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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.

Anonymous Referee #2

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Title: Seasonal hydrology drives rapid shifts in the flux and composition of dissolved and particulate organic carbon and mercury in the Fraser River, Canada

Authors: B.M. Voss, B. Peucker-Ehrenbrink, T. I. Eglinton, R. G. M. Spencer, E. Bulygina, V. Galy, C. H. Lamborg, P. M. Ganguli, D. B. Montluçon, S. Marsh, S. L. Gillies, J. Fanslau, A. Epp, and R. Luymes

Reference Number: bgd-12-7613-2015

Summary: This paper presents a comprehensive daily time series of water chemistry

during the early stages of the Fraser River's spring freshet in 2013, in conjunction with less complete data sets from 2011, 2012, and the remainder of 2013, to analyze trends in organic matter composition in relation to hydrologic dynamics in the basin. A very limited set of mercury samples was also collected and the results were discussed as a function of changing organic matter composition.

GENERAL COMMENTS

Originality: The article presents a new data set characterizing water chemistry from a moderately sized, relatively un-impacted, temperate river watershed. The intensive sampling effort over the initial rise in the freshet hydrograph showed distinct trends in organic matter fractions and optical properties that may have been missed under less frequent sampling protocols.

Language: The language in this article is generally excellent, clear, and concise. There were a few places in the text where sentences could be reworded for greater clarity (see detailed comments below).

Layout and Format: There was a decent narrative and fairly logical flow to this article.

Title: The title is generally descriptive of the content and conclusions in the study.

Abstract: The abstract summarizes some of the findings in the study. A sentence stating broader implications for the findings would have been useful.

Introduction: This section is generally clear and a thorough introduction to the DOC/DOM literature, the DOC/DOM issues at hand, and the objectives of the study. Mercury dynamics are not discussed to nearly the same extent as DOC/DOM in the introduction and there is no discussion of the literature concerning mercury transport during snowmelt. Recommend some additional references below:

Mitchell, Carl PJ, Brian A. Branfireun, and Randall K. Kolka. "Total mercury and methylmercury dynamics in upland–peatland watersheds during snowmelt." Biogeochemistry 90.3 (2008): 225-241.

Demers, Jason D., Charles T. Driscoll, and James B. Shanley. "Mercury mobilization and episodic stream acidification during snowmelt: Role of hydrologic flow paths, source areas, and supply of dissolved organic carbon." Water resources research 46.1 (2010).

Haynes, Kristine M., and Carl PJ Mitchell. "Inter-annual and spatial variability in hillslope runoff and mercury flux during spring snowmelt." Journal of Environmental Monitoring 14.8 (2012): 2083-2091.

Mann, Erin, et al. "Mercury fate in ageing and melting snow: Development and testing of a controlled laboratory system." Journal of Environmental Monitoring 13.10 (2011): 2695-2702.

Materials and methods: The materials and methods section is organized and explains the study design. The authors described sampling and analysis activities with enough detail for reader to understand how the study was carried out. Despite description of standard reference materials and numbers of replicates run, actual QAQC data were limited and sporadic. A summary statement of QAQC for each analysis would be helpful. Also it is not clear if field duplicates or field/equipment blanks were collected and analyzed. The latter are particularly important for dissolved mercury analyses especially because glass bottles were used instead of Teflon (the standard material).

Results and discussion: The overall presentation of results and discussion is well organized and generally addresses the importance of DOM/DOC findings in the context of the literature. The section titles are informative. There were a couple sentences that could be reworded (see detailed comments).

My biggest criticism is that mercury seems to be an afterthought in this study. The use of mercury in the title indicates to me as a reader that I will learn something about how seasonal hydrology drives a shift in the composition and flux of mercury as well as organic matter. However, a total of 6 samples were collected over the early freshet in 2013 (at least that was all the data that were presented), which doesn't really seem like

enough to characterize compositional shifts caused by seasonal hydrologic drivers. It is true that there is a major shift captured in the limited data set that is presented, but I don't find this to be a particularly compelling data set. I think that shows in the inability of the authors to conclude much at all about what drives the changes in mercury export. I also do not think that the authors have enough data to make conclusions about total mercury export from the basin, nor the contribution from legacy Hg from mining activities to total export.

Conclusions: DOM/DOC conclusions follow from the data presented in the article. Some of the conclusions concerning Hg export are somewhat overreaching and speculative (see detailed comments).

Data presentation: Figures are clear and show many different relationships.

DETAILED COMMENTS

Abstract:

Pg 7615, Lines 17-19: The single inconclusive sentence about mercury in the abstract does not follow from the stated ability to identify rapid changes in the flux of dissolved material (focus on mercury) at the beginning of the abstract. Furthermore daily mercury samples were not collected over the early freshet in 2013 according to the data presented in table 1 and figures 10 and 12. A concluding "global implications" statement on the abstract would be useful.

Methods:

Pg 7619, Lines 9-10: The stated reason for using the discharge data at the Hope station was that it was the most downstream site that did not experience tidal influence. Given that the Hope station is 100 km upstream from Fort Langley, where the 2013 freshet sampling occurred, it stands to reason that there is likely more tidal influence. What might be the expected effect not only on samples, but also on the DOM and Hg transport processes? If there is tidal influence does it slow movement of water

downstream and allow for more DOM and Hg cycling? How do concurrent data from the two sites compare? This seems like a relevant issue to address because the authors mix data sets in the results and discussion.

Pg 7621, Lines 13-16: Some discussion of the operational definition of "dissolved" may be warranted. Standard water quality methods for determining suspended solids use a 1.5 μm pore-size filter and most utilize 0.45 μm as the operational definition of dissolved. How does the use of 0.22 μm change the results of your analyses relative to those presented in other studies?

Results and discussion:

Pg 7629, Lines 12-30 and Pg 7630, Lines 1-4: This section of the discussion could use more connection to the results of the study. Yes the Fraser River may be expected to behave differently, but do you see differences in water chemistry between the Fraser and other type systems that are explained by the physical differences described in this section?

Pg 7630, Lines 13-16: More discussion of why the Fraser exports a similar amount of DOC as the Yukon (which we expect to be different based on the previous paragraph) and why exports are so different from the Columbia would be helpful here.

Pg 7632, Lines 12-25: This paragraph is very dense and could use some rewording in places for clarity. The two sentences preceding lines 12-25 set up an explanation for an observed trend in the data and then state the complexity introduced by seasonal changes and physical geography. Are lines 12-25 meant to disentangle the complexity? How deep is deep soil? Do the data support one interpretation or the other (shallow and deep DOM decoupling vs coupled and slow degradation)? And if some soil DOM doesn't enter the deeper soil pool wouldn't the deeper pool become depleted over time? If only a small fraction of basin NPP is exported isn't this process happening to some extent? I'm not certain of the purpose intended for this section.

Pg 7634, Lines 20-21: How deep is deep soil-derived DOC?

Pg 7636, Lines 19-20: The report of Hg concentrations that are not well correlated with DOC is a good addition to the literature.

Pg 7637, Lines 14-15: Yes THg concentrations increase during the freshet period described, but TDHg essentially remains constant. It is not clear why the authors invoke Hg leaching from the solid to dissolved phase in these lines when concentrations don't really change. Wouldn't leaching from the solid increase the dissolved concentrations given the high levels of solids?

Pg 7637, Lines 18-24: Was there a trend in the Kd for Hg? Data are not presented. Other things may also affect Kd values (e.g. ligands, pH). Or was it simply variable? Variation between 4.5 and 4.9 doesn't seem that dramatic. I agree that changing nature of the OC on the solids could affect affinity for Hg, but it is also likely that the concentrations of Hg observed are well below concentrations that would saturate preferential sites on the OC, even with the change.

Pg 7639, Lines 19-26: This is pretty speculative. Hg export is based on 6 samples? And your THg trends do not match your SPM trends over the freshet so solids don't explain all of the Hg data.

Pg 7639, Lines 26-29: The conclusions here do not agree with some of your findings earlier in this section where you found higher Hg concentrations in the Fraser River than expected based on the findings of other studies from the Yukon and NE US and Eastern Canada (Pg

7636, Lines 21-26). With so little data can you really support these numbers?

Conclusions:

Pg 7640, Lines 12-13: "hydrologic control of [...] snowmelt-dominated hydrology" is a tautology, consider rewording

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