Biogeosciences Discuss., 12, C4515–C4530, 2015
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Interactive comment on "Seasonal hydrology drives rapid shifts in the flux and composition of dissolved and particulate organic carbon and mercury in the Fraser River, Canada" *by* B. M. Voss et al.

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Received and published: 21 August 2015

The comments of both reviewers are summarized below point-by-point. Each comment is followed by a statement of how the comment was addressed in the revised manuscript. The revised manuscript, with changes marked, is attached to this comment.

Reviewer 1

Have a single section describing watershed characteristics, rather than having such

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Interactive Discussion

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information interspersed throughout the text. No info given on watershed size or flow contribution to the coast relative to other rivers.

Author response: In the original manuscript, descriptions of watershed characteristics occur in the Introduction (pg. 7617, lines 20-28), as well as the opening of the Discussion (pg. 7629, lines 15-28). These sections were combined in the Introduction, and metrics for basin size and discharge were added.

Reduce the total amount of figures, some can go to supplemental info (specifically numbers 2, 4, 5, and 12).

Author response: These figures have been made supplemental material as follows: Fig 2 → Fig. S1; Fig. 4 → Fig. S2; Fig. 5 → Fig. S3. Figure 12 has been kept in the main text, as readers interested in DOC-Hg dynamics will very likely want to see this relationship.

Caution against broad conclusions regarding Hg dynamics from such a limited dataset

Author response: The estimates we present for Hg deposition and export are given with numerous caveats and the assumptions clearly stated. We acknowledge the limited size of the dataset at the beginning of the Discussion: "While the size of this dataset is limited..." (pg. 7636, lines 26-27). We believe that our conclusions are valid as a starting point for future studies with a larger focus on Hg specifically by providing first-order estimates and some historical and global context, and we hope that others will see this as an invitation for more detailed work on Hg in the Fraser basin. As we point out in the Introduction, there are currently no reliable published Hg datasets for the Fraser River. This manuscript will serve to bring attention to that fact while offering a window into the Hg dynamics of this system. However, we understand that our flux estimates are preliminary due to the limitations of the dataset, and we have added more comments pointing that out throughout section 4.3. We do agree that the inclusion of mercury in the manuscript's title may lead readers to assume that the Hg dataset is similarly comprehensive to that of DOM; therefore, we have chosen to modify

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the title to read "Seasonal hydrology drives rapid shifts in the flux and composition of dissolved and particulate organic carbon and major and trace ions in the Fraser River, Canada." We also modified the wording of the Abstract to reflect the distinction between the carbon-focused dataset and the smaller Hg dataset. We also added the following statement to the beginning of the Hg discussion (section 4.3): "Although sampling for dissolved, total, and sedimentary Hg was not as comprehensive as that for OM and other dissolved species, this contemporaneous dataset allows for an initial assessment of Hg dynamics in an understudied watershed." Finally, we have removed unnecessary discussion from this section, as well as the reference to a lack of mining contamination from the Conclusions.

Highlight the main contribution of the manuscript (how DOM dynamics in a large, relatively undisturbed system with unique hydrology compares to other systems) in the abstract.

Author response: The following sentence was added to the Abstract: "The snowmelt-dominated hydrology, forested land cover, and minimal reservoir impoundment of the Fraser River may influence the DOC yield of the basin, which is high relative to the nearby Columbia River and of similar magnitude to that of the Yukon River to the north. Anticipated warming and decreased snowfall due to climate changes in the region may cause an overall decrease in DOM flux from the Fraser River to the coastal ocean in coming decades."

Clarify the meaning of DOC/POC ratio results (Introduction versus data presented).

Author response: The ratio given in the Introduction represents relative DOC and POC concentrations at specific points in time, while the value from Ludwig et al. (1996) and the data presented in the Discussion (pg 7635) represent relative annual fluxes of DOC and POC. It is expected that individual points will exhibit larger variability than annual averages, and the point measurements are only from a portion of the annual cycle. We removed the reference to the literature average ratio in the Introduction, as such a

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comparison is not entirely appropriate and potentially confusing.

Filtered vs in situ FDOM and relation to DOC data should be presented in Results, not Methods, or moved to supplemental material.

Author response: The description of FDOM results and correlations with DOC and SPM concentrations were moved to the Results (section 3.1), and Figure 4 is now Figure S2.

Hg detection limit info should be in Results, not Methods.

Author response: The description of blanks and detection limits was moved to the Results (section 3.3).

Description of UV concepts belongs in Intro or Methods, not Results.

Author response: The description of UV parameters ("Absorbance at specific wavelengths can be diagnostic of certain DOM properties... The use of multiple optical proxies provides support from multiple metrics for interpretations of the data.") was moved from the Results to the Methods (section 2.3).

Relationship between SPM and POC belongs in Discussion, not Results. Author response: The section describing the relationship between SPM and POC ("A negative exponential relationship...lower capacity for OC loading (Mayer, 1994).") was removed as it is not critical to the interpretation of our data.

Add a summary of sampling frequencies for various parameters, and time period for in situ samples, to beginning of Methods.

Author response: A summary of sampling frequencies for the various parameters, and distinguishing between the early freshet and 2-year records, was added to the beginning of the Methods (section 2.2).

Describe changes in nutrient and dissolved major element data in "Water Quality Trends" section of Results. State whether these parameters would be expected to

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change in concert with OC.

Author response: A paragraph each describing early freshet changes in dissolved nutrients and major ions was added to the Results (section 3.1). Supplemental figures S2 and S3 were added to visualize these results.

Speculate on why DOC yield of Fraser might be different or similar to that of Columbia or Yukon

Author response: A few sentences were added to the final section of the Discussion (section 4.1) describing differences and similarities between Fraser, Columbia, and Yukon rivers which likely contribute to the observed differences in DOC yields among these basins. These comments are reiterated in the Conclusions.

Are fall and spring DOC mobilization quantities (pg. 7631, line 19-21) presented in Results?

Author response: Fall and spring DOC mobilization quantities refer to the relative size of the DOC pulses apparent in the time series records of DOC concentrations (i.e. fall DOC pulses are much smaller than those occurring during spring freshet), they are not explicitly quantified. These lines have been expanded to clarify this: "The smaller quantity of DOC mobilized by fall soil flushing compared to that of the spring freshet (evident in the smaller fall pulses of DOC exhibited by the long-term Environment Canada DOC record)..."

The estimate of fluvial Hg export as a fraction of deposition of 24-47% is high relative to more recent studies (e.g. Brigham et al. 2009).

Author response: The study cited in our manuscript for Hg export in other basins (Swain et al. 1992) reports fluvial export of $\sim$25% relative to total deposition. Brigham et al. (2009) reports fluvial Hg export of 3-44%. Our estimate of total Hg deposition in the Fraser basin (14-28 μg m-2 a-1) is also higher than those reported for the basins in the Brigham et al. (2009) study. The most comparable basin in this study to the

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Fraser River, based on biogeoclimatic characteristics, is most likely the forested Lookout Creek in Oregon, for which the authors report total deposition of 9-21 μg m-2 a-1 and fluvial Hg export as 8-19% of total deposition. In light of the assumptions used in our estimate of total Hg deposition and fluvial Hg export in the Fraser basin, the differences between our estimates and those reported by Brigham et al. (2009) are not surprising. We have modified our description of these results to read "24-47% of total Hg deposition, which represents a watershed delivery efficiency that is similar to or somewhat higher than other temperate watersheds" and added the reference to Brigham et al. (2009).

Speculate on future changes in DOM dynamics resulting from increased precipitation vs snow precipitation and earlier onset to freshet.

Author response: A paragraph was added to the end of Discussion section 4.2 describing the likely responses of DOM cycling to anticipated future changes in climate. We conclude that such changes are most likely to result in decreased DOM flux to the coastal ocean.

Section of Discussion devoted to Hg and C dynamics should be shortened, but consider some relevant publications not cited (Burns et al. 2013, Demers et al. 2010, Oswald and Branfireun 2014, Riscassi and Scanlon 2011, Shanley et al. 2002, Shanley et al. 2005, Shanley et al. 2008, Schuster et al. 2008).

Author response: We appreciate these suggestions. We have removed unnecessary material from the Hg discussion (specifically material on pg. 7638). References to Demers et al. (2010), Riscassi and Scanlon (2011), Shanley et al. (2002, 2008), and Schuster et al. (2008) were added to Discussion section 4.3. We also added a citation to Oswald and Branfireun (2014) to Discussion section 4.2, as it supports the hypothesis that warm, dry conditions (e.g. summer) can cause accumulation of soil DOM (and associated Hg), which is released in subsequent precipitation events (e.g. fall rainstorms). Burns et al. (2013) was cited in the Introduction (pg. 7618, line 5), but

incorrectly shown as 2012.

Methods: Define spectral slope

Author response: Spectral slope (SR) is defined in Methods section 2.3 along with other DOM optical parameters. This material was in Results section 3.2 in the original manuscript.

Tables and Figures

Table 1: Why are units for nutrients and major elements not in heading like for all other parameters?

Author response: Unit labels were added to the table and removed from table caption.

Table 2: Add "at" to caption "Sampling in 2012 was not sufficiently high frequency." Define spectral parameters.

Author response: Added.

Table 3: Note difference in sample frequency of different study periods.

Author response: The time period for each study is indicated in the column headings (1998-2013 for Environment Canada, 2011-2013 for our data). A description of sampling frequencies was added to the caption.

Table 4: Clarify meaning of "fraction."

Author response: An explanation of "fraction" as well as the shallow and deep soil DOM end-members was added to the caption.

Figure 2: Clarify meaning of "daily fluctuations in water temperature creating diurnal discharge pulses." Daytime snowmelt? Evapotranspiration? Industrial discharges? Why does time axis begin on March 18, rather than March 25 like all other freshet figures?

Author response: The caption was amended to read "daily fluctuations in air temper-

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ature are transmitted to the observed water temperature, and create daily pulses of snowmelt, seen in diurnal peaks in discharge." The bounds of this plot were extended in order to show hydrologic conditions preceding the freshet.

Figure 3: Define "SPM"

Author response: Definition added to caption.

Figures 3, 6, 8, 9: Add an overall description of what is shown to captions. "Take-home messages" useful but secondary.

Author response: Interpretive statements were removed from captions for Figs. 3, 8, and 9. We believe the current caption for Fig. 6 is strictly descriptive.

Figure 3B: What are "two measurements" used to calculate "SPM concentration difference"?

Author response: The meanings of SPM concentration and SPM concentration difference presented in these figures was clarified in the caption. The captions for panels A and B now read: "(A) Measured suspended particulate matter (SPM) concentration determined from the mass of sediment recovered from filtered water correlated strongly with turbidity measured with a nephelometer. (B) SPM concentration difference was calculated as the difference between the SPM concentration determined from the mass of sediment recovered from filtered water and that estimated from the linear correlation in panel A."

Figure 4: Why not report r2 for panel 4A as in 4B?

Author response: Linear regression and r2 value were added to panel A (now Fig. S1).

Figure 5: "Very rapid" changes in 1-month freshet period appear consistent with record from other years, even if inadequate sampling frequency didn't fully capture changes.

Author response: The distinctive feature of the freshet δD change we intended to highlight was its large magnitude relative to the full annual cycle. The wording of the caption

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for panel B has been changed to "In the context of the 4-year record of δD in the Fraser River (total variability $\sim$40 ‰, the changes observed during the 1-month period of the early freshet ($\sim$16 ‰ are significant." An interpretive statement in the caption for panel A was also removed.

Figure 8: Caption labels for panels A and B should precede descriptions, not follow. Change time axis label from Julian Day to months as in other figures.

Author response: The panel labels in the caption were changed as suggested. Time axes are now labeled in months.

Figure 12: Include correlation coefficients since they are referenced.

Author response: Correlation coefficients were added to the caption. As the correlations are not very strong, regression lines were not added to the figures.

Reviewer 2

Add a sentence stating broader implications of the study in the Abstract.

Author response: The following sentence was added to the Abstract: "The snowmelt-dominated hydrology, forested land cover, and minimal reservoir impoundment of the Fraser River may influence the DOC yield of the basin, which is high relative to the nearby Columbia River and of similar magnitude to that of the Yukon River to the north. Anticipated warming and decreased snowfall due to climate changes in the region may cause an overall decrease in DOM flux from the Fraser River to the coastal ocean in coming decades."

Add references to Hg dynamics and transport during snowmelt to Introduction (Mitchell et al. 2008, Demers et al. 2010, Haynes and Mitchell 2012, Mann et al. 2011).

Author response: We added a citation to Demers et al. (2010) to the Introduction. We did not add citations to Mitchell et al. (2008) or Haynes and Mitchell (2012) because only total Hg, not dissolved Hg, were measured in these studies, and the Mann et al.

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(2011) study does not contain DOC data.

Add a summary statement of QAQC for each analysis to Methods, and state whether field duplicates or field/equipment blanks were collected and analyzed.

Author response: Values of measurement accuracy and precision were added for nutrient, cation, and anion concentrations and stable isotope (δD, δ18O) analyses. QAQC information is already shown for DOC concentration, SPM elemental and isotopic compositions, and Hg analyses. Field blanks or duplicates were not collected and a statement of that was added to the first paragraph of Methods section 2.2. Regarding the materials and methods chosen for Hg water samples, we refer to our citation of Hammerschmidt et al. 2011 (Storage bottle material and cleaning for determination of total mercury in seawater. Limnol. Oceanogr. Methods 9, 426-431.), which found that careful cleaning and handling procedures using glass bottles, which we employed, are equally clean for trace-level aqueous samples of Hg as Teflon bottles.

Hg dataset too limited to warrant inclusion in paper title or the estimation of total Hg export from the basin or possible contributions from legacy gold mining.

Author response: See response to the third comment from Reviewer 1.

Statement about Hg in Abstract does not support claim of identification of "rapid changes in flux of dissolved material."

Author response: Mercury has been removed from the statement in the Abstract about "rapid changes in the flux and composition of dissolved material."

Abstract should include a concluding statement of "global implications."

Author response: See response to the first comment from Reviewer 2.

If Fort Langley sampling site experiences tidal influence, what might be expected effects on DOM and Hg transport? Can tides slow movement of water and allow for more DOM and Hg cycling? How do concurrent data from Hope and Fort Langley compare?

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Author response: Tidal influence at Fort Langley is significant enough to complicate discharge measurements; however, it is far upstream of the zone which experiences mixing with salt water even at very low flow conditions. Sediment concentration and composition, as well as species which are significantly influenced by them (which may include Hg), may experience some effect from tidal fluctuations and attendant changes in flow velocity resulting in particle settling and resuspension. We do not have samples across a tidal cycle which could elucidate whether or not such effects are detectable. However, based on the overlap of our DOC concentration record with that of Environment Canada (Fig. 1 below), we are confident that tidal and other differences between the Fort Langley and Hope sites are not sufficient to significantly affect most chemical parameters.

Discuss operational definition of "dissolved" (pg. 7621, lines 13-16), considering standard water quality definition of suspended solids is >1.5 μm and most dissolved defined as <0.45 μm. How does this affect comparability with other studies?

Author response: The majority of dissolved constituents we present (Ca, Mg, Na, K, Cl, SO4, NO3+NO2, N4, H4SiO4, PO4, DOC) are not likely to exist to a significant extent as colloidal material which could span the size range between 0.22 and 0.45 μm, therefore we do not expect this distinction to complicate comparability of other studies with our results. It is possible that our dissolved Hg results would be different had we used 0.45 μm filters, and other studies using this definition of "dissolved" should be cautious in comparing with our results. We added a sentence to the beginning of the sampling methods section (2.2) explicitly stating this definition, and a reference to the filtration pore size was added to the section describing DOM methods (2.3; such a reference already exists in the Hg methods section, 2.4). Our suspended sediment sampling methods were designed in order to identify OM properties of the sediment, and since OM is preferentially associated with finer particle sizes, the use of a filter with a relatively large pore size may have excluded OM which is important to the processes we aimed to characterize. The difference between our measurement of SPM as mate-

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rial retained on a 0.22 μm filter would likely result in significantly different results from investigators using 1.5 μm filters. For this reason, we refer to suspended sediment as SPM (rather than terms with more rigorous definitions such as TSS) and we do not attempt to use our SPM concentration data to estimate loads or fluxes of sediment.

Results & Discussion

pg. 7629, lines 12-30 and pg. 7630, lines 1-4: How do unique characteristics of basin relate to expected differences in water chemistry compared to other basins?

Author response: The basin description in the Introduction (including material that was moved from pg. 7630 of the Discussion) contains descriptions of how the climatic, hydrologic, and land cover features of the Fraser basin are expected to impact DOM dynamics relative to other river types.

pg. 7630, lines 13-16: Expand on differences in DOC yield of Fraser vs Yukon and Columbia.

Author response: We added comments on similarities and differences between these basins as they relate to DOC dynamics (see response to Reviewer 1 comment on the same topic).

pg. 7632, lines 12-25: Improve clarity of this dense paragraph related to interactions between deep and shallow soil DOM pools.

Author response: The section beginning "If, however, a portion of shallow soil DOM escapes mobilization..." through the end of the paragraph has been significantly condensed and reworded. It now reads "A stronger understanding of the nature of interaction between shallow and deep soil DOM pools would further inform the results of this study. An investigation of seasonal changes in soil DOM properties (e.g. concentration, optical properties, biolability, 14C age) with depth could build on the results presented here by identifying whether hydrologic flushing imparts a 'fresh' DOM signature on deep soil DOM and how long such a signature persists."

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pg. 7634, lines 20-21: How deep is deep soil-derived DOC?

Author response: The terms "shallow" and "deep" soil DOM are used conceptually as end-members for relatively fresh versus aged/degraded DOM sources to the river. We do not define the depth of deep soil DOM a priori, but the calculation on pg 7633 using optical parameters and discharge volumes attempts to set constraints on the depth of the cutoff between shallow and deep sources. This paragraph contains many caveats emphasizing the propositional nature of the estimate of the depth of the shallow soil DOM pool.

pg. 7637, lines 14-15: Why invoke Hg leaching from particles when TDHg concentration does not change?

Author response: This sentence has been reworded to indicate that changes in SPM conditions may change the distribution of solid vs dissolved Hg, not necessarily in a particular direction. It now reads "Regarding the TDHg concentrations, it is possible that the exchange of Hg between solid and dissolved phases changes with changes in SPM concentration."

pg. 7637, lines 18-24: Was there a trend in Hg Kd?

Author response: There was no distinct temporal trend in Kd' (Fig. 2 below).

pg. 7639, lines 19-26: Estimate of Hg export based on 6 samples is quite speculative. Since SPM and THg not perfectly correlated over sampling period, something besides particles must be influencing export.

Author response: We added a statement highlighting the preliminary nature of this estimate: "This is necessarily a first-order estimate, as SPM concentration and THg are not perfectly correlated in our dataset, indicating that other factors play an important role in Hg export." We have also reworded the final portion of discussion section 4.3 to be less definitive in the result that legacy mining contamination is not evident based on the deposition and export flux estimates. We now conclude with: "As the poten-

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tial additional sources of Hg to the Fraser River, including natural weathering, legacy mining contamination, and contemporary pollution, do not elevate the Hg load beyond what is deposited by the atmosphere, it appears that soils and sediments within the basin are accumulating Hg and/or releasing a portion of the deposited Hg back to the atmosphere."

pg. 7639, lines 26-29: Conclusions do not agree with the finding that [dissolved] Hg concentrations in Fraser are higher than expected for DOC concentrations based on previous studies. Perhaps due to limited dataset?

Author response: The statement that additional sources (beyond atmospheric deposition) do not appear to cause elevated Hg concentrations in the Fraser River is based on the previous statement that the Fraser exports a typical fraction of its basin Hg deposition. In light of Reviewer 1's observation that the estimated Hg export relative to deposition is likely on the high end, these conclusions may not be contradictory.

pg. 7640, lines 12-13: Reword "hydrologic control of [...] snowmelt-dominated hydrology"

Author response: This sentence has been changed to "hydrologic control of OM dynamics in a snowmelt-dominated river basin..."

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/12/C4515/2015/bgd-12-C4515-2015-supplement.pdf

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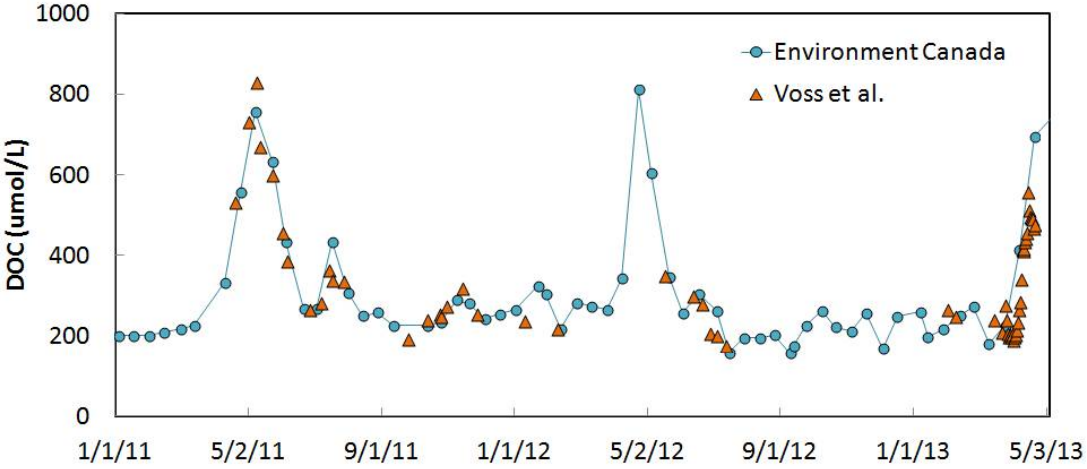

Fig. 1. The DOC record of Environment Canada compared with that presented in this study for their period of overlap

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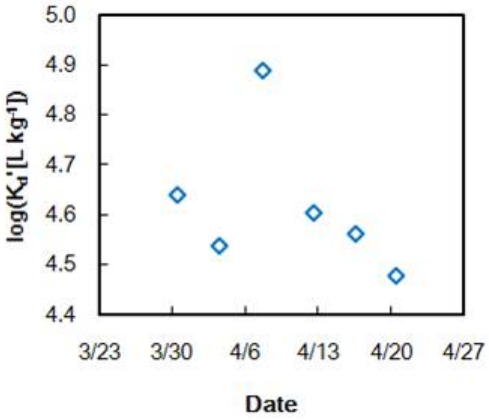

Fig. 2. Mercury partition coefficient during the 2013 early freshet

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