Biogeosciences Discuss., doi:10.5194/bg-2017-5, 2017
Manuscript under review for journal Biogeosciences
Published: 19 January 2017


Biogeosciences Discussions Open Access EGU

# Globally significant yields of dissolved organic carbon from small watersheds of the Pacific coastal temperate rainforest.

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Biogeosciences Discuss., doi:10.5194/bg-2017-5, 2017
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Published: 19 January 2017


**Abstract**

The perhumid region of the Pacific coastal temperate rainforest of North America (PCTR) 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 outer-coast region of the PCTR. 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 examined using absorbance and fluorescence spectroscopy, including 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 in the world exported to the ocean. We observed strong seasonality in the quantity and composition of exports, with the majority of DOC export occurring during the extended wet period of the year (September-April). Stream flow from catchments reacted quickly to rain inputs, resulting in rapid flushing of relatively fresh, highly terrestrial-like DOM. DOC concentration and measures of DOM composition were correlated with watershed attributes, including the extent of lakes and wetlands, and thickness of organic and mineral soils. Our discovery of high DOC yields from these small catchments on the outer-coast of the temperate rainforest is especially compelling as they represent the delivery of relatively fresh, highly terrestrial organic matter directly to the coastal ocean. This suggests that

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this coastal margin may play an important role in the global 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; Raymond et al., 2013). Export via running waters is an important mechanism in the removal of carbon from watersheds. 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., 2010; 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; Kling et al., 2000; 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 regions where empirical data are currently scarce, quantifying land-to-ocean DOC export is a clear priority for improving the accuracy of watershed and coastal carbon models. The transfer of water and organic matter from watersheds to the coastal ocean may represent an important pathway for carbon cycling and ecological subsidies between ecosystems. Therefore, better understanding of these linkages is needed for constraining predictions of ecosystem productivity and food webs in response to perturbations such as climate change.

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

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processing along the watershed terrestrial-aquatic continuum, and as a result can show significant spatial and temporal variation (Hudson et al., 2007; Fellman et al., 2009a; 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 Pacific coastal temperate rainforests of North America extend from the Gulf of Alaska, through British Columbia, to Northern California and span a wide range of precipitation and climate regimes. The wettest part of this region is described as the "perhumid" zone and is characterized by annual precipitation >1400mm, largely composed of rain and transient snow (Alaback, 1996)(Fig. 1). The perhumid Pacific coastal temperate rainforest (PCTR) extends from southeast Alaska through the outer coast of central British Columbia and contains forests and soils that have accumulated large amounts of carbon and store substantial quantities of organic matter relative to most other temperate forests (Gorham et al., 2012). Due to high 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. Previous studies have shown that streams in this region can contain high concentrations of DOC (Fellman et al., 2010; D'Amore et al., 2015a) and high DOC yields (D'Amore et al., 2015b; D'Amore et al., 2016) but these studies have largely focused on southeast Alaska and relatively little is known about carbon exports from the perhumid PCTR of British Columbia, an area of approximately 97,824 $km^2$ (calculated

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from spatial data adapted from Wolf et al., 1995). In addition, due to the logistical challenges of conducting fieldwork in this remote region, previous studies have derived DOC flux from point measurements of DOC concentrations and modelled river discharge (e.g., Mayorga et al., 2010; Stackpoole et al., 2016). In this study, we conduct the first field-based estimates of DOC flux from relatively undeveloped perhumid Pacific coastal temperature rainforest watersheds of the British Columbia outer-coast. We examine temporal and spatial trends in flux, and describe compositional characteristics of DOM exported from these watersheds to the coastal ocean. Finally, we describe relationships between measures of DOC quantity, DOM character, and watershed attributes.

## 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. 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,

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2014; Thompson et al., 2016). Forest stands are generally short with open canopies reflecting the lower productivity of the outer-coast forests compared to the rest of the perhumid rainforest (Banner et al., 2005). Dominant trees are western red cedar, yellow cedar, shore pine and western hemlock with composition varying across topographic and edaphic gradients. Widespread understory plants include several 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 habituation 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 outer coast – 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) (Gonzalez Arriola et al., 2015). We then used GIS to summarize watershed characteristics for each watershed polygon and for all watersheds combined (Table 1). Topographic measures were estimated from the DEM (Gonzalez Arriola et al., 2015); lake and wetland cover from Province of British Columbia Terrestrial Ecosystem Mapping (TEM) (Green, 2014); soil material thickness from unpublished digital soil maps (Supplemental S1).We recorded thickness of organic soil material, thickness of mineral soil material, and total soil depth to bedrock at a total of 353 field sites. In addition to field-

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148 sampled sites, 40 sites with exposed bedrock (0 cm soil depth) were located using aerial
149 photography. Soil thicknesses were combined with a suite of topographic, vegetation, and
150 remote sensing (LiDAR and RapidEye satellite imagery) data for each sampling point and used
151 to train a random forest model (randomForest package in R; Liaw and Wiener, 2002) that was
152 used to predict soil depth values. Soil material thicknesses were then averaged for each
153 watershed (Table 1). For additional details on field site selection and methods used for soil
154 depth predictions, see Supplemental S1.1.

155 **2.3 Sample Collection and Analysis**

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

167 In May 2014, we began collecting stream samples for stable isotopic composition of $\delta^{13}C$
168 in DOC ($DO\delta^{13}C$; n= 173) and optical characterization of DOM using absorbance spectroscopy
169 (n= 259). Beginning in January 2016, we also analyzed samples using fluorescence
170 spectroscopy (see section 2.6). Samples collected for $DO\delta^{13}C$ were filtered into 40mL EPA glass

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vials and preserved with $H_3PO_4$. DO$\delta^{13}$C samples were analyzed at GG Hatch Stable 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 125mL 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 0.2mm resolution (Campbell Scientific Ltd.) located in watershed 708 (elevation= 16m 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 (0-4m 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).

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194 **2.5 DOC flux**

195 From October 1, 2014 to April 30, 2016, we estimated DOC flux for each watershed
196 using measured DOC concentrations (n= 224) and continuous discharge recorded at 15-minute
197 intervals. The watersheds in this region respond rapidly to rain inputs and as a result DOC
198 concentrations are highly variable. To address this variability, routine DOC concentration data
199 (as described in section 2.2) were supplemented with additional grab samples (n= 21) collected
200 around the peak of the hydrograph during several high flow events throughout the year. We
201 performed watershed-specific estimates of DOC flux using the "rloadest" package (Lorenz et al.,
202 2015) in R (version 3.2.5, R Core Team, 2016), which replicates functions developed in the U.S.
203 Geological Survey load-estimator program, LOADEST (Runkel et al., 2004). LOADEST is a
204 multiple-regression adjusted maximum likelihood estimation model that calibrates a regression
205 between measured constituent values and stream flow across seasons and time and then fits it to
206 combinations of coefficients representing nine predetermined models of constituent flux. To
207 account for potentially small sample size, the best model was selected using the second order
208 Akaike Information Criterion (AICc). Input data were log-transformed to avoid bias and centered
209 to reduce multicollinearity. For additional details on model selection, see Supplemental Table
210 S3.1.

211 **2.6 Optical characterization of DOM**

212 Prior to May 2014, absorbance measures of water samples (n= 99) were conducted on a
213 Varian Cary-50 (Varian, Inc.) spectrophotometer at the BC Ministry of the Environment
214 Technical Services Laboratory (Victoria, BC, Canada) and used to determine specific UV
215 absorption at 254 nm ($SUVA_{254}$). After May 2014, we determined optical characterization of
216 DOM by absorbance and fluorescence spectroscopy at the Hakai Institute field station (Calvert

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Island, BC, Canada) using an Aqualog fluorometer (Horiba Scientific, Edison, New Jersey, USA). Samples were run in 1 cm quartz cells and strongly absorbing samples were diluted prior to analysis to avoid excessive inner filter effects (Lakowicz, 1999). We used absorbance scans 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) and used the Horiba Aqualog to apply 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).

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To further characterize features of DOM composition, we performed PARAFAC analysis using EEMs 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.

**2.7 Data analysis and statistics**

We evaluated relationships between stream water DOC and watershed characteristics by relating DOC concentration and measures of DOM character 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

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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

Annual precipitation for both water years (WY2015= 2661 mm; WY2016= 2587 mm), was lower than the predicted historical mean annual precipitation estimated at the location of our rain gauge (Fig. 1), which was approximately 2890 mm $yr^{-1}$ for the years 1981-2010 (Wang et al., 2012; available at http://www.climatewna.com/). It is worth noting that annual precipitation at our rain gauge location (elevation = 16 m) is substantially lower than the average amount received at higher elevations, which for years 1981-2010 was approximately 5027 mm $yr^{-1}$ at an elevation of 1000m within our study area. Annually, this area receives a very high amount of annual rainfall relative to most regions of the world (http://data.worldbank.org) but also experiences strong 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;

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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, and exhibited clear seasonal patterns (Fig. 2). Similar to precipitation data, higher Q occurred during the wet versus the dry period. Total Q for all watersheds combined was 22% greater (range for individual watersheds= 4% to 27% greater in WY2015 versus WY2016) 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 total Q for all watersheds in the wet period of WY2016 (total Q= 182.89 * $10^6$; range= 4.17 * $10^6$ – 91.45 * $10^6$ $m^3$).

### 3.2 Temporal and spatial patterns in DOC concentration and DOC flux

Stream waters were high in DOC concentration relative to the global average concentrations in 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 the average measured DOC concentrations (11.1 mg $L^{-1}$, Table 2), and also resulted in slightly different ranking of the watersheds for highest to lowest DOC concentration. Within watersheds, flow-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). 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 2; box plots, Figure 3). Low DOC concentration and variability in DOC concentrations were also observed for watershed 703, which lacks a high lake area but had the highest water yield as a result of having both the largest

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total watershed area and the highest maximum elevation (resulting in greater precipitation delivered to the catchment). On an annual basis, DOC concentrations decreased through the wet period, and then increased through the dry period.

Annual and monthly watershed 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 $km^{-2}$). For the complete water year of 2015, 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 much 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 $km^{-2}$ $mo^{-1}$).

On a per-watershed basis, DOC load generally increased with total watershed area, but this pattern was not maintained for DOC yield (Fig. 5). During WY2015, per-watershed yields ranged from 24.1 to 43.6 Mg C $km^{-2}$ (Table 1). Overall, 94% of the export in WY2015 occurred during the wet period, with a clear decrease in area-normalized export between WY2015 and WY2016 (Fig. 5).

### 3.3 Temporal and spatial patterns in DOM composition

Iron-corrected $SUVA_{254}$ values were relatively high compared to the range typically found in 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) suggesting DOM exported from these watersheds is comprised of highly aromatic carbon compounds. Values of $SUVA_{254}$ were relatively consistent across watersheds, however there was a strong seasonal trend that countered seasonal trends in DOC concentration; $SUVA_{254}$ values

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generally increased over the wet period and decreased over the dry period (Fig. 3). In contrast to $SUVA_{254}$, $S_R$ showed clear variation between watersheds, indicating systematic differences in the average molecular weight of the DOM pool between watersheds. Overall values of $S_R$ were low (average $S_R$ = 0.78, std= 0.04; range= 0.71 to 0.89) compared to the range typically observed in surface waters. This suggests that DOM was of high molecular weight, i.e., comprised of larger molecules that have not been chemically or biologically degraded through processes such as microbial utilization or photodegradation, and therefore are potentially more biologically available (Amon and Benner, 1996). Similar to $SUVA_{254}$, $S_R$ also appeared to fluctuate seasonally, with values decreasing (increasing in molecular weight) during the wet season and showing higher, more variable values during the dry season.

The stable isotopic composition of dissolved organic carbon ($DO\delta^{13}C$) was relatively similar across watersheds (average $DO\delta^{13}C$= -26.53‰, std= 0.36; range= -27.67‰ to -24.89‰) and exhibited some seasonal variation; values became slightly less depleted throughout the wet period relative to the dry period. Values for $DO\delta^{13}C$ suggested that terrestrial carbon sources originating from C3 plants and soils were the dominant input to catchment stream water DOM (Finlay and Kendall, 2007).

**3.4 Characterization of DOM- PARAFAC**

PARAFAC analysis indicated that terrestrial-derived organic carbon dominated spectral signatures across watersheds and across time. Six fluorescence components were identified through PARAFAC ("C1" through "C6")(Table 2). Additional details on PARAFAC 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 other two (C2 and C4) were found to have similar peaks

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355 represented in the literature. The first four components (C1 through C4) are described as
356 terrestrial-derived and comprised the majority of total fluorescence across all watersheds (Fig. 6).
357 C1 was by far the most dominant component in terms of percent contribution to total
358 fluorescence, suggesting a high and consistent supply of humic-like terrestrial material that is
359 relatively fresh (less-processed). Of the terrestrial-like components, C1, C2, and C4 exhibited
360 similar patterns to each other in their contribution to total fluorescence (Fig. 6) (Supplemental
361 Fig. S4.4), whereas component C3 appeared inversely related to the other terrestrial-like
362 components and exhibited the lowest spatial variability in percent contribution to total
363 fluorescence. Components C5 and C6 had spectral patterns indicative of autochthonous or
364 microbial-like origins, with C6 being the only component representing a distinct protein or
365 tryptophan-like contribution. Concentrations of C5 and C6 were correlated to one another ($F_{max}$
366 C5 vs. $F_{max}$ C6, $r^2 = 0.22$, $p < 0.001$), but neither appeared to covary with terrestrial components.
367 Relative to other components, C5 and C6 demonstrated the greatest variation between
368 watersheds (Supplemental Fig. S4.4). In general, the rank order of the components' percent
369 contribution to total fluorescence and variability between watersheds was maintained over time,
370 although on average percent composition of C2 and C4 was higher, and C3 was lower for
371 watersheds 819 and 844 relative to the other watersheds (Supplemental Fig. S4.4). The relative
372 importance of various components appeared consistent across the wet and dry periods, although
373 slightly more variation was observed during the dry period.

374 **3.5 Relationships between watershed characteristics and DOC exports**

375 Results of the partial-RDA (type 2 scaling) were significant in explaining variability in
376 DOM concentration and composition (semi-partial $R^2 = 0.33$, $F = 7.90$, $p < 0.0001$)(Fig. 7). Axes 1
377 through 3 were statistically significant at $p < 0.001$, and the relative contribution of each axis to

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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 inundation from lakes versus wetlands, with lake area and mean mineral soil material thickness showing a strong positive contribution, and wetlands showing a strong negative contribution to this axis. The Freshness Index, Fluorescence Index, $S_R$ and fluorescence component C6 were all positively correlated with this axis, while component C4 showed a clear negative correlation. Axis 2 described a subtler gradient of soil composition from greater mean organic soil material thickness to greater mean mineral soil material thickness. DOC concentration, DO$\delta^{13}$C, SUVA, 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 percent wetland area and thickness of organic soil material. DO$\delta^{13}$C showed the most positive correlation with Axis 3, whereas fluorescence components C1 and C4 showed the most negative.

## 4. Discussion

### 4.1 DOC flux: High DOC yields from small catchments to the coastal ocean

Freshwater DOC yields from Calvert and Hecate Island watersheds are some of the highest recorded globally, and in the upper range for this region when compared to previous regional predictions from global models (Mayorga et al., 2010) and DOC exports quantified for southeastern Alaska (D'Amore et al., 2015a; D'Amore et al., 2016; Stackpoole et al., 2016). On a global scale, DOC yields from Calvert and Hecate Island watersheds were higher than estimates from many tropical rivers including the Congo River (Spencer et al., 2016),

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401 Amazonian blackwater rivers (Moreira-Turcq et al., 2003; Waterloo et al., 2006) and southeast
402 Asian rivers draining virgin tropical peatlands (Baum et al., 2007), even though these types of
403 tropical rivers are often regarded as having disproportionately high carbon export compared to
404 temperate and Arctic rivers (Aitkenhead and McDowell, 2000; Borges et al., 2015).
405 While comparable DOC yields have been estimated from other high-latitude catchments
406 that receive high amounts of precipitation and contain organic soils (e.g. Naiman, 1982; Ågren et
407 al., 2007), these are typically small catchments containing low (first or second) order headwater
408 streams draining to higher order stream reaches. While headwater streams have been shown to
409 export up to 90% of the total annual carbon in stream flow (Leach et al., 2016), DOC exported
410 from headwaters and low order streams may potentially undergo significant processing before
411 reaching the ocean. In that regard, our discovery of high DOC yields from Calvert and Hecate
412 Island watersheds is especially compelling because these catchments drain directly to the ocean,
413 therefore providing a large and concentrated supply of relatively fresh terrestrial DOC directly to
414 a low DOC marine environment. Over much of the complex, incised outer coast of the perhumid
415 Pacific coastal temperate rainforest, small, rainfall-dominated catchments are the most direct
416 source of freshwater runoff to the coastal ocean (Eaton and Moore, 2010; Hill et al., 2015;
417 Royer, 1982). Our findings suggest that the small catchment of this region enable geographically
418 distributed inputs of high DOC flux directly to the coastal ocean, and that this region could
419 represent a significant biogeochemical hotspot for coastal carbon cycling.
420 Flashy stream hydrographs indicate that hydrologic residence times for Calvert and
421 Hecate Island watersheds are typically short, presumably as a result of small catchment size, high
422 drainage density, and relatively shallow soils with high hydraulic conductivity (Gibson et al.,

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423 2000; Fitzgerald et al., 2003). Precipitation is a well-established driver of stream DOC export
424 (Alvarez-Cobelas et al., 2012) particularly in systems containing organic soils and wetlands
425 (Olefeldt et al., 2013; Wallin et al., 2015; Leach et al., 2016). In general, frequent high
426 precipitation events and short residence times are expected to result in pulsed exports of stream
427 DOC that is rapidly shunted downstream, thus reducing time for in-stream processing (Raymond
428 et al., 2016). Rapid runoff is presumably accompanied by rapid increases in water tables and
429 lateral movement of water through shallow soil layers rich in organic matter (Fellman et al.,
430 2009; D'Amore et al., 2015b) We observed distinct seasonality of DOC delivery to the coastal
431 ocean, which may be important for determining downstream effects on ecological processes.

432 **4.2. DOM character: Sources, variability, and implications for coastal marine foodwebs**

433 On Calvert and Hecate Islands, short catchment residence times reduce opportunities for
434 in-stream production and processing, and, in conjunction with water flowing through abundant
435 sources of DOM from organic-rich soils, wetlands, and forests, result in high quantities of
436 terrestrial DOM export from watersheds to the ocean. This is consistent with findings from
437 previous studies on DOM exports from streams draining small headwater catchments
438 (Yamashita et al., 2011), and undisturbed catchments comprised of mixed forest and wetlands
439 (e.g. Wickland et al., 2007; Fellman et al., 2009a; Spencer et al., 2010). Seasonal variability in
440 DOM composition may be attributed to differences in DOM source due to seasonal changes in
441 biological activity or as a result of shifting flow paths that affect hydrologic interactions with
442 different DOM source materials (Fellman et al., 2009b). Rising water tables can establish strong
443 hydraulic gradients that initiate and sustain prolonged increases in metrics like $SUVA_{254}$, until
444 the progressive drawdown of upland water tables constrain flow paths (Lambert et al., 2013).
445 For example, during the wet and cooler period DOM increased in aromaticity and molecular

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weight, indicating an increase in contributions of more plant and soil-derived material as saturated conditions promote the mobilization of a wide range of DOM source materials (McKnight et al., 2001; Kalbitz et al., 2002). However, this trend was reversed during the dry and warmer period, suggesting a shift in the source of DOM and/or increased contributions from microbial products and plant exudates, and perhaps deeper flow paths that contribute to mineral binding and export of older, more processed terrestrial material (McKnight et al., 2001; van Hees et al., 2005). Similarly, proportions of fluorescence components were more consistent across watersheds during the wet period compared to the dry period, further suggesting that water table draw down and unsaturated soils lead to more diverse flow paths and interaction with different sources of DOM. The interaction of sources and flow paths during wet versus dry periods may have important consequences for the downstream fate of this material.

Biological utilization of DOM is influenced by its composition (e.g. Judd et al., 2006; Fasching et al., 2014), therefore differences in the nature of DOM exports will likely alter the downstream fate and ecological role of freshwater-exported DOM. 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), and thus may represent a relatively fresh, seasonally-consistent contribution of terrestrial material from streams to the coastal ecosystem. This may have ecological significance as a potential subsidy for downstream microbial production. In lakes, for example, pulsed contributions of less-processed humic material exported from rivers have been shown to stimulate bacterial production (Bergström and Jansson, 2000). In comparison to the more humic fractions, the tryptophan-like component, C6, represents a portion of the DOM pool comprised of a higher proportion of proteins that are preferred and readily utilized by microbial communities (Stedmon and Markager, 2005). Although C6

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represents a minor, more variable proportion of total fluorescence in comparison to the more humic compounds such as C1, 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). While previous studies have suggested that bacteria prefer autochthonous carbon sources, they also readily utilize allochthonous terrestrial DOC subsidies (Bergström and Jansson, 2000; Kritzberg et al., 2004; McCallister and Giorgio, 2008), enabling humic and fulvic material to potentially fuel a low but continuous level of bacterial productivity after more labile sources have been consumed (Guillamette and Giorgio, 2011). Given that the small watersheds of this region export very high amounts of terrestrial DOC, there is clear potential for this stream-exported DOM to provide pulsed contributions of terrestrial subsidies to coastal foodwebs.

**4.3 Relationships between watershed attributes and exported DOM**

While previous studies have implicated wetlands as a major driver of DOM composition, the analysis of relationships between Calvert and Hecate Island landscape attributes and variation in DOM character suggests that controls on DOM composition are more nuanced than being driven solely by the influence of wetlands. Ågren et al. (2008) found that when wetland area comprised >10% of total catchment area, wetland DOM was the most significant driver of stream DOM composition during periods of high hydrologic connectivity. Wetlands comprise an average of 37% of the total area of the watersheds used in this study, so, based on Agren et al. (2008) they should be a primary driver of DOC concentration and DOM composition. In our study, although we observed characteristics of DOM commonly found in wetland exports, wetlands do not appear to be the single leading driver of variability. Other factors, such as the depth of organic and mineral soil materials, alternative DOC-source pools, and watershed

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492 residence time appear to be important drivers of DOC concentration and DOM composition. In
493 these watersheds, soils with pronounced accumulations of organic matter are not restricted to
494 wetland ecosystems. While Hemists occur in the latter, which comprise 27.8% of the watersheds,
495 Folic Histosols occur on hillslopes over an additional 25.7% of the study area (Supplemental
496 S1.2). This suggests the importance of widely distributed, alternative soil DOM source-pools,
497 such as Folic Histosols and associated Podzols with thick forest floors on hillslopes, available to
498 contribute high amounts of terrestrial carbon for export.

499 Although lakes make up a relatively small proportion of the total landscape area, their
500 influence on DOM export appears to be important. The proportion of lake area can be a good
501 predictor of organic carbon loss from a catchment since lakes often increase hydrologic
502 residence times and thus increase opportunities for biogeochemical processing (Algesten et al.,
503 2004; Tranvik et al., 2009). In our study, watersheds with a larger percentage of lake area
504 exhibited lower DOC yields, and lake area was correlated with parameters that represent greater
505 autochthonous DOM production or microbial processing such as higher Freshness Index, $S_R$,
506 Fluorescence Index, and higher proportions of component C6. In contrast, watersheds with a
507 high percentage of wetlands contributed a different composition of DOM than watersheds with a
508 high percentage of lakes, therefore the proportion of different landscape types, such as wetlands
509 or lakes, appears to be an important factor influencing aspects of DOM export. In addition,
510 watersheds with the slowest response to rain events had lakes close to their catchment outlet
511 (e.g., watershed 1015, data not shown) that appear to dampen the response to rain events and
512 increased residence time low in the watershed. Therefore, the relative location of wetlands and
513 lakes within the catchment and their proximity to the watershed outlet also likely plays an
514 important role in the overall composition of DOM exports.

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515 Soil composition also plays a role in the quantity and character of DOM exported from
516 Calvert and Hecate Island watersheds. Organic and mineral soil materials provide different
517 environments for the production, retention, and degradation of DOM. It is generally known that
518 where peat has accumulated enough to form organic soils (Hemists), DOM is the most mobile
519 fraction of organic matter and accumulates under conditions of soil saturation and limited
520 drainage, resulting in the enrichment of poorly biodegradable, more stable humic acids
521 (Stevenson, 1994; Marschner and Kalbitz, 2003). However, on hillslopes where Folic Histosols
522 have formed under more freely drained conditions, high rates of respiration in organic soils can
523 result in further enrichment of aromatic and more complex molecules, and this material may be
524 rapidly mobilized and exported to streams (Glatzel et al., 2003). Preferential retention of certain
525 DOM fractions by sorption to mineral horizons can increase stability of the DOM pool by
526 reducing biodegradation, and is postulated as the main process by which DOM is retained in
527 forest soils (Kalbitz et al., 2005; Kaiser et al., 1997). In our study, the presence of thicker organic
528 soil material was positively correlated to higher DOC concentrations, as well as higher
529 proportions of C1, representing less processed, humic-like compounds. Steeper slopes were also
530 correlated with C1 (RDA Axis 3), suggesting that steeper slopes and adequate drainage may
531 result in the rapid mobilization of this material from organic soil horizons.
532 Changing environmental conditions, such as shifting precipitation and temperature
533 regimes, may affect future DOC fluxes. Long term patterns in DOC flux have been observed in
534 many places (e.g., Worrall et al., 2004; Borken et al., 2011; Lepistö et al., 2014) and continued
535 monitoring of this system will allow us to better understand the underlying drivers of export. For
536 example, changes in soil temperature and moisture could influence the stability of the organic
537 matter pool, as processes such as organic matter production and sorption have strong

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538 relationships with temperature and oxidation state. Therefore, additional research is needed to
539 assess soil properties relevant to DOM mobility (e.g., texture, sesquioxide content), landscape
540 attributes, and flow paths for predicting DOM export in this region and the consequences of
541 shifting conditions such as those associated with altered land use or climate change.

542 **5. Conclusions**

543 Previous work has demonstrated freshwater discharge is substantial along the coastal
544 margin of the Pacific temperate rainforest, and plays an important role in processes such as ocean
545 circulation (Royer, 1982; Eaton and Moore, 2010). Our finding that small catchments in this
546 region export some of the highest yields of terrestrial DOC in the world to coastal waters
547 suggests that freshwater inputs may also influence ocean biogeochemistry and food web
548 processes through terrestrial organic matter subsidies. Our findings also suggest that this region
549 may be currently underrepresented in terms of its role in global carbon cycling. Currently, there
550 is no region-wide carbon flux model for the Pacific coastal temperate rainforest or the greater
551 Gulf of Alaska, which would quantify the importance of this region within the global carbon
552 budget. Our estimates represent the hypermaritime outer-coast zone, where subdued terrain, high
553 rainfall, ocean moderated temperatures and poor bedrock have generated a distinctive 'bog-
554 forest' landscape mosaic within the greater temperate rainforest (Banner et al. 2005). To quantify
555 regional scale fluxes of rainforest carbon to the coastal ocean, further research will be needed to
556 estimate DOC yields across the west-to-east, and north to south, gradients of topography,
557 climate, hydrology, soils and vegetation. Further study on the controls of DOC export from these
558 watersheds, such as the role of landscape type (e.g., different wetland and forest types within the
559 ecosystem mosaic), watershed attributes (e.g., stream connectivity, slope, etc.), and detailed
560 characterization of soils, are warranted. Coupled with current studies investigating the fate of

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561 terrestrial material in ocean food webs, this work will improve our understanding of coastal
562 carbon patterns, and increase capacity for predictions regarding the ecological impacts of climate
563 change.
564
565 **Author Contributions**
566 The authors declare that they have no conflict of interest.
567 A.A. Oliver prepared the manuscript with contributions from all authors, designed analysis
568 protocols, analyzed samples, performed the modeling and analysis for dissolved organic carbon
569 fluxes, parallel factor analysis of dissolved organic matter composition, and all remaining
570 statistical analyses. S.E. Tank assisted with designing the study and overseeing laboratory
571 analyses, crafting the scope of the paper, and determining the analytical approach.
572 I. Giesbrecht led the initial DOC sampling design, helped coordinate the research team, oversaw
573 routine sampling and data management, and led the watershed characterization.
574 M.C. Korver developed the rating curves, and conducted the statistical analysis of discharge
575 measurement uncertainties and rating curve uncertainties. W.C. Floyd lead the hydrology
576 component of this project, selected site locations, installed and designed the hydrometric
577 stations, and developed the rating curves and final discharge calculations. C. Bulmer and P.
578 Sanborn collected and analyzed soil field data and prepared the digital soils map of the
579 watersheds. K.P. Lertzman conceived of and co-led the overall study of which this paper is a
580 component, helped assemble and guide the team of researchers who carried out this work,
581 provided input to each stage of the study.
582
583 **Acknowledgements**

Biogeosciences Discuss., doi:10.5194/bg-2017-5, 2017
Manuscript under review for journal Biogeosciences
Published: 19 January 2017




584 This work was funded by the Tula Foundation and the Hakai Institute. The authors would like to
585 thank many individuals for their support, including Skye McEwan, Bryn Fedje, Lawren McNab,
586 Nelson Roberts, Adam Turner, Emma Myers, David Norwell, and Chris Coxson for sample
587 collection and data management, Clive Dawson and North Road Analytical for sample
588 processing and data management, Keith Holmes for creating our maps, Matt Foster for database
589 development and support, Shawn Hateley for sensor network maintenance, Jason Jackson and
590 the entire staff at Hakai Energy Solutions for installing and maintaining the sensors and
591 telemetry network. Thanks to Santiago Gonzalez Arriola for generating the watershed summaries
592 and associated data products, and Ray Brunsting for overseeing the design and implementation
593 of the sensor network and the data management system at Hakai. Additional thanks to Lori
594 Johnson and Amelia Galuska for soil mapping field assistance, and Francois Guillamette for
595 PARAFAC consultation. Thanks to Dave D'Amore for inspiring the Hakai project to investigate
596 aquatic fluxes at the coastal margin and for technical guidance. Lastly, thanks to Eric Peterson
597 and Christina Munck who provided significant guidance throughout the process of designing and
598 implementing this study.

599

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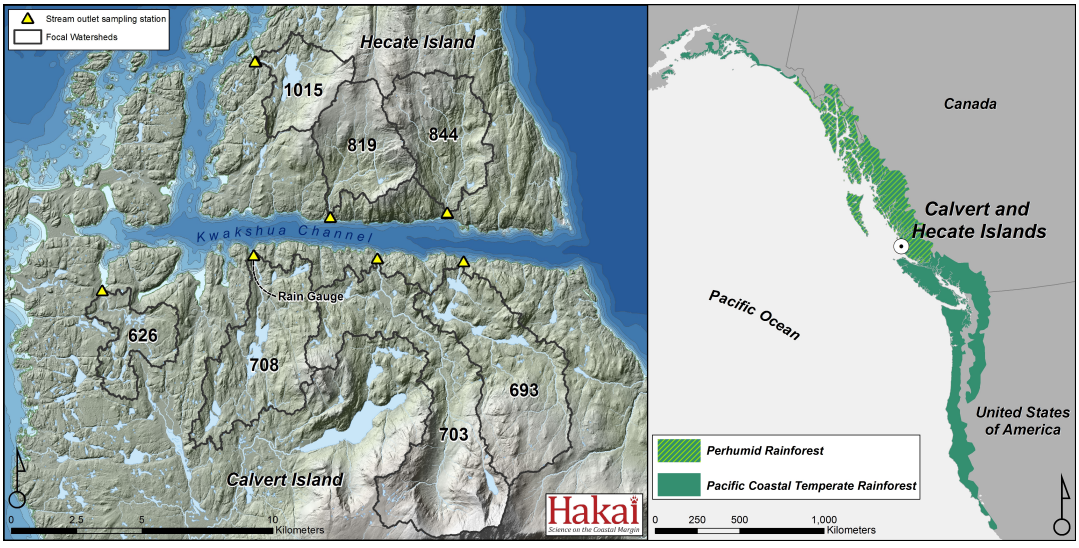
Published: 19 January 2017




**Figure 1.** The location of Calvert Island, British Columbia, within the perhumid region of the Pacific 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.



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1041 **Figure 2.** Hydrological patterns reflect the high amounts of precipitation and rapid runoff
1042 response typical of watersheds located in the study area (a) the hydrograph and precipitation
1043 record from Watershed 708 illustrates seasonal patterns in runoff and rainfall for the study period
1044 of October 1, 2015-April 30, 2016. Grey shading indicates the wet period (September 1-April
1045 30) and the unshaded region indicates the dry period (May 1-August 30) (b) Correlation of daily
1046 (24 hour) areal runoff (discharge of all watersheds combined) to 48 hour total rainfall recorded at
1047 watershed 708. For the period of study, comparisons of daily runoff to 48-hr rainfall
1048 (runoff:rainfall mean= 0.92, std ±0.27) indicated that the response in discharge from catchments
1049 is relatively rapid following precipitation.

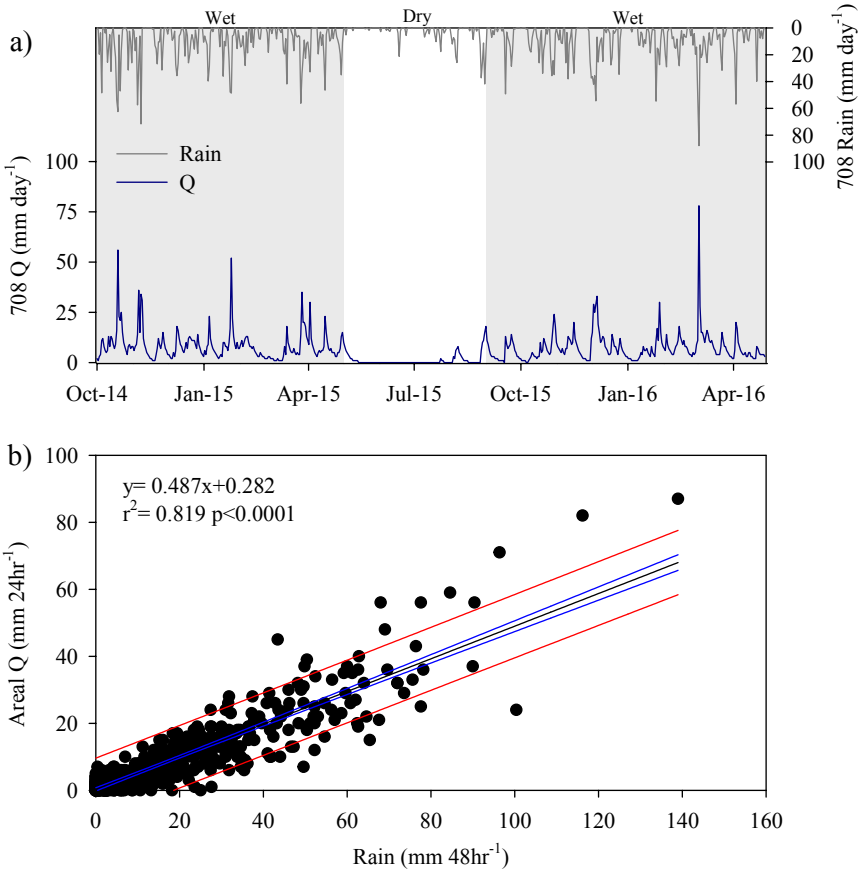


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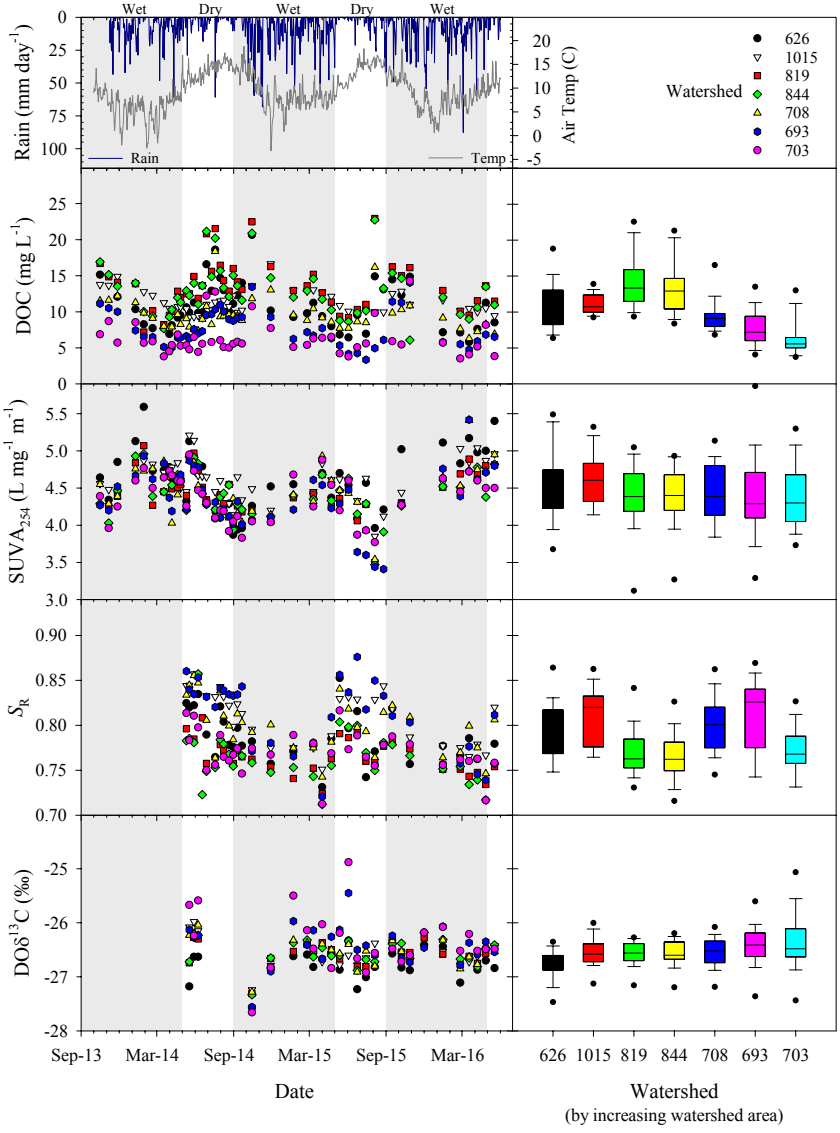
**Figure 3.** Seasonal (timelines, by date) and spatial (boxplots, by watershed) patterns in DOC concentration and DOM composition for stream water collected at the outlets of the seven study watersheds on Calvert and Hecate Islands. Daily precipitation and annual temperature are shown in the top left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



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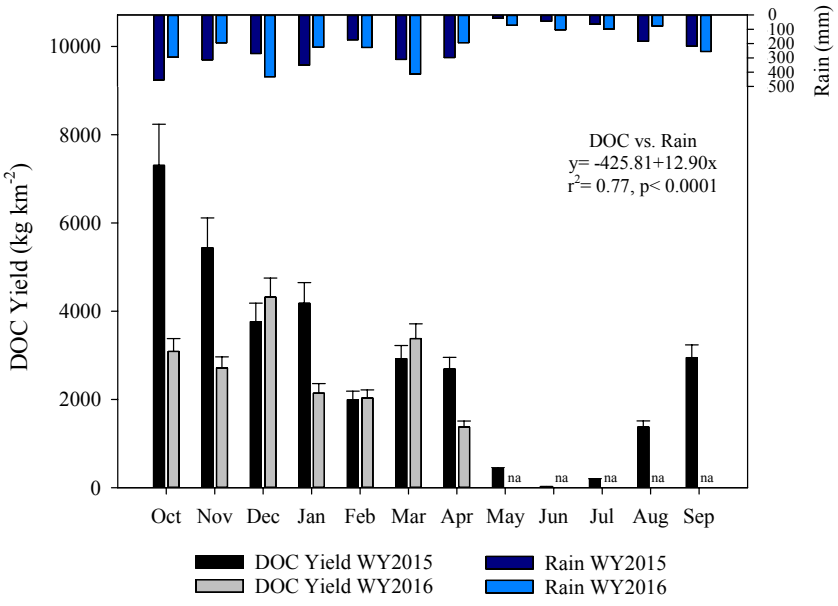
1059 **Figure 4.** Monthly areal DOC yields and precipitation for water year 2015 (WY2015) and the
1060 wet period (October 1-April 30) of water year 2016 (WY2016). Error bars represent standard
1061 error. Total rain and DOC yield were significantly correlated ($r^2$ = 0.77) and months of higher
1062 rain produced higher DOC yields. In WY2015, the majority of DOC export (~94% of annual
1063 load) occurred during the wet period (~88% of annual precipitation).

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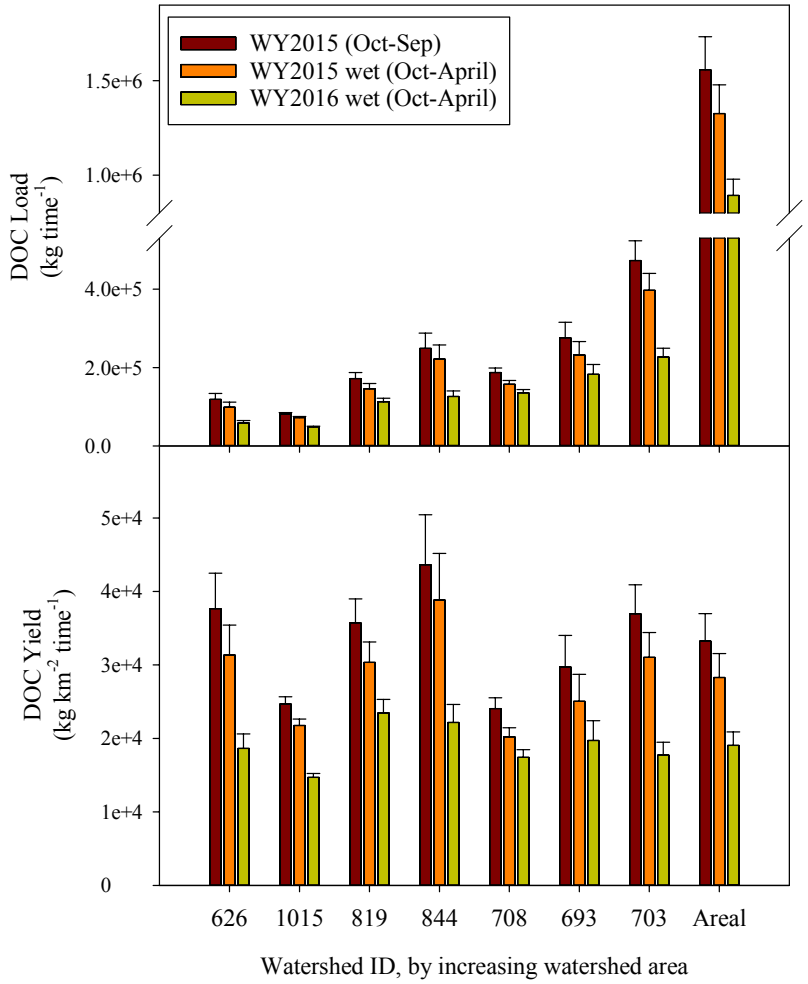
1082 **Figure 5:** DOC loads and yields for the seven study watersheds and the total area of study (all
1083 watersheds combined, or "areal") on Calvert and Hecate Islands for the complete water year
1084 2015 (WY2015; Oct 1 - Sep 30), and October 1- April 30 of the wet period for water year 2015
1085 (WY2015 wet) and water year 2016 (WY2016 wet). Because DOC yields were only available
1086 for September in WY2015, this month was excluded from the wet period totals in order to make
1087 similar comparisons between years. Error bars represent standard error. Total DOC load tended
1088 to increase by increasing watershed area, and the total amount of DOC exported during the wet
1089 period was higher in WY2015 compared to WY2016. DOC yield was also higher for the wet
1090 period of WY2015 compared to WY2016, but differences between watersheds were independent
1091 of total watershed area, indicated different drivers of DOC export on a per-area basis.

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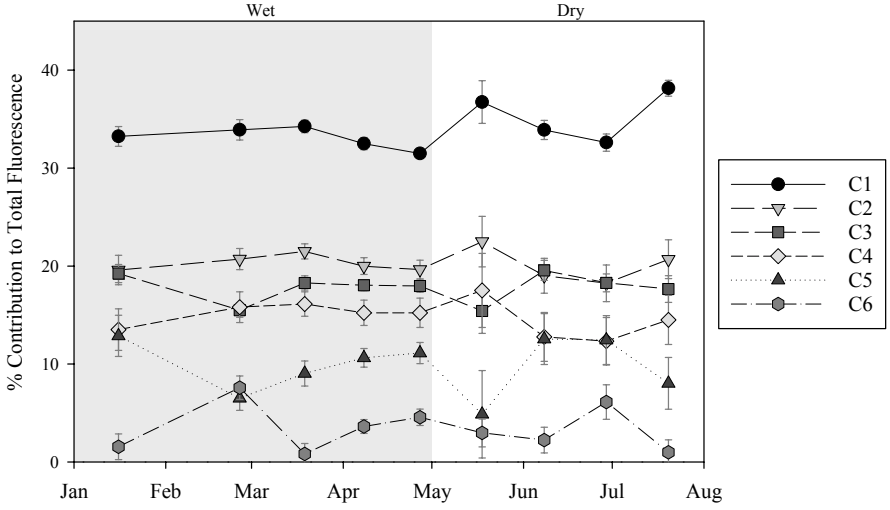
Published: 19 January 2017




1093 **Figure 6:** Percent contribution of the six components identified in parallel factor analysis
1094 (PARAFAC) for samples collected every three weeks from January-July, 2016 from the seven
1095 study watersheds on Calvert and Hecate Islands study watersheds. Points represent means ±
1096 standard deviation for all watersheds combined. The grey shading indicates the wet period and
1097 the unshaded region indicates the dry period.

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Published: 19 January 2017


**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.

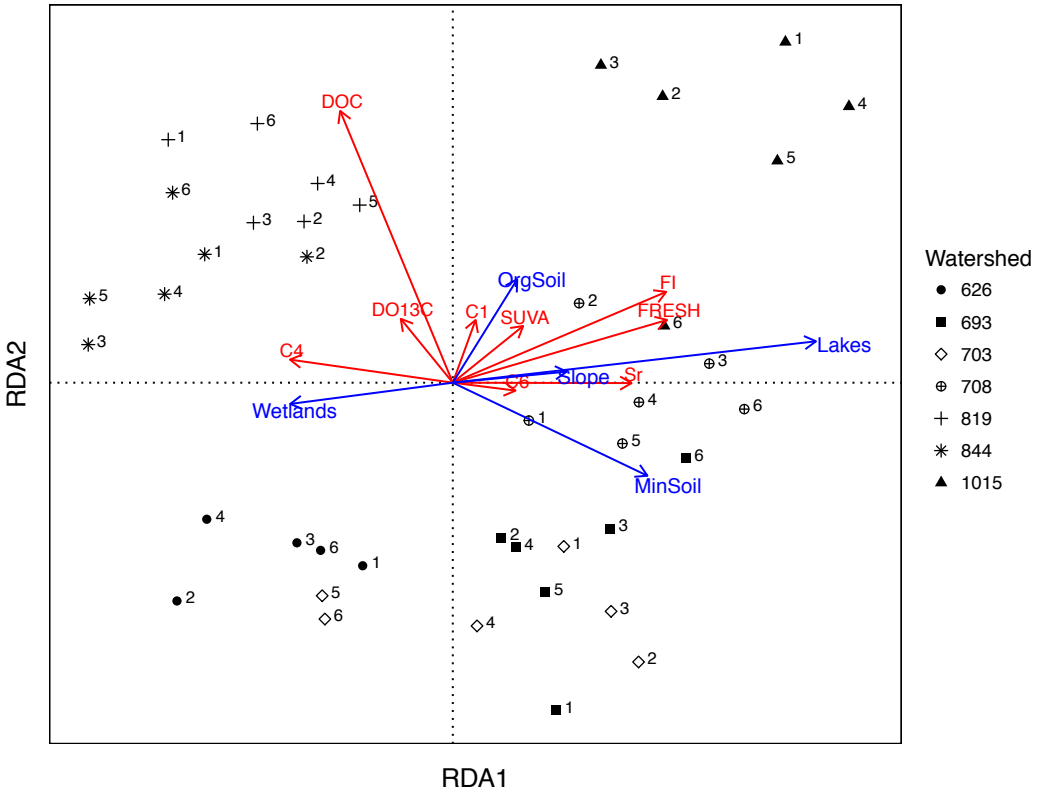

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**Table 1:** Watershed characteristics, discharge, DOC concentrations, and DOC yields for the seven study watersheds on Calvert and Hecate Islands. Additional details on the methods used to determine watershed characteristics can be found in Supplementary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

| Water-shed | 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

Biogeosciences Discuss., doi:10.5194/bg-2017-5, 2017
Manuscript under review for journal Biogeosciences
Published: 19 January 2017


**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.

| 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, low molecular weight, enriched fulvic acid | Coble, 2007; Garcia et al. 2015; Graeber et al. 2012; Walker et al. 2014; Yamashita et al. 2011. |
| C2 | 270/ 380 | 484 | 20.2 ±1.9 (16.1-25.6) | Not commonly reported, similarities to humic-like, more processed terrestrial, high molecular weight | Boehme & Coble, 2000; Coble et al. 1998; La Pierre et al. 2014; Stedmon et al. 2003; |
| C3 | 270 | 478 | 17.8 ±1.8 (12.8-20.8) | Humic-like, highly processed terrestrial; refractory, oxidized quinone-like | Stedmon & Markager, 2005; Yamashita et al. 2010 |
| 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; Stedmon et al., 2003 |
| C5 | 325 | 442 | 9.8 ±3.5 (0.0-15.9) | Aquatic humic-like terrestrial; autochthonous, microbial produced; may be photoproduced | Boehme & Coble, 2000; Coble et al. 1998; Stedmon et al., 2003 |
| 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; Shutova et al. 2003; Stedmon et al. 2007; Yamashita et al. 2003 |

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