June 15, 2017

Author response to re-review of Oliver et al., bg-2017-5, “A global hotspot for dissolved organic carbon in hypermaritime watersheds of coastal British Columbia.”

Dear Associate Editor,

Please find below our response to the reviewer’s comments. We appreciate all of the reviewer’s insight and helpful comments, and believe we have addressed them all. However, we are happy to discuss if you would like to see something additional or different.

Thank you for your consideration and best regards,

Allison Oliver, lead author

Minor revisions: Comments Referee #1

“However, even in its revised version, I consider that the current MS is not suitable for publication and must deserve more intensive work in the interpretation of the seasonal variations and the identification of the drivers leading to seasonal changes in stream DOM concentration and composition in this part of the globe. Thus, the discussion about seasonal changes in DOM concentration and composition (sections 4.2 and 4.3, could be merged) is limited to a comparison between wet and dry periods. However, there are significant and gradual changes occurring both during wet and dry periods. For example, DOC concentrations decrease in all catchment during the wet period of the water year 2014-2015 and these decreases are linked with clear changes in DOM composition (increasing d13C-DOC, increasing SUVA and decreasing Sr). Such fluctuations contrast markedly with those reported during the previous dry period that is characterized by gradual increasing DOC concentrations, decreasing SUVA, Sr and d13C-DOC values.

Author response: In the last iteration of this paper, we worked hard to further investigate the relationship between seasonality and DOC/DOM beyond just “wet” vs “dry” periods. To do so, we looked at changes in DOC/DOM in relation to drivers of stream temperature and discharge as they changed throughout the year. This gave us more insight into seasonal patterns including within the predefined “wet” and “dry” periods and revealed changes in DOC/DOM parameters associated with warmer temperatures and higher discharge, both of which vary on a seasonal basis. We appreciate the reviewer’s observations of seasonal patterns within the predefined “wet” and “dry” periods, and believe the results of our investigation into drivers of temperature and discharge reflect these observations. To better communicate this, and to further develop the concepts behind DOC flushing (per the reviewer’s recommendation, see next comment below) we have restructured sections 4.2 and 4.3 and changed some of the wording surrounding the discussion of temperature and discharge (i.e., seasonal patterns) to avoid the misunderstanding that we are only comparing between wet and dry periods. We also specifically included the reviewer’s observation that DOC concentrations increase and decrease during the dry and wet periods (revised manuscript lines 535-538) and that these changes are also associated with changes in DOM composition. We incorporated this along with the discussion of seasonally-variable measures of stream temperature and discharge to expand the discussion of seasonality beyond the predefined periods of "wet" and "dry" (new draft lines 534-542)

The authors refer well to several studies that have investigated the DOC flushing process in other small catchments, but it has to be noted that DOC flushing is a generic term and several flushing mechanisms have been reported (Boyer et al., 1996; Sanderman et al., 2009; Lambert et al., 2013 and also Pacific et al., 2010 DOI 10.1007/s10533-009-9401-1). How the authors can better constrain DOC export in their catchments with all their dataset on DOM composition? Are these fluctuations related to (1) changes in DOM sources mobilized along the soil profile (topsoil versus subsoil, e.g. Sanderman et al., 2009), (2) changes in the production mechanisms of terrestrial DOM (e.g. Lambert et al., 2013), (3) depletion of a DOM pool depleted in 13C during the wet period (e.g. Boyer et al., 1996), (4) increasing in-stream production during the dry period…? Fluorescence data (Freshness Index, FI values and PARAFAC model) are poorly included in this part of the discussion while they can provide critical information on DOM sources and dynamic. Is there some relationships between d13C-DOC and other proxies of DOM composition that could support one of these explanations? A more robust and convincing discussion on these aspects would represent a major improvement for the MS."

Author response: We appreciate the reviewer's thoughtful consideration of different mechanisms related to DOC flushing and emphasis on considering these mechanisms as possible explanations for DOC/DOM export within our study. However, given the scale and scope of our study, we suggest that higher-resolution data is likely needed to specifically test these hypotheses and make conclusions about flushing mechanisms. For example, we have looked extensively at these data and expected to find relationships between DOC, d13C-DOC, and fluorescence proxies, however we were surprised not to find anything of significance. The objectives of this manuscript were to describe DOC quantity and measures of DOM composition exported from this region of the world, but not to test specific hypotheses of DOC flushing. Therefore, the next logical step for follow up to this work is to conduct studies targeted at understanding mechanisms of export. This work is currently in progress and will be included in future publications. Based on the data collected for the present study, we do not feel we are able to exclude any of the reviewer's suggested flushing mechanisms as candidates that might explain controls on export. Instead, we suggest that these possible mechanisms need to be explored further. To emphasize the reviewer's point that there are multiple possible explanations for mechanisms of DOC flushing, we have included additional points of discussion on these different mechanisms and how they may potentially apply in our study watersheds
(new manuscript lines 543-580).

Specific comments:

Lines 373-375: From my perspective, I see clear variation in d13C-DOC. Considering for example the catchment 703 (but it is also applicable for the others catchments), there is a clear and significant decrease from the dry period to the beginning of the wet period in 2014, then d13C-DOC increase along the wet period. This pattern is less obvious for the water year 2015-2016, but we can also observe a gradual increase in d13C-DOC from August 2015 to march 2016. Seasonal changes is also supported by the fact that the authors reported positive relationships between d13C-DOC, discharge and temperature (line 539). There is something here that should be investigated more deeper.

Author response: We would like to thank the reviewer for their detailed comment. We have changed the wording here to reflect the observation of seasonal variability/changes rather than referring to whether or not we observe a consistent and directional seasonal trend across all watersheds. In our previous revision, we made a concerted effort to further investigate drivers of seasonal patterns by looking at the specific relationship between various DOC/DOM parameters and discharge/temperature. Our results indicate that for some of our parameters, discharge and temperature, and therefore seasonal variability in these drivers, appear to be important predictors of DOC or DOM. If the reviewer (or Associate Editor) would like further analysis on seasonal changes beyond the role of discharge and temperature, we are happy to consider accommodating any suggestions that are within the scope of our dataset.

Line 482: this is partly true for the upland catchment studied by Boyer et al. (1996) (note that drier period in their catchment = winter period), but there is different "forms" of DOC flushing (See Sanderman 2009; Lambert 2013; Pacific et al., 2010 DOI 10.1007/s10533-009-9401-1).

Author response: To underscore the reviewer's point that there are different mechanisms and forms of DOC flushing, we have incorporated some additional text (new document lines 503-511).

Line 501: "highly terrestrial" is quite odd. "mainly terrestrial"?

Author response: We changed to "mainly terrestrial".

Line 519: Please clarify "wider range of DOM from soil material".

Author response: For clarification, we changed to "mobilization of DOM from across a wider range of the soil profile".

Line 529: Caution should be taken when interpreting relationships based on the relative contribution of PARARAC components as when one goes up, another goes down. For example, the increase in C6 suggested by the authors is not clear in Figure 7 (very low increase observed at only one date of the dry period). It will be more relevant to use maximal fluorescence intensity of components to investigate absolute increase or decrease.

Author response: We agree that the increased percent contribution of C6 during the dry season is largely observed during one of the sampling points. We note that the same pattern is observed in maximum fluorescence intensity (data not shown). We have removed the mention of C6 from the sentence.

Lines 539-542: these suggestions cannot be made simply based on the relationships observed between d13C-DOC and discharge and temperature. Moreover, changes in d13C-DOC are significant (> 1 ‰).

Author response: We removed the part of our discussion ("suggestions") highlighted by the reviewer, and included δ^{13}C-DOC in the sentence below this section (updated manuscript lines 571-572) that discusses the relationship between various parameters and temperature.

Lines 542-543: Higher freshness index values do not necessary imply higher biodegradability.

Author response: We were not trying to connect higher Freshness Index values with higher biodegradability, rather we are suggesting that warmer temperatures lead to DOM being freshly produced, apparently from both terrestrial and microbial sources, which could potentially serve as additional source of DOM available for microbial use. To clarify this point, we have changed the language and removed the phrase "available for microbial degradation" to simply, "contribute a fresh supply of DOM exported from terrestrial sources"

Lines 546-565: this is a long discussion on an aspect of DOM cycling that has not been investigated in the study (the authors have no estimation on the biodegradability of DOM in their catchments).

Author response: We feel that it is important to include some preliminary discussion on the potential downstream (e.g., marine environment) implications of the high amounts of terrestrial DOC/DOM exported from these watersheds, partly to provide context for the importance of this work but also as a prelude to follow up work in preparation looking at the fate of this material in the ocean. However, we recognize the reviewer's concern about the length of a section based on information not specifically investigated in this study. In response, we have shortened this paragraph to a few sentences which are now included at the end of the previous paragraph. We also removed the citations associated with the deleted text.

Lines 578-590: is there some correlation between the relative repartition of Hemist and Folic Histosols and stream DOM concentration and composition? As data seems to be available (supplements S1.2), this would represent a strong argument to support this hypothesis.

Author response: While investigating specific relationships between detailed soil properties within watersheds and DOC fluxes is a next logical step, we feel it is beyond the scope of the current paper. We do, however, thank the reviewer for this insightful comment!

Lines 591-604: additional figures for illustrating the different links between lakes/wetlands and stream DOM will be great here.

Author response: The discussion here is related to the results of our RDA analysis, which illustrates the relationship between different DOM variables and lake and wetland area (Fig. 7). We also included an additional series of figures in the supplement (Supplemental Fig. S2.2) showing the different hydrologic responses of catchments with/without extensive lake area, as we mention lakes being important for increasing response/residence time. To aid in the assessment of ties between lake area, wetland area, and stream DOM, we have added text to the caption of Figure S2.2 to direct the reader to relevant information (Table 1) on these catchment characteristics. If the reviewer can provide more detail on a possible figure in addition to what we already provide, we would be happy to consider contributing additional information.

Reference Lambert et al. (2013) is still missing.
Author response: Reference now included.

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

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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.

Deleted: global

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

2.3 Sample Collection and Analysis

From May 2013 to July 2016, we collected stream water grab samples from each watershed stream outlet every 2-3 weeks (n_{total}= 402), with less frequent sampling (~ monthly) during winter (Fig. 1). All samples were filtered in the field (Millipore Millex-HP Hydrophilic PES 0.45μm) and kept in the dark, on ice until analysis. DOC samples were filtered into 60 mL amber glass bottles and preserved with 7.5M H_3PO_4. Fe samples were filtered into 125 mL

HDPE bottles and preserved with 8M HNO_3. DOC and Fe samples were analyzed at the BC Ministry of the Environment Technical Services Laboratory (Victoria, BC, Canada). DOC concentrations were determined on a TOC analyzer (Aurora 1030; OI-Analytical) using wet chemical oxidation with persulfate followed by infrared detection of CO_2. Fe concentrations were determined on a dual-view ICP-OES spectrophotometer (Prodigy; Teledyne Leeman Labs) using a Seaspray pneumatic nebulizer.

In May 2014, we began collecting stream samples for stable isotopic composition of $\delta^{13}C$ in DOC ($\delta^{13}C$-DOC; n= 173) and optical characterization of DOM using absorbance spectroscopy (n= 259). Beginning in January 2016, we also analyzed samples using fluorescence spectroscopy (see section 2.6). Samples collected for $\delta^{13}C$-DOC were filtered into 40 mL EPA glass vials and preserved with H_3PO_4. $\delta^{13}C$-DOC 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 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.

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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

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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 $R^2= 0.09$).

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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

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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

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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

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

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

The process of "DOC flushing" has been shown to increase stream water DOC during higher flows in coastal and temperate watersheds (e.g., Sanderman et al., 2009; Deirmendjian et al., 2017). Flushing can occur through various mechanisms. For example, Boyer et al. (1996) observed that during drier periods, DOC pools can increase in soils and are then flushed to

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streams when water tables rise. Rising water tables can establish strong hydraulic gradients that initiate and sustain prolonged increases in metrics like SUVA$_{254}$, until the progressive drawdown of upland water tables constrain flow paths (Lambert et al., 2013). DOC concentrations can vary during flushing in response to changing flow paths, which can shift sources of DOC within the soil profile from older material in deeper soil horizons to more recently produced material in shallow horizons (Sanderman et al., 2009), or from changes in the production mechanism of 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 composition suggests that controls on DOM composition are more nuanced than being solely driven by the extent 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. Although wetlands comprise an average of 37% of our study area, they do not appear to be the single leading driver of variability in DOC concentration and DOM composition. Other factors, such as watershed slope, the depth of organic and mineral soil materials, and the presence of lakes also appear to be influence DOC concentration and DOM composition. The presence of cyptic wetlands (Creed et al., 2003) and

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limitations of the wetland mapping method could also weaken the link between wetland extent, DOC, and DOM.

In these watersheds, soils with pronounced accumulations of organic matter are not restricted to wetland ecosystems. Peat accumulation in wetland ecosystems results in the formation of organic soils (Hemists), where mobile fractions of DOM accumulate under saturated soil conditions and limited drainage, resulting in the enrichment of poorly biodegradable, more stable humic acids (Stevenson, 1994; Marschner and Kalbitz, 2003). Although Hemist soils comprise 27.8% of our study area, Folic Histosols, which form under more freely drained conditions, such as steeper slopes, occur over an additional 25.7% of the area (Supplemental S1.2). In freely drained organic soils, high rates of respiration can result in further enrichment of aromatic and more complex molecules, and this material may be rapidly mobilized and exported to streams (Glatzel et al., 2003). This suggests the importance of widely distributed, alternative soil DOM source-pools, such as Folic Histosols and associated Podzols with thick forest floors on hillslopes, available to contribute high amounts of terrestrial carbon for export.

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Although lakes make up a relatively small proportion of the total landscape area, their influence on DOM export appears to be important. The proportion of lake area can be a good predictor of organic carbon loss from a catchment since lakes often increase hydrologic residence times and thus increase opportunities for biogeochemical processing (Algesten et al., 2004; Tranvik et al., 2009). In our study, watersheds with a larger percentage of lake area exhibited slower response following rain events (Supplemental Fig. S2.2), lower DOC yields, and lake area was correlated with parameters that represent greater autochthonous DOM production or microbial processing such as higher Freshness Index, S_{R}, Fluorescence Index, and higher proportions of component C6. In contrast, watersheds with a high percentage of wetlands contributed DOM that was more allocthonous in composition. Lakes are known to be important landscape predictors of DOC, as increased residence time enables removal via respiration, thus reducing downstream exports from lake outlets (Larson et al., 2007). The proximity of wetlands and lakes to the watershed outlet can also play an important role in the composition of DOM exports (Martin et al., 2006).

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5. Conclusions

Previous work has demonstrated freshwater discharge is substantial along the coastal margin of the North Pacific temperate rainforest, and plays an important role in processes such as ocean circulation (Royer, 1982; Eaton and Moore, 2010). Our finding that small catchments in this region contribute high yields of terrestrial DOC to coastal waters suggests that freshwater inputs may also influence ocean biogeochemistry and food web processes through terrestrial organic matter subsidies. Our findings also suggest that this region may be currently underrepresented in terms of its role in global carbon cycling. Currently, there is no region-wide carbon flux model for the Pacific coastal temperate rainforest or the greater Gulf of Alaska, which would quantify the importance of this region within the global carbon budget. Our estimates point to the importance of the hypermaritime outer-coast zone of the CTR, where subdued terrain, high rainfall, ocean moderated temperatures and poor bedrock have generated a distinctive 'bog-forest' landscape mosaic within the greater temperate rainforest (Banner et al. 2005). However, even within our geographically limited study area, we observed a range of DOC yields across watersheds. To quantify regional scale fluxes of rainforest carbon to the coastal ocean, further research will be needed to estimate DOC yields across complex spatial gradients of topography, climate, hydrology, soils and vegetation. Long term changes in DOC

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flux have been observed in many places (e.g., Worrall et al., 2004; Borken et al., 2011; Lepistö et al., 2014; Tank et al., 2016) and continued monitoring of this system will allow us to better understand the underlying drivers of export and evaluate future patterns in DOC yields. Coupled with current studies investigating the fate of terrestrial material in ocean food webs, this work will improve our understanding of coastal carbon patterns, and increase capacity for predictions 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.

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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.

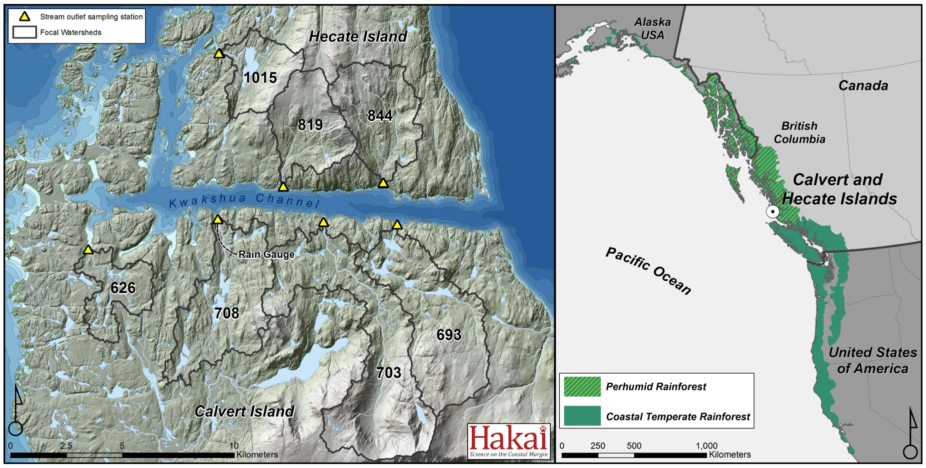


Figure 2. Hydrological patterns typical of watersheds located in the study area (a) the hydrograph and precipitation record from Watershed 708 for the study period of October 1, 2015-April 30, 2016. Grey shading indicates the wet period (September 1-April 30) and the unshaded region indicates the dry 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.

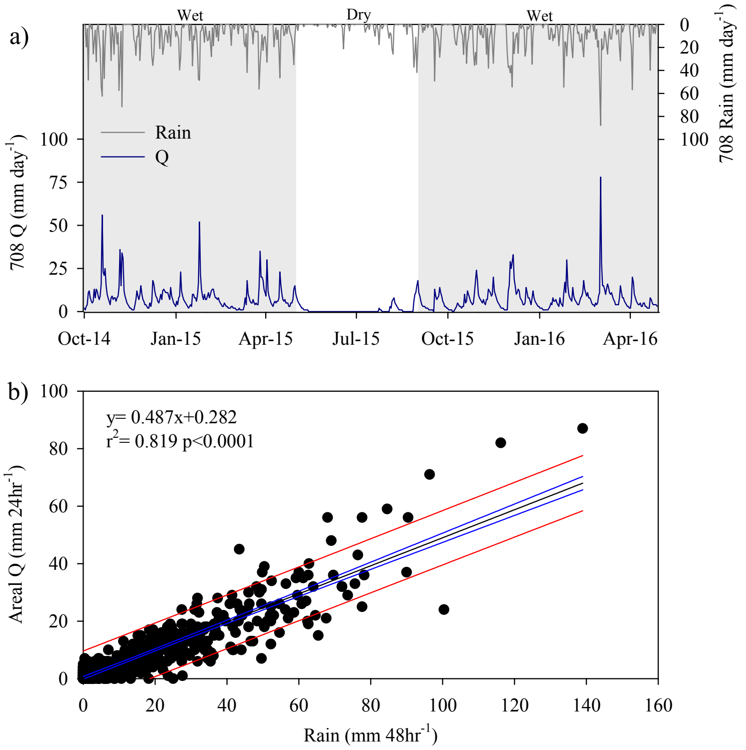


Figure 3. Seasonal (timelines, by date) and spatial (boxplots, by watershed) patterns in DOC concentration and DOM composition for stream water collected at the outlets of the seven study watersheds on Calvert and Hecate Islands. Boxes represent the 25th and 75th percentile, while whiskers represent 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.

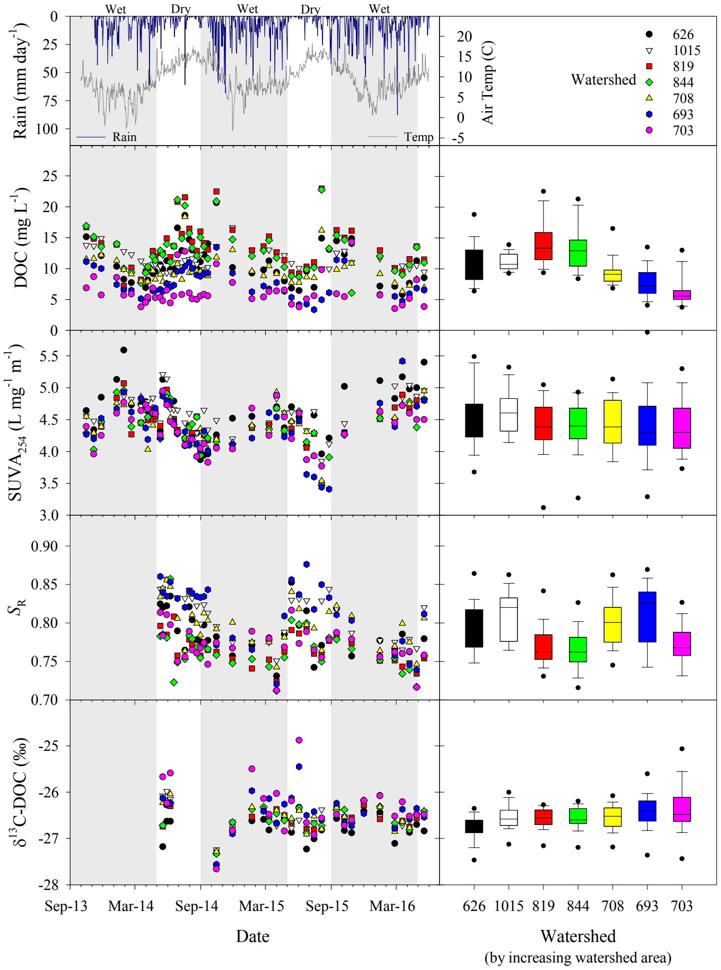


Figure 4. Monthly areal DOC yields and precipitation for water year 2015 (WY2015) and the wet period (October 1-April 30) of water year 2016 (WY2016). Error bars represent standard error. Total rain and DOC yield were significantly correlated ($r^2 = 0.77$) and months of higher rain produced higher DOC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

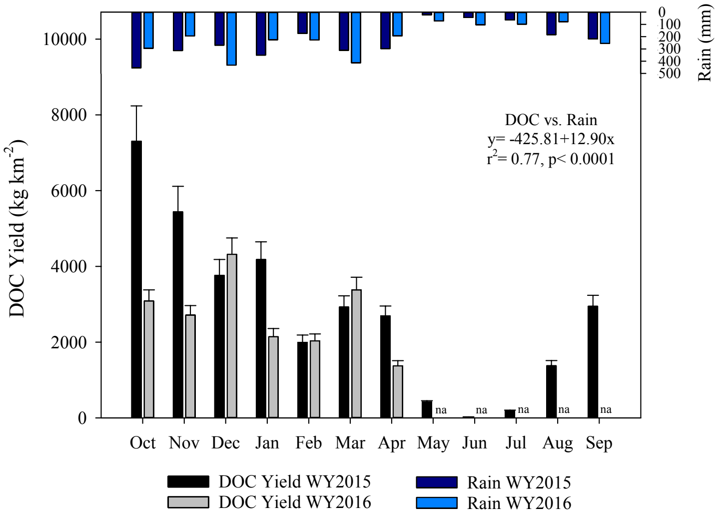


Figure 5: DOC fluxes and yields for the seven study watersheds and the total area of study ("areal", all watersheds combined) on Calvert and Hecate Islands for water year 2015 (WY2015; Oct 1 - Sep 30), and October 1- April 30 of the wet period for water year 2015 (WY2015 wet) and water year 2016 (WY2016 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.

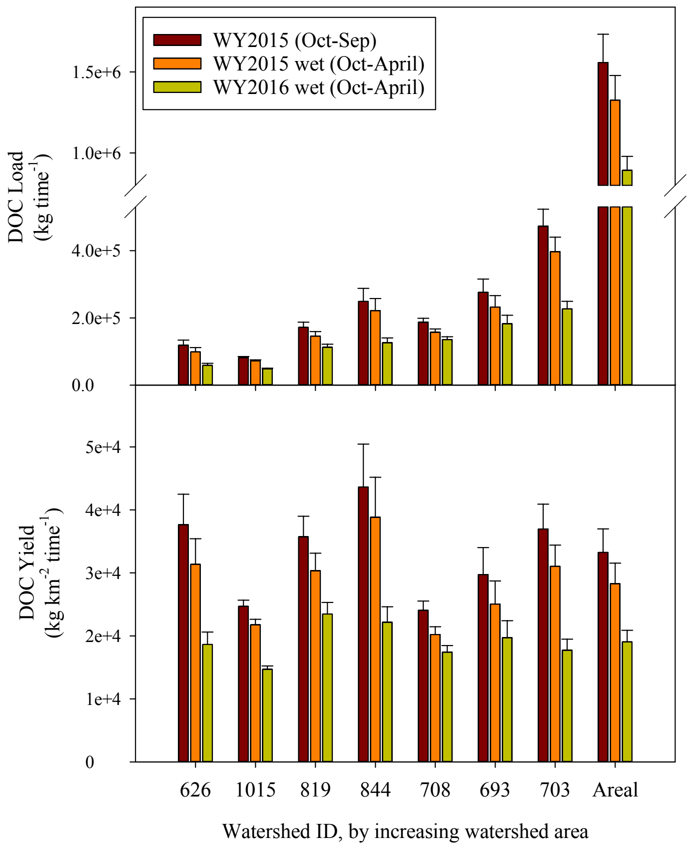


Figure 6: Percent contribution of the six components identified in parallel factor analysis (PARAFAC) for samples collected every three weeks from January-July, 2016 from the seven study watersheds on Calvert and Hecate Islands. The grey shading indicates the wet period and

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.

Comment [AO9]: New figure created and inserted. New figure shows individual points for each watershed instead of mean +- std.

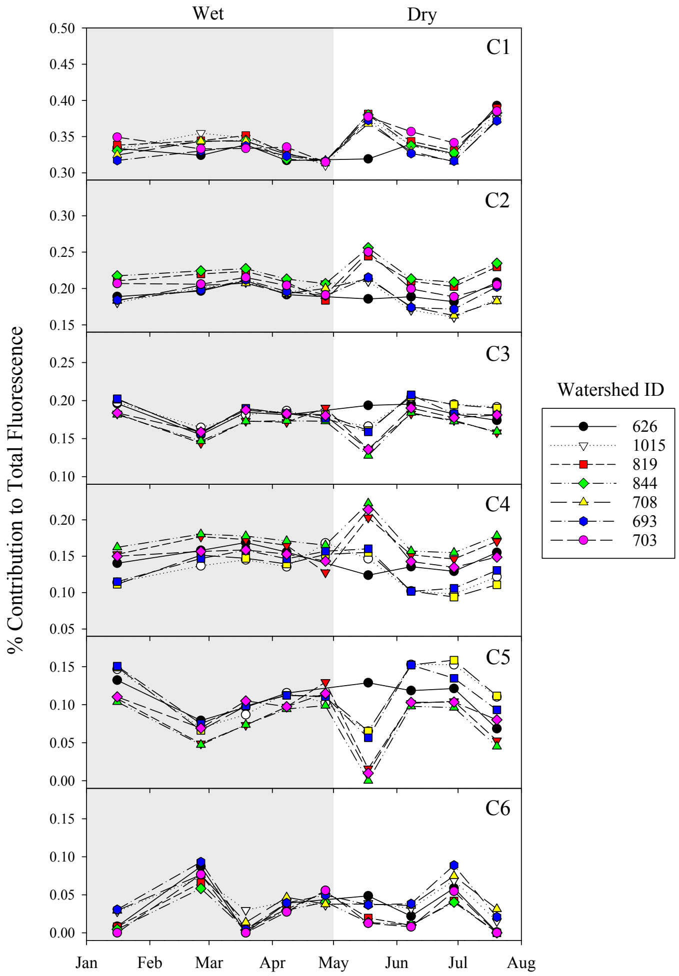
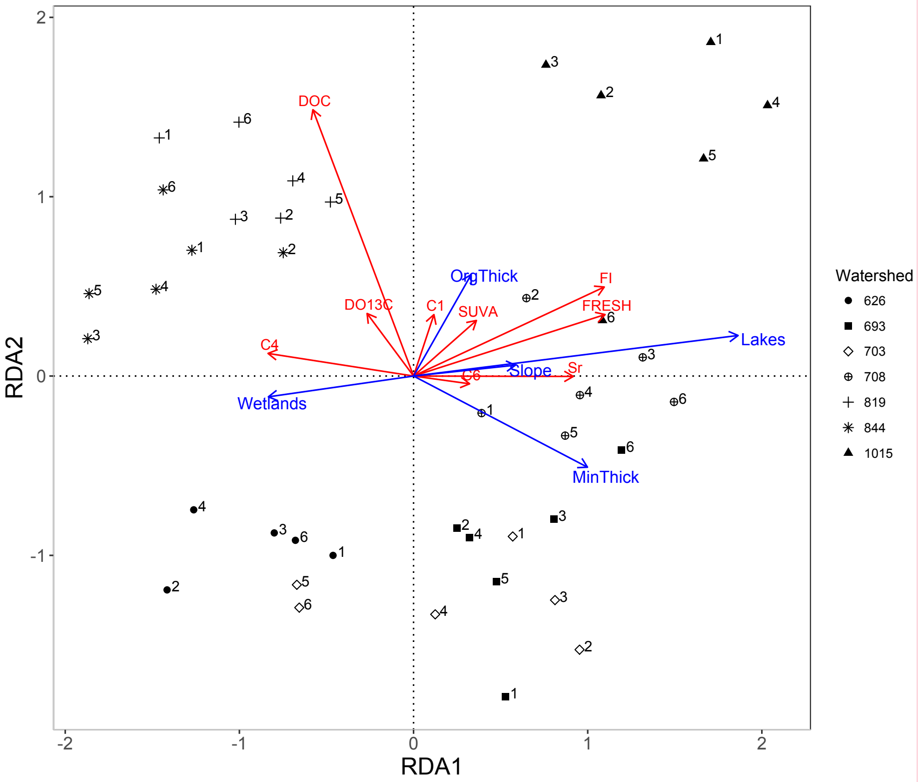


Figure 7: Results from the partial-Redundancy analysis (RDA; type 2 scaling) of DOC concentration and DOM composition versus watershed characteristics. Angles between vectors represent correlation, i.e., smaller angles indicate higher correlation. Symbols represent different

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.



Comment [AO10]: Remade figure renaming “OrgSoil” and “MinSoil” as “OrgThick” and “MinThick”

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.

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

Comment [AO11]: Table modified per comments from Reviewer 1

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During drier periods DOC pools increase in soils and are flushed to streams when water tables rise (Boyer et al., 1996)

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 downstream, thus reducing time for in-stream processing (Raymond et al., 2016). On Calvert and Hecate Islands, the combination of high rainfall, rapid runoff, and abundant sources of DOC from organic-rich soils, wetlands, and forests, result in high DOC fluxes. The process of "DOC flushing" has been shown to increase stream water DOC during higher flows in coastal and temperate watersheds (e.g., Sanderman et al., 2009; Deirmendjian et al., 2017). In our study, the relationship between DOC concentration and discharge varied by watershed (see Supplemental Fig. S6.1[A01]), but overall DOC concentrations increased with both discharge and temperature. This indicates that while watershed characteristics are important for influencing the magnitude and variability of DOC concentrations and export, the hydrologic coupling of precipitation and discharge with seasonal production and availability of DOC is an overarching driver of DOC export (Fasching et al., 2016).

4.3 DOM character: Sources and variability

Measures of [S2]DOM composition from Calvert and Hecate Islands suggest that carbon and organic matter exported from these systems is highly terrestrialsufficient. Values for δ^{13}C-DOC were relatively constrained, suggesting 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).

Seasonal variability in DOM composition may be attributed to seasonal changes in biological activity and shifting flow paths that affect hydrologic interactions with different DOM source materials (Fellman et al., 2009b). On Calvert and Hecate Island watersheds, Walso[S3] some measures of DOM composition, such as δ^{13}C-DOC and S_R, exhibited seasonal patterns[A04]. In our study, discharge was significantly related to δ^{13}C-DOC and S_R, with higher discharge resulting in more terrestrial-like DOM (i.e., more depleted δ^{13}C-DOC and lower S_R) as saturated conditions promote the mobilization of a wider range of DOM from soil material (McKnight et al., 2001; Kalbitz et al., 2002). This is similar to findings of Sanderman et al. (2009), who observed distinct relationships between discharge and both δ^{13}C-DOC and SUVA$_{254}$, and postulated that during the rainy season, hillslope flushing shifts DOM sources to more aged soil organic material because plant productivity is not rapid enough to meet microbial demand, forcing microbes to switch to metabolizing more aged DOM within soils. It has also been shown that rising water tables can establish strong hydraulic gradients that initiate and sustain prolonged increases in metrics like SUVA$_{254}$, until the progressive drawdown of upland water tables constrain flow paths (Lambert et al., 2013).

During the drier and warmer period, DOM decreased in molecular weight (S_R) and Freshness Index, as well as increased in C6, a component comprised of protein-like composition. This suggests 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), 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). Proportions of fluorescence components were generally consistent across watersheds during the dry period, but diverged during the wet period, further suggesting that water table draw down and unsaturated soils lead to more diverse flow paths and hydrologic interaction with different sources of DOM[A05].

Interestingly, more depleted values of δ^{13}C-DOC were also related to warmer temperature. The positive relationship between δ^{13}C-DOC and both discharge and temperature, as well as the overall low variability in δ^{13}C-DOC, suggests that the availability or production of terrestrial DOM is enough to keep up with microbial demand, allowing the supply of terrestrial material to remain relatively seasonally consistent. The positive relationship of temperature and Freshness Index, as well as with C1 and C4, further suggests that warmer periods contribute to a fresh supply of terrestrial material available for microbial degradation and export (Fellman et al., 2009a; Fasching et al., 2016).

The interaction of sources and flow paths during wet versus dry periods may have important consequences for the downstream fate of this material. For example, 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). This may represent a relatively fresh, seasonally-consistent contribution of terrestrial subsidy from streams to the coastal ecosystem, which is relatively lower in carbon and nutrients throughout much of the year (Whitney et al., 2005; Johannessen et al., 2008). For example, pulsed contributions of less-processed humic material exported from rivers to lakes have been shown to stimulate bacterial production (Bergström and Jansson, 2000). While previous studies have suggested that bacteria prefer autochthonous carbon sources, they readily utilize allochthonous terrestrial DOC subsidies (Bergström and Jansson, 2000; Kritzberg et al., 2004; McCallister and Giorgio, 2008; Berggren et al., 2010), enabling humic and fulvic material to fuel a low but continuous level of bacterial productivity after more labile sources have been consumed (Guillamette and Giorgio, 2011). In addition, although the tryptophan-like component C6, 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).

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