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Interactive comment on "Partial coupling and differential regulation of biologically and photo-chemically labile dissolved organic carbon across boreal aquatic networks" *by* J.-F. Lapierre and P. A. del Giorgio

Anonymous Referee #4

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Partial coupling and differential regulation of biologically and photo-chemically labile dissolved organic carbon across boreal aquatic networks J.-F. Lapierre1*, P. A. del Giorgio1

While this manuscript clearly reflects a significant amount of field and lab effort, I found it extremely difficult to follow the thread of the author's points both due to its overall poor organization and overuse of ill-defined technical terms. Because of this, I found it challenging to provide specific comments (its hard to just say, "I didn't follow"). I hope

the authors find the below review useful.

GENERAL COMMENTS (in no particular order): If the authors are clear on what the main objectives of this study were, it was not made clear to me as a reader. Is it to look at whether Bd-DOC and Pd-DOC pools different across lakes/streams/wetlands? If they are linked more or less in lakes vs. streams vs. wetlands? Is it to use Bd-DOC and Pd-DOC measurements to gain insight into DOC source? To its diagenic state? Is it to think about C processing prior to reaching oceans? Is it to understand how "landscapes" control DOM composition? To use optical properties to predict Bd-DOC and Pd-DOC concentration or percent? Even though the headers in the discussion try to break out the different topics, the introduction and results did not adequately set-up these questions. The paper requires significant rewriting to convey the authors' points in a clear, and much more concise, manner.

Investigating links between different DOM (or DOC, whatever term you choose) pools is challenging, because it is a heterogeneous pool of compounds and we typically measure bulk properties (e.g. DOC concentration), or sub-pools (Bd-DOC, Pd-DOC, A440, Ex370/Em460, PARAFAC components), or bulk composition (SUVA, %Components, Abs ratios, %bioavailable, %photodegradable), and/or net changes in these pools or properties and try to say something about DOM origin. I think it would help the authors to make a venn diagram depicting how they imagine these different parameters relate. For example, Bd-DOM and Pd-DOM both would fit within a large circle representing the total DOM pool, and these two sub-sets of DOM would overlap to a variable extent depending on DOM source and environmental processing. Then for each parameter you measure, determine how that fits within that model. For example, the DOM that absorbs at A440 should largely overlap with the Pd-DOM pool (since both are by definition photoreactive), and probably overlap much less with the Bd-DOM pool. I also imagine "fresh" - meaning un-alterned not necessarily of a certain age - DOM largely overlaps with the Bd-DOM pool (80%?) and depending on its source (algal vs. plant) can have a variable Pd-DOM overlap but still much lower as a percent compared to

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humified DOM. Assuming terrestrial derived DOM has already been degraded and is no longer fresh (an assumptions I believe the authors make, although not explicitly), the reverse would be true. Overall lakes, wetlands and rivers have DOM from both terrestrial and algal sources, but the proportions differ, HOWEVER more importantly how "fresh/altered/environmentally processed/humified" the DOM is varies. This changes the sizes and overlap of all of the circles in the venn diagram.

Another common challenge when investigating DOM pools is being aware of when you are dealing with CONCENTRATION based parameters (parameters that reflect the AMOUNT of DOC in your sample) and COMPOSITION based parameters (parameters that reflect the TYPE of material in the sample). The AMOUNT of Pd-DOC and Bd-DOC in the sample provides completely different information than the PERCENT in the samples. #1: Please come up with a clear way to distinguish between when you refer to conc and percent – please use different abbreviations! I did not understand why the authors spend so much time pointing out there is a strong correlation between [Pd-DOC] and [Bd-DOC], and between these terms an other concentration based measurements. You would expect that given MORE of something (DOC) , the sub-pools would also generally increase. To me the more interesting question is how does %Pd-DOC and %Bd-DOC correlate. For the PCA analysis, I think including both concentration based and composition based terms in the analysis is confusing. Again, I would expect all of the concentration based parameters to be highly correlated. I think it would be much more informative to run the PCA analysis, and also the multiple linear regression analyses, on the COMPOSITIONALLY based parameters alone.

I do not follow how the authors believe they can separate terrestrial from aquatic derived DOM pools based on the sampling approach and methods used. They seem to suggest that "CDOM" (which I assume refers to A440, pleae define on first use and remind the reader later too), is a measure of terrestrial DOM, however that is certainly not the case. This is a major flaw in the paper if this is being assumed.

It is not clear how the authors separate out terrestrial vs. aquatic DOM, especially in

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wetland environments. Freshly leached plant DOM (e.g. likely present in wetlands) can look very similar to freshly produced phytoplankton derived DOM. Where does aquatic vegetation fall?

Please be more careful and far more sparing in the use of technical sounding terms, and clearly define their meanings. Many of the terms included, though frequently used in the literatrue, mean different things to different people. For example:

*regulation: this term is in the title, but was not used very often in the paper (except the abstract and last page). Regulation by what?

*Landscape scale – this term is used, but never clearly explained what/how any landscape scale parameters were collected or examined. When I hear this term I think of things like soil type, vegetation type and cover, precipitation, climate, anthropogenic influence (fertilizer inputs, erosion, etc.)... If you just mean lakes vs. wetlands vs. rivers, I would take out this term entirely.

*Landscape gradients – gradients of what landscape features? This term is used so broadly it isn't useful.

*Allocthounous/autocthonous – how does this relate to terrestrial/algal? Most often the authors seem to compare autocthonous to terrestrial, so why use authocthonous at all? I found the discussion of "age" and "freshness" useful, but wasn't sure how this then relates back to the idea of initial source/origin. Regarding age, what types of environmental processing besides biodeg. and photdeg. do you think occur?

*coupled/coupling: is this synonymous with correlated, or linked? I also like to use this term to think about pools of DOM, but there were times I wasn't certain what was meant by these terms. Especially when you use the term "partial coupling". Please use more specific (clear) language.

*functional pools: what does this mean? instead of using different terms to mean the same thing, I suggest you try to define specific terms and use them consistently.

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This sentence from the last paragraph is an example of how the authors used complex language that may sound good, but I can't figure out what they are trying to say: "This result also suggested an additive behavior of DOC degradability along a gradient of terrestrial influence, and here we show that the role of land as a major source of both biologically and photo-chemically degradable DOC to boreal aquatic networks results in a pattern of co-variation between these two key pools of carbon at the whole landscape scale, despite fundamental contrasts in terms of their composition and regulation". I suggest you write in a more concise manner.

Why suddenly use "water retention time" "DOC freshness" and "regulation" in the last page when you barely used these terms prior to this? What do you mean by these terms? Do have you have any information about residence times for these samples?

There was recently an article in Nature about the reliance of P values indicating significance, when in cases where R2 values were in fact so low that the relationship was so weak that the significance is meaningless. I suggest the authors take a look at this paper: Nature, 152 vol 506 13Feb2014 by Regina Nuzzo.

I felt the total N and P data was included more of an aside and never satisfactorily presented. Did you look at C:N, C:P or N:P ratios for insight into DOM source and processing?

Please add a correlation matrix for all of the parameters discussed: preferably one matrix that contains only concentration based parameters, and one that contains compositionally based parameters. Unless, for some reason you want to see how composition trends with concentration – in which case please explain/justify the difference between comparing SUVA to [Pd-DOC] and %Pd-DOC.

By definition absorbance and fluorescence measures the photoreactive pool of DOM, thus it is well-known that these measurements should be linked to the pool of C that is photodegradable. It is interesting to examine which specific optical measurement can best predict Pd-DOC and Bd-DOC, however the authors did not take a clear statistical

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approach to this question (or if you did, I didn't focus on that). Again, a correlation matrix of all parameters would be useful, followed by the multiple linear regression results shown in Table 1. As mentioned above, I found it puzzeling that parameters of both concentration and composition were included in the same analysis [C6] and %C6. Is this confounded?

Overall, this data set has a tremendous amount of potential, but these statistical analyses, interpretation, and discussion require significant reworking.

SPECIFIC COMMENTS: 13 The first sentence of the abstract mentions the flow of carbon from continents to oceans – I do not believe the paper addresses this (suggest it is removed). I did not find that after reading this paper I had an understanding of the "large scale patters in BDOC and PDOC" across continental watersheds".

17 Pd-DOC concentration or percent? Or both? Please specify.

18 What do you mean by system trophy and terrestrial influence? What "landscape level" parameters did you examine?

21 Don't you use absorbance as well as fluorescence to identify DOM pools? Do you mean differences in DOM composition, not just different pools?

22 What nutrients? Nutrient concentration or content? N:P ratios? Very unclear. Should say "protein-like DOM fluorescence". However, fluorescence in the "Peak T and Peak B" regions are not necessarily proteins!! Tannins and other compounds also fluoresce here. Perhaps use 'fluorescence in the lower UV region". See for example, Hernes et al, 2009; Beggs et al, 2011.

25 Please state what you mean by CDOM here (A440?) I have never seen CDOM used as a proxy for terrestrial influence! This is a major flaw if the authors are making this assumption. Many papers show a good relationship between DOC concentration and "CDOM" (A254, A440, etc.), and it is not surprising that if you have higher concentrations of DOC you have higher concentrations of degradable DOC too. But does

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the fraction (%) of these pools differ and why? To me it is more interesting why the %s change: why in some cases is there still labile/photoreactive DOC in water. The most simple explanation to high %BDOC or %PDOC is that there have been recent inputs of fresh DOM, or the water has been cold and there is no light so it hasn't been altered, or the bacterial community is nutrient limited, or. . . (This type of discussion is missing).

27 Putative bio-labile fluorescence component? What does this mean? Please do not use the term "browner"; use an optically measured property. Avoid using autocthonous without defining it clearly.

31. After reading the paper, there is still no indication the authors examined any type of "landscape gradients". The only classes I saw were river vs. wetland vs. lake, which I would not classify as landscape gradients but rather simply three types of water bodies.

31 I do not know what this last sentence is saying, and I read it many times. It is already well known that terrestrial sources of DOM are major contributors to surface waters DOM. I am not convinced that the authors can in any way determine the origin of DOM: terrestrial vs. autocthonous, per their definitions.

38 what is the difference between sources and origins? I believe these are synonyms.

50 I am not clear on how Pd-DOC pools relate to the aquatic food web. Upon photoxidation, isn't this DOC "lost" to the foodweb if it is converted completely to CO2?

56 "factors that are intrinsic to DOC" is too vague. This point needs to be elaborated – and linked to the optical properties subsequently measured and discussed.

51-63: I agree with the authors' first point that the two pools overlap. Then they suggest the pools are "broadly" distinct? While this might be true in some cases, I would argue that it certainly does not hold up for less biologically degraded (ie "fresh") material. Certainly after biological processing of the DOM pool has been exhausted the remaining pool can still have high photolability. I don't believe anyone would suggest the sources and origins of BDOC and PDOC differ, since they both originate from photosynthesis by

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plants (terrestrial and/or aquatic). The authors are clearly aware of these complexities, as they reference a lot of key papers that cover these topics.

62. Here you define source vs. origins, but I actually don't understand your definitions. The words are nouns but the definition for sources is a verb? What "environments" are you considering? How does the aquatic environment relate to the terrestrial environment? Terrestrial derived DOM is being added to water all the time, not just at the headwaters.

82 I am still not clear on the authors' conceptual model of "sources and origins" and how this relates to PDOC and BDOC, bulk DOC concentration, and "functional pools" of DOC.

Methods:

Please summarize clearly the sample numbers and how many were analyzed for DOC concentration, nutrients, BDOC, PDOC, etc. Preferably in a table.

Define CDOM, TN, TP

There is a fair amount of results included in the Methods (e.g. lines 107-114)

115: I don't understand where samples were collected from. Why the deepest measured point of lakes? Why not near the outflow or center? Near the shore of streams and wetlands from what depth? Were these just grab samples?

117 I suggest you look at C:N, C:P, and N:P ratios.

120 Two weeks is a fairly long time to store samples for optical analysis, but okay.

122 Please provide references for all of these analyses.

130 Please report stdev or error associated with the duplicates.

138 Please check this. Didn't Spencer use A250:A365? (although A254 is practically the same).

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147 blank corrected too? How many samples were ambient versus photochemically degraded?

163 How was %BDOC calculated?

177 Add “Photoexposure incubation time”. You might like to state that you assume this light exposure represents the “maximum potential” for photodegradation for each sample, if you think that is the case.

192: Did you consider combining the results and discussion? I usually find that makes it easier to write and read. There is a fair amount of discussion in the results.

196. This is an impressive range!

203: “typically lower” “no relationship at all” is not very satisfying or specific. What did the statistics say?

209 Here although the stats say the relationship is significant, the r2 values are low (<0.4). I think the POOR relationship is surprising and warrants discussion. However, I would be more interested in discussion of the data in terms of % (i.e., proportion, fraction). You could plot % BDOC and PDOC against DOC concentration, to show whether there is a relationship between CONC and quality.

220 Be careful: Peak T and Peak B like fluorescence are also associated with polyphenols, and should not be assumed to represent proteins only. When discussing your PARAFAC results, it wold be helpful to link your components to more familiar peaks like C, A, T, B (put them into context). Also point out how your components are similar / different to commonly identified PARAFAC components.

224: by “extreme” do you mean high? Do you need to include these 43 samples?

236 I do not see much distinction between lakes, wetlands, rivers in Fig 5. It seems obvious, and already knonw, that they would group along a concentration gradient. I believe seeing how they would group by “composition/reactivity” alone would be more

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informative.

241-244: This seems to state the obvious: more DOC means more PDOC and BDOC. More interesting/informative is how does DOC conc. relate to %PDOC and %BDOC?

247 remind the reader what A254:A365 is a proxy for.

252: this PCA analysis does not convince me PDOC and BDOC are distinct pools.

259 I see that the authors looked at pH, Chl-a, TP, TN, but I do not see how this translates to "systematic ecosystem-specific or region-specific" interpretations. The only grouping I am aware of are their 3 aquatic environments (lake, river wetland). I strongly encourage the authors to avoid fancy sounding terms and instead stick with "the three different aquatic groupings" they use. Similarly, what is meant by "drivers"? No drivers (light exposure, temperature, residence time) have been defined let alone presented.

260 This sentence does not make any sense to me. Do you mean "DOC composition, including nutrient content"? DOC composition (its chemical makeup and structure) is determined by its source, type of aquatic environment, region it is found in. This seems circular.

263 Please consistently use DOC vs. DOM. Please include a full correlation matrix. How correlated was C5 to C6? C3 to C2?

266 One expects the photodegradable pool to be more highly correlated with optical properties, since by definition you are limited to measuring the photreactive pool of DOM with this approach.

273-276 This is interesting.

277-294 Interesting, but already established in the literature. Include references to prior work.

294-313 I am lost here: what evidence is there that CDOM at A440 represents ter-

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restrial derived DOM? I assure you that if you extract algae it will absorb at A440, especially if you let it degrade. I am concerned that your “low-CDOM” relationship is an artifact of your analysis and detection limits. What are the %C6 values associated with this low [C6] values? Could this just be PARAFAC picking up noise?

At this time I feel the discussion needs major revision, and will not provide further comments.

Interactive comment on Biogeosciences Discuss., 11, 6673, 2014.