Response to Reviewer No 2

Although the dataset is interesting, there is a lack of focus in the manuscript through which the reader gets lost in all the details and has difficulties to follow the reasoning of the authors and to understand what's the actual outcome of the study. We agree about the overloading of the mansucript by details. This is mainly due to large spread of geographical transect and significant number of major and trace elements (~ 50) considered in the same work. We would like to point out that the general objective and specific tasks, the working hypothesis and specific objectives are presented in L1-26 p. 17862, whereas the synthehtic outcome of the work is illustrated in Fig. 13 and explained in Conclusions on p.17886.

In addition, the English is overall average to poor, which does not contribute to a clear presentation of results and interpretation. We agree with this comment and greatly revised the English of the manuscript. We would like to point out that the paper was English proof read by BGD office (payed service)

As the title suggests, the focus should be more on the permafrost gradient. The authors refer frequently to latitude patterns. If they use latitude pattern as a synonym for permafrost gradient, then I would suggest to use the latter. In the end we are interested in the effect of the permafrost gradient on the elemental chemistry and not the change in latitude of the watershed. We totally agree and replaced the term "latitudidnal gradient" by "permafrost gradient" throughout the text. However, we have to use the latitude for data presentation because it bears quantittiave meaning. Note that in accord with other reviewer request, we added the treatment of the data that included the percentage of permafrost coverage of the watershed (see reply to Reviewer No 3).

Another general comment, the authors should be more clear why we are interested in the distribution of certain elements such as Mo, V, Ba,: : : Also on what basis did the authors decide to show the distribution of Mo in the manuscript while for other elements (e.g. Ti) it has been included in the supplementary information? In other words, why are certain elements considered to be more interesting/important than others and therefore merit to be in the manuscript and not in the supplementary information? Following the first round of review of this ms, we have to place significant part of figures in the Supplement. Therefore, we decided to keep representative elements (metals, micronutrients, toxicants in the main text). The distinction between different groups is simply based on the element behavior as a function of latitude or permafrost coverage: only the elements exhibiting clear and statistically significant trends are discussed in details in the manuscript and presented in the main figures. These are elements most senstive to the permafrost presence. As it is stated in L7-18 (p. 17868),

"In the results presentation below, we will focus on few distinct groups of similar elements according to their chemical properties (i.e., alkalis, alkaline-earths, divalent metals, tri- and tetravalent hydrolysates, oxyanions and neutral molecules), following the similarity of element behavior in surface waters of western Siberia (e.g., Manasypov et al., 2014, 2015; Vorobyev et al., 2015). Special attention will be given to Fe and Al, the major colloidal carriers whose concentration and transport essentially control the migration of all other trivalent and tetravalent hydrolysates in surface waters of western Siberia (Pokrovsky et al., 2011, 2013; Shirokova et al., 2013). Besides, we analyzed in details the behavior of Sr, Mo

and U because these elements are most affected by the permafrost abundance, or the latitudinal position of the watershed, the central question of this study."

Abstract Lines 25-32 : this section needs restructuring. Three trends (categories) are suggested but in the end there are so many exceptions that it becomes very unclear what the actually trend is for each element. Maybe the authors could first subdivide the elements into two groups : (1) elements that show the same trend throughout the year and (2) elements that show seasonal differences. Then discuss the variability per season, e.g. in spring elements Fe, Al, REEs, Pb, Zr, Hf, Mn, Co, Zn and Ba show a northward increase while elements Ni, Cu , Zr, Rb show a southward decrease. We agree and revised the Abstract significantly (see below).

Note that the authors contradict themselves, they mention that Zr both increases (line 27) and decreases (line 35) northward during spring. Agree and corrected this contardiction: Zr decreases northward during spring and increases during winter.

Line 25 : specify the meaning of TE. Trace elements, fixed.

Line 31 : Ti does already appear in category 1 (line 27). Do the authors mean that Ti does not show any distinct trend in spring and autumn? This needs to be made more clear. Yes, we corrected the text accordingly: Ti does not show any distinct trend in spring and autumn.

Line 32 : Very confusing, category 1 does already describe the metals which show a northward increase in spring (line 26) so why is this trend discussed again in this line? We completely revised this part of the Abstract as following:

"Two groups of elements were distinguished: (1) elements that show the same trend throughout the year and (2) elements that show seasonal differences. The first group included decreasing northward during all seasons (Sr, Mo, U, As, Sb) marking the underground water influence of river feeding. The elements of second group exhibited variable behavior in the course of the year. A northward increase during spring period was mostly pronounced for Fe, Al, Mn, Co, Zn and Ba and may stem from a combination of enhanced leaching from the topsoil and vegetation and bottom waters of the lakes (spring overturn). The increase of element concentration northward only in winter was observed for Ti, Ga, Zr and Th whereas Fe, Al, REEs, Pb, Zr, Hf, increased northward both in spring and winter, which could be linked to leaching from peat and/or redox processes and transport in the form of Fe-rich colloids. A spring time northward decrease was observed for Ni, Cu, Zr and Rb. The southward increase in summer was strongly visible for Fe, Ni, Ba, Rb and V, probably due to peat/moss release (Ni, Ba, Rb) or groundwater feeding (Fe, V). Finally, B, Li, Cr, V, Mn, Zn, Cd, Cs did not show any distinct trend from S to N whose variations within each latitude range were higher than the difference between latitudinal ranges."

Introduction The introduction lacks discussion of the elements discussed in the paper. Why are we interested in the distribution of the discussed trace elements (e.g. REE, Mo, V, Ga, Be, : :)? How is their distribution in other similar regions e.g. Alaska, Canada. What parameters control their distribution in those regions? All measured trace elements (ca. 40 elements) are discussed in our manuscript. We are afraid that discussing them in the Introduction will make the reading very difficult and greatly enhance this already long paper. Note that the available information on trace elements in other boreal and subarctic rivers is discussed in section 4.1 and 4.2. To our knowledge, no information on TE in rivers of different size over full hydrological cycle of the year, covering large gradient of the permafrost are available for Alaska and Canada.

Line 68 : What do the authors mean by geochemical traces ? We corrected as following: ”biogeochemical cycles of essential micronutrients (Fe, Zn, Ni, Mn, Mo), geochemical traces (Sr, REE) and contaminants (Cd, Pb, As…) at the Earth surface.”

Study site and methods line 186 : After storage, were the samples dried down before analysis on the Agilent ? No, filtered river water samples were processed directly on the ICP MS.

Line 221: Did the authors apply any transformations to the dataset before PCA? Concentrations are a closed system as everything is calculated relative to 100% to get out of this system, which is essential for PCA, generally log transformations are applied. Yes, we did applied the log transformation. Both rang-transformed and non-transformed data were used for analyses.

Results line 234 : Can the authors explain why they chose Fe and Al as tracers. As it is stated in the text (L 18-22 p. 17866), Fe and Al were chosen as main tracers of TE mobilization from surface and underground reservoirs and TE colloidal carriers in Siberian rivers and lakes, whose presence may limit the transport of heavy metals and hydrolysates in the form of high molecular weight organic and organo-mineral colloids, see Pokrovsky et al., 2006, 2012).

line 237 : On the other hand: : : Can the authors explain why and/or add a reference ?
We added: Voronkov, 1966; Beaulieu et al., 2012; Tank et al., 2012:

Voronkov, P. P., Sokolova, O. K., Zubareva, V. I., and Naidenova, V. I.: Hydrochemical features of local discharge during spring flood from the soil coverage of European territory of the USSR, Trudy GGI (Proceedings of State Hydrological Institute), 137, 3–57, 1966 (in Russian).

Tank, S. E., Raymond, P. A., Striegl, R. G., McClelland, J. W., Holmes, R. M., Fiske, G. J., and Peterson, B. J.: A land-to-ocean perspective on the magnitude, source and implication of DIC flux from major Arctic rivers to the Arctic Ocean, Global Biogeochem. Cy., 26, GB4018, doi:10.1029/2011GB004192, 2012.

Line 256: I don’t really see how the first factor is marked by DOC and UV_{280nm}, both are located within the cloud of data points. The negative trend seems to be controlled by DIC on the one hand: the distribution of Ca, Sr and Mg, defined by DIC and thus ground-water feeding of rivers and water-rock interactions in the basement (line 238). The other end of the negative trend is marked by REE.
Among major components, the DOC exhibited the highest PCA value (0.70), and thus it is tentatively considered as first factor. Based on novel information on watershed bog/forest/lake coverage, requested by the 3rd reviewer, we completely revised the description of PCA results, as presented in revised version of the paper attached to our response to reviewer No 3.

The correlation/ or lack of correlation with DOC and Al, Ti, : : : could be verified with correlation plots. We agree with this remark but we believe that the matrix correlation table given in the Supplement (Table S2) with significant ($p < 0.05$) correlations indicated in bold allows compact representataion of all correlations. Addding requested plots will enormously increase the length of the paper.
As a result I am not convinced that the PCA results really contribute to the interpretation of the data. Also both factors explain less than 50% of the variability in

the data. It would be nice to see the fractionation of communalities. We believe that simultaneous consideration of 50 element concentration and physico-geographical parameterss of the watershed (size, latitude, forest/bog/lake coverage) requires a PCA treatment. We tried to condense our PCA results presentation as much as possible and can place it to the Supplement.

Line 268: seems an over-interpretation of the data; The focus should not be on what explains the 5% variability in the dataset but the 70% which is not discussed in the paper. We agree and removed this paragraph accordingly.

line 276 : this sentence should be moved to line 234. Agree.

line 278 : Is this a general statement our specific to this project? If it is specific to the project then this sentence belongs in the discussion section otherwise add a reference. We removed this general sentence from the presentation of results. The groups of elements according to their chemical properties and affinity to DOM are discussed in section 4.2.

line 294 : Mn seems to be rather constant for all three seasons especially compared to Zn and Pb. I don't think you can say that Mn increases northward in spring. We agree and corrected the text and Abstract accordingly.

line 329 : which elements ? Trivalent hydrolysates such as Al, Ga, Y, REEs.

lines 380-384 : What is the interest of calculating fluxes across latitudinal gradients for all elements when clearly from figs. 4-11 there are elements which are not affected by latitudinal changes ? The calculating of TE annual fluxes in WSL rivers can be averaged over full latitudinal range for most elements which are not systematically affected by the latitude (or permafrost). These values can be compared with available fluxes in other boreal rivers of the world. Such a comparison is crucial for discussion of weathering and TE export. The elements strongly affected by latitudinal changes cannot be used for such a flux calculation.

Discussion Overall, references and/or a more detailed explanation are missing for made statements. We greatly revised the Discussion and provided necessary explanations.

Line 428 in contradiction with line 427: If mobile element concentrations decrease northwards regardless season then this can not be due to change in chemical weathering with temperature as temperatures change with seasons. A decrease of mobile element such as alkalis and alkaline-earths, oxyanions concentration northward in the WSL may be due to decrease of chemical weathering intensity with the temperature as it is known from both temperate and boreal catchment (Oliva et al., 2003; Beaulieu et al., 2012). The temperature changes with season both in the south and in the north. It is essentially the open-water period (spring to fall) which determines the intensity of chemical weathering, and during this period the temperature of soils in the south is higher than that in the north.

Line 434 in contradiction with line 430 and 428: if the distribution of elements is not dependant on the river size (line 428) than their distribution cannot be explained by a decrease in degree of groundwater feeding (430) as the river size impacts the impact of groundwater input (line 434). We agree with this and above given comment of the reviewer and removed the term "regardless of the season and the river size" from the revised text.

Line 472: "clearly" is not appropriate here, see previous comments. Agree and modified as " The PCA results revealed two possible factors…"

Line 533: What does the latter refer to? Unclear transition in text, please clarify. Revised as "The decrease of Sr, Mo and U concentration northward is detectable in all four main compartments…"

Line 569:What does "re-increase" refer to? Revised as "An increase of element concentration in rivers north of 66°N compared to permafrost-free zone, especially visible for…"

Line 574: add reference. There doesn't exist any geochemical profiles of peatlands in Siberia to have an idea of how much of these metals are stored in these bogs? If these bogs are ombrotrophic then they are only fed by atmospheric deposition. Accordingly, it would seem rather unlikely that large amounts of metals would be leached from these bogs. We agree and removed second explanation. The revised text states now "We can hypothesize the influence of marine sediments underlying frozen peat in the 50-100 km vicinity of the shoreline (see section 4.3 below for surface profile). Indeed, the ground vegetation may be enriched in seawater aerosols transported from unfrozen coastal waters in the form of rain and fog. An increase of B, Sr, Mo, Rb, U and also Na, Mg, K, Ca of marine origin in large thermokarst lakes north of 68°N relative to discontinuous permafrost zone was reported for the northern part of the WSL (Manasypov et al., 2014)."

Line 599: add reference. We added "(Tyrtikov, 1973; Khrenov, 2011)."

Line 614: Can the location of active layer not be included in the PCA? Unfortunately, we do not have the information of the average thickness of active layer (ALT) for all individual rivers of our data set. This remark is very pertinent, and PCA treatment of the river chemistry together with permafrost coverage and ALT will be a subject of future research.

Line 620: add reference. We added Kremenetsky et al., 2003

Lines 507 and 626: Does this mean that melt in Spring is minimal? Yes, it does not contribute very much in the total annual flux in the northern, permafrost-affected regions. However, the surface-frozen peat in early spring in the south does prevent the infiltration of surface waters to deep mineral horizons in the southern, permafrost-affected zones.

Line 695: How were these factors calculated? The PCA analyses of full dataset identified two possible factors. We revised the text accoridngly.

Line 720: latitude should be replaced by permafrost gradient. Changes with latitude, is not really what is interesting. As the title indicates, changes with permafrost is what matters. We fully agree and corrected the text accordingly.

Technical corrections:
Title: Please replace "trace elements transport" by "Trace element transport". Fixed.

Line 25 : three categories We revised as “Two groups of elements were distinguished:” in accord with previous remarks of this reviewer

Line 32 : a northward increase - Fixed.
Line 67 : rephrase “Transport of trace element” into “Trace element transport” - Fixed
Line 68 : Earth’s surface -Fixed
Line 89 : colloidal form - Fixed
Line 92 : major and trace elements - Fixed
Line 93 : of these regions to climate change - Fixed
Line 116 : was first the assessment of TE concentrations and fluxes across significant gradients of permafrost – Corrected
Line 123 : major element transport - Fixed
Line 137 : this study aims at - Fixed
Line 147 : and are represented - Fixed
Line 148 : WSL, carbonate concretions and shells - Fixed
Line 212 : trace element concentrations in rivers - Fixed
Line 228 : major and trace element concentrations - Fixed
Line 252 : trace element carriers - Fixed
Line 312: TE concentration variations - Fixed
Line 325 : pronounced than those - Fixed
Line 488: not allow to explain - Fixed
Line 511: by the TE concentration trend observed in the WSL rivers (Figs. 9-11 and Figs. S7-S8 and section 3.2). - Fixed
Line 702: On the other hand - Fixed
Line 739: On the other hand - Fixed

We thank reviewer No 2 for his/her very constructive and insightful comments.