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Interactive comment on "Permafrost coverage, watershed area and season control of dissolved carbon and major elements in western Siberian rivers" *by* O. S. Pokrovsky et al.

Anonymous Referee #1

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Pokrovsky et al. analyze water samples collected from nearly 100 rivers across western Siberia to identify the major controls on carbon species and major ions, focusing on the effects of latitude, permafrost extent, watershed area, and season. They use statistical techniques to determine the relative importance of environmental factors on water chemistry, and combine their chemistry data with historical and derived river discharge data to calculate fluxes from different latitudinal zones. The authors use chemical trends with latitude to infer hydrologic and biogeochemical processes responsible for changing river chemistry, and argue that latitude followed by season were more important than watershed size.

The study is quite ambitious, in that it covers such a large and data-sparse area. I think

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that the chemical trends in space and time are interesting and important, and worthy of publication. However, I often felt that the explanation for the causes of the trends were speculative, or at least that the authors' arguments were not explained clearly enough that I believed it. Generally I think that it is very hard to attribute chemical changes to a combination of physical and biogeochemical parameters without specific information at smaller scales. The authors cite many papers that give examples of the relevant processes, but it is hard to tell if these processes are ubiquitous across these large scales, or if there might be alternative explanations for the observed trends. I also did not trust the flux calculations, which were based on a very small number of water samples (one to five samples) and discharge data derived from historic records or incomplete data. While there is a compelling dip in fluxes in the discontinuous permafrost zone (Figures 9 and 10), I believe that a robust error analysis needs to be presented to quantify the uncertainty around the chemistry and discharge values, and extrapolation from a few point measurements to an annual solute flux budget. Overall, I would suggest that the authors focus on the chemistry trends, and correlations between the different species which might provide a more robust picture of the processes responsible for chemical trends (eg. linking DOC, DIC, and pH). I think that the discussion could be shortened, with a focus on removing speculation and strengthening the argument for the coupled hydrological and biogeochemical processes that they find most important.

Major Comments 1. Parsing hydrology from biogeochemistry: The discussion includes quite a bit of speculation and relies on complex logic arguments to infer the coupled hydro/biogeo processes responsible for the observed trends. The logic of these arguments is not always clear, and there are many assumptions that are not justified. It is difficult to attribute the trends found in this paper to physical or chemical processes without some other line of evidence.

2. Discharge: The methods paragraph on discharge is rather vague. In some cases it appears that discharge was estimated based on data from 1970 to 1972, or from 1973-1992 or was estimated based on discharge in other basins. The number of river

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discharges determined using these various methods should be quantified, and uncertainty needs to be rigorously considered for each (in order to support the flux calculations. Perhaps the location and dates for discharge measurements could be included in Figure 1.

3. Fluxes: Fluxes aren't mentioned in the methods at all, instead they are included in the results, and never fully explain how point measurements are used to determine annual fluxes. It is problematic that discharge is so uncertain, and mostly based on historical data that cannot be directly related to discharge at the time that water chemistry was collected. This suggest major uncertainty in the actual discharge, and thus on the fluxes. The authors report an uncertainty of 30% on the flux measurements, but it is difficult to determine how this value was selected – it seems arbitrary. I think it is likely that this uncertainty is way too small, especially for the spring pulse, where sampling just before or after the peak can lead to incorrectly quantifying discharge and concentrations by orders of magnitude. In many cases, and especially on Arctic rivers, discharge uncertainty by itself may be much larger than 30%, especially for the spring pulse. On top of this, water samples were only collected at 1 to 5 days over the year (and for the fall period were only collected below 60°N (p.10633 line 25)). It seems highly unlikely that these few samples represent seasonal averages, and thus there is large uncertainty in seasonal chemistry, thus compounding the flux uncertainty. For this reason I think that the spring fluxes at least are likely highly inaccurate, and given that the majority of the annual flux occurs in the spring in Arctic systems, calculating annual fluxes based on this data is a real stretch. If the authors can provide many more details on how discharge was quantified, and thus a realistic estimate of uncertainty, it is possible that seasonally-averaged fluxes for the summer and winter could still be meaningful, albeit with very large error bars.

4. Objectives: Objective 2 intends to relate chemistry to active layer depth, peat thickness, and permafrost coverage. However, these were not determined in this study and no data is provided from other studies. I don't think that this objective can be properly

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tested without this data. And how was permafrost extent determined? Likely based on latitude. So correlating latitude to permafrost extent (Figures 6 and 7) doesn't seem all that meaningful or useful. Especially since you didn't quantify permafrost extent.

Minor comments

10622-4: Samples were not collected in Autumn over the 1500 km latitudinal gradient according to the text (p. 10633, line 25).

10622-11: I'm not sure which trend "The trend of inorganic components was. . .." Refers to.

10622-15-17: This logic is not totally clear.

10622-22: Maybe change 'until' to 'below'.

10623:3-18: Much of this paragraph seems reasonable, but speculative and not related to the results from this study. I would suggest removing or at least greatly abbreviating this paragraph.

10625-13: Year for 'Frey et al.'?

10625-17 – Is river size really the only influence on groundwater discharge? It seems like regional topography and sedimentology should also play an important role

10625-17 – This assumes that a talik exists in all cases.

10625-18-19 – unclear how the previous statement leads to this one

10626-15: What's a 'flood zone'?

10629-23: What were you comparing with the ANOVA?

10629-26&27: 'elemental' should be changed/removed, because some of these are compounds.

10630-9: By 'normed' do you mean 'normalized'?

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10630-14-20: This information should be in the methods rather than results

10631-14-16: It is unclear if the ranges refer to the seasons or the three factors. And the major PCA factors should add up to a large value (towards 100%) to be meaningful – here the three factors only add up to 12% at best, suggesting that they are telling you very little about the variance in the data. This makes me question the analysis and its utility.

10631-18: "...the first factor which is presumably latitude...." It is unclear exactly what Table S2 is showing (the legend provides little guidance), but it appears to be the correlation coefficients between various factors and the principal components. If my guess is correct, then it is not a good assumption that the first factor is latitude - Latitude appears to correlate well to the first component in the spring and winter, but not in the summer. Furthermore, many other variables including calcium, DIC, and Mg have higher correlations that are consistent across seasons.

10632-5-8: This information should be in the methods rather than results

10632-22-25 and 26-27: This information should be in the discussion.

10633-1-9: This information should be in the methods. At this point, there is no mention of flux determinations at all in the methods.

10633-7: It's possible that the contributing area changes in time, but the watershed area should not change.

10633-24: It seems important to highlight that October samples were only collected in 12 of the 96 rivers, all below 60° N. This has major implications for the results and conclusions of this study.

10633-14-29: There are no results here. This is a mix of methods and discussion.

10633-10634: "The dominant factor controlling the uncertainty of seasonal flux...was the standard deviation of the average value of individual rivers". To what does 'value'

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refer? Also, I think that a much more thorough and transparent uncertainty analysis is necessary to support the reported fluxes.

20 – The second and third factors each explain less than 5% of the variability? That is really small. Are they actually important?

10646-11: Isn't the highest discharge in the spring? What do you mean by seasonal discharge?

10647-11: 'Reactive' is not the appropriate word. Maybe 'active', or simply '. . .the mineral layer is 'frozen'

106747-25: This seems rather speculative. Warming will also increase peat growth, leading to greater insulation of frozen boundaries.

10648-1-2: Generally, clay is impermeable and should not result in greater infiltration.

10648-7: I agree that sorption will be greater for DOC, but water moving across this mineral boundary may also leach and transport other solutes.

10648-14-25: I'm not sure that this paragraph is needed. It doesn't tie well to the rest of the story and while it's interesting, it's unclear why we're being told this.

10648-28: What about Walvoord references from 2007 and 2012?

10649-1: But won't ET also increase with the potential to balance increasing precip and runoff?

10649-2-3: How does your data support this statement?

10649-5: Vegetation productivity is also likely to affect C export. Why isn't this considered?

Table 1 – What do the codes under the months represent? And how was the annual runoff calculated?

Figure 1:

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It is very difficult to distinguish winter and spring sampling markers.

What is a runoff contour line, how is it calculated, and how was it used in this study? This isn't mentioned in the text.

It is hard to distinguish the rivers and their names

Where is the Kara Sea basin from which you used data?

1b- Again, the rivers are not well labeled, difficult to distinguish, and it's unclear how this relates to Figure 1a.

Figures 2 – 4: Why is autumn not included here? Is it worth even mentioning Autumn in the text if it can't be used in the analysis? Figures 9-11: I don't believe these values at all. And the methods don't mention quantifying an annual load. How can you have any confidence in this based on the fact that 1) the rivers were only sampled 1 to 5 times over the year and 2) the discharge data is often from 20 to 40 years earlier than the chemistry data?

Figure 12: Are these two cross sections really representative of the entire domain? They are very detailed, but how representative are they of all of the variability in the system?

Interactive comment on Biogeosciences Discuss., 12, 10621, 2015.