more than 50% of total carbon flux from terrestrial systems to the ocean (Milliman and Syvitski, 1992; Masiello and Druffel, 2001). Extrapolating our estimate of annual DOC yield from Calvert and Hecate Island watersheds to the entire hypermaritime subregion of British Columbia's CTR (29,935 km^2), generates an estimated annual DOC flux of 0.997 Tg C yr^{-1} (0.721 to 1.305 Tg C yr^{-1} for our lowest to highest yielding watersheds, respectively), with the caveat that this estimate is rudimentary and does not account for spatial heterogeneity in controlling factors such as wetland extent, topography, and watershed size. Regional comparisons estimate that Southeast Alaska (104,000 km^2), at the northern range of the CTR, exports approximately 1.25 Tg C yr^{-1} (Stackpoole et al., 2016), while south of the perhumid CTR, the wet northwestern United States and its associated coastal temperate rainforests export less than 0.153 Tg C yr^{-1} as DOC (reported as TOC, Butman et al., 2016). This suggests that the hypermaritime coast of British Columbia plays an important role in the export of DOC from coastal temperate rainforest ecosystems of western North America, in a region that is already expected to contribute high quantities of DOC to the coastal ocean.

4.2 DOM composition

The composition of stream water DOM exported from Calvert and Hecate Island watersheds is mainly terrestrial, indicating the production and overall supply of terrestrial material is sufficient to exceed microbial demand, and thus a relatively abundant supply of terrestrial DOM is available for export. Values for δ^{13}C-DOC suggest terrestrial carbon sources from C3 plants and soils were the dominant input to catchment stream water DOM (Finlay and Kendall, 2007). Measures of S_R and $SUVA_{254}$ were typical of environments that export large quantities of high molecular weight, highly aromatic DOM such as some tropical rivers (e.g.,

Lambert et al., 2016; Mann et al., 2014), streams draining wetlands (e.g., Ågren et al., 2008, Austnes et al., 2010), or streams draining small undisturbed catchments comprised of mixed forest and wetlands (e.g. Wickland et al., 2007; Fellman et al., 2009a; Spencer et al., 2010, Yamashita et al., 2011). This suggests the majority of the DOM pool is comprised of larger molecules that have not been extensively chemically or biologically degraded through processes such as microbial utilization or photodegradation, and therefore are potentially more biologically available (Amon and Benner, 1996).

Biological utilization of DOM is influenced by its composition (e.g. Judd et al., 2006; Fasching et al., 2014), therefore differences in DOM can alter the downstream fate and ecological role of freshwater-exported DOM. For example, the majority of the fluorescent DOM pool was comprised of C1, which is described as humic-like, less-processed terrestrial soil and plant material (see Table 2). In addition, although the tryptophan-like component C6, represents a minor proportion of total fluorescence, even a small proteinaceous fraction of the overall DOM pool can play a major role in overall bioavailability and bacterial utilization of DOM (Berggren et al., 2010; Guillamette and Giorgio, 2011). These contributions of stream-exported DOM may represent a relatively fresh, seasonally-consistent contribution of terrestrial subsidy from streams to the coastal ecosystem, which in this region is relatively lower in carbon and nutrients throughout much of the year (Whitney et al., 2005; Johannessen et al., 2008).

4.3. DOC and DOM export: Sources and seasonal variability

On Calvert and Hecate Islands, the relationship between DOC concentration and discharge varied by watershed (see Supplemental Fig. S6.1), as might be expected given the known influence of watershed characteristics (e.g., lake area, wetland area, soils, etc) on DOC concentration and export. However, overall DOC concentrations increased in all watersheds with both discharge and temperature indicating the overarching drivers of DOC export are the hydrologic coupling of precipitation and runoff from the landscape with the seasonal production and availability of DOC (Fasching et al., 2016).

Precipitation is a well-established driver of stream DOC export (Alvarez-Cobelas et al., 2012), particularly in systems containing organic soils and wetlands (Olefeldt et al., 2013; Wallin et al., 2015; Leach et al., 2016). Frequent, high intensity precipitation events and short residence times are expected to result in pulsed exports of stream DOC that are rapidly shunted

512 downstream, thus reducing time for in-stream processing (Raymond et al., 2016). Flashy stream
513 hydrographs indicate that hydrologic response times for Calvert and Hecate Island watersheds
514 are rapid, presumably as a result of small catchment size, high drainage density, and relatively
515 shallow soils with high hydraulic conductivity (Gibson et al., 2000; Fitzgerald et al., 2003).
516 Rapid runoff is presumably accompanied by rapid increases in water tables and lateral movement
517 of water through shallow soil layers rich in organic matter (Fellman et al., 2009b; D'Amore et
518 al., 2015b). It appears that on Calvert and Hecate Islands, the combination of high rainfall, rapid
519 runoff, and abundant sources of DOC from organic-rich wetlands and forests, result in high DOC
520 fluxes.

521 The relationship between DOC, stream temperature, and discharge indicates that seasonal
522 dynamics play an important role in the variability of DOC exported from these systems. For
523 example, DOC concentrations decrease in all watersheds during the wet period of the year, these
524 decreases are associated with clear changes in DOM composition, such as increasing δ^{13}C-DOC,
525 $SUVA_{254}$, and decreasing S_R. This is in contrast with patterns observed during the dry period,
526 when DOC concentrations gradually increase, while δ^{13}C-DOC, $SUVA_{254}$ decrease. Fluctuations
527 in DOC and DOM composition occur throughout the wet and the dry season, suggesting that
528 temperature and runoff – and perhaps other seasonal drivers - are important year-round controls
529 on DOC concentration as well as certain measures of DOM composition, such as δ^{13}C-DOC and
530 S_R.

531 The process of "DOC flushing" has been shown to increase stream water DOC during
532 higher flows in coastal and temperate watersheds (e.g., Sanderman et al., 2009; Deirmendjian et
533 al., 2017). Flushing can occur through various mechanisms. For example, Boyer et al. (1996)
534 observed that during drier periods, DOC pools can increase in soils and are then flushed to
535 streams when water tables rise. Rising water tables can establish strong hydraulic gradients that
536 initiate and sustain prolonged increases in metrics like $SUVA_{254}$, until the progressive drawdown
537 of upland water tables constrain flow paths (Lambert et al., 2013). DOC concentrations can vary
538 during flushing in response to changing flow paths, which can shift sources of DOC within the
539 soil profile from older material in deeper soil horizons to more recently produced material in
540 shallow horizons (Sanderman et al., 2009), or from changes in the production mechanism of
541 DOC (Lambert et al., 2013). For example, Sanderman et al. (2009), observed distinct

relationships between discharge and both δ^{13}C-DOC and $SUVA_{254}$, and postulated that during their rainy season, hillslope flushing shifts DOM sources to more aged soil organic material. In addition, instream production can also provide a source of DOC, and therefore affect seasonal variation in DOC concentration and composition (Lambert et al., 2013). The extent of these effects can shift seasonally; relationships between flow paths and DOC export in rain-dominated catchments can vary within and between hydrologic periods depending on factors such as the degree of soil saturation, duration of previous drying and rewetting cycles, soil chemistry, and DOM source-pool availability (Lambert et al., 2013).

Our observations of changes in DOC and DOM related to discharge and stream temperature suggest that a variety of mechanisms may be important for controlling dynamics of seasonal export in Pacific hypermaritime watersheds. We observed elevated DOC concentrations during precipitation events following extended dry periods, suggesting DOC may accumulate during dry periods and be flushed to streams during runoff events. Increased discharge was significantly related to δ^{13}C-DOC and S_R, with higher discharge resulting in more terrestrial-like DOM. One possible explanation is that hydrologic connectivity increases during higher discharge as soil conditions become more saturated, therefore promoting the mobilization of DOM from across a wider range of the soil profile (McKnight et al., 2001; Kalbitz et al., 2002). In addition, the mechanisms of DOC production and sources of DOC appear to shift seasonally. Relationships between increased temperature and lower values of δ^{13}C-DOC, and higher values of Freshness Index, C1 and C4, suggest that warmer conditions result in a fresh supply of DOM exported from terrestrial sources (Fellman et al., 2009a; Fasching et al., 2016). This may represent a shift in the source of DOM and/or increased contributions from less aromatic, lower molecular weight material, such as DOM derived from increased terrestrial primary production (Berggren et al., 2010). Further, fine-scaled investigation into the mechanistic underpinnings of the relationship between discharge, stream temperature, and DOM, represents a clear priority for future research in this region.

4.4 Relationships between watershed attributes and exported DOM

Previous studies have implicated wetlands as a major driver of DOM composition (e.g., Xenopoulos et al., 2003; Ågren et al., 2008; Creed et al., 2008), however the analysis of relationships between Calvert and Hecate Island landscape attributes and variation in DOM

572 composition suggests that controls on DOM composition are more nuanced than being solely
573 driven by the extent of wetlands. Ågren et al. (2008) found that when wetland area comprised
574 >10% of total catchment area, wetland DOM was the most significant driver of stream DOM
575 composition during periods of high hydrologic connectivity. Although wetlands comprise an
576 average of 37% of our study area, they do not appear to be the single leading driver of variability
577 in DOC concentration and DOM composition. Other factors, such as watershed slope, the depth
578 of organic and mineral soil materials, and the presence of lakes also appear to be influence DOC
579 concentration and DOM composition. The presence of cyptic wetlands (Creed et al., 2003) and
580 limitations of the wetland mapping method could also weaken the link between wetland extent,
581 DOC, and DOM.
582 In these watersheds, soils with pronounced accumulations of organic matter are not
583 restricted to wetland ecosystems. Peat accumulation in wetland ecosystems results in the
584 formation of organic soils (Hemists), where mobile fractions of DOM accumulate under
585 saturated soil conditions and limited drainage, resulting in the enrichment of poorly
586 biodegradable, more stable humic acids (Stevenson, 1994; Marschner and Kalbitz, 2003).
587 Although Hemist soils comprise 27.8% of our study area, Folic Histosols, which form under
588 more freely drained conditions, such as steeper slopes, occur over an additional 25.7% of the
589 area (Supplemental S1.2). In freely drained organic soils, high rates of respiration can result in
590 further enrichment of aromatic and more complex molecules, and this material may be rapidly
591 mobilized and exported to streams (Glatzel et al., 2003). This suggests the importance of widely
592 distributed, alternative soil DOM source-pools, such as Folic Histosols and associated Podzols
593 with thick forest floors on hillslopes, available to contribute high amounts of terrestrial carbon
594 for export.
595 Although lakes make up a relatively small proportion of the total landscape area, their
596 influence on DOM export appears to be important. The proportion of lake area can be a good
597 predictor of organic carbon loss from a catchment since lakes often increase hydrologic
598 residence times and thus increase opportunities for biogeochemical processing (Algesten et al.,
599 2004; Tranvik et al., 2009). In our study, watersheds with a larger percentage of lake area
600 exhibited slower response following rain events (Supplemental Fig. S2.2), lower DOC yields,
601 and lake area was correlated with parameters that represent greater autochthonous DOM

602 production or microbial processing such as higher Freshness Index, S_R, Fluorescence Index, and
603 higher proportions of component C6. In contrast, watersheds with a high percentage of wetlands
604 contributed DOM that was more allocthonous in composition. Lakes are known to be important
605 landscape predictors of DOC, as increased residence time enables removal via respiration, thus
606 reducing downstream exports from lake outlets (Larson et al., 2007). The proximity of wetlands
607 and lakes to the watershed outlet can also play an important role in the composition of DOM
608 exports (Martin et al., 2006).

609 **5 Conclusions**

610 Previous work has demonstrated freshwater discharge is substantial along the coastal
611 margin of the North Pacific temperate rainforest, and plays an important role in processes such as
612 ocean circulation (Royer, 1982; Eaton and Moore, 2010). Our finding that small catchments in
613 this region contribute high yields of terrestrial DOC to coastal waters suggests that freshwater
614 inputs may also influence ocean biogeochemistry and food web processes through terrestrial
615 organic matter subsidies. Our findings also suggest that this region may be currently
616 underrepresented in terms of its role in global carbon cycling. Currently, there is no region-wide
617 carbon flux model for the Pacific coastal temperate rainforest or the greater Gulf of Alaska,
618 which would quantify the importance of this region within the global carbon budget. Our
619 estimates point to the importance of the hypermaritime outer-coast zone of the CTR, where
620 subdued terrain, high rainfall, ocean moderated temperatures and poor bedrock have generated a
621 distinctive 'bog-forest' landscape mosaic within the greater temperate rainforest (Banner et al.
622 2005). However, even within our geographically limited study area, we observed a range of
623 DOC yields across watersheds. To quantify regional scale fluxes of rainforest carbon to the
624 coastal ocean, further research will be needed to estimate DOC yields across complex spatial
625 gradients of topography, climate, hydrology, soils and vegetation. Long term changes in DOC
626 flux have been observed in many places (e.g., Worrall et al., 2004; Borken et al., 2011; Lepistö et
627 al., 2014; Tank et al., 2016) and continued monitoring of this system will allow us to better
628 understand the underlying drivers of export and evaluate future patterns in DOC yields. Coupled
629 with current studies investigating the fate of terrestrial material in ocean food webs, this work
630 will improve our understanding of coastal carbon patterns, and increase capacity for predictions
631 regarding the ecological impacts of climate change.

Author Contributions

The authors declare that they have no conflict of interest.

A.A. Oliver prepared the manuscript with contributions from all authors, designed analysis protocols, analyzed samples, performed the modeling and analysis for dissolved organic carbon fluxes, parallel factor analysis of dissolved organic matter composition, and all remaining statistical analyses. S.E. Tank assisted with designing the study and overseeing laboratory analyses, crafting the scope of the paper, and determining the analytical approach.

I. Giesbrecht led the initial DOC sampling design, helped coordinate the research team, oversaw routine sampling and data management, and led the watershed characterization.

M.C. Korver developed the rating curves, and conducted the statistical analysis of discharge measurement uncertainties and rating curve uncertainties. W.C. Floyd lead the hydrology component of this project, selected site locations, installed and designed the hydrometric stations, and developed the rating curves and final discharge calculations. C. Bulmer and P. Sanborn collected and analyzed soil field data and prepared the digital soils map of the watersheds. K.P. Lertzman conceived of and co-led the overall study of which this paper is a component, helped assemble and guide the team of researchers who carried out this work, provided input to each stage of the study.

Acknowledgements

This work was funded by the Tula Foundation and the Hakai Institute. The authors would like to thank many individuals for their support, including Skye McEwan, Bryn Fedje, Lawren McNab, Nelson Roberts, Adam Turner, Emma Myers, David Norwell, and Chris Coxson for sample collection and data management, Clive Dawson and North Road Analytical for sample processing and data management, Keith Holmes for creating our maps, Matt Foster for database development and support, Shawn Hateley for sensor network maintenance, Jason Jackson, Colby Owen, James McPhail, and the entire staff at Hakai Energy Solutions for installing and maintaining the sensors and telemetry network, and Stewart Butler and Will McInnes for field support. Thanks to Santiago Gonzalez Arriola for generating the watershed summaries and associated data products, and Ray Brunsting for overseeing the design and implementation of the sensor network and the data management system at Hakai. Additional thanks to Lori Johnson

and Amelia Galuska for soil mapping field assistance, and Francois Guillamette for PARAFAC consultation. Thanks to Dave D'Amore for inspiring the Hakai project to investigate aquatic fluxes at the coastal margin and for technical guidance. Lastly, thanks to Eric Peterson and Christina Munck who provided significant guidance throughout the process of designing and implementing this study.

References

Ågren, A., Buffam, I., Jansson, M. and Laudon, H.: Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export, J. Geophys. Res. Biogeosci., 112(G3), doi:10.1029/2006JG000381, 2007.

Ågren, A., Buffam, I., Berggren, M., Bishop, K., Jansson, M. and Laudon, H.: Dissolved organic carbon characteristics in boreal streams in a forest-wetland gradient during the transition between winter and summer, J. Geophys. Res. Biogeosci., 113(G3), doi:10.1029/2007JG000674, 2008.

Akaike, H.: Likelihood of a model and information criteria, J. Econometrics, 16(1), 3-14, doi:10.1016/0304-4076(81)90071-3, 1981.

Aitkenhead, J.A., and McDowell, W.H.: Soil C:N ratio as a predictor of annual riverine DOC flux at local and global scales, Global Biogeochem. Cycles, 14(1), 127–138, doi:10.1029/1999GB900083, 2000.

Alaback, P.B.: Biodiversity patterns in relation to climate: The coastal temperate rainforests of North America, Ecol. Stud., 116, 105–133, doi:10.1007/978-1-4612-3970-3_7, 1996.

Algesten, G., Sobek, S., Bergström, A., Ågren, A., Tranvik, L. and Jansson, M.: Role of lakes for organic carbon cycling in the boreal zone, Global Change Biol., 10(1), 141–147, doi:10.1111/j.1365-2486.2003.00721.x, 2004.

Alvarez-Cobelas, M., Angeler, D., Sánchez-Carrillo, S. and Almendros, G.: A worldwide view of organic carbon export from catchments, Biogeochemistry, 107(1-3), 275–293, doi:10.1007/s10533-010-9553-z, 2012.

Amon, R.M.W., and Benner, R.: Bacterial utilization of different size classes of dissolved organic matter, Limnol. Oceanogr., 41, 41-51, 1996.

Aufdenkampe, A., Mayorga, E., Raymond, P., Melack, J., Doney, S., Alin, S., Aalto, R., and Yoo, K.: Riverine coupling of biogeochemical cycles between land, oceans, and atmosphere, Front. Ecol. Environ., 9(1), 53–60, doi:10.1890/100014, 2011.

703 Austnes, K., Evans, C.D., Eliot-Laize, C., Naden, P.S., and Old, G.H.: Effects of storm events on
704 mobilisation and in-stream processing of dissolved organic matter (DOM) in a Welsh peatland
705 catchment, Biogeochem., 99, 157-173, doi:10.1007/s10533-009-9399-4, 2010.
706
707 Banner, A., LePage, P., Moran, J., and de Groot, A. (Eds.): The HyP3 Project: pattern,
708 process, and productivity in hypermaritime forests of coastal British Columbia -
709 a synthesis of 7-year results, Special Report 10, Res. Br., British Columbia Ministry Forests,
710 Victoria, British Columbia, 142 pp., available at:
711 http://www.for.gov.bc.ca/hfd/pubs/Docs/Srs/Srs10.htm, 2005.
712
713 Battin, T.J., Kaplan, L.A., Findlay, S., Hopkinson, C.S., Marti, E., Packman, A.I., Newbold, D.,
714 and Sabater, F.: Biophysical controls on organic carbon fluxes in fluvial networks, Nature
715 Geosci., 1, 95–100, 2008.
716
717 Bauer, J.E., Cai, W.J., Raymond, P.A., T.S., Bianchi, Hopkinson, C.S., and Regnier, P.A.G.: The
718 changing carbon cycle of the coastal ocean, Nature, 504(7478), 61-70, doi:10.1038/nature12857,
719 2013.
720
721 Berggren, M., Laudon, H., Haei, M., Ström, L., and Jansson, M.: Efficient aquatic bacterial
722 metabolism of dissolved low-molecular-weight compounds from terrestrial sources, ISME J.,
723 doi:10.1038/ismej.2009.120, 2010.
724
725 Boehme, J. and Coble, P.: Characterization of Colored Dissolved Organic Matter Using High-
726 Energy Laser Fragmentation, Environ. Sci. Technology, 34(15), 3283–3290,
727 doi:10.1021/es9911263, 2000.
728
729 Borcard, D., Gillet, F., and Legendre, P.: Numerical ecology with R, Springer, New York,
730 United States, doi:10.1007/978-1-4419-7976-6, 2011.
731
732 Borken, W., Ahrens, B., Schultz, C. and Zimmermann, L.: Site-to-site variability and temporal
733 trends of DOC concentrations and fluxes in temperate forest soils, Global Change Biol., 17:
734 2428–2443, doi:10.1111/j.1365-2486.2011.02390.x, 2011.
735
736 Borges, A.V., Darchambeau, F., Teodoru, C.R., Marwick, T.R., Tamooh, F., Geeraert, N.,
737 Omengo, F.O., Guérin, F., Lambert, T., Morana, C., Okuku, E., and Bouillon, S.: Globally
738 significant greenhouse-gas emissions form African inland waters, Nature Geosci., 8, 637–642,
739 doi:10.1038/ngeo2486, 2015.
740
741 Boyer, E.W., Hornberger, G.M., Bencala, K.E., and McKnight, D.: Overview of a simple model
742 describing variation of dissolved organic carbon in an upland catchment, Ecol. Modell., 86, 183-
743 188, 1996.
744
745 Burnham K.P., and Anderson, D.R.: Model selection and multimodel inference, 2nd edn.
746 Springer, New York, 2002.
747

748 Carmack, E., Winsor, P., and William, W.: The contiguous panarctic Riverine Coastal Domain:
749 A unifying concept, Prog. Oceanogr., 139, 13-23, doi:10.1016/j.pocean.2015.07.014, 2015.
750
751 Castillo, M.M., Allan, J.D., Sinsabaugh, R.L., and Kling, G.W.: Seasonal and interannual
752 variation of bacterial production in lowland rivers of the Orinoco basin, Freshwater Biol., 49(11),
753 1400-1414, doi:10.1111/j.1365-2427.2004.01277.x, 2004.
754
755 Clark, J.M., Lane, S.N., Chapman, P.J., and Adamson, J.K.: Export of dissolved organic carbon
756 from an upland peatland during storm events: Implications for flux estimates, J. Hydrol., 347(3-
757 4), 438-447, doi: 10.1016/j.jhydrol.2007.09.030, 2007.
758
759 Coble, P., Castillo, C. and Avril, B.: Distribution and optical properties of CDOM in the Arabian
760 Sea during the 1995 Southwest Monsoon, Deep Sea Res. Part II, Oceanogr., 45(10-11), 2195–
761 2223, doi:10.1016/S0967-0645(98)00068-X, 1998.
762
763 Cole, J., Prairie, Y., Caraco, N., McDowell, W., Tranvik, L., Striegl, R., Duarte, C., Kortelainen,
764 P., Downing, J., Middelburg, J. and Melack, J.: Plumbing the Global Carbon Cycle: Integrating
765 Inland Waters into the Terrestrial Carbon Budget, Ecosystems, 10(1), 172–185,
766 doi:10.1007/s10021-006-9013-8, 2007.
767
768 Cory, R.M., and McKnight, D.M.,: Fluorescence spectroscopy reveals ubiquitous presence of
769 oxidized and reduced quinines in dissolved organic matter, Environ. Sci. Technol., 39, 8142 -
770 8149, doi:10.1021/es0506962, 2005.
771
772 Creed, I.F., Beall, F.D., Clair, T.A., Dillon, P.J., and Hesslein, R.H.: Predicting export of
773 dissolved organic carbon from forested catchments in glaciated landscapes with shallow soils,
774 Glob. Biogeochem. Cycles, 22, GB4024, doi:10.1029/2008GB003294, 2008.
775
776 Creed, I.F., Sanford, S.E., Beall, F.D., Molot, L.A., and Dillon, P.J.: Cryptic wetlands:
777 integrating hidden wetlands in regression models of the export of dissolved organic carbon from
778 forested landscapes, Hydrol. Process., 17, 3629-3648, 2003.
779
780 D'Amore, D.V., Edwards, R.T., and Biles, F.E.: Biophysical controls on dissolved organic
781 carbon concentrations of Alaskan coastal temperate rainforest streams, Aquat. Sci.,
782 doi:10.1007/s00027-015-0441-4, 2015a.
783
784 D'Amore, D.V., Edwards, R.T., Herendeen, P.A., Hood, E., and Fellman, J.B.: Dissolved
785 organic carbon fluxes from hydropedologic units in Alaskan coastal temperate rainforest
786 watersheds, Soil Sci. Soc. Am. J., 79:378-388, doi:10.2136/sssaj2014.09.0380, 2015b.
787
788 D'Amore, D.V., Biles, F.E., Nay, M., Rupp, T.S.: Watershed carbon budgets in the southeastern
789 Alaskan coastal forest region, in: Baseline and projected future carbon storage and greenhouse-
790 gas fluxes in ecosystems of Alaska, U.S. Geological Survey Professional Paper, 1826, 196 p.,
791 2016.
792

Dai, M., Yin, Z., Meng, F., Liu, Q. and Cai, W.J.: Spatial distribution of riverine DOC inputs to the ocean: an updated global synthesis, Curr. Opin. Sust., 4(2), 170–178, doi:10.1016/j.cosust.2012.03.003, 2012.

Deirmendjian, L., Loustau, D., Augusto, L., Lafont, S., Chipeaux, C., Poirier, D., and Abril., G.: Hydrological and ecological controls on dissolved carbon concentrations in groundwater and carbon export to surface waters in a temperate pine forest watershed, Biogeosciences Discuss., doi:10.5194/bg-2017-90, in review, 2017.

DellaSala, D.A.: Temperate and Boreal Rainforests of the World, Island Press, Washington, D.C., 2011.

Emili, L. and Price, J.: Biogeochemical processes in the soil-groundwater system of a forest-peatland complex, north coast British Columbia, Canada, Northwest Sci., 88, 326–348, doi:10.3955/046.087.0406, 2013.

Fasching, C., Behounek, B., Singer, G. and Battin, T.: Microbial degradation of terrigenous dissolved organic matter and potential consequences for carbon cycling in brown-water streams, Sci. Rep., 4, 4981, doi:10.1038/srep04981, 2014.

Fasching, C., Ulseth, A., Schelker, J., Steniczka, G. and Battin, T.: Hydrology controls dissolved organic matter export and composition in an Alpine stream and its hyporheic zone, Limnol. Oceanogr., 61(2), 558–571, doi:10.1002/lno.10232, 2016.

Fellman, J., Hood, E., D'Amore, D., Edwards, R. and White, D.: Seasonal changes in the chemical quality and biodegradability of dissolved organic matter exported from soils to streams in coastal temperate rainforest watersheds, Biogeochemistry, 95, 277–293, doi:10.1007/s10533-009-9336-6, 2009a.

Fellman, J., Hood, E., Edwards, R. and D'Amore, D.: Changes in the concentration, biodegradability, and fluorescent properties of dissolved organic matter during stormflows in coastal temperate watersheds, J. Geophys. Res. Biogeosci., 114, doi:10.1029/2008JG000790, 2009b.

Fellman, J., Hood, E. and Spencer, R.: Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: A review, Limnol. Oceanogr., 55, 24522462, doi:10.4319/lo.2010.55.6.2452, 2010.

Fellman, J., Nagorski, S., Pyare, S., Vermilyea, A.W., Scott, D., and Hood, E.: Stream temperature response to variable glacier cover in coastal watersheds of Southeast Alaska, Hydrol. Process., 28, 2062-2073, doi:10.1002/hyp.9742, 2014

Finlay, J.C., and Kendall, C.: Stable isotope tracing of temporal and spatial variability in organic matter sources and variability in organic matter sources to freshwater ecosytems, in Stable Isotopes in Ecology and Environmental Science, 2, Michener, R., and Lajtha, K. (Eds), Blackwell Publishing Ltd, Oxford, UK, 283-324, 2007.

Fitzgerald, D., Price, J., and Gibson, J.: Hillslope-swamp interactions and flow pathways in a hypermaritime rainforest, British Columbia, Hydrol. Process., 17, 3005-3022, doi:10.1002/hyp.1279, 2003.

Gibson, J.J., Price, J.S., Aravena, R., Fitzgerald, D.F., and Maloney, D.: Runoff generation in a hypermaritime bog-forest upland, Hydrol. Process, 14, 2711-2730, doi: 10.1002/1099-1085(20001030)14:15<2711::AID-HYP88>3.0.CO;2-2, 2000.

Glatzel, S., Kalbitz, K., Dalva, M., and Moore, T.: Dissolved organic matter properties and their relationship to carbon dioxide efflux from restored peat bogs, Geoderma, 113, 397-411, 2003.

Gonzalez Arriola S., Frazer, G.W., Giesbrecht, I.: LiDAR-derived watersheds and their metrics for Calvert Island, Hakai Institute, doi:dx.doi.org/10.21966/1.15311, 2015.

Gorham, E., Lehman, C., Dyke, A., Clymo, D., and Janssens, J.: Long-term carbon sequestration in North American peatlands, Quat. Sci. Review, 58, 77-82, 2012.

Graeber, D., Gelbrecht, J., Pusch, M., Anlanger, C. and von Schiller, D.: Agriculture has changed the amount and composition of dissolved organic matter in Central European headwater streams, Sci. Total Environ., 438, 435–446, doi:10.1016/j.scitotenv.2012.08.087, 2012.

Green, R.N.: Reconnaissance level terrestrial ecosystem mapping of priority landscape units of the coast EBM planning area: Phase 3, Prepared for British Columbia Ministry Forests, Lands and Natural Resource Ops., Blackwell and Associates, Vancouver, Canada, 2014.

Guillemette, F. and Giorgio, P.: Reconstructing the various facets of dissolved organic carbon bioavailability in freshwater ecosystems, Limnol. Oceanogr., 56, 734–748, doi:10.4319/lo.2011.56.2.0734, 2011.

Hansen, A.M., Kraus, T.E.C., Pellerin, B.A., Fleck, J.A., Downing, B.D., and Bergamaschi, B.A.: Optical properties of dissolved organic matter (DOM): Effects of biological and photolytic degradation, Limnol. Oceanogr., 61, 1015-1032, doi:10.1002/lno.10270, 2016.

Harrell, F.E., Dupont, C., and many others.: Hmisc: Harrell Miscellaneous. R package version 4.0-2. https://CRAN.R-project.org/package=Hmisc, 2016.

Harrison, J., Caraco, N. and Seitzinger, S.: Global patterns and sources of dissolved organic matter export to the coastal zone: Results from a spatially explicit, global model, Global Biogeochem. Cycles, 19, doi:10.1029/2005gb002480, 2005.

Helms, J., Stubbins, A., Ritchie, J., Minor, E., Kieber, D. and Mopper, K.: Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter, Limnol. Oceanogr., 53, 955–969, doi:10.4319/lo.2008.53.3.0955, 2008.

Helton, A., Wright, M., Bernhardt, E., Poole, G., Cory, R. and Stanford, J.: Dissolved organic carbon lability increases with water residence time in the alluvial aquifer of a river floodplain ecosystem, J. Geophys. Res. Biogeosciences, 120, 693–706, doi:10.1002/2014JG002832, 2015.

Hoffman, K.M., Gavin, D.G., Lertzman, K.P., Smith, D.J., and Starzomski, B.M.: 13,000 years of fire history derived from soil charcoal in a British Columbia coastal temperate rain forest, Ecosphere, 7, e01415, doi:10.1002/ecs2.1415, 2016.

Hope, D., Billett, M.F., and Cresser, M.S.: A review of the export of carbon in river water: Fluxes and processes, Environ. Pollut., 84(3), 301-324, doi:10.1016/0269-7491(94)90142-2, 1994.

Hopkinson, C.S., Buffam, I., Hobbie, J., Vallino, J. and Perdue, M.: Terrestrial inputs of organic matter to coastal ecosystems: An intercomparison of chemical characteristics and bioavailability, Biogeochemistry, 43, 211–234, 1998.

Hudson, N., Baker, A. and Reynolds, D.: Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters-a review, River Res. Appl., 23, 631–649, doi:10.1002/rra.1005, 2007.

Hurvich, C.M., and Tsai, C.: Regression and time series model selection in small samples, Biometrika, 76(2), 297-307, doi:10.2307/2336663, 1989.

International Union of Soil Sciences (IUSS) Working Group: World Reference Base for Soil Resources, International soil classification system for naming soils and creating legends for soil maps, World Soil Resources Reports No. 106, Food and Agricultural Organization of the United Nations, Rome, Italy, 2015.

ISO Standard 9196: Liquid flow measurement in open channels - Flow measurements under ice conditions, International Organization for Standardization, available online at www.iso.org, 1992.

ISO Standard 748: Hydrometry - Measurement of liquid flow in open channels using current-meters or floats, International Organization for Standardization, available online at www.iso.org, 2007.

Johannessen, S.C., Potentier, G., Wright, C.A., Masson, D., and Macdonald, R.W.: Water column organic carbon in a Pacific marginal sea (Strait of Georgia, Canada), Mar. Environ. Res., 66, S49-S61, doi:10.1016/j.marenvres.2008.07.008, 2008.

Johnson, P.C.D.: Extension of Nakagawa & Schielzeth's R^2_{GLMM} to random slopes models. Methods Ecol. Evol., DOI: 10.1111/2041-210X.12225, 2014.

Johnson, M., Couto, E., Abdo, M. and Lehmann, J.: Fluorescence index as an indicator of dissolved organic carbon quality in hydrologic flowpaths of forested tropical watersheds, Biogeochemistry, 105, 149–157, doi:10.1007/s10533-011-9595-x, 2011.

Judd, K., Crump, B. and Kling, G.: Variation in dissolved organic matter controls bacterial production and community composition, Ecology, 87, 2068–2079, doi:10.1890/0012-9658(2006)87[2068:VIDOMC]2.0.CO;2, 2006.

Kalbitz, K., Schmerwitz, J., Schwesig, D. and Matzner, E.: Biodegradation of soil-derived dissolved organic matter as related to its properties, Geoderma, 113, 273–291, doi:10.1016/S0016-7061(02)00365-8, 2003.

Kling, G., Kipphut, G., Miller, M. and O'Brien, W.: Integration of lakes and streams in a landscape perspective: the importance of material processing on spatial patterns and temporal coherence, Freshwater Biol., 43, 477–497, doi:10.1046/j.1365-2427.2000.00515.x, 2000.

Koehler, A.-K., Murphy, K., Kiely, G. and Sottocornola, M.: Seasonal variation of DOC concentration and annual loss of DOC from an Atlantic blanket bog in South Western Ireland, Biogeochemistry, 95, 231–242, doi:10.1007/s10533-009-9333-9, 2009.

Lakowicz, J.R.: Principles of Fluorescence Spectroscopy, 2, Kluwer Academic, New York, 1999.

Larson, J.H., Frost, P.C., Zheng, Z., Johnston, C.A., Bridgham, S.D., Lodge, D.M., and Lamberti, G.A.: Effects of upstream lakes on dissolved organic matter in streams, Limnol. Oceanogr., 52(1), 60-69, doi:10.4319/lo.2007.52.1.0060, 2007.

Leighty, W.W., Hamburg, S.P., and Caouette, J.: Effects of management on carbon sequestration in forest biomass in Southeast Alaska, Ecosystems, 9, 1051, doi:10.1007/s10021-005-0028-3, 2006.

Lalonde, K., Middlestead, P., Gélinas, Y.: Automation of 13C/12C ratio measurement for freshwater and seawater DOC using high temperature combustion, Limnol. Oceanogr. Methods, 12, 816-829, doi:10.4319/lom.2014.12.816, 2014.

Lambert, T., Bouillon, S., Darchambeau, F., Massicotte, P., and Borges, A.V.: Shift in the chemical composition of dissolved organic matter in the Congo River network, Biogeosci., 13, 5405-5420, doi:10.5194/bg-13-5405-2016, 2016.

Leach, J., Larsson, A., Wallin, M., Nilsson, M. and Laudon, H.: Twelve year interannual and seasonal variability of stream carbon export from a boreal peatland catchment, J. Geophys. Res. 121, 1851–1866, doi:10.1002/2016JG003357, 2016.

Legendre, P., and Durand, S.: rdaTest, Canonical redundancy analysis, R package version 1.11, available at http://adn.biol.umontreal.ca/~numericalecology/Rcode/, 2014.

Lepistö, A., Futter, M.N. and Kortelainen, P.: Almost 50 years of monitoring shows that climate, not forestry, controls long-term organic carbon fluxes in a large boreal watershed, Glob. Change Biol., 20, 1225–1237, doi:10.1111/gcb.12491, 2014.

977
978 Liaw, A., and Wiener, M.: Classification and Regression by randomForest, R News, 2(3), 18-22,
979 2002.
980
981 Lochmuller, C.H., Saavedra, S.S.: Conformational changes in a soil fulvic acid measured by time
982 dependent fluorescence depolarization, Anal. Chem., 38, 1978-1981, 1986.
983
984 Lorenz, D., Runkel, R., and De Cicco, L.: rloadest, River Load Estimation, R package version
985 0.4.2, available at https://github.com/USGS-R/rloadest, 2015.
986
987 Ludwig, W., Probst, J. and Kempe, S.: Predicting the oceanic input of organic carbon by
988 continental erosion, Global Biogeochem. Cycles, 10, 23–41, doi:10.1029/95GB02925, 1996.
989
990 Mann, P.J., Spencer, R.G.M., Dinga, B.J., Poulsen, J.R., Hernes, P.J., Fiske, G., Salter, M.E.,
991 Wang, Z.A., Hoering, K.A., Six, J., and Holmes, R.M.: The biogeochemistry of carbon across a
992 gradient of sreams and rivers within the Congo Basin, J. Geophys. Res. Biogeosci., 119, 687-
993 702, doi:10.1002/2013JG002442, 2014.
994
995 Marschner, B., and Kalbitz, K.: Controls on bioavailability and biodegradability of dissolved
996 organic matter in soils, Geoderma, 113, 211–235, 2003.
997
998 Martin, S.L., and Soranno, P.A.: Lake landscape position: Relationships to hydrologic
999 connectivity and landscape features, Limnol. Oceanogr., 51(2), 801-814,
1000 doi:10.4319/lo.2006.51.2.0801, 2006.
1001
1002 Masiello, C.A., and Druffel, E.R.M.: Carbon isotope geochemistry of the Santa Clara River,
1003 Global Biogeochem. Cycles, 15, 407-416, doi:10.1029/2000GB001290, 2001.
1004
1005 Mayorga, E., Seitzinger, S., Harrison, J., Dumont, E., Beusen, A., Bouwman, A.F., Fekete, B.,
1006 Kroeze, C. and Drecht, G.: Global Nutrient Export from WaterSheds 2 (NEWS 2): Model
1007 development and implementation, Environ. Model. Softw., 25, 837–853,
1008 doi:10.1016/j.envsoft.2010.01.007, 2010.
1009
1010 McClelland, J., Townsend‐Small, A., Holmes, R., Pan, F., Stieglitz, M., Khosh, M. and Peterson,
1011 B.: River export of nutrients and organic matter from the North Slope of Alaska to the Beaufort
1012 Sea, Water Resour. Res., 50, 1823–1839, doi:10.1002/2013WR014722, 2014.
1013
1014 McKnight, D., Boyer, E., Westerhoff, P., Doran, P., Kulbe, T. and Andersen, D.:
1015 Spectrofluorometric characterization of dissolved organic matter for indication of precursor
1016 organic material and aromaticity, Limnol. Oceanogr., 46, 38–48, doi:10.4319/lo.2001.46.1.0038,
1017 2001.
1018
1019 McLaren, D., Fedje, D., Hay, M.B., Mackie, Q., Walker, I.J., Shugar, D.H., Eamer, J.B.R., Lian,
1020 O.B., and Neudorf, C.: A post-glacial sea level hinge on the central Pacific coast of Canada,
1021 Quat. Sci. Review., 97, 148-169, 2014.

Meybeck, M.: Carbon, nitrogen, and phosphorus transport by world rivers, Am. J. Sci., 282, 401-450, Available from: http://earth.geology.yale.edu/~ajs/1982/04.1982.01.Maybeck.pdf, 1982.

Milliman, J.D., and Syvitski J.P.M.: Geomorphic tectonic control of sediment discharge to the ocean: The importance of small mountainous rivers, J. Geol., 100, 525-544, 1992.

Moore, R.D.: Introduction to salt dilution gauging for streamflow measurement part III: Slug injection using salt in solution, Streamline Watershed Management Bulletin, 8(2), 1-6, 2005.

Morrison, J., Foreman, M.G.G., and Masson, D.: A method for estimating monthly freshwater discharge affecting British Columbia coastal waters, Atmoshere-Ocean, 50, 1-8, doi:10.1080/07055900.2011.637667, 2012.

Mulholland, P. and Watts, J.: Transport of organic carbon to the oceans by rivers of North America: a synthesis of existing data, Tellus, 34, 176–186, doi:10.1111/j.2153-3490.1982.tb01805.x, 1982.

Murphy, K., Stedmon, C., Graeber, D. and Bro, R.: Fluorescence spectroscopy and multi-way techniques. PARAFAC, Anal. Methods, 5, 6557–6566, doi:10.1039/C3AY41160E, 2013.

Murphy K., Stedmon, C., Wenig, P., Bro, R.: OpenFluor- A spectral database of auto-fluorescence by organic compounds in the environment, Anal. Methods, 6, 658-661, DOI:10.1039/C3AY41935E, 2014.

Naiman, R.J.: Characteristics of sediment and organic carbon export from pristine boreal forest watersheds, Can. J. Fish. Aquat. Sci., 39(12), 1699-1718, doi:10.1139/f82-226, 1982.

Nakagawa, S., and Schielzeth, H.: A general and simple method for obtaining R^2 from generalized linear mixed-effects models, Methods Ecol. Evol., 4(2): 133-142. DOI: 10.1111/j.2041-210x.2012.00261.x, 2013.

Olefeldt, D., Roulet, N., Giesler, R. and Persson, A.: Total waterborne carbon export and DOC composition from ten nested subarctic peatland catchments- importance of peatland cover, groundwater influence, and inter-annual variability of precipitation patterns, Hydrol. Process., 27, 2280-2294, doi:10.1002/hyp.9358, 2013.

Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D., and R Core Team: nlme: Linear and Nonlinear Mixed Effects Models, R package version 3.1-128, 2016.

Pojar, J., Klinka, K., and Demarchi, D.A.: Chapter 6, Coastal Western Hemlock Zone, in: Special Report Series 6, Ecosystems of British Columbia, Meidiner, D., and Pojar, J. (Eds.), Ministry of Forests, British Columbia, Victoria, 330 p., 1991.

Poulin, B., Ryan, J. and Aiken, G.: Effects of iron on optical properties of dissolved organic matter, Environ. Sci. Technol., 48, 10098–106, doi:10.1021/es502670r, 2014.

R Core Team, R: A language and environment for statistical computing, R Foundation for Statistical Computing, Vienna, Austria, http://www.R-project.org/, 2013.

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

Regnier, P., Friedlingstein, P., Ciais, P., Mackenzie, F., Gruber, N., Janssens, I., Laruelle, G., Lauerwald, R., Luyssaert, S., Andersson, A., Arndt, S., Arnosti, C., Borges, A., Dale, A., Gallego-Sala, A., Goddéris, Y., Goossens, N., Hartmann, J., Heinze, C., Ilyina, T., Joos, F., LaRowe, D., Leifeld, J., Meysman, F., Munhoven, G., Raymond, P., Spahni, R., Suntharalingam, P. and Thullner, M.: Anthropogenic perturbation of the carbon fluxes from land to ocean, Nat. Geosci., 6, 597–607, doi:10.1038/ngeo1830, 2013.

Roddick, J.R.: Geology, Rivers Inlet-Queens Sound, British Columbia, Open File 3278, Geological Survey of Canada, Ottawa, Canada, 1996.

Royer, T.C., Coastal fresh water discharge in the northeast, Pacific, J. Geophys. Res., 87, 2017-2021, 1982.

Runkel, R.L., Crawford, C.G., and Cohn, T.A.: Load Estimator (LOADEST): A FORTRAN program for estimating constituent loads in streams and rivers, U.S. Geological Survey Techniques and Methods Book 4, Chapter A5, 65 pp., 2004.

Sanderman, J., Lohse, K.A., Baldock, J.A., and Amundson, R.: Linking soils and streams: Sources and chemistry of dissolved organic matter in a small coastal watershed, Water Resourc. Res., 45, W03418, doi:10.1029/2008WR006977, 2009.

Spencer, R., Butler, K. and Aiken, G.: Dissolved organic carbon and chromophoric dissolved organic matter properties of rivers in the USA, J. Geophys. Res. Biogeosciences, 117(G03001), doi:10.1029/2011JG001928, 2012.

Spencer, R.G., Hernes, P.J, Ruf, R., Baker, A., Dyda, R.Y., Stubbins, A., and Six, J.: Temporal controls on dissolved organic matter and lignin biogeochemistry in a pristine tropical river, Democratic Republic of Congo, J. Geophys. Res., 115, G03013, doi:10.1029/2009JG001180, 2010.

Stackpoole, S.M., Butman, D.E., Clow, D.W., Verdin, K.L., Gaglioti, B., and Striegl, R.: Carbon burial, transport, and emission from inland aquatic ecosystems in Alaska, in: Baseline and projected future carbon storage and greenhouse-gas fluxes in ecosystems of Alaska, Zhiliang, Z., and David, A. (Eds.), U.S. Geological Survey Professional Paper, 1826, 196 p., 2016.

Stackpoole, S.M., Butman, D.E., Clow, D.W., Verdin, K.L., Gaglioti, B.V., Genet, H., and Striegl, R.G.: Inland waters and their role in the carbon cycle of Alaska, Ecol. Appl., Accepted Author Manuscript, doi: 10.1002/eap.1552, 2017.

Stedmon, C. and Bro, R.: Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial, Limnol. Oceanogr. Methods, 6, 572–579, doi:10.4319/lom.2008.6.572b, 2008.

Stedmon, C. and Markager, S.: Tracing the production and degradation of autochthonous fractions of dissolved organic matter by fluorescence analysis, Limnol. Oceanogr., 50(5), 1415–1426, doi:10.4319/lo.2005.50.5.1415, 2005.

Stedmon, C., Markager, S., Bro, R., Stedmon, C., Markager, S. and Bro, R.: Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy, Mar. Chem., doi:10.1016/S0304-4203(03)00072-0, 2003.

Stevenson, F.J.: Humus Chemistry: Genesis, Composition, Reactions, 2, Jon Wiley and Sons Inc., New York, United States of America, 1994.

Symonds, M.R.E., and Moussalli, A.: A brief guide to model selection, multimodel inference, and model averaging in behavioural ecology using Akaike's information criterion, Behav. Ecol. Sociobiol., 65:13-21, DOI: 10.1007/s00265-010-1037-6, 2011.

Tallis, H.: Kelp and rivers subsidize rocky intertidal communities in the Pacific Northwest (USA), Marine Ecology Progress Series, 389, 8596, doi:10.3354/meps08138, 2009.

Tank, S., Raymond, P., Striegl, R., McClelland, J., Holmes, R., Fiske, G. and Peterson, B.: A land-to-ocean perspective on the magnitude, source and implication of DIC flux from major Arctic rivers to the Arctic Ocean, Global Biogeochem. Cycles, 26, GB4018, doi:10.1029/2011GB004192, 2012.

Tank, S., Striegl, R.G., McClelland, J.W., and Kokelij, S.V.: Multi-decadal increases in dissolved organic carbon and alkalinity flux from the Mackenzie drainage basin to the Arctic Ocean, Environ. Res. Lett., 11(5), doi:10.1088/1748-9326/11/5/054015, 2016.

Thompson, S.D., Nelson, T.A., Giesbrecht, I., Frazer, G., and Saunders, S.C.: Data-driven regionalization of forested and non-forested ecosystems in coastal British Columbia with LiDAR and RapidEye imagery, Appl. Geogr., 69, 35–50, doi: 10.1016/j.apgeog.2016.02.002, 2016.

Trant, A.J., Niijland, W., Hoffman, K.M., Mathews, D.L., McLaren, D., Nelson, T.A., Starzomski, B.M.: Intertidal resource use over millennia enhances forest productivity, Nature Commun., 7, 12491, doi: 10.1038/ncomms12491, 2016.

van Hees, P., Jones, D., Finlay, R., Godbold, D. and Lundström, U.: The carbon we do not see-the impact of low molecular weight compounds on carbon dynamics and respiration in forest soils: a review, Soil Biol. Biochem., 37, 1–13, doi:10.1016/j.soilbio.2004.06.010, 2005.

Wallin, M., Weyhenmeyer, G., Bastviken, D., Chmiel, H., Peter, S., Sobek, S. and Klemedtsson, L.: Temporal control on concentration, character, and export of dissolved organic carbon in two hemiboreal headwater streams draining contrasting catchments, J. Geophys. Res. Biogeosci. 120, 832–846, doi:10.1002/2014jg002814, 2015.

Wang, T., Hamann, A., Spittlehouse, D.L., and Murdock, T.Q.,: ClimateWNA- High resolution spatial climate data for Western North America, J. Appl. Meterol. Climatol., 51, 16-29, doi:dx.doi.org/10.1175/JAMC-D-11-043.1, 2012.

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

Whitney, F.A., Crawford, W.R. and Harrison, P.J.: Physical processes that enhance nutrient transport and primary productivity in the coastal and open ocean of the subarctic NE Pacific, Deep Sea Research Part II: Topical Studies in Oceanography, 52, 681–706, 2005.

Wickland, K., Neff, J., and Aiken, G.: Dissolved Organic Carbon in Alaskan Boreal Forest: Sources, Chemical Characteristics, and Biodegradability, Ecosystems, 10, 1323-1340, 2007.

Wilson, H.F. and Xenopoulos, M.A.: Effects of agricultural land use on the composition of fluvial dissolved organic matter, Nat. Geosci., 2, 37–41, doi:10.1038/ngeo391, 2009.

Wolf, E.C., Mitchell, A.P., and Schoonmaker, P.K.: The Rain Forests of Home: An Atlas of People and Place, Ecotrust, Pacific GIS, Inforain, and Conservation International, Portland, Oregon, 24 pp., available at: http://www.inforain.org/pdfs/ctrf_atlas_orig.pdf, 1995.

Worrall, F., Burt, T., and Adamson, J.: Can climate change explain increases in DOC flux from upland peat catchements?, Sci. Total. Environ., 326, 95–112, doi:10.1016/j.scitotenv.2003.11.022, 2004.

Xenopoulos, M.A., Lodge, D.M., Frentress, J., Kreps, T.A., Bridgham, S.D., Grossman, E., and Jackson, C.J.: Regional comparisons of watershed determinants of dissolved organic carbon in temperate lakes from the Upper Great Lakes region and selected regions globally, Limnol. Oceanogr., 48(6), 2321-2334, 2003.

Yamashita, Y. and Jaffé, R.: Characterizing the Interactions between Trace Metals and Dissolved Organic Matter Using Excitation−Emission Matrix and Parallel Factor Analysis, Environ. Sci. Technol., 42, 7374–7379, doi:10.1021/es801357h, 2008.

Yamashita, Y., Kloeppel, B., Knoepp, J., Zausen, G. and Jaffé, R.: Effects of Watershed History on Dissolved Organic Matter Characteristics in Headwater Streams, Ecosystems, 14, 1110–1122, doi:10.1007/s10021-011-9469-z, 2011.

Figure 1. The location of Calvert Island, British Columbia, Canada, within the perhumid region of the coastal temperate rainforest (right) and the study area on Calvert and Hecate Islands, including the seven study watersheds, corresponding stream outlet sampling stations, and location of the rain gauge (left). Characteristics of individual watersheds are described in Table 1.

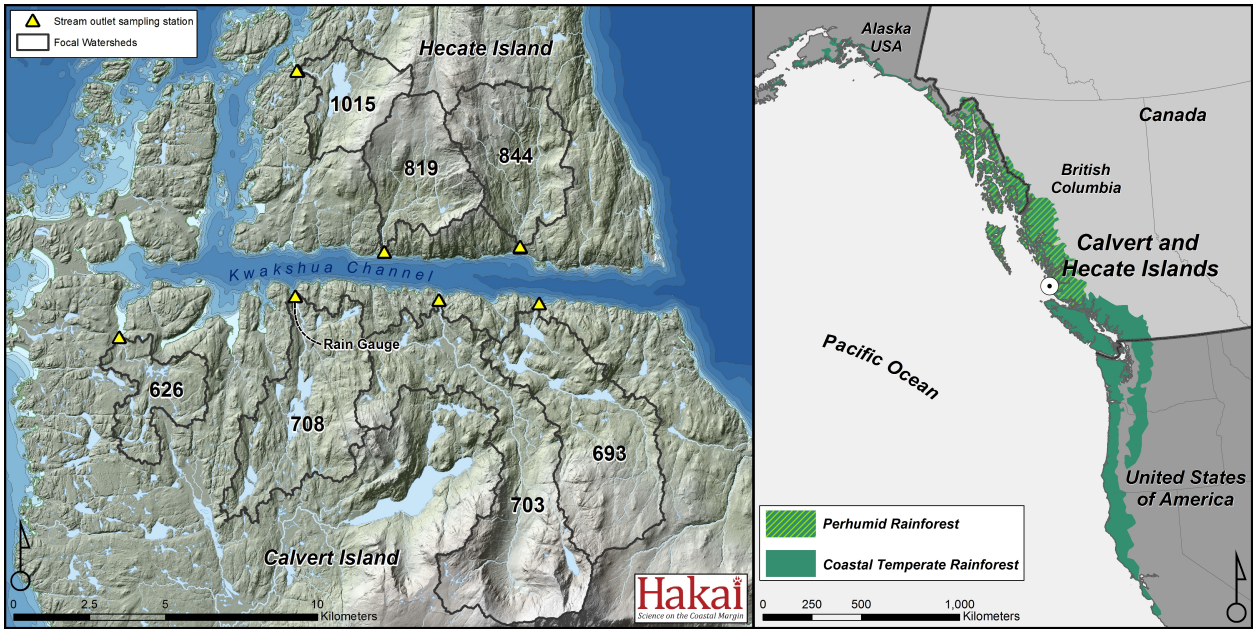

Figure 2. Hydrological patterns typical of watersheds located in the study area (a) the hydrograph and precipitation record from Watershed 708 for the study period of October 1, 2015-April 30, 2016. Grey shading indicates the wet period (September 1-April 30) and the unshaded region indicates the dry period (May 1-August 30) (b) Correlation of daily (24 hour) areal runoff (discharge of all watersheds combined) to 48 hour total rainfall recorded at watershed 708. For the period of study, comparisons of daily runoff to 48-hr rainfall (runoff:rainfall mean= 0.92, std ±0.27) indicated rapid discharge response to rainfall.

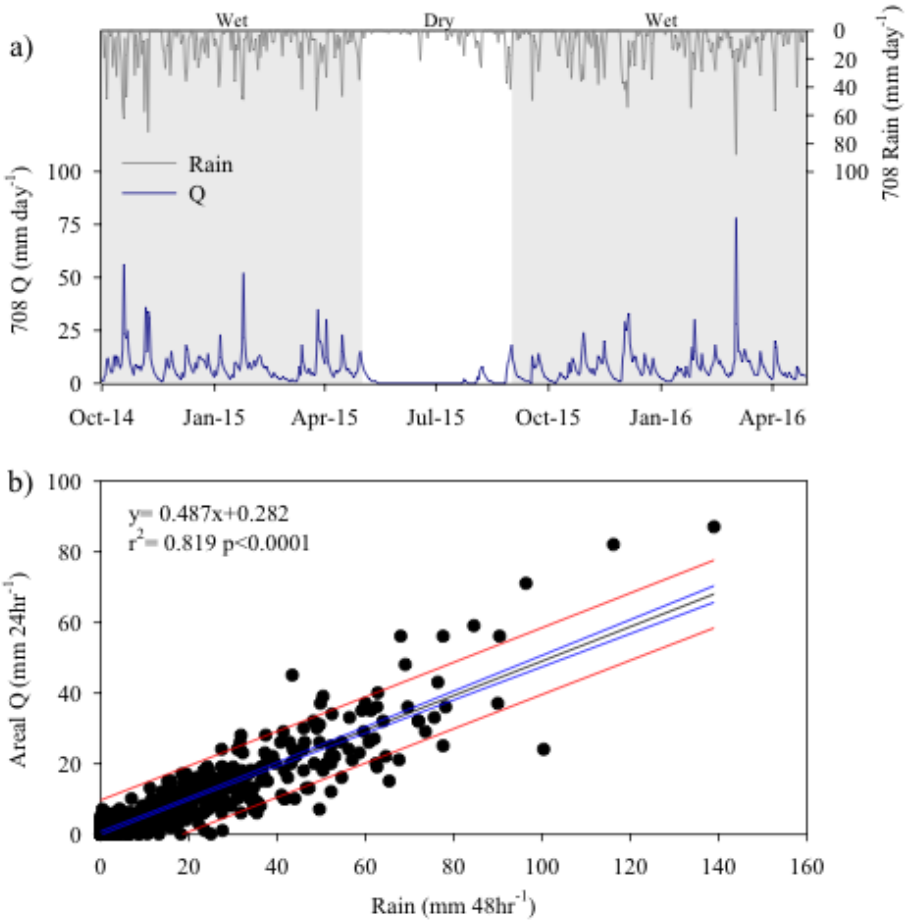

Figure 3. Seasonal (timelines, by date) and spatial (boxplots, by watershed) patterns in DOC concentration and DOM composition for stream water collected at the outlets of the seven study watersheds on Calvert and Hecate Islands. Boxes represent the 25th and 75th percentile, while whiskers represent the 5th and 95th percentile. Daily precipitation and annual temperature are shown in the top left panel. Grey shading indicates the wet period (September 1-April 30) and the unshaded region indicates the dry period of each water year.

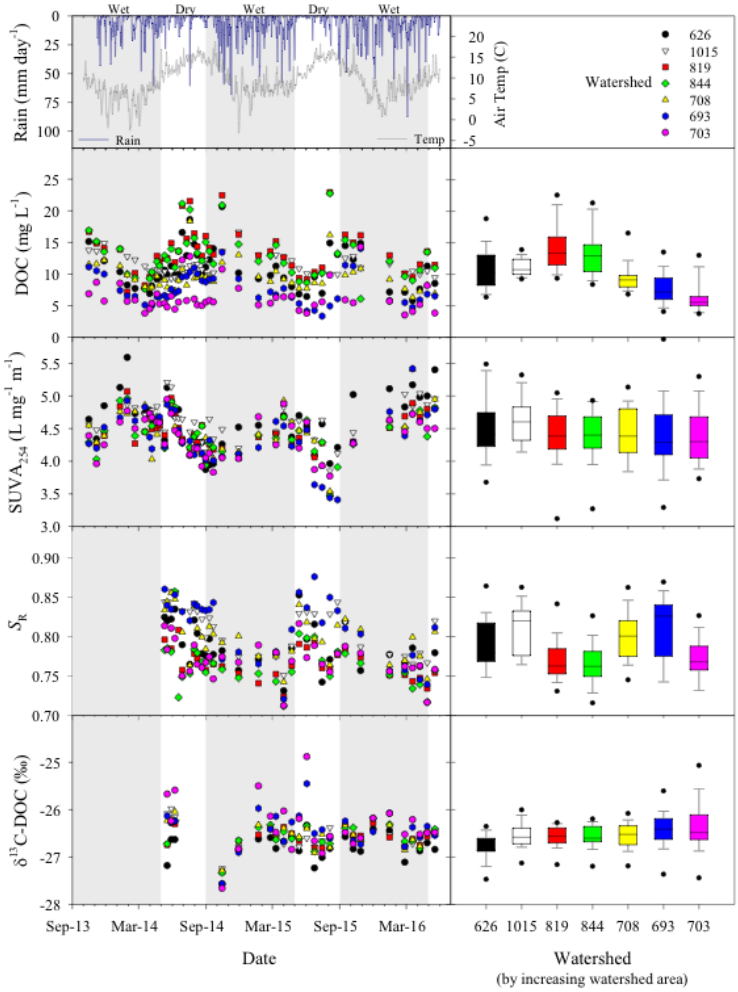

Figure 4. Monthly areal DOC yields and precipitation for water year 2015 (WY2015) and the wet period (October 1-April 30) of water year 2016 (WY2016). Error bars represent standard error. Total rain and DOC yield were significantly correlated ($r^2 = 0.77$) and months of higher rain produced higher DOC yields. In WY2015, the majority of DOC export (~94% of annual flux) occurred during the wet period (~88% of annual precipitation).

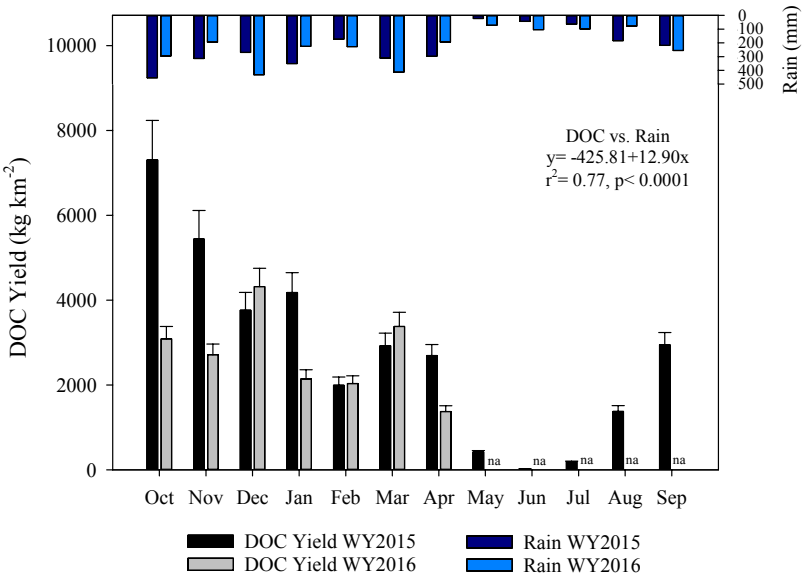

Figure 5: DOC fluxes and yields for the seven study watersheds and the total area of study ("areal", all watersheds combined) on Calvert and Hecate Islands for water year 2015 (WY2015; Oct 1 - Sep 30), and October 1- April 30 of the wet period for water year 2015 (WY2015 wet) and water year 2016 (WY2016 wet). Because DOC yields were only available for September in WY2015, this month was excluded from the wet period totals in order to make similar comparisons between years. Error bars represent standard error.

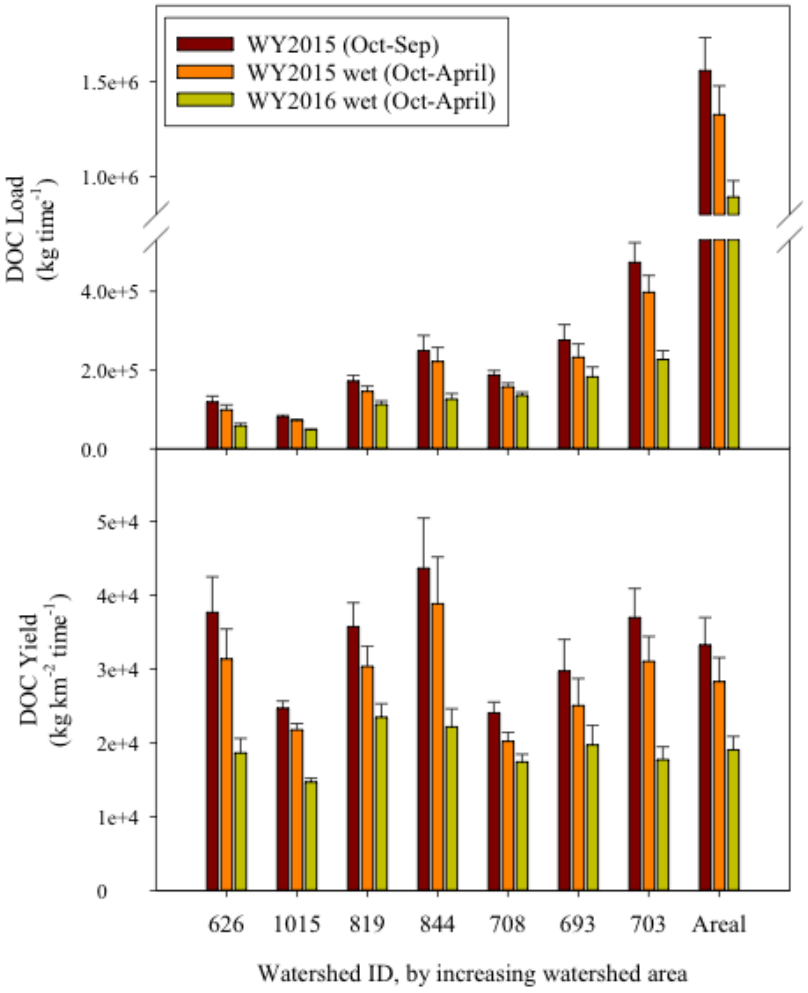

Figure 6: Percent contribution of the six components identified in parallel factor analysis (PARAFAC) for samples collected every three weeks from January-July, 2016 from the seven study watersheds on Calvert and Hecate Islands. The grey shading indicates the wet period and the unshaded region indicates the dry period. Note that while the y-axis for each panel has a range of 20%, the max and min for each y-axis varies by panel.

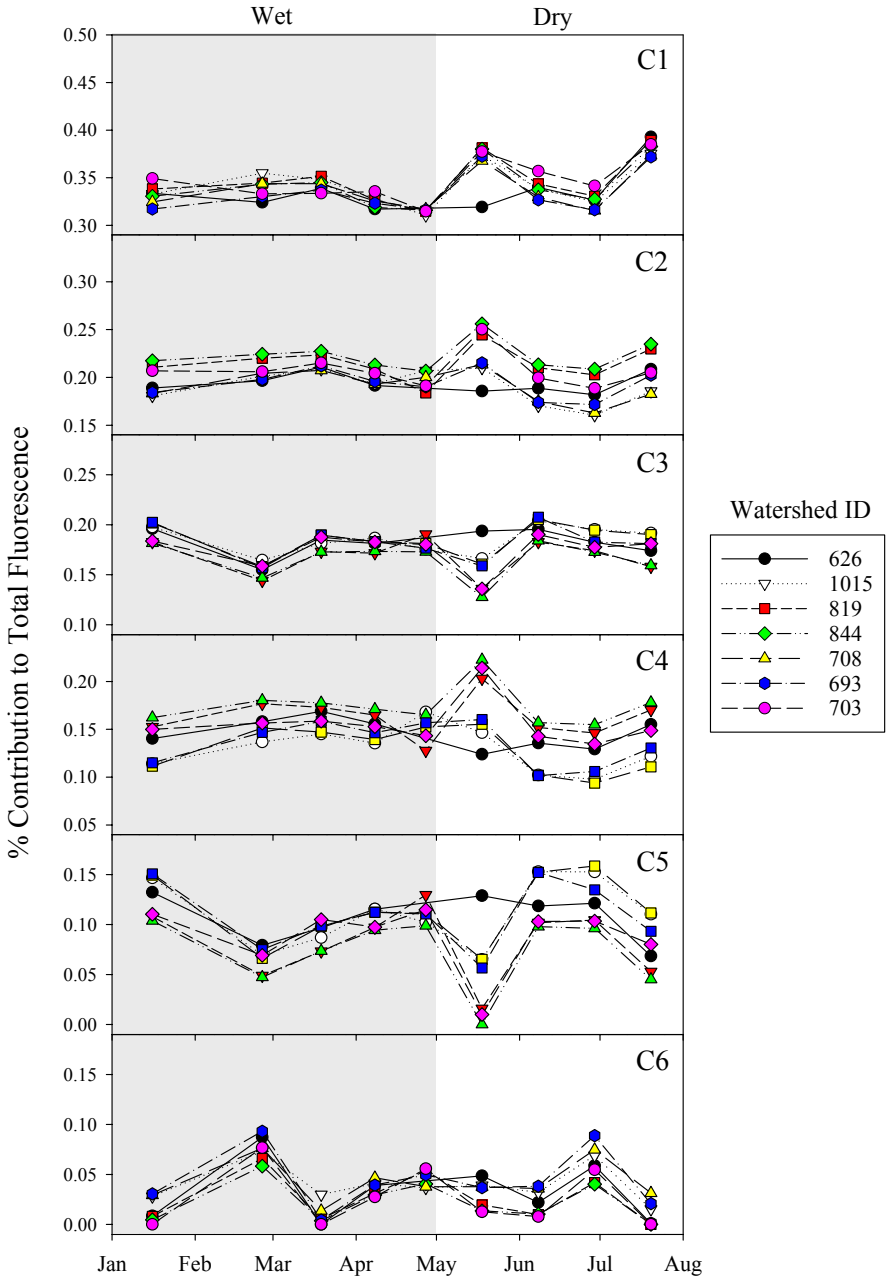

Figure 7: Results from the partial-Redundancy analysis (RDA; type 2 scaling) of DOC concentration and DOM composition versus watershed characteristics. Angles between vectors represent correlation, i.e., smaller angles indicate higher correlation. Symbols represent different watersheds, and numbers on symbols represent the sample month in 2016: 1= January, 2= February, 3= March, 4= early April, 5= late April, and 6= May.

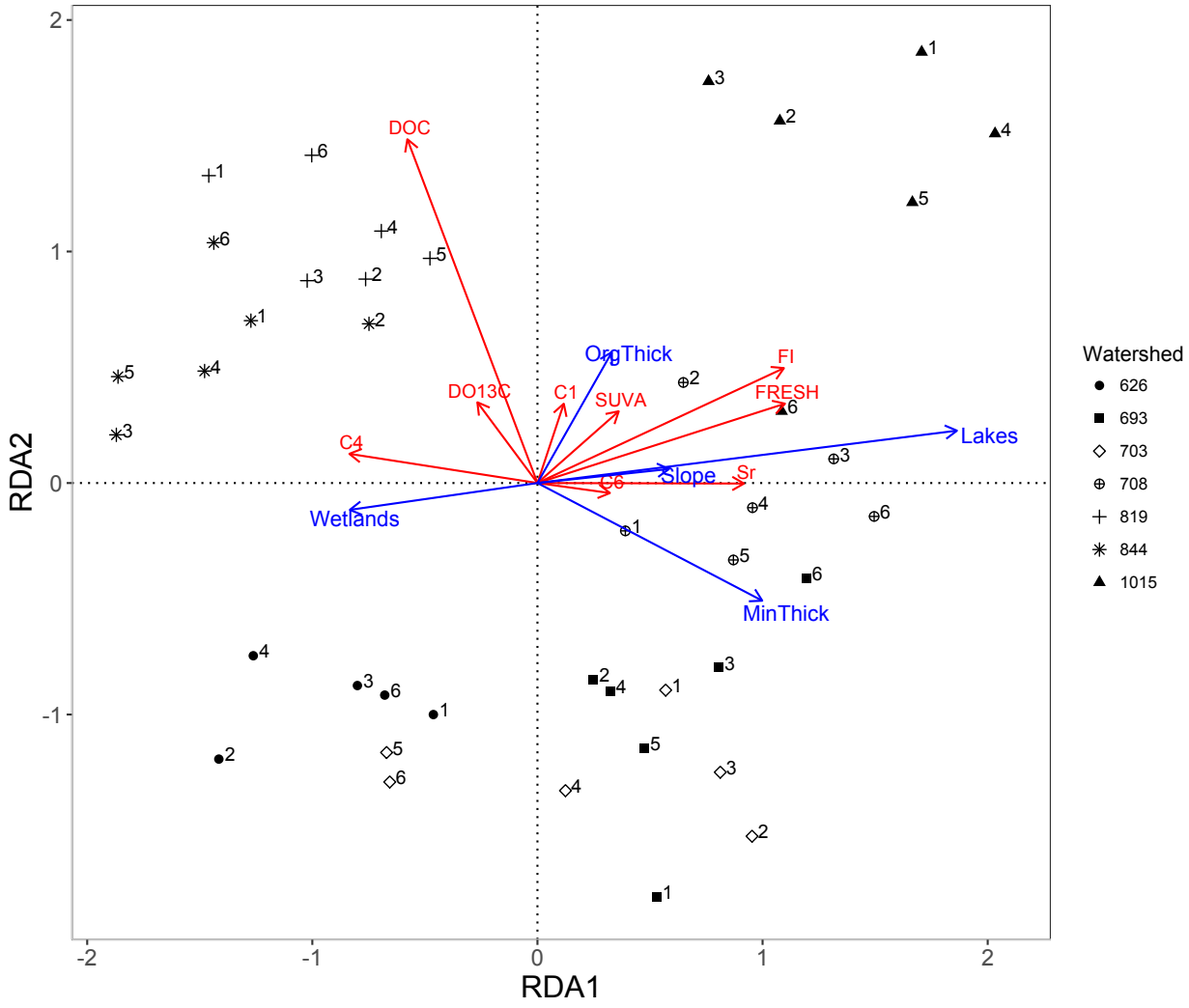

Table 1: Watershed characteristics, discharge, DOC concentrations, and DOC yields for the seven study watersheds on Calvert and Hecate Islands. Additional details on the methods used to determine watershed characteristics can be found in Supplemental Material.

Watershed	Area (km^2)	Avg. Slope (%)	Lakes (% Area)	Wetlands (% Area)	Avg. Depth Organic Soils (cm)	Avg. Depth Mineral Soils (cm)	Total Q Yield* (mm)	DOC*[a] (mg L^{-1})	Q-weighted Avg. DOC* (mg L^{-1})	DOC Annual Yield[b] WY2015* (Mg C km^{-2})	DOC Monthly Yield[b] Wet Season** (Mg C km^{-2})	DOC Monthly Yield[b] Dry Season*** (Mg C km^{-2})
626	3.2	21.7	4.7	48.0	39.4 ±24.3	30.8 ±8.3	3673	11.0 ±3.5	15.3	37.7 (31.9 – 44.2)	3.59 (3.05 – 4.18)	0.62 (0.49 – 0.77)
1015	3.3	34.2	9.1	23.8	39.5 ±17.2	33.7 ±8.6	3052	11.2 ±1.6	12.9	24.7 (23.6 – 25.8)	2.56 (2.45 – 2.78)	0.27 (0.25 – 0.28)
819	4.8	30.1	0.3	50.2	37.9 ±19.1	29.8 ±5.7	3066	14.0 ±3.5	19.3	35.7 (31.7 – 40.2)	3.80 (3.37 – 5.10)	0.57 (0.48 – 0.67)
844	5.7	32.5	0.3	35.2	35.4 ±18.0	29.1 ±6.4	4129	13.1 ±3.6	15.9	43.6 (34.2 – 54.9)	4.24 (3.36 – 5.30)	0.54 (0.36 – 0.77)
708	7.8	28.5	7.5	46.3	36.2 ±19.7	29.9 ±6.0	3805	9.5 ±2.4	10.9	24.1 (22.2 – 26.0)	2.67 (2.46 – 4.07)	0.38 (0.34 – 0.43)
693	9.3	30.2	4.4	42.8	35.4 ±16.1	30.2 ±6.4	5866	7.7 ±2.5	8.4	29.7 (25.9 – 34.0)	3.19 (2.79 – 4.94)	0.41 (0.32 – 0.52)
703	12.8	40.3	1.9	24.3	37.3 ±16.5	35.8 ±13.4	6058	6.3 ±2.6	9.0	37.0 (32.5 – 42.0)	3.48 (3.07 – 4.02)	0.64 (0.52 – 0.77)
All	46.9	32.7	3.7	37.1	37.4 ±17.7	32.2 ±9.2	4730	10.4 ±3.8	11.1	33.3 (28.9 – 38.1)	3.35 (2.94 – 4.40)	0.50 (0.41 – 0.62)

* Calculated for water year 2015 (WY2015; Oct 1, 2014-Sep 30, 2015)
** Wet period average monthly yield calculated from October-April and September, WY2015 and October-April, WY2016
*** Dry period average monthly yield calculated from May-August, WY2015
[a] Mean ± standard deviation
[b] Total ± 95% confidence interval

Table 2: Spectral composition for the six fluorescence components identified using PARAFAC, including excitation (Ex.) and emission (Em.) peak values, percent composition across all samples, and likely structure and characteristics of the fluorescent component based on previous studies.

1307

Component	Ex. (nm)	Em. (nm)	% Composition[a]	Potential structure/Characteristics	Previous studies with comparable results
C1	315	436	34.1 ±2.2 (31.1-39.3)	Humic-like, less processed terrestrial, high molecular weight, widespread but highest in wetland and forest environment	Garcia et al. 2015(C1); Graeber et al. 2012(C1); Walker et al. 2014(C1); Yamashita et al. 2011(C1); Cory & McKnight, 2005(C1)
C2	270/ 380	484	20.2 ±1.9 (16.1-25.6)	Humic-like, resembles fulvic acid, widespread, high molecular weight terrestrial	Stedmon and Markager, 2005(C2); Stedmon et al. 2003(C3); Cory & McKnight, 2005(C5)
C3	270	478	17.8 ±1.8 (12.8-20.8)	Humic-like, highly processed terrestrial; suggested as refractory	Stedmon & Markager, 2005(C1); Yamashita et al. 2010(C2)
C4	305/ 435	522	14.8 ±2.6 (9.4-22.3)	Not commonly reported, similarities to fulvic-like, contributed from soils	Lochmuller & Saavedra, 1986(E)
C5	325	442	9.8 ±3.5 (0.0-15.9)	Aquatic humic-like from terrestrial environments; autochthonous, microbial produced; may be photoproduced	Boehme & Coble, 2000(Peak C); Coble et al. 1998(Peak C); Stedmon et al., 2003(C3)
C6	285	338	3.4 ±2.5 (0.0-9.3)	Amino acid-like/Tryptophan-like. Freshly added from land, autochthonous. Rapidly photodegradable	Murphy et al. 2008(C7); Shutova et al. 2003(C4); Stedmon et al. 2007(C7); Yamashita et al. 2003(C5)

[a] Mean ± stdev (min-max) from all samples

1308