

## ***Interactive comment on “Trace elements transport in western Siberia rivers across a permafrost gradient” by O. S. Pokrovsky et al.***

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General comments:

The reviewer correctly pointed out that “To get full use of a PCA landscape data is needed to get the bigger picture more complete (with this mean I the proportion forest, wetland, lakes etc).”. In response to this comment, we performed a GIS work on most studied watersheds of western Siberia. We determined the proportion of lakes, bogs and forest on river watersheds and we performed PCA with all available parameters (see Figure 1). Although detailed analysis of the role of lakes, bogs and forest on element concentrations and fluxes in WSL Rivers is beyond the scope of this (already long) paper, this first assessment allowed to conclude that forest play the major role of

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DOC and insoluble elements mobilization from the soil to the river and that bogs and lakes retain TE and diminish their export from the watershed. This is consistent with recent observations of researchers (group of H Laudon) in Krycklan watershed.

Especially the proportion of wetlands and concepts like hydraulic load (see Behrendt 2000, Behrendt H, Opitz D. Retention of nutrients in river systems: dependence on specific runoff and hydraulic load. *Hydrobiologica*. 2000, 410:111–22) can give information about TE transport. This is very pertinent remark and we thank the reviewer for pointing out this useful reference. In fact, for the range of typical annual runoff of the WSL (200-300 mm), up to 75% of N and P exported to the river from the watershed can be retained by the river. In this work, we did not address N and P behavior but Si retention can be important. To which degree the concepts developed for N, P and metal pollutants in western European rivers (Behrendt and Opitz, 2000; Vink et al., 1999) can be applied for biotically inert TE transport in pristine, half-year-frozen WSL rivers is uncertain. At quite low annual runoff of the WSL, significant retention of dissolved Fe, Mn, Al as oxyhydroxides and Si as coastal grass and diatoms in the river may occur. However, given that the size of the river and thus, water residence time in the channel) have insignificant effect on concentration of these and other TE (see section 3.3.1), we argue on negligible impact of TE retention on element transport in WSL rivers. We added this in the Discussion (L674-L682).

The English in the ms is variable, from good to poor, especially in the introduction it is poor. This makes it hard to understand sometimes what the authors mean and I think some of the sentences should be rephrased. Presumably, the referee used our first version of the ms, submitted to BGD. The revised version of this ms posted on the website is significantly different from the first one, and some comments of the referee were addressed during first round of review. This is especially true for English proofread (done by BG office) and careful reference correction.

Line 132-134, 'However, it remains unknown, to which degree retaining of downward migrating DOC (and thus, organic complexes of TE) on mineral horizons in the south

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may be outweighed by enhanced TE mobilization from mineral horizons and waterrock interaction at the depth., what this means I don't know, I may guess, but it is better if the authors clarify what they mean. We removed this sentence and completely revised this part of the text (see L 132-137)

Specific comments of reviewer No 3 Line 72 Clarify what you mean by that the size of catchment determines the amount of groundwater feeding. I cannot see that this is mentioned in the Beaulieu text, is this motivated by the critical zone concept or has it to do with the fact that permafrost is in the region, please clarify. We revised this sentence as: "Because in the permafrost zone the size of the watershed determines the degree of groundwater feeding, river specific discharge and water residence time (i.e., Nikitin and Zemtsov, 1986; Novikov et al., 2009), the effect of the river size on TE transport becomes an issue of high academic and practical importance. This may become especially relevant for testing various models of chemical weathering and element migration in the Critical Zone of the Arctic and sub-arctic (i.e., Beaulieu et al., 2012)."

Line 151 What is meant by the 400 30, I guess that is the variation of some sort (standard deviation, range, confidence interval). Please specify. See also line 152. This is s.d. Added in the text accordingly.

Line 189 Do you have any idea why the contamination from Zn was so high? Can this have an effect on other elements as well? Zn is one of the major contaminant during sampling and filtration. This is especially true for winter period in WSL, given that the snow water concentration exceeds river water concentration by a factor of 10 to 100 (see Figure 2).

Line 200 Did you recalibrate when the certified standard was too far away or did you drift correct using another standard? We applied drift correction using another standard (highly diluted digested BCR-482 lichen or EPOND in-house standard). Added.

Line 201 What is meant by intrinsic uncertainty? Analytical (instrumental) uncertainty. Corrected.

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Line 216 Kruskal-wallis test is new to me, I guess that the authors mean Kruskal-Wallis test. Please check the spelling throughout the ms, different variants exists (like kryckalwallis in line 339) in the text. We corrected as “Kruskal-Wallis”.

Line 248 Should be  $R > 0.55$ ,  $p < 0.05$ . Agree and corrected.

Line 253 Figure 2 is rather hard to read, is it possible to to do a loadings plot instead with lines ending with the component names? We revised this figure and clearly identified variables and factors. We also generated a loading plot as requested (Figure 3). However, a F1 x F2 diagram allows better judge the factorial structure of the data and see the relative role of first or 2nd factor on each component.

Line 279, 280, 292, 294, 384 Please provide statistical test for significant/significantly or rephrase (for example much lower, higher). I think the word significant only should be used when referring to statistical tests. We replaced the terms as recommended or provided the statistical tests.

Line 350 Trend were statistically significant for Sr, Mo and U, why do you think it is so, two redox elements and one that is not? This finding is also intriguing for us. We do not think that strongly anoxic conditions capable to immobilize Mo and U are encountered in WSL shallow soils and river watersheds. Rather, we hypothesize concomitant increase of Sr and uranyl (as carbonate complexes) from carbonate-bearing mineral soils (L 550-555) and pH control of Mo and other oxy-anions (L 556-568)

Line 402 Please provide what 30% means, confidence interval, standard deviation, range. Corrected as “from 10 to 70%”.

Line 430 How common is it to find clay minerals in soils in the northern river catchments? Clay minerals are quite common in WSL (Vasil'evskaya et aal., 1986; Tyrtikov, 1973).

Line 462 Watershed area and discharge does not have an effect on the TE transport, as postulated in the introduction. DIC and DOC seems to be the most important factors

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controlling TE. This was also evident from analysis of major cations. I think it is surprise that discharge does not have any effect since this control the amount of DIC and DOC (depending where the water comes from in the soil). I think that this needs a comment. In this §we state that “the watershed size (and thus discharge) do not control element concentration”. We have no doubt that the discharge has primary effect on DOC, DIC, and all TE fluxes in rivers. DOC does control the element mobilization from the soil to the river as we stated in the revised version (L496-500).

Line 556, 559 Give an explanation for the +/-5 and +/-30. Revised as range of %.

Line 567 Intrinsic uncertainty, explain what you mean. The uncertainties on the flux evaluation, revised accordingly (L 610)

Line 568-575 In view of this information it would be interesting to also have information on bedrock and soil. These data can then also be used, by for example performing a PCA to give statistical information on the control of element fluxes. Is this information available? Quantification of different rock lithology on watersheds of 60 rivers of WSL was beyond the goal of this study. However, this work is in progress and a PCA of lithological/landscape control of element concentration in WSL rivers will make a subject of separate publication. If not please give information, with for example a reference, about the extension of carbonate and silicate rocks in the Dvina area. We added a pertinent reference as requested.

References Should be sorted by author and then chronologically. Revised. Pokrovsky et al, 2002, missing in reference list. Removed from the text. Huh et al 1998 is 1998b in the list. Corrected. Frey and Smith (2007) is not in the list, only 2005 not 2007. Added Frey and Smith (2007) Pokrovksy and Schott (2002) is missing in the list. Removed from the text. Huh et al (1998) in the text but in the list Huh et al (1998b) Dahlqvist et al (2007) but in the list 2005. Corrected. Frey and McClellan (2009) is in the list but not in the text. Corrected.

We thank Referee No 3 for very helpful suggestions and remarks.

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Please also note the supplement to this comment:

<http://www.biogeosciences-discuss.net/12/C9704/2016/bgd-12-C9704-2016-supplement.pdf>

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Interactive comment on Biogeosciences Discuss., 12, 17857, 2015.

**BGD**

12, C9704–C9712, 2016

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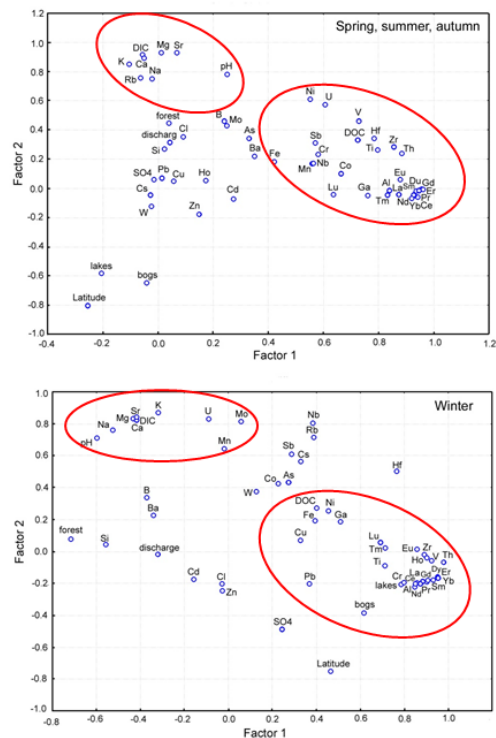
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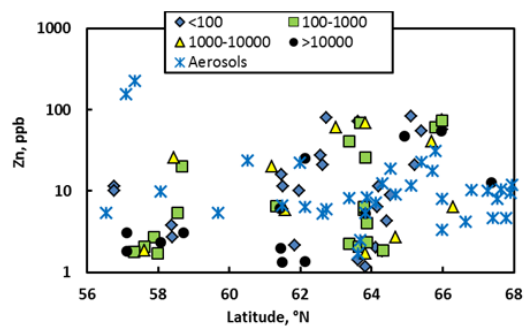
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- A** **Figure 1.** A PCA analysis. PCA analysis of ~50 variables in ~60 rivers sampled during open-water period (A) and in winter (B). The first factor (21% Var.) comprises DOC and insoluble trivalent and tetravalent hydrolysates. The second factor (18% Var.) is latitude which is inversely correlated with soluble major and trace elements, alkali and alkaline earth metals, oxyanions and U whose concentration decreases with increasing latitude. This factor is linked to the proportion of bogs and lakes on the watershed: bogs and lakes decrease the input of elements to the rivers, whereas the forest increased the element export. The impact of bogs, forest and lakes is mostly visible during open-water season but the impact of latitude is strongly pronounced in winter.
- B**

Fig. 1.



**Figure 2.** Winter snow soluble concentration of Zn (blue asterisk) compared with actual concentrations in rivers during spring flood (May-June) of different size of the watershed (diamonds, squares, triangles and circles correspond to < 100, 100-1000, 1000-10,000 and > 10,000 km<sup>2</sup> surface area, respectively) in western Siberia along the latitudinal gradient (Shevchenko et al., 2016 in preparation).

**Fig. 2.**

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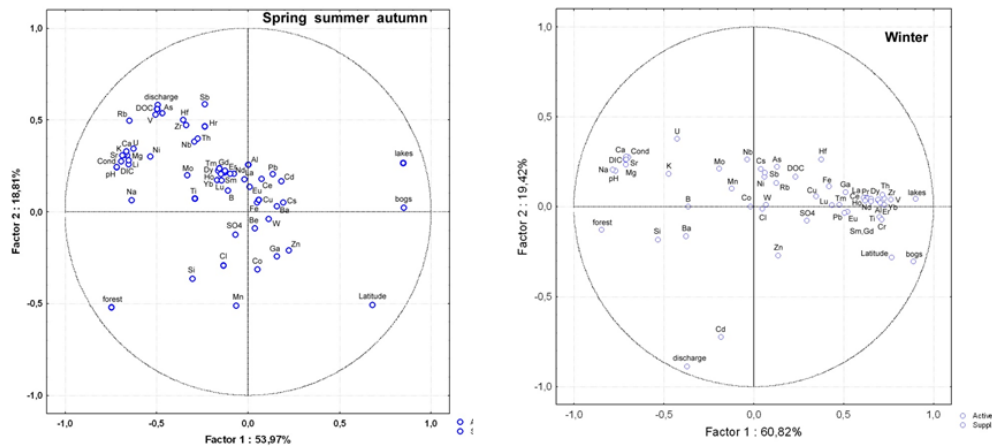


Figure 3. PCA results presented as loadings plot.

Fig. 3.

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