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.