16 May 2017

Responses- Anonymous Referee #1

Responses to General Comments (GC):

Thank you for taking the time to review our manuscript and for your positive feedback on the overall scope of the paper. Below you will find our responses to your comments, which are greatly appreciated and have improved the paper. Please feel free to contact us with any additional questions or comments.

GC1: Overall, manuscript is highly descriptive. Could regret the lack of more specific goals/questions for this study.

Author response: The outer-central coast of British Columbia's perhumid coastal temperate rainforest is largely unstudied with respect to DOC exports, so a primary goal of this manuscript is to establish in the literature a detailed description of DOC exports for this region and put them into a global context. However, we agree that a more specific statement of goals and questions will further strengthen the quality of the manuscript. We have clarified our objectives in terms of quantifying flux and determining compositional characteristics to identify sources and drivers of DOM. We have also included some new simple statistical measures to look at differences between seasons and correlations between variables, as well as conducted a simple regional estimate of DOC flux to emphasize the importance of our results and put them into a global and regional global context.

GC2: Some approximation regarding DOC fluxes/yields that need to be corrected and/or clarified.

Author Response: We have attempted to clarify DOC fluxes/yields per the reviewer's comments. Please see SC19 below for complete description of our approach.

GC3: Data poorly included in the section aiming to describe temporal dynamics of DOM.

Author Response: We have added analysis of the role of both discharge and temperature in relation to our data and have conducted additional analysis examining differences in temporal dynamics in the dynamics of DOM compositional variables and DOC concentration. Please see SC13 and SC24 below for more information.

Responses to Specific Comments (SC):

SC1: Lines 107-110: the scientific objectives of this paper are too general.

Author Response: We have included more specific objectives/hypotheses to replace the text of lines 107-110.

SC2: Line 142: please define GIS.

Author Response: Text was changed to define "GIS" as "geographic information system"

SC3: Line 146: how have been defined the boundaries between organic and mineral soils? It would be very informative to compare a soil map and a map showing the location of wetlands and lakes within catchments.

Author Response: We have added some explanation of the distinction between organic and mineral soil materials in S1.2: “Mineral soil horizons have ≤17% organic C, while organic soil horizons have >17% organic C, as per the Canadian System of Soil Classification (Soil Classification Working Group, 1998). Boundaries between surface organic horizons and the underlying mineral soil were usually obvious, based on colour, consistence, and presence/absence of mineral grains, but for occasional ambiguous cases, grab samples were collected for laboratory determination of C content by a ThermoFischer Scientific Flash 2000 CHNS analyser at the Ministry of Environment laboratory in Victoria, B.C.”

Further documentation of the soil characteristics of the watersheds will be provided elsewhere by publications in preparation, so in this manuscript we presented only the summary data needed to support the interpretations related to DOC export.

SC4: Line 168: I suggest to use the more common notation ‘13C’ or ‘13CDOC’.

Author Response: Notation was changed to δ^{13}C-DOC throughout the document.

SC5: Line 175: what size of filtration?

Author Response: All samples were filtered in the field using a Millipore Millex-HP Hydrophilic PES 0.45μm as described in the information on sample collection, lines 158-159.

SC6: Line 240: define PARAFAC.

Author Response: included definition, “..we performed parallel factor analysis (PARAFAC)…”

SC7: Line 301 and 306: change for ‘Table 1’ in the brackets.

Author Response: Changed to “Table 1” in the brackets.

SC8: Lines 304-310: I am not sure that is very significant. Maybe a statistical test could support this.

Author Response: We have conducted additional statistical tests that compare watersheds and seasons (wet versus dry) and that explore the relationships between DOC, stream discharge and temperature. We have reworded parts of this section to include information supported by this new analysis.

SC9: Line 312: why there is no DOC fluxes/yield for WY2014 while sampling for DOC has started in October 2014?

Author Response: We don't have DOC fluxes/yields for Water Year 2014 because "Water Years" are defined by the year they end (defined at the beginning of Section 3.1 "Hydrology"), and we did not have discharge data for the period of September 1, 2013 to October 1, 2014. Discharge data began October 1, 2014, and so the first year of record is Water Year 2015. This is noted in the next line, Line 313.

SC10: Lines 326-328: Such elevated SUVA values are commonly found in tropical rivers (e.g. Lambert et al., 2016, Biogeosciences, 13, 5405-5420) or in streams draining wetlands (e.g. Agren et al., 2008). This should be noted as it is not an exception but rather typical of environments exporting large quantities of highly aromatic DOM.

Author Response: Great point. We included a statement to clarify this, that values were "typical of environments that export large quantities of highly aromatic DOM, such as some tropical rivers (e.g., Lambert et al., 2016) or streams draining wetlands (e.g., Ågren et al., 2008)." We also added the Lambert citation to our references.

SC11: Lines 345-347: maybe this should be moved into the discussion as its interpretation of d13C-DOC data.

Author Response: We agree, we moved this into the discussion under Section 4.2 on "DOM Character" as an additional component aimed at better developing the interpretation of DOM sources and temporal trends/controls per the Reviewer's general comment (GC3).

SC12: Lines 325-347: where are the Fluorescence Index and the Freshness Index? Even if they have been measured over a short period, they should be described as they are included in the RDA.

Author Response: We included a paragraph within Section 3.3 ("Temporal and spatial patterns in DOM composition"), on the results of the Fluorescence and Freshness Index data.

SC13: Lines 348-373 & table 2: it would be informative that the corresponding number of PARAFAC components in other studies appears in table 2. For example, it's not clear what component identified in Graeber et al. (2012) matches C1. Also, according to Fellman et al. (2010), components similar to C2 are commonly reported in freshwaters. Overall this paragraph is hard to follow, mainly because figures 6 and S4.4 are not very efficient to support the text. Y-axis in figure S4.4 should be adapted for each PARAFAC component, and figure 6 could be modified in order to present temporal variability for some representative catchments. Also, some statistical tests are welcome in order to support the variability between catchments and between seasons.

Author Response: 1) The corresponding numbers for each of the components identified in previous studies was added to Table 2. A few references from the table were missing so they were also added to the reference list. 2) We edited the text in lines 348-373 for clarity and included some additional language to clarify that C1 and C2 are both considered to be widespread and commonly reported. 3) We adapted the Y-axis in S4.4 for each PARAFAC component and also added means and standard errors across all watersheds to give a better idea of the spatial variability across watersheds for each component. 4) Figure 6 was modified to a panel figure in order to represent each component for all watersheds. We are hoping this addresses the reviewer's comments and better shows temporal variability for all the catchments. 5). To support the variability described between catchments and seasons, we conducted statistical comparisons to test the difference between seasons and between catchments for each component. We also looked at correlations between PARAFAC components, these are presented in a correlation matrix in the Supplementary material. These relationships are discussed in the text. A table of Pearson correlation coefficients is included as Table S4.2 in Supplementary Material.

SC14: Line 374: DOC export is not investigated in RDA, please change the title accordingly.

Author Response: Title changed to "Relationships between watershed characteristics, DOC concentration, and DOM composition"

SC15: Line 374: because PARAFAC components track different fractions of the DOM pools I would suggest to perform the RDA with all components, or at least to include C3 and C5.

Author Response: We understand the argument here and why utilizing all the components for this type (or other types) of analysis would make sense in some circumstances. Here, we are trying to identify the most important characteristics of DOM as they relate to watershed attributes. C3, C4, and C5 were removed because they were found to be highly correlated and therefore they do not appear to be significantly different from other variables as far as identifying the most important drivers of differences in bulk DOM that can be related to different watershed attributes. Because the RDA is a statistical test, leaving the correlated variables in the analysis inflates the standard errors and increases the variance of the remaining independent variables, making them more difficult to interpret in regards to teasing apart differences in watersheds and drivers of DOM/DOC concentration.

SC16: Line 380: I don't think that the term 'inundation' is relevant here as wetlands are wet environments. Clearly the RDA1 identifies two elements of the landscape (i.e. wetlands and lakes) as being important drivers for the spatial variability in DOC concentrations and DOM composition.

Author Response: The term 'inundation' used in this context was meant to suggest that the gradient of wetlands to lakes was a gradient of increasing water coverage (i.e., wetlands being "less inundated" to lakes being "more inundated" with water). However, it seems as though this term may be introducing confusion in this context, so we have replaced the word "inundation" with, what we hope, is a more comprehensive explanation: "a gradient of watershed coverage by inundated ecosystem types, ranging from more wetland coverage to more lake coverage".

SC17: Line 384: there is no information about soil composition as only the depths of organic and mineral soil horizon have been measured.

Author response: Changed "soil composition" to "soil material thickness", however an overview of the main soil types for the study area is given in lines 183-188 of the revised manuscript, as well as in supplementary section S1.2 More details are forthcoming in publications in preparation.

SC18: Lines 394: the title of the section 4.1 needs to be corrected because DOC yields and DOC fluxes are calculated differently and therefore have not the same meaning. See the next comment.

Author response: This is a good point, as we do not discuss DOC flux *per se* in this section, but rather yield as the flux per unit area of watershed. Accordingly, the title of section 4.1 has been corrected to "DOC export from small catchments to the coastal ocean" as export encompasses both flux and yield.

SC19: Lines 395-404: this section is confusing because DOC yields and DOC fluxes have not the same meaning: DOC fluxes are the amount (mass) that passes a given point on the river over a given period of time while DOC yields are the flux per unit drainage area. If it is true that DOC yields of the study sites are higher or comparable to those estimated for some tropical rivers (higher than the Congo and the Amazon rivers but comparable relative to the Siak River), DOC fluxes are clearly lower compared to these systems (see figure). Moreover, as shown by Agren et al. (2007), DOC yields trend to decrease with catchment areas because of (1) better connection between terrestrial and aquatic ecosystems in headwater catchments, (2) reduced in stream losses in small streams and (3) increasing contribution of DOC-poor groundwater in large rivers. Consequently, the authors should compare their DOC yields to tropical catchments having similar drainage areas to support the statement that DOC yields from Calvert and Hecate Island are some of the highest recorded globally (lines 395-396). Furthermore, this statement should be taken with caution because very high DOC concentrations (> 15 mg/l) are commonly found in tropical rivers (e.g. Mayorga et al., 2003), especially in the central part of the Congo Basin where small streams < 100 km2 can have DOC concentrations up to 70 mg/l (e.g. Lambert et al., 2016, Biogeosciences, 13, 5405-5420), having thus likely among the highest DOC yields and export for streams.

Author Response: The reviewer makes some very good points. We have made the following changes:

1) To put numbers into a more regional and global context we have included a simple regional estimate for total DOC flux from the hypermaritime region of B.C.'s perhumid coastal temperate rainforest.
2) We included flux estimates from global to regional scales.
3) We removed comparisons of our DOC yields with much larger rivers and instead include comparisons of watersheds of similar size, in particular those that have high amounts of precipitation, and contain extensive organic soils and wetlands. We emphasize that to the best of our knowledge, this is the first study that represents the role that these types of small catchments (high latitude, temperate, wetland and peat or organic soil-dominated) play in delivery of DOC directly to the ocean.

SC20: Lines 408-409: is it valid for the sites studied by the authors?

Author Response: We are emphasizing that while our sites represent small catchments, they are not first or second order headwater streams that drain to higher order catchments, but rather low to mid-order streams that drain directly to the ocean.

SC21: Lines 405-431: this part of the manuscript is quite long and looks like more as an introduction for the section 4.2 rather than a discussion including the data.

Author Response: This section of the manuscript was shortened and includes more discussion of the data. Lines 406-420 from the original manuscript were incorporated into the previous paragraph along with the changes discussed in the response to SC19. Lines 421-432 (from original manuscript) have been re-worded and incorporated into the beginning of Section 4.2.

SC22: Line 414: do you have a reference?

Author Response: Sorry, not sure of what is being referenced? Line 414 is a statement about the results of this study. We would be happy to provide a reference, or more detailed response, with clarification.

SC23: Lines 415-417: do you have an idea about how much represent freshwater masses compared to coastal water masses?

Author Response: It is estimated that the coastal freshwater discharge in the northeast Pacific Ocean is at least 40% of the total of freshwater that enters from the atmosphere, and is significant enough to create a freshwater-influenced water mass known as the Riverine Coastal Domain (RCD; Carmack et al. 2015). The RCD fluctuates in size but is influenced by variability in continental runoff (Morrison et al. 2012). We incorporated a sentence in the text that describes the significance of freshwater discharge and its role in the development of the RCD in this region and added the two citations mentioned above.

SC24: Lines 428-430: this phenomenon is commonly referred as 'DOC flushing' (Boyer et al., 1996, Ecological modelling, 86, 183-188) and should be moved to the beginning of section 4.2 (nothing to do with DOC fluxes/yields). Maybe the authors could also exploit their data to discuss about hypothesis around 'DOC flushing'? Indeed, d13CDOC values been found to investigate change in sources and pathways of DOC in small catchments (e.g. Sanderman et al., 2009, WRR, 45, W03418; Lambert et al., 2013). It is a pity that isotopic measurements made for this study are not discussed and related to the temporal and spatial variability of DOC.

Author Response: We moved the discussion of seasonal patterns in DOC to a new section ("Section 4.2: Seasonal variability in DOC export"). We also followed your suggestion to use our delta13C-DOC data, along with other measures of DOM quality and DOC concentration per comments below (SC26 re: lines 433-456), and comments from other reviewers, to further explore the relationship between discharge, temperature, DOC concentration and DOM quality. We refined our objectives to include the rationale for this additional analysis (e.g., possible seasonal and spatial trends and drivers) and to address general comments regarding incorporating

DOM data to look at temporal and cross-watershed patterns. Results are included as a figure (Figure S6.1) and two tables (Table S6.1, S6.2) in Supplementary Material.

SC25: Line 432: the manuscript presents no data allowing to investigate the effects of fresh DOC fluxes in coastal waters. Even if I agree that the delivery of fresh terrestrial material likely impact coastal marine foodwebs I would suggest to modify the title of the section.

Author Response: We changed the title of this section to "Sources of DOM and seasonal variability"

SC26: Lines 433-456: it is not clear what are driving the changes in DOM composition. What are the 'microbial products and plants exudates' (line 450)? I strongly suggest to use d13C-DOC values to go deeper in this section in parallel with optical properties of DOM. How vary the fluorescence index and the freshness index and % of PARAFAC components? Is there difference in temporal variability between catchments?

Author Response: We clarified that "microbial products and plant exudates" represent increased terrestrial primary production and microbial degradation products of lower molecular weight, less aromatic materials. Our RDA analysis looks at the role of various watershed attributes in influencing DOM composition, and in addition to box and whisker plots in Figure 2, is used to identify and discuss differences between catchments. To address questions of temporal variability, we conducted additional analysis with linear mixed effects models to see if there were relationships between DOC concentration, DOM character, and stream discharge or stream temperature. Methods and results are presented in new sections 2.7 and 3.5 "Evaluating relationships in DOC concentration and DOM composition with stream discharge and stream temperature", as well as additional discussion in section 4.3. Also see response to SC24 above for details. We also modified Figure 6 to show temporal differences between catchments for PARAFAC components. This is noted in the text under Results Section 3.3 (formerly Section 3.4).

SC27: Lines 457-479: ok but speculative. Maybe this could be moved at the end of the discussion. Also, potential implications of the data are included several times along the text (lines 412-414, 417-419, 431. . .) and consequently are quite redundant.

Author Response: To address the redundancy of certain points in the text related to coastal subsidies of DOC/DOM, we removed several lines of text (e.g., 417-419, 431, 478-480 (see below)). We chose to leave the text from lines 457-479 but reduced the length, because it relates to implications of patterns in the sources of DOM.

SC28: Section 4.3: This section can be shortened. Wetlands and lakes are known to be two major elements of the landscape having contrasting effects on DOC and DOM quality (e.g. Frost et al., 2006, Aquatic Science, 68, 40-51; Lambert et al., 2016, Biogeosciences, 13, 2727-2741) and it is relatively obvious from RDA1 that DOM concentrations and composition are largely driven by wetlands and lakes in this study. The authors should better explain the role of wetlands/lakes rather than looking for additional *and questionable drivers that cannot be supported by their data.*

Author Response: We agree, DOM concentrations and compositions are largely driven by wetlands and lakes in this study. However, the results of our RDA also indicate other factors have significant relationships with DOM, such as depths of organic and inorganic soil types and physical watershed features such as slope. We believe it is important to include this information here, but agree that this section can be shortened. We condensed and removed much of the text on soils (lines 516-532), and text was moved to the end of the first paragraph to emphasize that the role of wetlands and underlying soils are important, but that there are also other types of non-wetland associated soils contributing sources of DOM.

SC29: Lines 491-492: What is the meaning of 'alternative DOC-source pools'?

Author response: We have changed the text from "DOC-source pools" to: "the contribution of DOC from sources other than organic soils associated with wetlands…"

SC30: Lines 491-492: watershed residence times are unknown so they can be not considered as a driver because changes between seasons could be very low due to the small size of the catchments.

Author Response: We have removed watershed residence time here as a potential driver.

SC31: Lines 503-506: could you add figures to illustrate this?

Author Response: This information is presented in Table 1 and in Figure 7.

SC32: Lines 515-516: this statement cannot be supported by the data included in the study. Soil analysis are limited to the measurements of organic and mineral horizons depths (please clarify how this has been done), and there is no information regarding soil composition (%Corg, C/N ratio, content in Al- or Fe- minerals. . .) that could help to investigate the role of soil composition on stream DOC dynamics. Moreover, the variability of soil organic and mineral horizons between catchments in table 1 is relatively limited. Finally, I am not convinced by the argumentation based on the RDA. For example, vectors DOC and OrgSoil have respectively negative and positive loadings along RDA1, suggesting a limited correlation. Also, the difference in the lengths of vectors C1 and Slope along RDA3 suggests that slopes are not a strong predictor for C1 (lines 529-531), as also suggested by the lack of relationship between these two vectors along RDA1.

Author Response: We entered additional text to clarify how organic and mineral soil depths were measured (also see response to comment SC3). We have removed most of this paragraph from the discussion (lines 516-532), including the discussion of slope as a predictor for C1 as we agree that the while slope and C1 are highly correlated along RDA3, the vector length of C1 suggests the relationship is not strong. We politely disagree with the comment on the relationship between DOC and OrgSoil, because although DOC and OrgSoil have opposite loading along Axis 1 (gradient of wetlands to lakes) they both show positive loading along Axis 2. In an RDA with type 2 scaling, the angle between the vectors represents the degree of correlation, with smaller angles representing more correlation. Although DOC is not the most highly correlated with OrgSoil, the angle between these vectors is <90 degrees suggesting some correlation. We changed the wording of the relationship between these variables from "important drivers of DOM composition" to "influence DOM composition" and include the caveat that this relationship is based only on depth: "However, because our study was limited to soil material depth, future work including more detailed measures of soil composition may help better describe the relationship between soils and DOM export from these watersheds."

SC33: Lines 524-526: according to recent concepts in soil science (e.g. Kaiser & Kalbitz, 2012, Soil biology & biogeochemistry, 52, 29-32), the retention of DOM in soils due to absorption processes on mineral surfaces leads to a greater biodegradation as the residence time in soil is increased. This is consistent with several studies reporting that DOC during base flow has a lower aromaticity as water pathways deepens along the soil profile (e.g. Sanderman et al., 2009, WRR, 45, W03418).

Author Response: This portion of text has been removed (see SC28).

SC34: Figure 7: the variables 'OrgSoil' and 'MinSoil' are confusing between they suggest different soil composition while they are only dealing with depths. Please change their name. It is surprising that SUVA is related more to lakes rather than wetlands as the latter trend to export aromatic material. Do the authors have an explanation? DOC, d13C-DOC and C4 are clearly related to wetlands, maybe this observation should deserve more attention in the section 4.3?

Author Response: We changed the names to "OrgThick" and "MinThick" on Figure 7.

In response to the reviewer's second comment, in a RDA of type 2 scaling, the angles between vectors of the ordination reflect their correlations, the longer a vector is along a given axis the more it contributes to that axis. With this in mind, we interpret the RDA as showing SUVA to be slightly more influenced by Axis 2 than Axis 1 (SUVA standardized coefficient score for Axis 1= 0.04, score for Axis 2= 0.07), which may represent a gradient of thicker organic to thicker mineral soil layers. However, SUVA is not strongly associated with any of the axis, suggesting the environmental variables do not explain much about our SUVA results. To help with this interpretation, we included a table (Table S5.6) of standardized coefficient scores for the DOC and DOM ("species") variables in Supplement Section 5. We also do not interpret the RDA as showing that DOC, d13C-DOC and C4 are clearly related to wetlands (also see Table S5.6). C4 is the most closely related to wetlands, but both DOC and d13C-DOC show similar or stronger correlations to OrgThick (thickness of organic soils) and Axis 2. This relates to our discussion point at the beginning of 4.3, regarding how wetlands appear not to drive the majority of observed variance in these variables. We added an additional line of text in the revised document, line 751, to restate and clarify this point.

SC35: Some references are missing in the reference list: Hopkinson et al., 1998; Tallis, 2009; Lambert et al., 2013

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Author Response: We have added those references.

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Responses- Anonymous Referee #2

Thank you for taking the time to review our manuscript and for your positive feedback on the overall scope of the paper. Below you will find our responses to your comments, which are greatly appreciated and have improved the paper. Please feel free to contact us with any additional questions or comments.

Responses to General Comments (GC):
GC1: A large amount of interesting data are presented however, they are not fully exploited to unpick specific research questions further than underlining the important role the catchments studied play in DOC export.

Author Response: A primary goal of this manuscript is to establish in the literature a detailed description of DOC exports for this region of British Columbia and the coastal temperate rainforest and to put the results into regional and global context. However, we agree that more specific goals and questions will further strengthen the quality of the manuscript. To address this comment, we have clarified our objectives and have included additional analysis to investigate controls of flow and temperature on DOC concentration and DOM composition, a more detailed investigation of the relationship between PARAFAC components, and some simple statistical comparisons of variables across both seasons and watersheds. We also included a simple regional estimate of DOC flux to emphasize the importance of our results and put them into a global and regional global context.

GC2: I would have liked to see further analysis of the DOM compositional proxies as at present the manuscript doesn't benefit significantly from the addition of the compositional measurements.

Author Response: We have conducted additional analysis using linear mixed models and multiple linear regression to investigate the of discharge and temperature in relation to DOC concentration and DOM compositional data. We have also conducted additional analysis to look at relationships between PARAFAC components. Please see specific responses below for more information.

Responses to Specific Comments (SC):
SC1: Line 140-142. For those not familiar with mapping software a definition of GIS would be useful. Also were catchments delineated using watershed analysis?

Author Response: We included the definition of GIS as "geographic information system". Catchments were delineated using a 3m resolution digital elevation model (DEM) derived from airborne laser scanning (LiDAR) (Gonzalez Arriola et al., 2015). This was included in the text at the beginning of Section 2.2.

SC2: Line 156-158. While less frequent sampling due to logistical constraints is understandable, have you considered how this may impact you load estimations given that large quantities of

DOC that are mobilised during periods of intense rainfall? As estimates of load can be skewed significantly if large events are under represented.

Author Response: We made a concerted effort to supplement our routine sampling with additional samples taken during larger events in order to better represent higher peak flows. Comparison of estimates using those additional points resulted in slightly higher load predictions for estimates that include samples from events, but no statistical comparison of the different methods has been made.

SC3: Line 218. What wavelength range did you scan over and at what interval?

Author Response: Included in text, "Samples were run in 1 cm quartz cells over an excitation range of 230-550 nm at 1nm increments."

SC4: Line 219. Were high absorbing samples diluted if they breached an absorbance threshold?

Author Response: Yes, we diluted if samples had absorbance > 0.05 at 250nm. This is included in text.

SC5: Line 228. What settings were used for your fluorescence scans (ex/em wavelengths etc.)?

Author Response: Included in text: "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 2nm increments."

SC6: Line 240. Define PARAFAC

Author Response: Included definition in text, "parallel factor analysis"

SC7: Line 301. Table listed in brackets should be Table 1 not Table 2

Author Response**:** Oops, sorry! Changed to Table 1.

SC8: Line 327. The range of SUVA254 values reported in the literature is large. Elevated SUVA254 values are commonly found in both tropical rivers (Mann, P. J., et al. (2014), The biogeochemistry of carbon across a gradient of streams and rivers within the Congo Basin, J. Geophys. Res. Biogeosci., 119, 687–702, doi:10.1002/2013JG002442.) and also have been found upland peat catchment of the UK (Austnes, Kari; Evans, Chrisptoher D.; Eliot-Laize, Caroline; Naden, Pamela S.; Old, Gareth H.. 2010. Effects of storm events on mobilisation and in-stream processing of dissolved organic matter (DOM) in a Welsh peatland catchment. Biogeochemistry, 99 (1-3). 157-173. 10.1007/s10533-009-9399-4). However, lower values (<3) are also observed in groundwater dominated catchments (Yates, C, Johnes, P & Spencer, R, 2016, 'Assessing the drivers of dissolved organic matter export from two contrasting lowland catchments, U.K'. Science of the Total Environment, vol 569-570., pp. 1330-1340).

Author Response: We have incorporated these references into the text under the discussion in 4.2.

SC9: Line 333-347. Discussion is creeping in to the results section. Consider deleting or moving some text.

Author Response: We deleted some of this text, and also moved some of it to the discussion section.

SC10: Line 372. Could this variability be quantified in some way?

Author Response: We modified figure 6 to show results from each individual watershed, which we hope better illustrates the variability between catchments. In addition to Figure 6 and Table 1, we don't feel that it is necessary to report and compare the standard deviation associated with each sampling date as this would list the variability between different watersheds at different points in time but the figure already shows this information.

SC11: Line 420-430. I agree with reviewer 1 one on this point. The data could be better exploited to evaluate temporal shifts in DOC/DOM composition as all the data were collected for this purpose. For example it would have been interesting if changes in DOM composition could be in some way evaluated in relation to these change in flow conditions (using either the optical measurements of 13C values). This would have given the paper more of a focus, as reviewer 1 states to investigate 'DOC flushing'.

Author Response: We conducted additional analysis using linear mixed model multiple regression to looking at the relationships between DOC concentration and DOM compositional variables, with discharge and temperature. We refined our objectives to include the rationale for this additional analysis (e.g., possible seasonal and spatial trends and drivers) and to address general comments regarding incorporating DOM data to look at temporal and cross-watershed patterns. The methods for this additional analysis are presented in the new Section 2.7, results are presented in the new Section 3.5, and additional discussion is provided in Section 4.3. Results are also included as a figure (Figure S6.1) and two tables (Table S6.1, S6.2) in Supplementary Material.

SC12: Line 432. Was any work done on investigating the implications of elevated DOC yields on marine foodwebs? If not then remove

Author Response: We removed.

SC13: Line 490-492. What do you mean by DOC-source pools? Are you referring to the flushing of different soil horizons or the mobilising of material from a different source i.e. a source that under normal flow conditions would not be hydrologically connected to the main channel of the river? Also you have not calculated retention time for your catchments? Smaller catchments will always respond quicker than larger ones as they are simpler systems.

Author Response: By "alternate DOC-source pools" we are referring to sources of high DOC that are not associated with wetlands, typically thought of as high-DOC sources. We changed this text to: "the contribution of DOC from sources other than organic soils associated with wetlands…" We have not calculated retention time, but based on stream flow and precipitation data we do know that catchment response time is rapid following rain events. We have provided some ancillary data in the supplementary material (Supplementary Figure S2.2) to provide a qualitative look at response time, or how quickly streams respond to precipitation. This shows, for example, the lag in response in watersheds with lakes, such as 1015 and 693. To clarify this issue, we have changed the wording "retention time" to "response time" in the text.

SC14: Line 353. Work has already been carried out investigating long term trends in DOC flux from a wide range of catchments in relation to changes in global temperatures. See Worrall (2003). Long term records in riverine DOM. Biogeochemistry 64(2), 165-178. Or Freeman (2001) Export of organic carbon from peat soils. Nature. 412(6849) 785- 785.

Author Response: We note this in the text and include references to previous work (including the one suggested above by Worrall).

SC15: Figure 2. Caption is too long and bordering on discussion. Consider making more concise.

Author Response: We made the caption more concise.

*SC16: Figure 3. Are the box-whisker plots showing 1.5*IQR?*

Author Response: Boxes represent the 25th and 75th percentile and whiskers represent the 5th and 95th percentile. We have included this in the caption for clarification.

SC17: Figure 7. This also applies to the discussion but did you study catchments dominated by organic vs mineral soils or is this referring to the soil horizons? If so then consider renaming for clarity.

Author Response: All watersheds contained varying areal proportions of organic (i.e. Histosols) and mineral (i.e. Podzols) soil types. The latter also contain organic horizons at the surface, of varying thickness, so the reported data for organic horizon thickness includes measurements for such cases, as well as for soils that would be classified as Histosols.

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Responses- Anonymous Referee #3

Thank you for taking the time to review our manuscript and for your positive feedback on the overall scope of the paper. Below you will find our responses to your comments, which are greatly appreciated and have improved the paper. Please feel free to contact us with any additional questions or comments.

Responses to General Comments (GC):
GC1: Statements about global relevance should be tempered accordingly because watersheds studied are so small.

Author Response: To put our watersheds into better context, we have included additional comparisons between our watershed yields and yields from watersheds of similar size from around the world. We have also done a simple calculation of regional flux to compare potential DOC export from the region studied here, to other regions within the coastal temperate rainforest. We hope this provides better context for our flux and yield measurements relative to regional and global estimates of riverine carbon exports.

GC2: The extensive dataset on DOM quality could also be better utilized to understand the mechanisms that are driving DOM export rather than just make broad observations about streamwater DOM quality.

Author Response: The outer-central coast of British Columbia's perhumid coastal temperate rainforest is largely unstudied with respect to DOC exports, so a primary goal of this manuscript is to establish in the literature a detailed description of DOC exports for this region and to identify potential sources and patterns in DOM composition. We have included the RDA analysis to assess potential watershed/landscape drivers of DOC concentration and DOM composition However, agree that the manuscript benefits from more utilization of the DOM dataset. To address this comment, we have included additional analysis on the relationship between DOC and DOM composition with discharge and stream temperature. We have also done additional analysis on the relationship between PARAFAC components that goes beyond the analysis presented in the RDA. Please see specific comments below for further information.

GC3: There is no such thing as a "globally important" DOC yield… The yields reported here are quite high, however this is largely a function of the fact that DOC yields (flux per area) are inversely related to watershed size and the watersheds in this study are very small and have high wetlands coverage. For this to represent a globally important finding, the authors would have to make the case that the fluxes measured here are broadly representative of the 100,000 km2 perhumid coastal forest in BC and thus provide evidence of a substantial mass flux of DOC to the coastal ocean. I understand that the purpose of this paper was not to calculate regional fluxes, however more directly addressing the issue of how regionally representative these high flux watersheds are would: 1) give readers a more concrete sense of the regional/global importance of these fluxes and 2) better justify statements such as "the small watersheds of this region export very high amounts of terrestrial DOC" (Line 477). The only place this issue is addressed in the paper is briefly in the conclusions (lines 552-554).

A similar issue arises in the discussion of the yields in section 4.1. Comparing DOC yields from these 3-10 km2 watersheds with yields from the Congo and Amazon doesn't make sense given the difference in scale. The Congo exports more than 10 Tg DOC/yr and all of the watersheds in this study together export probably 1/1000th of a Tg DOC/yr. The claim that DOC yields measured in this study are higher than those reported in southeast Asia should also be clarified given that Moore et al. (2011, 2013) have reported DOC yields >2x those reported here for watersheds in Indonesia that are several orders of magnitude larger than the watersheds in this study (doi:10.5194/bg- 8-901-2011; doi:10.1038/nature11818).

Author Response: Thank you for this comment, you make some good points. We have made the following changes:

1) To put numbers into a more regional and global context we have included a simple regional estimate for total DOC flux from the hypermaritime region of B.C.'s perhumid coastal temperate rainforest.
2) We included flux estimates from global to regional scales.
3) We removed comparisons of our DOC yields with much larger rivers and instead include comparisons of watersheds of similar size, in particular those that have high amounts of precipitation, and contain extensive organic soils and wetlands. We emphasize that to the best of our knowledge, this is the first study that represents the role that these types of small catchments (high latitude, temperate, wetland and peat or organic soil-dominated) play in delivery of DOC directly to the ocean.

GC4: This is a very rich data set in terms of DOM compositional information. That said, the compositional data were somewhat underutilized in the study. For example, the 13C data were not even mentioned in the Discussion. In addition, the stream gage data are not utilized to elucidate how streamflow impacts DOM quality. Instead there are general statements about how compositional data change between wet and dry seasons (e.g. lines 445-456).
In Fig. 3 it appears that streamwater DOC concentrations are correlated with air temperature. If this is the case it would suggest that there is a link between soil temperature and soil water DOC production that influences the export of DOC to streams. Thus, temperature may be useful for predicting seasonal changes in streamwater DOC concentrations.

Author Response: We conducted additional analysis using linear mixed effects models to look at relationships between DOM compositional data (including 13C-DOC), DOC concentration, discharge and temperature. We refined our objectives to include the rationale for this additional analysis (e.g., possible seasonal and spatial trends and drivers) and to address general comments regarding incorporating DOM data to look at temporal and cross-watershed patterns. The methods for this additional analysis are presented in the new Section 2.7, results are presented in Sections 3.3 and 3.4, as well as included as a figure (Figure S6.1) and two tables (Table S6.1, S6.2) in Supplementary Material. Additional discussion is provided in Section 4.3.

Responses to Specific Comments (SC):
SC1: There is some discussion material mixed in to the Results section of the paper. Examples include: Lines 336-339 and 345-347.

Author Response**:** This text (and other text that bordered on discussion) has been removed from Results and is now included in Discussion. Examples given by the reviewer are now included in Section 4.3.

SC2: There are a number of references to watershed residence time in the Discussion (for example, lines 433, 492, 502), but it is not clear how this was quantified and whether it was function solely of lake influence or if watershed slope played a role as well.

Author Response: We did not specifically quantify residence time for watersheds, however we do know that based on the very rapid hydrograph response to precipitation events, the response time of these catchments is short. Where appropriate (such as example from line 433) we have changed this to hydrologic "response" time. In other places (such as example from 492) we removed the sentence entirely. Line 502 is providing an example from the literature, so that reference to residence times was left in the text, similar to line 512, but the text was changed here to be more explicit that this wasn't something we measured directly but an effect we would expect to see based on other watershed factors. In addition to lakes, watershed slope definitely plays a role in response/residence time, this is mentioned in line 530 of the original document and also in the results and discussion related to the RDA analysis. We have also included a figure in the Supplement (Fig. S2.2) that illustrates the response times of our watersheds with and without a high extent of lake area.

SC3: Line 74: The phrase "predictions of ecosystem productivity and food webs" is extremely Vague

Author Response: Changed this to just "predictions of ecosystem productivity"

SC4: Lines 100-101: How and why would you expect DOC export from perhumid forests in Alaska to be different from perhumid forests in British Columbia? In other words, is there a reason to think that the work done in Alaska would not be valid in the same forest type in British Columbia?

Author Response: We have included a few sentences in the text (inserted in 2nd to last paragraph of Introduction in new manuscript) that describe how and why we would expect DOC export to be different in the study region of B.C. versus Alaska:

"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. 2015) and glacial cover (Fellman et al. 2014). Previous studies have shown that streams in southeast Alaska can contain high DOC concentrations (Fellman et al., 2010; 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."

SC5: Lines 104-105: The fact that discharge was directly measured is a strength of this study, however it is somewhat misleading to compare this highly localized study to continental and global scale studies where modeling discharge is a necessity.

Author Response**:** This information was originally included to highlight the need for studies in this region that include the direct measurement of discharge, because the only work that has attempted to quantify DOC flux have been large scale studies using modeled discharge. These studies may not be appropriately capturing the heterogeneity of this complex region (see response to comment 4 above) and highlights the challenge of working in these remote locations (modelling discharge has been the only option until our paper). However, we have removed this specific text and comparison with global scale studies and now only make comparisons with regional, smaller scale studies and estimates of flux.

SC6: Line 273: It seems redundant to report climatewna data in the study site and in the results. Also the values reported for mean annual precipitation differ between the study site (line 115) and the results (line 273).

Author Response: We removed the second reference to climatewna in the results. Mean annual precipitation (MAP) for the study sites (line 115) is taken from sea level and central to all the study watersheds. The MAPs reported in the results (line 273 and 276) are taken from the exact location of our rain gauge and from the location of our high elevation weather station. The spatial distribution of rain in this area is extremely heterogeneous, and the range of values is presented to illustrate the differences across the landscape.

SC7: Line 278: The comparison of precipitation at the study site to "most regions of the world" is vague and does not illustrate anything meaningful.

Author Response: We removed "most regions of the world"

SC8: Lines 291-295: This sentence is repetitive and very hard to follow with all of the parenthetical data references. Recommend simplifying it to make the point about the difference in wet season flow without all of the Q data. It is also interesting that wet season Q differed by >20% between the two years while wet season precipitation only varied by 5%.

Author Response: We removed most of the parenthetical data references except for two that describe total discharge and range for water year 2015 and water year 2016. The difference in precipitation and flow between the two years is a function of, 1) precipitation arriving as snow at higher elevations that is not captured in the rain gauge, and 2) heterogeneity of rainfall across the study region. The rain gauge is centrally located in one catchment within the study region, however this gauge probably does not capture the full range of precipitation being delivered across the islands. However, these differences would more likely be reflected in differences in Q.

SC9: Line 326: It would be more clear to say that SUVA values were at the high end of the range rather than "relatively high compared to the range".

Author Response: Modified the text as recommended.

SC10: Line 417: "Catchment" looks like it should be plural.

Author Response: This sentence has been removed.

SC11: Line 419: The term "a significant biogeochemical hotspot for coastal carbon cycling" is somewhat vague. Many of the studies cited in this paper calculate end of pipe DOC fluxes "directly to the coastal ocean". It would be helpful to more specifically explain why the watershed DOC fluxes in this study are "significant" from the standpoint of the coastal C cycle.

Author Response: The paragraph containing this sentence has been removed during modification of this section based on other reviewer comments.

SC12: Lines 425-6: Does the term "high precipitation event" refer to intensity or magnitude. Also, it seems like the slope of these watersheds (typically >30%) is an important factor in the short hydrologic residence times that is not mentioned in this paragraph.

Author Response: "High precipitation event" refers to both. We modified this sentence to reflect those details "Therefore, frequent precipitation of high magnitude or intensity …." We agree that slope is potentially an important factor influencing DOC export, and have mentioned it in Section 4.2 several times both in reference to high-gradient catchments, and the role of slope in variation between watersheds.

SC13: Lines 430-431: I agree that seasonality is important for ecological processes and it would be helpful to provide more analysis about why this would be the case in this region.

Author Response: These specific lines have been removed during modification of this section, however, we have incorporated text in the same area of discussion to highlight that the seasonal contribution of DOC from these watersheds to the ocean "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)." The importance of seasonality in ecological processes is widely known in terms of production (both primary and secondary), and additional analysis on the importance of seasonality in terms of broader ecological processes is outside the scope of this paper.

SC14: Line 455-456: Again, the consequences should be explained or this sentence should be removed.

Author Response: This sentence was moved to the beginning of the following paragraph (last paragraph of Section 4.3) where we describe some of the effects of composition on biological utilization.

SC15: Line 546: Because yields are a measure of the per area export (flux) of DOC the term “export the highest yields” is redundant.

Author Response: Changed “export” to “contribute”

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

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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; 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

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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; 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.

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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

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Comment [AO2]: Objectives redefined.

Deleted: 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.

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).

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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.

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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).

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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 ($S_{350\text{-}400}$).

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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).

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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

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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

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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).

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

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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

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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 (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; WY2016 dry= 352 mm, average air temp= 13.1°C). Overall, although WY2015 was slightly wetter than WY2016, the two years were comparable in relative precipitation during the wet versus dry periods.

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

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

Stream waters were high in DOC concentration relative to the global average for DOC concentration 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

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than average measured DOC concentrations (11.1 mg L^{-1}, Table 1), and also resulted in slightly different ranking of the watersheds for highest to lowest DOC concentration. Within watersheds, 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), and concentrations were significantly different between watersheds (Kruskal-Wallis test, $p < 0.0001$). Seasonal variability tended to be higher in watersheds where DOC concentration was also high (watersheds 626, 819, and 844) and lower in watersheds with greater lake area (watersheds 1015 and 708) (Table 1; box plots, Figure 3). On an annual basis, DOC concentrations generally decreased through the wet period, and increased through the dry period, and concentrations were significantly lower during the wet period compared to the dry period (Mann-Whitney test, $p = 0.0123$). Results of our linear mixed effects (LME) model (Supplemental Table S6.1) indicate that DOC concentration was positively related to both discharge ($b = 0.613$, $p < 0.001$) and temperature ($b = 0.162$, $p = 0.011$) (model conditional $R^2 = 0.57$, marginal $R^2 = 0.09$).

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

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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 did not observe an obvious seasonal trend in δ^{13}C-DOC (Fig. 3), but LME model results (Supplemental Table S6.1) indicate that δ^{13}C-DOC declined with increasing discharge (b= -0.049, p= 0.014) and stream temperature (b= -0.024, p< 0.001) (model conditional R^2=

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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).

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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

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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 previous studies, our estimate of freshwater DOC yields from Calvert and Hecate Island watersheds are in the upper range predicted for this region based on 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., 2017). 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 determined 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};

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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, 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. Seasonal variability in DOC export

Despite having an ocean-moderated climate compared to continental interiors, the study area experiences seasonal patterns in precipitation dominated by a longer wet period and a shorter, drier period. 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). During drier periods DOC pools increase in soils and are flushed to streams when water tables rise (Boyer et al., 1996).

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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

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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), 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 DOM composition from Calvert and Hecate Islands suggest that carbon and organic matter exported from these systems is highly terrestrial. 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).

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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, some measures of DOM composition, such as δ^{13}C-DOC and S_R, exhibited seasonal patterns. 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

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water table draw down and unsaturated soils lead to more diverse flow paths and hydrologic interaction with different sources of DOM.

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.,

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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).

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 beign solely driven by the presence 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.

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

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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 region (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.

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 within the catchment and their proximity to the watershed outlet can also play an important role in the composition of DOM exports (Martin et al., 2006).

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Changing environmental conditions, such as shifting precipitation and temperature regimes, may affect future DOC fluxes. Long term patterns in DOC flux have been observed in many places (e.g., Worrall et al., 2004; Borken et al., 2011; Lepistö et al., 2014) and continued monitoring of this system will allow us to better understand the underlying drivers of export. For example, changes in soil temperature and moisture could influence the stability of the organic matter pool, as processes such as organic matter production and sorption have strong relationships with temperature and oxidation state. Therefore, additional research is needed to assess soil properties relevant to DOM mobility (e.g., texture, sesquioxide content), landscape attributes, and flow paths for predicting DOM export in this region and the consequences of shifting conditions such as those associated with altered land use or climate change.

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 represent 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). 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 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.

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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.

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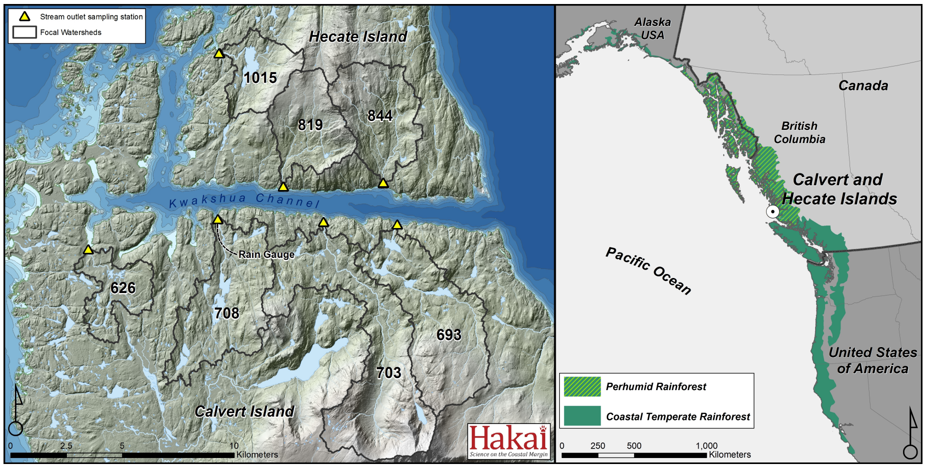

Figure 2. Hydrological patterns typical of watersheds located in the study area (a) the hydrograph and precipitation record from Watershed 708 for the study period of October 1, 2015-April 30, 2016. Grey shading indicates the wet period (September 1-April 30) and the unshaded region indicates the dry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

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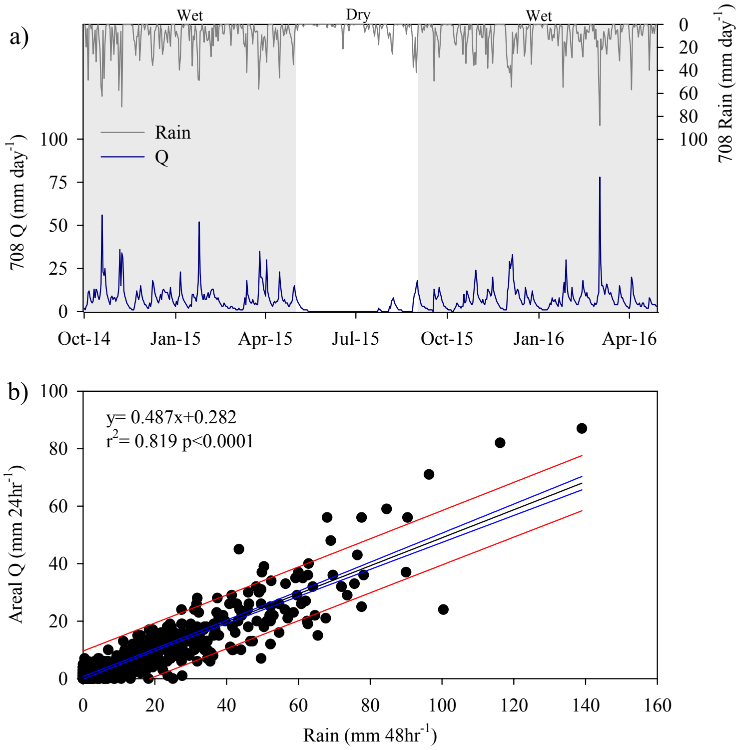

Figure 3. Seasonal (timelines, by date) and spatial (boxplots, by watershed) patterns in DOC concentration and DOM composition for stream water collected at the outlets of the seven study watersheds on Calvert and Hecate Islands. Boxes represent the 25th and 75th percentile, while whiskers represent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

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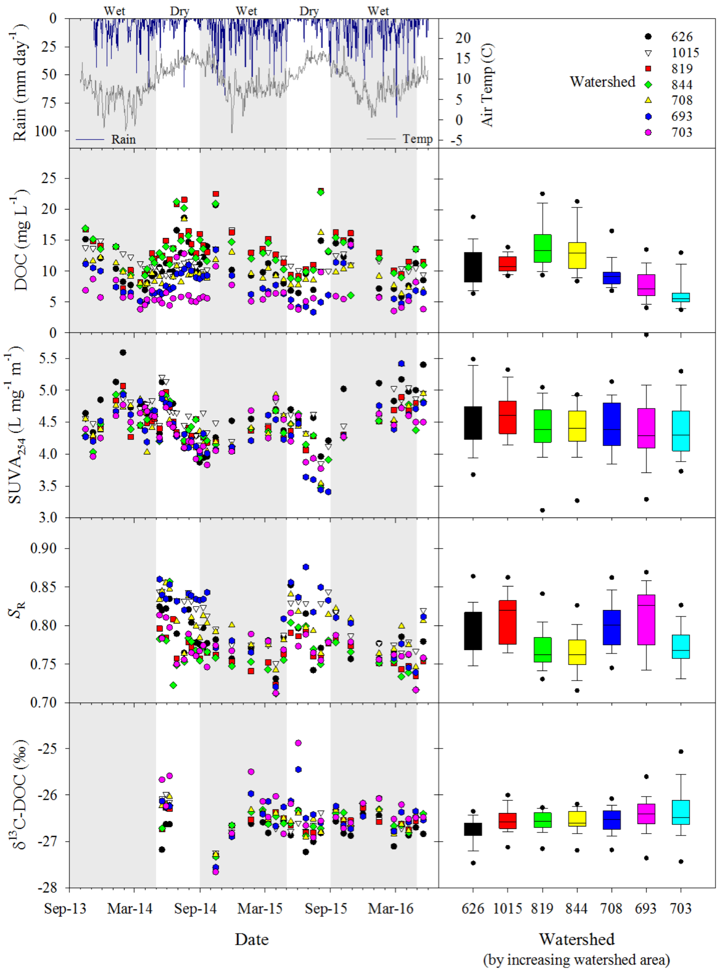

Figure 4. Monthly areal DOC yields and precipitation for water year 2015 (WY2015) and the wet period (October 1-April 30) of water year 2016 (WY2016). Error bars represent standard error. Total rain and DOC yield were significantly correlated ($r^2 = 0.77$) and months of higher rain produced higher DOC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

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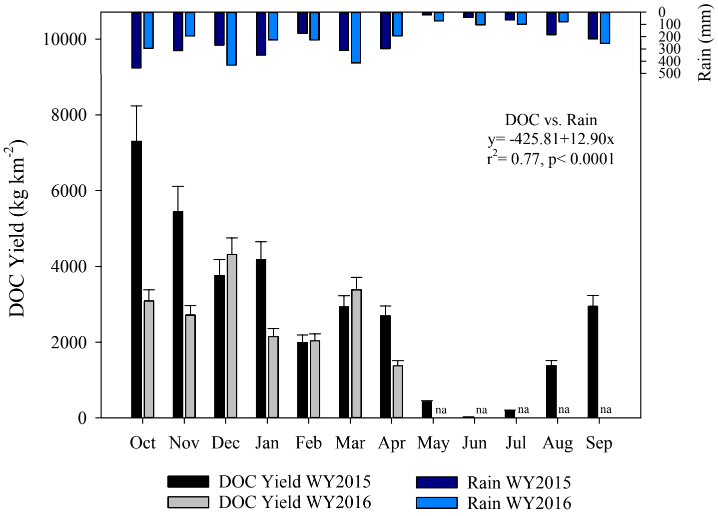

Figure 5: DOC fluxes and yields for the seven study watersheds and the total area of study (“areal”, all watersheds combined) on Calvert and Hecate Islands for water year 2015 (WY2015; Oct 1 - Sep 30), and October 1- April 30 of the wet period for water year 2015 (WY2015 wet) and water year 2016 (WY2016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

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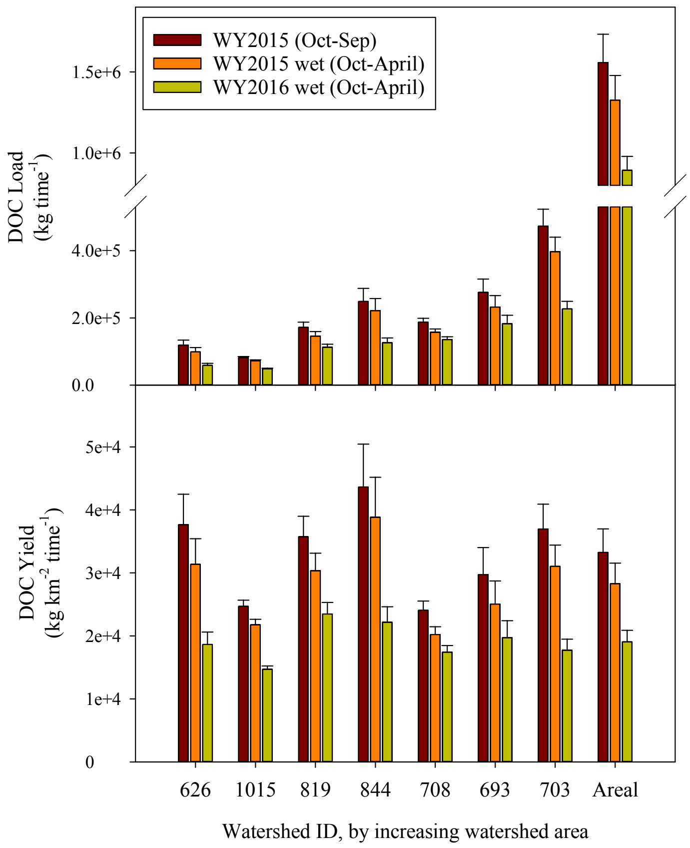

Figure 6: Percent contribution of the six components identified in parallel factor analysis (PARAFAC) for samples collected every three weeks from January-July, 2016 from the seven study watersheds on Calvert and Hecate Islands. The grey shading indicates the wet period and

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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.

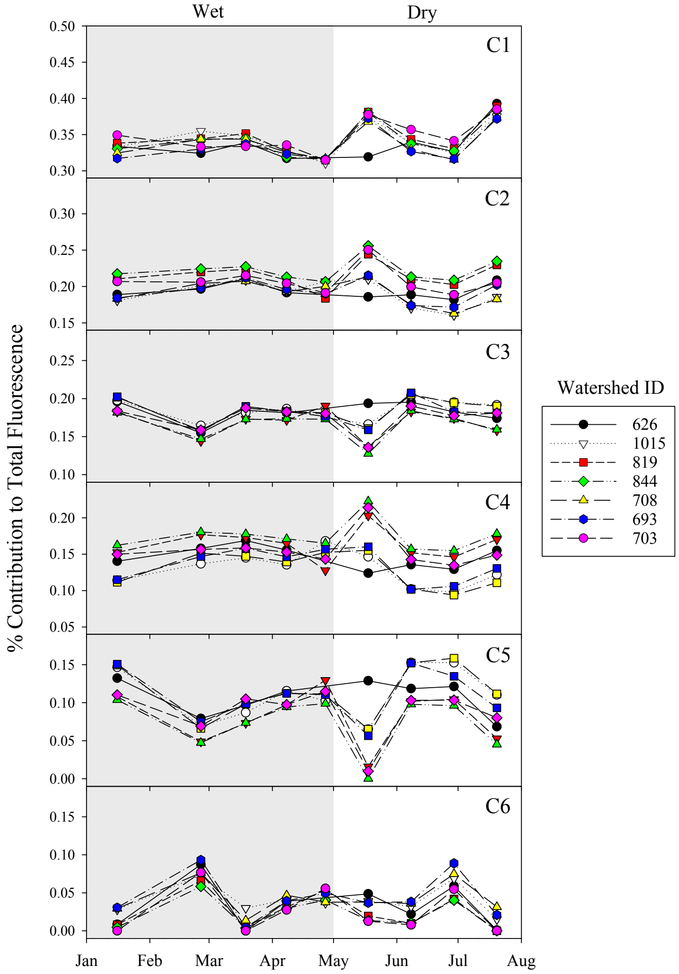

Figure 7: Results from the partial-Redundancy analysis (RDA; type 2 scaling) of DOC concentration and DOM composition versus watershed characteristics. Angles between vectors represent correlation, i.e., smaller angles indicate higher correlation. Symbols represent different

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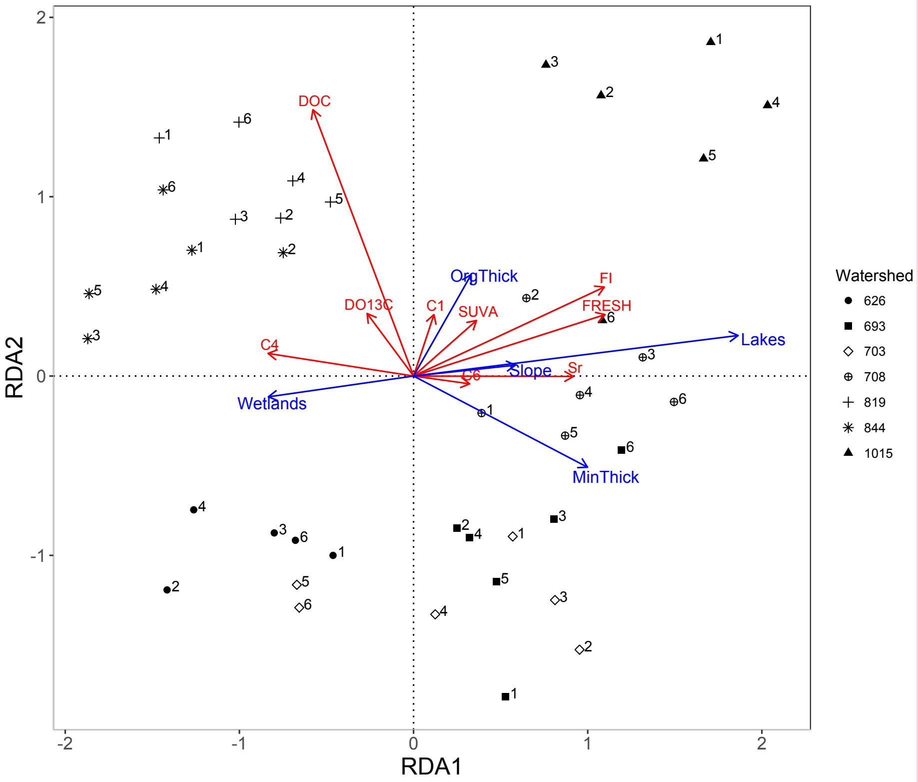
watersheds, and numbers on symbols represent the sample month in 2016: 1= January, 2= February, 3= March, 4= early April, 5= late April, and 6= May.



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.

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

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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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3.3 Characterization of DOM- PARAFAC

[A01] 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 other 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-derivedC1 comprised the majority of total fluorescence across all watersheds (Fig. 6), representing a consistent supply of humic-like terrestrial material in stream water outflows that is relatively fresh (i.e., less-processed). omponents C5 and C6 are described as autochthonous or microbially-derived. C5 likely represents autochthonous-produced material of humic-like composition, whereas C6 was the only component representing a distinct protein or tryptophan-like contribution likely derived from autochtonous production. In general, the rank order of the components' percent contribution to total fluorescence and variability between watersheds was maintained over time. C1 comprised the majority of total fluorescence across all watersheds (Fig. 6), representing a consistent supply of humic-like terrestrial material in stream water outflows that is relatively fresh (i.e., less-processed).

Over time, components were relatively synchronous across watersheds although slightly more variation was observed during the beginning of the dry period relative to other times of the year (Fig 6). Of the terrestrial-like components, C1, C2, and C4 exhibited similar temporal patterns in contribution to total fluorescence (Fig. 6;) and were positively correlated with one another (Supplemental[AO2] Table S4.2) [AO3]Component C3 exhibited the lowest spatial variability and was negatively correlated to C1 through C4 but positively correlated to C5 Concentrations of C5 and C6 were not correlated and negatively correlated to C1 through C4, with the exception of a strong positive correlation between C5 and C3.

Percent composition of components C1, C3, C5 and C6 were not significantly different across watershed (for all components Kruskal-Wallis test, $p > 0.05$), however percent composition of both C2 and C4 different (Kruskal-Wallis $p = 0.0306$ and $p= 0.0307$, respectively) and higher for watersheds 819 and 844 relative to the other watersheds (Supplemental Fig. S4.4).

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