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Interactive comment on "Seasonal contribution of terrestrial organic matter and biological oxygen demand to the Baltic Sea from three contrasting river catchments" *by* H. E. Reader et al.

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We would like to thank the reviewer for their thoughtful and detailed comments. We have responded to all of the comments below:

Reviewer #1.

General Comments Analytical issues: BOD and organic matter quality. BOD is a common measurement for community oxygen demand, and generally unfiltered whole water samples are used for this measurement. Here, the authors adapted this method to measure oxygen demand of filtered water samples. Because bacteria causes DOM decomposition and filtration removes a large fraction of bacteria, this adapted method

may underestimate BOD of DOM.

Response: The approximate pore size of a GFF filter is $\sim$0.7 μm. Unlike other filters the pores are not uniform in size, and this represents a average pore size. So the process is not a sterile filtration, however will retain some bacteria as well as all larger organisms which can contribute to respiration and particulate detritus which can act as additional substrate. During the two week period the bacterial community should re-establish. This is now clarified in the Methods section lines 161-169, revised manuscript: "Samples were filtered through ashed GF/F filters directly into 60-mL Winkler bottles which were sealed without headspace. The fitration was done to remove larger organisms and their contribution to respiration, as well as to remove particulate and detritus which may act as additional substrate for microbial degradation. Three bottles were fixed immediately with Winkler reagents, and three more were incubated in the dark at 20.5°C for two weeks. The two-week incubation period was chosen to give the bacterial community time to re-establish from the filtration, as well as be short enough to minimize any contribution to oxygen consumption from nitrification."

Comment: In addition, BOD can be used as an indicator of la- bile DOM, but BOD is not exact the same as BDOM because other components (e.g., oxidation of ammonium) may also consume oxygen. To overcome this problem, DOC changes (before and after bioassays) are also determined along with DO measure- ment. In doing so, a linear regression between bioavailable DOC (BDOC) and BOD can be set up, and BDOC can be estimated from BOD using this regression. However, BDOC has not measured in this study.

Response: While standardized BOD measurements can be used to measure community oxygen demand (and this is normally done using unfiltered waters), our goal was not to measure the community oxygen demand, but rather the potential oxygen demand from the bacterial breakdown of DOM. The approach was standardized for all samples and the measurements represent a degradation potential, which can be easily compared across sites and seasons. Nitrification would contribute to oxygen demand

although in light of the short incubation times it is unlikely to have made a considerable contribution. Data from the Baltic Sea (Stedmon unpublished) indicates nitrification occurring after one month incubation. We did not measure post-incubation DOC, and so an absolute measurement of BDOM is not done. In figure 3b, where we show BOD as a fraction of total DOC, we state that we are using a respiratory quotient (RQ) of 1. Please see above for the clarifications made to the text lines 161-169, in the revised manuscript.

Comment: Lastly, although BOD is an indicator for organic matter quality, BOD measurement is done in lab in dark. In nature, photochemical oxidations (or sunlight bleaching) can break down refractory molecules to small labile DOM. This mechanism for BDOM generation should be mentioned in discussion sec- tion.

Response: Photochemical processes in natural waters can both produce and destroy labile DOM (and consumes O2 in the process), for this reason, incubations were done in the dark, in order to remove potential complications from competing processes, since the goal was to understand the biological signal alone. Text has been added to the methods (2.1) explaining this choice (lines: 169-173 revised manuscript) “The incubation was performed in the dark to eliminate further complications from photochemical processes. Photochemistry is known to both produce and destroy biologically labile DOM and competition between microbes and photochemical processes could complicate the interpretation of results (Reader and Miller, 2014).”

Comment: Data analysis can be improved in a few places in this paper: 1) DOC and BOD flux calculations. Current flux calculations use one concentration data for a whole month, and large errors may be generated because DOC/BOD concentration may change with flow even within a month. Since there are relationships between DOC or BOD concen- tration and river flow, these relationships can be used to improve DOC/BOD flux esti- mations. There are many established approaches (e.g., US Geological Survey’s Load Estimator or LOADEST) for flux calculation with continuous flow but discrete DOC data. LOADEST can be downloaded and is free to the public.

Response: Q-C graphs were attempted for all of the rivers and variables (TOC, CDOM, BOD) as is done in the LOADEST type models. However, we were not able to determine valid relationships for all variables on all rivers. For those that we were able to determine relationships we found that the difference between using that and using the monthly average method used in the manuscript was between -3.5% and +3.8% (for those Q-C relationships with R2 = 0.3-0.5) and between -1.1% and +1.0% (for those Q-C relationships with R2 = 0.6-0.9). Because these differences are minimal and there were multiple cases where a Q-C relationship could not be determined, we opted to use the monthly average method for all data presented in the manuscript for the purpose of consistency. There was no hysteresis noted in any of the Q-C relationships.

Text describing this has been added to section 2.2 (lines 187-194, revised manuscript): “An alternative method of determining flow relationships with carbon variables (i.e. Q-C relationships) was attempted. This method is often successfully employed in smaller catchments (Strohmeier et al., 2013;Jollymore et al., 2012). When a valid Q-C relationship was obtained, the difference between loadings obtained using the monthly average method and the Q-C method was between -3.5% and +3.8%. However, valid Q-C relationships were not found for all rivers and all variables. Because the differences between the methods were small, the monthly average method was used for all rivers and variables to ensure consistency.”

Comment: 2) The linkages of DOC and BOD fluxes or yields with watershed land-use, climate parameters (air temperature, precipitation and river flow) have not been explored quantitatively. Once such a linkage have been established (e.g., linear regression with multiple variables), it can be used to predict changes in DOC and BOD exports with future climate and land-use changes.

Response: While this is an interesting idea this dataset is limited with only three catchments and therefore unsuitable for this type of analysis (essentially a regression with three data points). We have therefore not pursued this further.

Comment: 3) This paper has not analyzed evolution of DOC (and aromaticity and BOD/DOC ratio) with river flow changes to test there is any hysteresis or not. Such analysis (even with monthly data) may provide insight on DOC transport in watershed. See Strohmeier et al. 2013, Biogeosciences, 10, 905–916.

Response: Please see above response about the Q-C relationships in this data set.

Comment: Finally, this paper did not present hypothesis in introduction, I would add it to clarify why 3 study sites were selected. I also suggest the author read more literature on DOC export, DOC quality and climate change, and compare the results of this paper with other watersheds.

Response: The aim of the study has been clarified and the hypotheses driving the study have now been clearly stated (lines 125-129, revised manuscript): “The aim of the study is to examine DOM fluxes from rivers to the Baltic Sea, and how loadings of reactive DOM vary spatially and seasonally. We hypothesize that DOM concentrations and reactivity will vary seasonally with the discharge of the rivers. We assess this in three contrasting Swedish rivers, occupying distinct climatic zones.” Specific Comments:

Comment: 1. Abstract, line 5-9, this sentence is too long and cannot catch the main idea than need to highlight.

Response: Sentence shortened and clarified revised manuscript lines 27-32: “Dissolved organic carbon (DOC) concentrations were positively correlated with discharge from forested catchments over the year. While the overall concentrations of DOC were several times higher in the southern two catchments, higher discharge in the northern catchment resulted in the annual loadings of DOC being on the same order of magnitude for all three catchments.”

Comment: 2. Abstract, line 13-14, “ . . . was twice as high in the northern catchment”, as high as what? Please complete.

Response: Sentence clarified lines 36-37, revised manuscript: Total annual BOD loading to the Baltic Sea was twice as high in the northern catchment than in the two southern catchments.

Comment: 3. Abstract, line 21-22. Do not under what the conclusion really means. It would be better to say something on the contribu- tion of this paper on the DOC increases in Artic region.

Response: Sentence clarified lines 44-46, revised manuscript: Our results indicate that DOM supply to the Baltic Sea from boreal rivers will be more stable throughout the year, and potentially have a lower bioavailability.

Comment: 4. Page 1357, line 12-14, it’s unnecessary to mention DOC cycles in lakes because this paper does not deal with lakes.

Response: This sentence has been shortened to remove the lake focus (lines 67-70, revised manuscript) “A large amount of this terrestrially derived DOM is actively cycled in the freshwater systems, however, despite this active cycling, a significant fraction of this DOM, up to 50% of the input or $\sim$0.9 Pg C yr-1 Âň(Cole et al., 2007;Tranvik et al., 2009;Battin et al., 2009), is subsequently transported to the coastal ocean and there continues to be degraded by marine microbial communities.”

Comment: 5. Page 1359, line 8-11, it would be better to have hypothesis here, e.g., qual- ity of DOC, or controls on DOC quantity or quality of the three rivers.

Response: Please see the above response about the aim of the study and hypothesis.

Comment: 6. Page 1359, line 19. Do these hydro dams affect DOC quality, quantity and seasonality? It might be another reason for high BOD in this river, due to algal input. I have not seen any discussions later on these dams.

Response: Interestingly, the primary effect of damming in Sweden is oligotrophication, so primary production in these dams (which is small to begin with in Sweden compared to regions like Brazil or China for example), should not be a significant addition of

autochthonous DOC in this way. Text has been added to the manuscript in the results section clarifying this. Lines 243-245, revised manuscript: “Despite the influence of these dams on the flow on the river, widespread oligotrophication of dammed water in Sweden means that these dams are not likely to be driving DOC concentrations (for example from autochthonous production) (Rydin et al 2008).”

Comment: 7. Page 1359, line 24, what is Baltic Proper? Please explain.

Response: The regions of the Baltic have now been labeled on figure 1.

Comment: 8. Page 1360, line 7-11, this method for BOD of DOM needs references. What causes BOD? Actually, when you filter water with GF/F, you probably remove a frac- tion of bacteria from the water, and thus BOD was probably under-estimated.

Response: This is addressed above in the general comments section.

Comment: 9. Page 1361, line 17-22, curious on why there is a large difference in hydrology (summer flow peak) between Emån and Lyckeby, because they are so close to each other. Please provide addition evidence (e.g., mean river flow for a few years) to support this differ- ence is repeatable and not special in that year.

Response: As mentioned on page 1361 line 19 (lines 222-228 in the revised manuscript), there was an anomalous precipitation event in the Emån catchment in July, which caused widespread flooding throughout the catchment. This precipitation event did not occur in the far south of Sweden. While the two catchments are relatively close together, the sampling points (and relative catchments areas) are separated by roughly 140 km. The anomalous precipitation event is not repeatable in other years. The text has been edited to clarify this (lines 222-228, revised manuscript): “The first was in January during the winter peak precipitation season and the second in July during an anomalous precipitation event, which caused widespread flooding throughout the catchment. In Lyckeby, flow peaked in the winter months, during the normal period of high precipitation. Though the two southern catchments are relatively close to

each other (separated by $\sim$140 km), the summer months in Lyckeby did not experience the same anomalous precipitation even and instead were characterised by low precipitation and consequently low flow.”

Comment: 10. Page 1362, page 1-2. There are no DOC concentration data in Table 2, please add. Add p value and statistic method for difference test when you say higher or lower.

Response: The average DOC concentrations and the range in concentrations across the season for each site have been added to the table so that the clear difference between the northern and southern catchments is apparent. p-value has been added to the text lines 215-216, revised manuscript.

Comment: 11. Page 1362, page 4-6. It’s better to examine the evolution of DOC, aromaticity and BOD/DOC with river flow changes, and see if there is hysteresis. Then you can discuss possible reason for the seasonal variations in DOC and DOC quality.

Response: The qualitative measures for DOM are taken up in the following section 3.3. Also, please see above comment about hysteresis.

Comment: 12. Page 1362, page 1-16, the main point of this paragraph is that DOC is flow controlled, but slight different for the Ume River. I am wondering if the hdro dams of the upper Ume may have some effect on this relation- ship.

Response: There is no correlation with the flow on the dammed portion of Ume river. However, there is a positive and significant correlation with the flow on the low-altitude forested portion of the river. The dams in northern Sweden are found to be oligotrophic, and are unlikely to affect DOC concentrations, so their main effect is to slightly obscure the DOC/flow relationship. The correlations can be found in table 3. A clarification that the undammed portion of the river is unlikely to affect DOC has been added to the text: lines 240-245, revised manuscript: “The existence of dams on the Upper Ume river part of the catchment obscures this relationship by changing the flow after the confluence

of the two parts of the catchment. Despite the influence of these dams on the flow on the river, widespread oligotrophication of dammed water in Sweden means that these dams are not likely to be driving DOC concentrations (for example from autochthonous production) (Rydin et al, 2008)."

Comment: 13. Page 1363, page 4-8, BOD/DOC < 5

Response: We have opted to leave the language as is, since it does not change the meaning.

Comment: 14. Page 1364, line 2-24. Although it is possible that labile organic carbon from river source may cause coastal hypoxia, this mechanism has not been total proved yet. The author may need to mention that decay of marine phytoplankton is an important reason.

Response: Certainly, DOM degradation is not the sole cause of coastal hypoxia, and we clarified this section to ensure that it was clear that we view this as a compounding affect to phytoplankton decay, which we know to be important in this system. We have clarified the text, see lines 299-302 (revised manuscript): "The Baltic Sea is a strongly terrestrially influenced system and the riverine delivery of reactive DOM has the potential to compound the already oxygen stressed conditions present in the region. The consumption of oxygen by microbial DOM degradation can add to the oxygen consumption driven by phytoplankton decay."

Comment: 15. Page 1364, line 27, "2

Response: This comment is unclear, but we read through the sentence and did not find any typos.

Comment: 16. Page 1365, line 19-20, I am wondering if it is possible that labile organic leachate from au- tumn deciduous leaves can be preserved in colder temperature and released in spring, if there are deciduous trees in watersheds.

Response: Ume river, the only river with consistent sub zero temperatures in the winter,

is primarily dominated by coniferous forests (as are the other two catchments for that matter). While the preservation of leaves after freezing could potentially have a small impact on this system, the release of DOM from the freezing of roots etc, is a previously established process, that occurs throughout the catchment. We believe this is the most important mechanism in this catchment. Text has not been amended.

Comment: 17. Page 1380-1381, Figure 2-3 are not clear, I would increase the size of dots for DOC and CDOM.

Response: We have increased size of data markers.

Please also note the supplement to this comment:
http://www.biogeosciences-discuss.net/11/C1150/2014/bgd-11-C1150-2014-supplement.pdf

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