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Trace elements transport in western Siberia rivers across a permafrost gradient

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Trace elements transport in western Siberia rivers across a permafrost gradient

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Abstract

Towards a better understanding of trace element transport in permafrost-affected Earth surface environments, we sampled ~ 60 large and small rivers (< 100 to ≤ 150 000 km^2 watershed area) of Western Siberia Lowland (WSL) during spring flood and summer and winter base-flow across a 1500 km latitudinal gradient covering continuous, discontinuous, sporadic and permafrost-free zones. Analysis of ~ 40 major and trace elements in dissolved (< 0.45 µm) fraction allowed establishing main environmental factors controlling the transport of metals and trace elements in rivers of this environmentally important region. No statistically significant effect of the basin size on most TE concentration was evidenced. Three category of trace elements were distinguished according to their concentration – latitude pattern: (i) increasing northward in spring and winter (Fe, Al, Ga (only winter), Ti (only winter), REEs, Pb, Zr, Hf, Th (only winter)), linked to leaching from peat and/or redox processes and transport in the form of Fe-rich colloids, (ii) decreasing northward during all seasons (Sr, Mo, U, As, Sb) marking the underground water influence of river feeding and (iii) elements without distinct trend from S to N whose variations within each latitude range were higher than the difference between latitudinal ranges (B, Li, Ti (except summer), Cr, V, Mn, Zn, Cd, Cs, Hf, Th). In addition to these general features, specific, northward increase during spring period was mostly pronounced for Fe, 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). A spring time northward decrease was observed for Ni, Cu, Zr, 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).

The Principal Component Analysis demonstrated two main factors potentially controlling the ensemble of TE concentration variation. The first factor, responsible for 16–20 % of overall variation, included trivalent and tetravalent hydrolysates, Cr, V, and DOC and presumably reflected the presence of organo-mineral colloids, as also confirmed by previous studies in Siberian rivers. The 2nd factor (8–14 % variation) was

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linked to the latitude of the watershed and acted on elements affected by the groundwater feeding (DIC, Sr, Mo, As, Sb, U), whose concentration decreased significantly northward during all seasons.

Overall, the rank of environmental factors on TE concentration in western Siberian rivers was latitude (3 permafrost zones) > season > watershed size. The effect of the latitude was minimal in spring for most TE but highly visible for Sr, Mo, Sb and U. The main factors controlling the shift of river feeding from surface and subsurface flow to deep underground flow in the permafrost-bearing zone were the depth of the active (unfrozen) seasonal layer and its position in organic or mineral horizons of the soil profile. In the permafrost-free zone, the relative role of carbonate mineral-bearing base rock feeding vs. bog water feeding determined the pattern of trace element concentration and fluxes in rivers of various size as a function of season.

Comparison of obtained TE fluxes in WSL rivers with those of other subarctic rivers demonstrated reasonable agreement for most trace elements; the lithology of base rocks was the major factor controlling the magnitude of TE fluxes. The climate change in western Siberia and permafrost boundary migration will affect essentially the elements controlled by underground water feeding (DIC, alkaline-earth elements (Ca, Sr), oxyanions (Mo, Sb, As) and U). The thickening of the active layer may increase the export of trivalent and tetravalent hydrolysates in the form of organo-ferric colloids. Plant litter-originated divalent metals present as organic complexes may be retained via adsorption on mineral horizon. However, due to various counterbalanced processes controlling element source and sinks in plants – peat – mineral soil – river systems, the overall impact of the permafrost thaw on TE export from the land to the ocean may be smaller than that foreseen by merely active layer thickening and permafrost boundary shift.

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1 Introduction

Transport of trace element (TE) by rivers is the main factor controlling biogeochemical cycles of essential micronutrients, geochemical traces and contaminants at the Earth surface. Whereas the majority of large rivers are systematically (Cooper et al., 2008; McClelland et al., 2015) or occasionally (Gordeev et al., 1996; Seyler et al., 2003; Pokrovsky et al., 2010) monitored for some TE concentration and fluxes, this is not the case for smaller rivers, unless these rivers are affected by anthropogenic activity or local pollution. Because the size of the watershed determines the degree of groundwater feeding, river specific discharge and water residence time, the effect of the river size on TE transport becomes an issue of high academic and practical importance, essential for testing various models of chemical weathering and element migration in the Critical Zone (i.e., Beaulieu et al., 2012). However, straightforward comparison of element concentrations and fluxes in watersheds of various sizes is possible only in pristine regions of homogeneous runoff and landscape types (equatorial forest, tundra, or boreal biome of the platforms), where the seasonal aspect is often hard to resolve due to the difficulty of year-round access to the river or the lack of hydrological background.

In this regard, orographically flat, homogeneous, peat-covered western Siberia Lowland (WSL) offers a unique chance of testing various aspects of riverine element transport on relatively pristine territory with reasonably good knowledge of hydrology and runoff across a very large gradient of climate and vegetation. A very important aspect of western Siberian rivers is the dominance of peat soils, producing high concentration of Dissolved Organic Matter (DOM) of allochthonous (humic and fulvic) character. In the presence of dissolved organic, many typically insoluble, low mobile elements, notably trivalent and tetravalent hydrolyzates and some divalent metals, become highly labile being present as organic or organo-mineral colloids, i.e., entities between 1 kDa (~ 1 nm) and 0.45 µm (Stolpe et al., 2013; Porcelli et al., 1997). This colloidal from of migration greatly enhances the fluxes of TE from the soil to the river and finally, to the ocean. As a result, even small rivers of this region may turn out to be very important vectors of TE fluxes.

At present, the interest to aqueous geochemistry of major and trace element in permafrost-affected regions is rising due to high vulnerability of these regions to the climate change and the possibility of release of solutes previously stored in frozen soils and ice (see Anticibor et al., 2014; MacMillan., 2015; Vonk et al., 2015). This is particularly true for WSL exhibiting (i) highly unstable permafrost, mostly sporadic and discontinuous, and (ii) high stock of frozen organic matter (peat horizons), potentially containing elevated concentrations of many metals (Cu, Zn, Pb, Cd, Ba) accumulated in peat. In this regard, WSL allows studying the mobilization of organic-bound metals from frozen soil to the river across more than 1500 km gradient of permafrost coverage (absent, sporadic, isolated, discontinuous and continuous), vegetation (southern and middle taiga to tundra) and climate (0 to −9 °C MAAT) while remaining within relatively homogeneous nature of underlining lithology (sands and clays), soils (peat and podzols) and runoff (200 to 300 $\mathrm{mm\,yr^{-1}}$). Note that, in contrast to extensive studies of TE in rivers and streams of boreal regions of Scandinavia (Ingri et al., 2000, 2005; Wallstedt et al., 2010; Huser et al., 2011, 2012; Oni et al., 2013; Tarvainen et al., 1997; Lidman et al., 2012, 2014; Temnerud et al., 2013), Alaska (Rember and Trefry, 2004), Canada (Wadleigh et al., 1985; Gaillardet et al., 2003; Millot et al., 2003); Central Siberia (Pokrovsky et al., 2006; Bagard et al., 2011, 2013) and European Russia (Pokrovsky et al., 2002, 2010; Vasyukova et al., 2010), even punctual measurements of TE in western Siberia rivers (Ob, Nadym, Taz and Pur basin) with the exceptions of the Ob and Irtush river (Moran and Woods, 1997; Alexeeva et al., 2001; Gordeev et al., 2004) are lacking. Moreover, similar to other Siberian rivers (Pokrovsky et al., 2006; Huh and Edmond, 1999; Huh et al., 1998; Dessert et al., 2012) seasonally-resolved measurements of trace elements in WSL rivers are absent. At the same time, monthly monitoring of large Arctic rivers at the terminal gauging stations (Holmes et al., 2000, 2012, 2013) provide neither sufficient number of TE measurements nor the information on smaller rivers located within various climate and permafrost context.

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Therefore, the general objective of this study was first assessment of TE concentration and fluxes across significant gradient of permafrost in the WSL. Specific tasks were the following: (i) quantifying the effect of the watershed area (or river discharge) on TE concentration; (ii) assessing the difference of element concentration during main hydrological seasons (spring flood, summer and winter baseflow); (iii) revealing annual TE fluxes in rivers as a function of watershed latitude, and (iv) preliminary evaluation of the degree of flux modification under climate warming scenario and northward migration of the permafrost boundary.

As a working hypothesis, and following the concepts developed for major elements transport in WSL river (Frey et al., 2007a, b; Frey and Smith, 2005; Pokrovsky et al., 2015) we expect northward decrease of fluxes and concentrations of elements linked to the groundwater feeding, i.e., those originated from water-rock interaction at depth. At the same time, an increase of elements bound to organic colloids and linked to mobilization from surface (organic-rich) horizons in permafrost-affected regions compared to permafrost-free regions can be anticipated. This increase may be linked to limited downward migration of TE-DOM complexes and their low retention on frozen mineral horizon in the northern part of WSL, as it is reported for DOC (Kawahigashi et al., 2004; Pokrovsky et al., 2015)

However, it remains unknown, to which degree retaining of downward migrating DOC (and thus, organic complexes of TE) on mineral horizons in the south may be overweighed by enhanced TE mobilization from mineral horizons and water-rock interaction at the depth. In this scenario, one expects three distinct families of TE in terms of latitudinal pattern of their concentration and fluxes: (i) increasing northward, (ii) decreasing northward and (iii) indifferent to the latitude. This study is aimed at verifying the above mentioned hypothesis using rigorous statistics for a large number of rivers sampled during main hydrological periods.

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2 Study site and methods

2.1 Physico-geographical setting

Western Siberia Lowland (WSL) includes the watersheds of rivers Ob, Pur, Nadym, Taz and left tributaries of the Yenisei River draining Pliocene sands and clays. These sedimentary deposits are covered by thick (1 to 3 m) peat and enclose boreal taiga, forest-tundra and tundra biomes. The thickness of Quaternary clays, sands, and silts ranges from several meters to 200–250 m. The Paleogene and Neogene deposits are rarely exposed on the earth surface and represented by sands, alevrolites and clays. In the southern part of WSL, the carbonate concretions and shells are present within the claystone and siltstones (Geological Composition, 1958). The mean annual temperature (MAT) ranges from −0.5 °C in the south (Tomskaya region) to −9.5 °C in the north (Yamburg) with annual precipitation of 400 ± 30 mm over 1500 km latitudinal gradient. The river runoff gradually increases northward, from 190±30 mm yr^{-1} in the permafrost-free Tomskaya region to 300±20 mm yr^{-1} in the discontinuous to continuous permafrost zone (Nikitin and Zemtsov, 1986). Further physico-geographical description, hydrology, lithology and soils can be found in Botch et al. (1995); Smith et al. (2004); Frey and Smith (2007); Beilman et al. (2009) and more recent studies of Shirokova et al. (2013), Manasypov et al. (2014, 2015), and Stepanova et al. (2015). A map of studied region together with main permafrost provenances, bedrock lithology, active (seasonally unfrozen) layer depth, and river runoff in WSP is given in Fig. 1. More detailed river description and localization of watersheds are presented in Pokrovsky et al. (2015).

The mean multi-annual monthly discharges of WSL rivers are available from systematic surveys of Russian Hydrological Survey (Hydrological Yearbooks of RHS), generalized in Nikitin and Zemtsov (1986) and also compiled in R-AcricNET database (www.r-arcticnet.sr.unh.edu). In this study, due to limited number of observation over the year, the river discharge for each river was averaged for each 3 seasons of sampling (May to June, July to September, and October to April). In addition, systematic hydrological study of State Hydrological Institute in 1973–1992 in the northern part

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of western Siberia allowed reliable evaluation of small and medium rivers discharges (Novikov et al., 2009). Details of small WSL rivers discharge calculation are presented in previous publication (Pokrovsky et al., 2015).

2.2 Sampling and analyses

We sampled 60 rivers in early June 2013 (spring flood), 66 rivers in August 2013 and 2014 (summer baseflow), 13 rivers in October 2013 (autumn) and 55 rivers in February 2014 (winter baseflow), see Table S1 in the Supplement. The sampling points were located some 100–200 m upstream the river where it was crossing the regional road. The traffic on WSL roads is quite low and thus the pollution from the road is expected to be minimal. Several tests were made during summer baseflow on the same rivers sampled at different distances from the road bridge. Regardless of the size of the river, from few to 10 000 km^2 watershed, this test did not yield any statistically significant difference ($p > 0.05$) in the concentration of all TE. The watershed area of sampled rivers ranged from 2 to 150 000 km^2, excluding Ob in its medium course zone. The waters were collected from the middle of the stream for small rivers or at 0.5 m depth 1–2 m offshore on the large rivers using vinyl gloves and pre-washed polypropylene (PP) jars. Collected waters were immediately filtered in cleaned 30 mL PP Nalgene® flacons through single-use pre-washed filter units Minisart (Sartorius, acetate cellulose filter) having a diameter of 33 mm and a pore size of 0.45 µm. The first 20 to 50 mL of filtrate was discarded. Filtered solutions for trace analyses were acidified (pH ∼ 2) with ultrapure double-distilled HNO_3 and stored in the refrigerator. The preparation of bottles for sample storage was performed in a clean bench room (ISO A 10 000). Blanks of MilliQ water were processed in the field in parallel to samples in order to control the level of pollution induced by sampling and filtration. For most trace elements except Zn, these blanks were less than 10 % of the element concentration in the sample. For several rivers in winter, the Zn blanks were 30 to 50 % of their sample concentration and these data were not used in the discussion. Analyses of DOC, pH, major cations and anions and their uncertainties are described in details in previous publication (Pokrovsky et al., 2015). Note that in February, all rivers north of 66° N, in the continuous permafrost zone, except the largest Khadutte watershed (4933 km^2) were completely frozen: under 1.5–2 m ice thick, no water was found within 20 cm of the solid mineral ground.

Trace elements were determined with an ICP-MS Agilent ce 7500 with In and Re as internal standards and 3 various external standards, placed each 10 samples in a series of river water. The SLRS-5 (Riverine Water Reference Material for Trace Metals certified by the National Research Council of Canada) was measured each 20 samples to check the accuracy and reproducibility of the analysis (Yeghicheyan et al., 2013). The typical agreement with certified values was better than 10 % except for some elements (Ga, Y, W, Th) that yielded 20 to 30 % agreement. However, the intrinsic uncertainty on these element analyses was at least 20 %, so the agreement was considered as acceptable. Further details of TE analysis in boreal organic-rich surface waters, uncertainties and detection limits are presented in previous publications of our group (Pokrovsky et al., 2013; Shirokova et al., 2013; Manasypov et al., 2014, 2015).

2.3 Statistical treatment of the data and element speciation in the river water

The concentration of carbon and major elements in rivers were treated using the least squares method, Pearson correlation and one-way ANOVA (SigmaPlot version 11.0/Systat Software, Inc). Regressions and power functions were used to examine the relationships between TE concentration and the watershed area, latitude, and seasons. Trace element concentration in rivers of (1) three main permafrost zones (continuous, discontinuous and permafrost-free regions), (2) 6 latitudinal classes of the watershed (56–58, 58–60, 60–62, 62–64, 64–66 and 66–68° N), (3) during three main seasons and (4) 4 watershed size classes (< 100, 100–1000, 1000–10 000, and > 10 000 km^2) were processed using non-parametric H criterium Kruskal–Wallis test. This test is suitable for evaluation of difference of each TE among several samplings simultaneously. It is considered statistically significant at $p < 0.05$. However, we found that a p level of < 0.0001 corresponding to $H > 30$ indicated more significant differences and thus it was also used in assessing the relative effect of season, latitude and the watershed size.

Principal Component Analysis (PCA) was used to compute and interpret the spatial structures of TE in rivers using the STATISTICA package (http://www.statsoft.com). This treatment was used both for the full set of sampled rivers for all seasons simultaneously and for each season individually. Here, we considered the average latitude of the watershed and its watershed area, pH, and all major and trace element concentration as numerical variables.

Metal speciation and complexation with DOM in the river water was modeled using visual Minteq code (version 3.1, Gustafsson, 2014). For vMinteq calculation, season-averaged major and trace concentration of permafrost-free, discontinuous and continuous permafrost zone were used.

3 Results

3.1 Pearson correlation coefficient and PCA results

Full dataset of TE concentration in sampled rivers is available from the corresponding author upon request. Pearson correlation coefficients of TE with organic and inorganic carbon, Fe and Al are listed in Table S2 of the Supplement. For these correlations, dissolved organic and inorganic carbon (DOC and DIC, respectively), 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). From the other hand, DIC is most efficient tracer of ground-water feeding of rivers and it reflects the water-rock interaction in the basement. It can be seen from Table S2 that during open-water period (spring, summer and autumn), the DOC is statistically significantly ($p < 0.05$) correlated with Be (0.63–0.80), Al (0.59–0.72), Ti (0.56–0.70), V (0.71–0.82), Cr (0.63–0.87), Ni

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(0.71–0.88), Cu (0.66), Ga (0.66), Zr (0.85–0.86), Nb (0.53–0.76), REEs (0.6–0.8 in summer and autumn), Hf (0.62–0.80), Th (0.79–0.88) with the highest correlations always observed during summer. Several elements (Li, B, As, Sr, Mo, Sb, U) were more significantly correlated with DIC rather than DOC. In winter, only Sr (0.82) and U (0.80) were linked to DIC and none of TE was strongly ($R > 0.60$) correlated with DOC.

All insoluble, low-mobile trace elements were highly correlated with Al. This was mostly pronounced during summer ($0.8 \le R \le 0.98$) for Be, Ti, Cr, Co, Ga, Zr, Cd, REEs and Th. The correlation of these elements with Al was also significant ($R > 0.55$ at $p < 0.05$) in spring and autumn. The correlation of TE with Fe was not statistically significant during all seasons except winter, when Ti, V, Cr, Mn, Ga, As and Zr were correlated ($R > 0.5$, $p < 0.05$) with Fe, although the correlation coefficient of Ti, V, Cr and Zr was higher with Al than with Fe.

These preliminary links between trace elements carriers (DOC, Fe, Al) or proxies (DIC) were further examined using PCA (Fig. 2). Two factors, F1 and F2 were found to be capable explaining 21.5 and 11.4 % of variability of TE in all sampled rivers during all seasons. Noteworthy that the watershed area was not linked to these factors (−0.01 for F1 and 0.38 for F2). The first factor, marked by DOC and $UV_{280\,nm}$, was mostly visible for Be (0.86), Al (0.79), Ti (0.66), Zr (0.81), Nb (0.77), REEs (0.96–0.98), Hf (0.88) and Th (0.88). The second factor was clearly linked to the negative latitude of the watershed and was mostly pronounced for variation of specific conductivity (0.93), Mg (0.92), Ca (0.90), K (0.84), pH (0.82), DIC (0.90), Li (0.85), V (0.76), As (0.81), Sr (0.89), Mo (0.69), Sb (0.70), W (0.59) and U (0.68). Very similar structure of factors has been revealed when treating each season individually. The first factor was mostly pronounced in spring (16.8 and 8.6 % of variability for F1 and F2, respectively) whereas in summer the difference in the relative role of F1 and F2 decreased (15.8 and 10.3 %, respectively). Simultaneous treatment of all data on river water chemistry during open water seasons (spring, summer and autumn) yielded very similar factorial structure with the F1 (16.1 %) acting on DOC, UV, Al, Ga, Ti, V, Cr, Zr, REEs, Hf and Th and F2 (9.2 %) negatively linked to latitude and positively to pH, DIC, Na, Mg, K, Ca, B, As,

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Rb, Sr, Sb, Cs and U. Overall, one may notice high stability of F1 × F2 structure during different seasons.

The other possible factors (not shown) contribute less than 5 % to overall variation of TE concentration and potentially reflect aerosol uptake by terrestrial ground vegetation (B, Zn, Ba), proximity to the sea, as detected by sea salts and alkali and alkaline-earth elements (Na, Cl, Cs, Sr), and watershed area and river discharge, also linked to the groundwater feeding (SO_4, Sb, U).

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 previously revealed 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.

3.2 TE concentration dependence on the average latitude of the watershed

Concentration of TE as a function of the watershed latitude is shown in Figs. 3–11 and S1–S12 in the Supplement for three main hydrological seasons. The variability of TE within each latitudinal range was the highest for small-size catchments ($< 100\,km^2$). Considering all watershed sizes, several group of elements can be distinguished according to their basic physico-chemical properties and affinities to DOM. Trivalent hydrolysates such as Al, Ga, Y, REEs demonstrate no link between concentration and latitude in spring and summer and a significant, a factor of 10 to 100, increase northward during winter (Figs. 4 and S1). Fe and tetravalent hydrolysates Ti, Zr and Th also demonstrated significant northward increase in winter, the lack of visible latitudinal trend in spring and a decrease of concentration northward in summer (Fig. 3 for Fe and Fig. S2 for Ti as an example, respectively). The divalent metals (Mn, Zn, Co, Ni, Cu, Cd and Pb) yielded high variability of element concentration for the same latitudinal range, without distinct latitudinal trend in summer and winter (Mn, Ni, Co, Cu, Zn, Pb, Cd), an increase northward of concentration in spring (Mn, Co, Zn), and a decrease in spring (Ni, Cu). This is illustrated for Mn, Cu, Zn and Pb in Figs. 5–8, respectively and for Ni, Co, and Cd in Figs. S3–S5, respectively. Cr showed significant northward decrease in spring and increase in winter, without distinct latitudinal trend in summer (Fig. S6).

A number of elements exhibited very strong latitudinal trends regardless of the season and the watershed size. These are Sr (Fig. 9), Mo (Fig. 10) and U (Fig. 11). In a lesser degree, seasonally-persistent trend of northward concentration decrease is observed for B (summer and winter only, Fig. S7), As (Fig. S8) and Sb (not shown). Significant decrease of Li and Rb concentration in spring and V concentration in spring and summer was also visible for all watershed sizes (not shown). In contrast to Sr, Ba concentration increased northward in spring while significantly decreased during summer (Fig. S9).

Statistical treatment of these trends is described in the next section.

3.3 Statistical treatment of trace element concentration in WSL rivers

All sampled watershed were separated into four main classes of area: $< 100\,km^2$, 100 to $1000\,km^2$, 1000 to $10\,000\,km^2$ and $> 10\,000\,km^2$. Six latitude ranges were considered during 3 main hydrological seasons (56 to 58° N, 58 to 60° N, 60 to 62° N, 62 to 64° N, 64 to 66° N and 66 to 68° N). The significance of TE concentrations variation of each watershed size as a function of each latitudinal class was tested separately for each season and for the full period of observation.

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3.3.1 Effect of the watershed size and season

Based on H criterion of Kruskal–Wallis, the differences between watershed of different sizes were found quite low. In spring, only Ti, Ni, Cu, Ga, Zr, REEs, Pb, Th and U yielded slight effect ($H < 10$–15 and $p > 0.001$) of the size whereas concentration of all other elements were statistically insensitive to the watershed area. In summer, weak effect ($H \sim 10$, $p > 0.01$) was seen for Al, V, Ni, Cu, Rb, Mo and U with only Mn and Co showing some link to the size of the river ($H = 18.5$, $p = 0.0003$; $H = 16.4$, $p = 0.0009$, respectively). In winter, only Al showed significant effect of latitude ($H = 21.8$, $p = 0.0001$) whereas Ti, V, Cr, Fe, Sr, Zr, Ba, REEs and Pb yielded weak effect ($H < 15$, $p < 0.0001$). Finally, considering all seasons together, only U yielded significant impact of the watershed size ($H = 30.2$, $p < 0.0001$) whereas all other elements had $H < 20$ at $p > 0.001$.

The seasonal effects were tested for all river size and latitudes simultaneously. Generally, the seasonal variations were more significantly pronounced that those of the watershed size. Considering all river sizes across the full latitudinal profile, the effect of seasons was highly pronounced ($H > 25$, $p < 0.0001$) for Al, Ti, Mn, Fe, Co, Ga, Rb, As, Sr, Mo, Cd, Cs, Ba, HREEs, Hf, W, U). It was less important although statistically significant ($8 < H < 30$, $p \geq 0.0001$) for Li, B, V, Ni, Cu, Zn, Sb, LREEs, Pb and Th) and not visible for other elements.

3.3.2 Three permafrost regions and latitudinal trends

An assessment of the permafrost effect on TE concentration in river water is possible via distinguishing three categories of permafrost distribution in the WSL: permafrost-free, discontinuous and continuous permafrost zones. For these plots, we consider all seasons and river watershed sizes simultaneously. In terms of global permafrost influence, only Li, Sr, Mo and U depicted significant, 2 to 3 orders of magnitude decrease of concentrations northward (Fig. S10), consistent with statistical treatments (see below). Fe, Al and other trivalent hydrolysates demonstrated more than an order of magnitude

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increase in concentration in discontinuous and continuous permafrost zone relative to southern, permafrost-free zones (Fig. S11). This increase was most likely linked to significant rise in TE^{3+} concentration in winter in northern watersheds (see Sects. 3.2).

Considering all seasons simultaneously, for 3 permafrost zones, statistical Kruskal–Wallis test yielded significant impact of permafrost ($40 < H < 110$, $p < 0.0001$) for Li, B, Ni, Cu, As, Rb, Sr, Mo, Sb, Hf, W and U. In a much lesser degree ($8 < H < 30$, but typically from 10 to 15 at $p < 0.01$) the permafrost impacted Ti, V, Fe, Cs, Ba, and all REEs. All other elements including divalent metal micronutrients (Zn, Mn, Co) and pollutants (Cd, Pb) exhibited non-significant differences between different permafrost zones as illustrated in Fig. S12.

The Kruckal–Wallis test of 6 latitudinal classes in spring yielded highly pronounced effect ($H > 30$, $p < 0.0001$) of latitude on Li, V, Cr, Ni, Cu, As, Rb, Sr, Zr, Mo, Sb and U. During this period, the latitude effect was less visible ($10 < H < 30$, $0.001 < p < 0.05$) for Mn, Fe, Co, Zr, Nb, Cs, REEs, Hf, W, Pb and Th. In winter, 6 latitudinal classes were highly pronounced ($H > 30$, $p < 0.0001$) for Ca, DIC, Sr and U and less visible ($10 < H \leq 20$, $p < 0.05$) for B, Al, Ti, Cr, Mn, Fe, Co, Ga, As, Rb, Mo, Sb, Ba, REEs, Pb. In summer, the latitudinal classes were distinct ($H > 30$, $p < 0.0001$) for B, Cu, As, Rb, Sr, Mo, Ba, and U, and less pronounced ($10 < H < 30$, $0.001 < p < 0.05$) for Be, Ti, V, Cr, Fe, Ni, Zr, Cs, REE, Pb, Hf, W.

Considering all season together, six latitudinal classes were strongly pronounced ($H > 30$, $p \leq 0.0001$) for DIC, DOC, major cations and anions, Li, Be, B, V, Fe, Ni, Cu, As, Rb, Sr, Mo, Sb, Ba, Cs, Hf, W and U. The impact of the latitude was significant ($11 < H \leq 25$, $0.0001 < p < 0.05$) for Co, Zr, Nb, REEs, Pb and Th, and not significant for Al, Mn, Zn, Ga and Cd. In accord with the trends shown in Figs. 9–11, the latitude effect is most strongly pronounced for Sr, Mo, and U ($H = 122$, 110, and 123).

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3.4 Trace element fluxes in western Siberia rivers across the latitudinal gradient

Trace element fluxes were computed based on mean multi-annual monthly average discharge of sampled rivers and measured concentrations during three main hydrological seasons (spring flood, summer and winter baseflow including October), normalized to the watershed area at the point of river sampling. Considering high variability of concentrations among individual rivers at each latitudinal size range during a given season, the typical uncertainties of the average of several rivers in each latitudinal class (56–58, 58–60, 60–62, 62–64, 64–66 and 66–68° N) are between 20 and 30 %. Note that TE flux calculation may be biased by insufficient number of observations over the year, namely during long winter baseflow, and one single measurement during hydrologically important spring flood period. As such, the overall uncertainty of the annual fluxes of TE in each latitudinal range ranged between ±20 and ±50 % of the mean value. This uncertainty was calculated as the sum of uncertainties of each season. The uncertainty of each season flux was proportional to the contribution of this season to the annual flux. We consider this as reasonable evaluation given large variations of chemical composition of small rivers over the year. Besides, significant number of rivers in each latitudinal class, integrating all sizes of the watersheds including small, previously not studied streams ($< 1000\,km^2$), greatly enforces the representativity of our flux calculations.

Taking into account the abovementioned uncertainties, the majority of trace elements did not demonstrate statistically significant (at $p < 0.05$) latitudinal trend of export fluxes which was the case for some typical hydrolysates (Al, Ti, La, Zr, Th), oxyanions (B, As, Sb), and metals (Cr, Mn, Co, Ba, Rb, Cu, Pb). At the same time, many elements (V, Cr, Mn, Cu, Co, Ni, As, Zr, REEs, Th) demonstrated elevated flux in the northernmost latitudinal range, without clear trend in rivers south of 66° N. This single latitude range was not considered significant as it marked the elevated concentration of elements in only one river in winter and 4 rivers in summer and thus could be biased by the low number of sampled rivers. Because all rivers north of 66° N except the largest Khadutte (67.41° N, 4933 km^2) were completely frozen, the river fluxes in winter in this latitudinal range can be considered as zero. Neglecting winter-time fluxes in the latitudinal range 66–68° N removed anomalously high annual values for Cr, Mn, Fe, Cu, Zn, Co, As, Rb, Zr, REEs, Cd and Th rendering the northernmost fluxes of continuous permafrost zone for these elements similar to those of permafrost-free and discontinuous permafrost regions without statistically significant ($p > 0.05$) trend across the 1500 km latitudinal transect. Fe, Zn, and Cd demonstrated clear increase ($p < 0.05$) of fluxes northward (Fig. S13). This increase was more significant than the individual uncertainties in each latitudinal range.

The TE annual fluxes in WSL rivers can be averaged over full latitudinal range and listed in Table 1. A few elements (Sr, Mo, U) yielded distinct decrease of annual fluxes northward, with some re-increase in continuous permafrost zone, persistent even after removal of anomalously high winter-time concentrations of *r*. Khadutte (Table 1, Fig. S14). For these elements, no definite value of WSL river flux could be recommended.

3.5 Trace element speciation in western Siberia rivers

Element speciation in dissolved (< 0.45 µm) phase calculated using Stockholm Humic Model (vMinteq) is illustrated as stack diagram in Fig. 12. This calculation was performed based on seasonal-averaged concentrations of major and trace elements in three distinct geographical zones of WSL: permafrost-free, discontinuous and continuous permafrost. Trivalent hydrolyzates including Fe, Pb^{2+} and Cu^{2+} were present as > 90 % organic complexes, regardless of the type of permafrost abundance. Alkaline-earth metals and Mn^{2+} were essentially in the form of free ions having < 15 % of organic complexes. Transition metals exhibited variable proportion of organic complexes (from 20 to 60 %), without any trend related to the type of permafrost abundance. Considering all divalent metals, the following order of organic complexation was observed: Co < Cd ~ Zn < Ni ≪ Pb < Cu. Uranium exhibited most contrasting speciation between permafrost-free, DIC-rich rivers (40 ± 30 % of organic complexes) and permafrost-bearing zones (> 90 %). This contrast was linked to elevated concentrations of HCO_3^- ions in southern rivers, where inorganic U(VI)-carbonate species were prevailing.

4 Discussion

4.1 General features of TE migration across the permafrost gradient and trace elements correlations with DOC, DIC, Fe and Al and Principal Component Analysis

From general knowledge of environmental control on trace element fluxes in rivers of the Russian and Siberian subarctic (Pokrovsky and Schott, 2002; Pokrovsky et al., 2006, 2012) and other boreal and subartic regions (Huh et al., 1998; Millot et al., 2003; Rember and Trefry, 2004; Huser et al., 2011), the element concentration evolution over the latitudinal profile of variable permafrost coverage and vegetation at otherwise similar bedrock lithology and physico-geographical settings will be governed by several counter-balanced processes. A decrease of mobile element (alkali and alkaline-earths, oxyanions) concentration northward in the WSL regardless of the season and the river size may be due to (1) decrease of chemical weathering intensity with the temperature (Oliva et al., 2003; Beaulieu et al., 2012), (2) decrease of the thickness of the active (unfrozen) soil layer (Beilman et al., 2009); and (3) decrease of the degree of groundwater feeding (Frey et al., 2007b). These factors will mostly act on elements whose transport is not limited by dissolved organic matter. The river size is expected to act essentially on the 3rd factor, via decreasing the degree of river feeding by underground taliks with the decrease of the watershed area: it is fairly well known that the larger the river, the stronger the impact of underground input, notably in the permafrost zone of western Siberia (Fotiev, 1989, 1991).

The factors capable to enhance element concentration and export flux in northern (permafrost-bearing) rivers relative to southern (permafrost-free) rivers are those controlling the export of DOM and related metal complexes: (1) the increase of DOC and related element leaching from plant litter and topsoil (Pokrovsky et al., 2012; Giesler et al., 2006; Fraysse et al., 2010) during more pronounced massive freshet event or summer high flow (Michel and Vaneverdingen, 1994; McClelland et al., 2006; White et al., 2007), (2) enhanced mobility of low soluble TE in more acidic solutions of the spring acid pulse (well established in other permafrost-free boreal regions, Buffam et al., 2007), which is pronounced only in permafrost-affected rivers of western Siberia (Pokrovsky et al., 2015); and (3) the decrease of DOM-metal complexes retaining (adsorption) on mineral soil horizon because clay horizon is typically frozen in the north (Kawahigashi et al., 2004). These enhancing factors will be tightly linked to the nature of colloidal carriers of TE (organic, organo-ferric or organo-aluminium species) and the efficiency of metal leaching from the organic topsoil and plant litter. A comprehensive database of rivers of various size across the full gradient of permafrost investigated during main hydrological seasons in this study allows testing the abovementioned environmental factors.

The DOC and Fe are not correlated in rivers ($R < 0.40$; $p > 0.05$) and this is consistent with decoupling of Fe and DOC during size separation procedure as two independent colloidal pools, already demonstrated for European boreal rivers (Lyvén et al., 2003; Neubauer et al., 2013; Vasyukova et al., 2010) and other Siberian rivers and WSL thermokarst lakes (Pokrovsky et al., 2006, 2011). The highest correlation coefficients between DOC and divalent metals and hydrolysates observed in summer may indicate on the importance of DOM in these elements mobilization from vegetation pool or from soil mineral horizons. The latter pool is poorly pronounced in spring. Significant correlation of Al with insoluble low mobile elements such as Be, Ti, Cr, Ga, Zr, Cd, REEs, Hf and Th was mostly pronounced during open-water period. A likely cause of this coupled transport is concomitant release of these elements from soil peat or mineral horizon. Most likely, organo-Al colloids, also highly abundant in western Siberia thermokarst lakes (Pokrovsky et al., 2011) act as carriers of insoluble hydrolyzates from the organic or mineral (clay) soil constituents to the river. A decoupling of total dissolved Fe concentration from these correlations during all seasons is due to Fe vulnerability to redox processes. As a results, although organo-ferric colloids may still be important carriers of TE, significant fraction of dissolved Fe in Fe-rich streams, especially in winter, can be in Fe(II) form. Reductive dissolution of Fe and Mn oxy(hydr)oxides in temperate soils is known to provoke the release of Ba, Cd, Cu, Co, Cr, Ni and V (Abgottspon et al., 2015; Hindersmann and Mansfeldt, 2014; Weber et al., 2009). Additional source of some low mobile metals can be underground water influx, reflected in 1–2 orders of magnitude higher Fe and Mn concentrations in winter (Figs. 3c and 5C) and in statistically significant correlation coefficient with Fe of Ti, V, Cr, Mn, Ga, As, and Zr (Table S2, Sect. 3.1)

The PCA results clearly demonstrated two main factors controlling element distribution in rivers during all seasons, across the latitudinal gradient: F1 is presumably linked to organic and organo-mineral colloids, acting on insoluble, low mobile element hydrolysates (Be, Al, Ti, Zr, Nb, REEs, Hf, Th) and F2 being directly linked to the negative latitude which controls specific conductivity, DIC, Ca, Mg, K, Li, V, As, Rb, Sr, Mo, Sb, W and U whose concentrations greatly decrease northward during all seasons (see Fig. 2a and b)

The lack of watershed area and discharge effect on F1 × F2 structure revealed during PCA treatment suggests that the watershed size is the least significant parameter controlling element concentration in rivers across the latitudinal gradient during various seasons (see results of Kruckal Wallis test in Sect. 3.3.1). An important result is the persistence of F1 x F2 factorial structure with relatively similar eigenvalues over all four hydrological seasons, including winter baseflow. This strongly indicates the dominance of two main processes controlling element migration in rivers: organo-colloidal DOC-rich surface flow and deep underground or subsurface feeding by DIC-rich, DOC-poor waters, as also evidenced in during analyses of major cations (Ca, Mg) of the WSL rivers (Pokrovsky et al., 2015).

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Despite significant latitudinal and geographical coverage of western Siberia rivers, the PCA analysis does not allow explain the observed variability of solute composition in western Siberia due to its highly homogeneous environmental context (Pokrovsky et al., 2015), unlike that of the Mackenzie River drainage basin (Reeder et al., 1972). In the latter, however, contrasting lithological and physico-geographical factors (carbonate, gypsum, clays, halite deposits, hot springs) create distinct component structure. Another reason of relatively low efficiency of PCA to explain TE concentration variability (only 33 %) is that a fair number of TE, such as divalent metals (Mn, Zn, Bi, Co, Cu, Cd, Pb) are linked neither to latitude (groundwater feeding) nor to Al/Fe-rich organic colloids. As a result, not all the variables respond to the observed PCA F1 x F2 structure.

4.2 Effect of latitude on TE concentration and export from the soil profile and groundwater to the river

The decrease of concentration of elements originated from water-rock interaction whose transport is not limited by the availability of DOM (Ca, Mg, DIC, Li, B, V, Cr, Sr, Rb, As, Sb, Mo, U) is expected to be directly related to the concentration of these elements in underground waters contacting basement rocks. In winter, when the contribution of the groundwater relative to the surface runoff is maximal (i.e., Walvoord et al., 2012; Walvoord and Striegl, 2007), one can expect most significant effect of the latitude on these element concentration in rivers. In addition, in the permafrost-bearing zone during winter baseflow, significant difference in element concentration in winter between small rivers (not affected or weakly affected by taliks) and large rivers (essentially fed by taliks) should occur. In contrast, in spring, when the majority of the soil column is frozen, the export from the watershed is dominated by surface flux over the frozen organic horizon and thus the difference in groundwater-related element concentration between small and large rivers or between north and south should be minimal. Similar to results for major river components such as DIC, Ca, and Mg (see Pokrovsky et al., 2015), these hypotheses are not supported by TE concentration trend observed in rivers (Figs. 9–11, S7 and S8) and Sect. 3.2. The groundwater feeding of WSL rivers ranges significantly from the southern permafrost-free zone (56 to 58° N) where it varies between 30 and 80 % (Frey et al., 2007b) to 20–30 % in the discontinuous and sporadic/isolated part of WSL and decreases down to 3–6 % in the northern, continuous permafrost zone (Novikov et al., 2009). This decrease of groundwater feeding is capable to partially explain an order of magnitude decrease of Sr, Mo and U across the studied gradient (Figs. 9–11 and S10). However, the latitudinal trend of soluble TE (Sr, Mo, As, Sb, and U) concentration achieves 2 orders of magnitude and persists regardless of the seasons and the watershed size thus implying more than one single source of soluble elements in the rivers.

We hypothesize, therefore, that, in addition to deep underground feeding, there is element leaching from the main constituents of the soil profile – peat and mineral horizons. This leaching essentially controls the gradual decrease of soluble element concentration in rivers northward, visible during all seasons. The capacity of soil substrate to release TE to the river can be evaluated based on available elemental composition of WSL peat (Stepanova et al., 2014). At present, this is the only source of information on TE concentration in moss cover, peat and mineral horizons of WSL soils over more than 1500 km latitudinal transect similar to that investigated in the present work. Among 50 major and trace element analyzed in main soil reservoirs of the WSL, only several TE demonstrated statistically significant ($p < 0.05$) latitudinal concentration trend. For example, an order of magnitude decrease of Sr, Mo, and U northward in peat and mosses of the WSL between 55 and 66° N (Fig. S15) may reflect the latitudinal evolution of the geographic background across the WSL. Tentatively, it corresponds to a decrease of the content of carbonate concretions in the clayey horizons. The latter should be detectable in all four main compartments feeding the river: (1) soluble products of rock weathering in the underground reservoirs, (2) deep soil/subsurface fluids interacting with mineral part of the soil profile, (3) interstitial soil solutions of the peat horizons, and (4) plant litter/moss layer leachates transported to the river via surface runoff in the permafrost free zone and suprapermafrost flow in the permafrost-bearing zone.

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Additional factor of enhanced Sr, Mo and U mobility in the southern rivers relative to northern rivers is the difference of the pH regime between permafrost-free and permafrost-bearing zones of WSL. The pH values of 7 to 7.5 in the southern rivers observed both in winter and spring are indicative of carbonate/silicate rock weathering in the underground reservoirs. The spring acid pulse, reported for other permafrost-free boreal regions (Buffam et al., 2007), is not pronounced in the south of WSL but becomes clearly visible in the permafrost-affected, northern regions where the spring-time pH decreases to 5.5 ± 0.5 (Pokrovsky et al., 2015). A decreased mobility of Mo and other oxyanions in more acidic solutions in the north may be directly linked to their adsorption on mineral and organic surfaces, whereas enhanced U concentrations in DIC-rich, circum-neutral solutions in the south may be due to strong carbonate and hydroxycarbonate complexes replacing organic colloids (Fig. 12) as it is also known for European subarctic rivers (Porcelli et al., 1997; Pokrovsky et al., 2010). Finally, high sensitivity of Sr to the latitudinal trend is likely to reflect its co-mobilization together with Ca and DIC from both surface and subsurface sources.

Winter-time increase of Fe concentration in permafrost-affected rivers relative to permafrost-free region (Fig. 3c) may reflect enhanced Fe(II) mobilization from anoxic underground reservoirs and Fe oxy(hydr)oxide dissolution in river sediments. This input is visible mostly during winter, when thick ice cover created partially anoxic conditions suitable for Fe(II) maintenance in solution. These conditions were most pronounced in northern, permafrost-affected regions, where the ice thickness was higher and some rivers even froze solid in February. At the same time, the lack of Mn increase northward in winter (Fig. 5c) suggests relatively weak control of solely anoxic conditions on metal transport. Alternatively, these anoxic conditions suitable for enhanced Mn mobilization remain similar across the latitudinal profile, as Mn concentration remains quasi-constant and systematically, 1 to 2 order of magnitude higher in all rivers in winter relative to spring and summer (Fig. 5). Note that enhanced Mn transport during winter period linked to its redox – driven mobilization from lake and river sediments is fairly well established for small Scandinavian rivers (Pontér et al., 1990, 1992). Con-

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cerning trivalent and tetravalent hydrolysates, we hypothesize mobilization of TE^{3+}, TE^{4+} by Fe(III) colloids in the riverwater. These colloids are produced in the hyporheic zone of the river, fed by taliks from underground reservoirs. Very strong association of these elements with Fe(III) colloids stabilized by DOM is fairly well established in WSL thermokarst lakes and small rivers of the discontinuous permafrost zone (Pokrovsky et al., 2011; Shirokova et al., 2013).

A re-increase of element concentration in rivers north of 66° N, especially visible for B, V, Ni, Rb, Sr, Mo, As, U during summer time (Figs. 9b, 10b, 11b, S3, S7 and S8) does not have a straightforward explanation. Two possible hypotheses can be suggested: (i) the influence of marine sediments underlying frozen peat in the 50–100 km vicinity of the shoreline (see Sect. 4.3 below for surface profile); (ii) elevated flux of TE leaching from the moss and lichen leaching during summer time. 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).

Despite contrasting hydrochemistry of WSL rivers in permafrost-free, discontinuous and continuous permafrost regions in terms of pH and DOC concentration (Frey and Smith, 2005; Pokrovsky et al., 2015), the percentage of organic complexes of TE remained quite similar among all three permafrost zones. Among metals available in the vMinteq database, Mg, Ca, Sr, Ba, and Mn are complexed to DOM within 10 ± 5 %; Co, Cd and Zn are complexes at 30 ± 10 %, Ni is complexes at 55–60 %, and Al, Pb, Cu, Fe(III), La, Ce and other REEs are bound to DOM by 90 to 98 % (Fig. 12). Only U(VI) exhibited contrasting speciation between permafrost-free and permafrost-bearing zones with 40 ± 30 % present as organic complexes in HCO_3^- rich, circum-neutral solutions of southern rivers but remained > 90 % DOM-complexed in acidic, DIC-poor northern rivers.

The annual TE fluxes of WSL rivers averaged over full latitudinal profile (Table 1) can be compared with available data of TE fluxes in other subarctic rivers. Such a com-

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parison is suitable for the Severnaya Dvina River, the largest European subarctic river whose watershed lay on the same latitudinal range (58–64° N) as most WSL rivers but in the permafrost-free zone (Pokrovsky et al., 2010). The ratio of annual element fluxes in the Severnaya Dvina River measured in 2007–2009 to mean fluxes of the WSL rivers is plotted in Fig. S16. Given the intrinsic uncertainties on the fluxes in each region ranging between ±30 and ±50 %, the agreement within a factor of 1.5 to 2 is within the uncertainty. The elevated flux of Sr and U in the Severnaya Dvina River relative to the WSL rivers is due to the dominance of carbonate rocks whereas the elevated fluxes of lithogenic elements (Zr, Th, REEs, Al, Ti) are due to silicate rock (granites and their moraine) on the watershed of Severnaya Dvina. The reasons for more than an order of magnitude higher fluxes of Ni, Cu, and Cd in the Severnaya Dvina River relative to the WSL rivers are multiple and may include (i) the presence of sedimentary sulfides in the former, (ii) enhanced uptake of these metals by peat mosses in the WSL and finally (iii) anthropogenic local pollution by these metals in the Severnaya Dvina river.

4.3 Mechanisms of TE mobilization from the soil to the river

Together with a comprehensive database on concentration, colloidal status and fluxes of trace elements in the Kalix River (i.e., Ingri et al., 2000, 2005; Andersson et al., 2001; Dahlqvist et al., 2005), the Kryckland watershed (Björkvald et al., 2008; Laudon et al., 2013), Alaskan rivers (Sugai and Burrell, 1984; Rember and Trefry, 2004), the present study contributes to our understanding of the nature and magnitude of element transport in boreal rivers. The main peculiarities of WSL territory is the presence of permafrost on almost half of its territory. This permafrost likely acts as a very strong barrier between surface organic and underlying mineral soil horizon thus regulating the degree of mineral vs. peat leaching depending on latitude and season as it is known for other subarctic environments (Bagard et al., 2011, 2013; Keller et al., 2007, 2010).

A tentative cartoon of WSL soil profiles in the permafrost-free, discontinuous and continuous permafrost zone presenting TE mobilization pathways from the soil to the river is illustrated in Fig. 13. The main difference of WSL permafrost-bearing regions

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from other, Scandinavian, Alaskan, and Central Siberian soils is location of active (seasonally unfrozen) layer within the organic rather than mineral horizon. As a result, unlike that of the non-peatland permafrost environments (i.e., Keller et al., 2007; Barker et al., 2014), element mobilization to the river over full duration of open-water season occurs essentially from the organic horizon.

We hypothesize 3 main sources of TE in rivers from the soil profile shown in Fig. 13a: (I) surface flow (water travelling on the top surface and leaching TE from plant litter and moss/lichen cover); (II) interstitial soil water of the peat horizons (up to 3 m thick), travelling to the river via less permeable clay interface and (III) subsurface water, interacted with mineral (sand, clays) horizons. Supplementary to these three main surface water source is (IV) deep underground water feeding the river during baseflow then the hydraulic pressure of surface waters in the river bed is low (Nikitin and Zemtsov, 1986; Anisimova, 1981; Roux et al., 2015). In the permafrost-free region, all four TE input fluxes are operating during the year. Note that in this zone, the frozen peat prevents infiltration only during spring melt (Laudon et al., 2007). In the permafrost-bearing regions, the third, shallow subsurface flux from mineral horizons, is absent during all seasons and the 1st and 2nd pathways are realized via suprapermafrost flow (Fig. 13b and c). The soil column is frozen below organic peat layer and the downward penetrating surface fluids transport DOM and DOM-TE complexes leached from upper soil horizons and litter layer, without DOM sorption onto underlying minerals. This mechanism is evidenced for DOC transport in WSL rivers (Frey and Smith, 2005; Pokrovsky et al., 2015) and the Yenisey basin (Kawahigashi et al., 2004). It is consistent with frozen peat context of most western Siberia peat soil profiles.

Indeed, given 1 to 3 m thickness of the peat even in the northern part of the WSL (Vasil'evskaya et al., 1986; Kremenetsky et al., 2003) and the typical active layer thickness of 50 ± 30 cm (Tyrtikov, 1973; Khrenov, 2011; Novikov et al., 2009), in the region of permafrost development, downward migrating peat soil interstitial solutions will not likely contact the underlying mineral horizon. The consequences of this reduced pathway are double. From the one hand, organic complexes of TE will not adsorb on clay

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minerals during DOM-TE migration from the litter horizons through the soil column and further to the river along the permafrost impermeable layer. As a result, the concentration and fluxes of TE controlled by leaching from moss and lichen cover and topsoil horizons and often originated from atmospheric depositions (Mn, Zn, Co, Ni, Cu, Pb, Cd) will not significantly decrease in the permafrost region relative to the permafrost-free zones. Given rather uniform distribution of divalent metals in moss and peat of the WSL latitudinal transect (Stepanova et al., 2015), this produces low variation of metal fluxes from 56 to 66° N (Table 1).

From the other hand, the lack of fluid contact with mineral layer may impede Fe and other insoluble elements to be leached from silicate minerals. The lack of mineral dissolution brings about a decrease of element concentration northward during active (summer) period, as it is seen for Fe (Fig. 3b), Ti (Fig. S2b) and Zr (not shown). Elements correlated with Al (see Sect. 3.1) are less affected by watershed latitude possibly because dissolved Al is stabilized by organic complexes, equally abundant during top soil/litter leaching in the south and in the north. Here, the coprecipitation step is less pronounced than that for Fe; rather, concomitant mobilization of Al-DOM and TE-DOM complexes may explain positive correlation between mainly insoluble, low mobile TE^{3+}, TE^{4+} and Al (Table S2).

4.4 Evolution of TE concentration and fluxes in western Siberia rivers under climate change scenario

There are four main sources of TE in the river – surface flow, shallow and deep subsurface flux and underground water input (Fig. 13). In response to permafrost thaw and active layer depth thickening, the relative role of organic soil vs. mineral subsoil fluxes may change. Specifically, the switch of river feeding from essentially peat (No II) to peat + mineral (No III+II, see Fig. 13) horizon may increase the export of elements whose concentration is much higher in mineral compared to peat horizons. These are Fe, Al, all trivalent and tetravalent hydrolysates, Ba, V and Cr. At the same time, the surface flux of Mn, Zn, Co, Ni, Cu, Cd, Pb, and in a lesser degree, Ba and Rb, essentially controlled by litter and moss leaching which is mostly pronounced during spring flood, will remain unaffected. In addition to the change of element source induced by active layer migration, the shift of the permafrost boundary to the north will expose more amount of organic peat to infiltrating waters. This will further attenuate the increase of the export flux for TE whose concentration in the peat decreases northward (B, Sr, Mo, U). As a result, the subsoil and shallow groundwater influx of highly soluble B, Li, Sr, Mo, As, Sb, W and U may remain unchanged as the concentrations of these elements in soil mineral horizons progressively decrease northward (see examples in Fig. S15), consistent with the trend in the river water concentration.

Under climate change scenario, the thickening of the active layer will increase the delivery of insoluble hydrolysates (in the form of organic complexes and organo-ferric colloids) while possibly decreasing the input of divalent metal micronutrients. The downward migrating organic complexes of the latter may be retained on mineral surfaces and in within the clay interlayers (Kaiser et al., 2007; Oosterwoud et al., 2010; Mergelov and Targulian, 2011; Gentsch et al., 2015), similar to that of DOC (Kawahigashi et al., 2004; Pokrovsky et al., 2015). Note however that the lack of TE analyses in the permanently frozen peat below the active layer in the northern region of WSL does not allow to foresee the consequences of permafrost thaw on TE leaching from previously frozen peat horizons.

Most elements did not yield any statistically significant dependence of annual export fluxes on the latitude. Very few elements demonstrated systematic and significant (more than a factor of 2) latitudinal trend of fluxes: Fe, Zn and Cd showed a northward increase and Sr, Mo and U showed a northward decrease. Therefore, the shift of the permafrost boundary northward may decrease the annual fluxes of Fe and some divalent metals originated from topsoil and mineral horizons while increasing the annual riverine export of Sr, Mo and U.

The change of the hydrological regime in the WSL (Karlsson et al., 2015), in particular the increase of the winter baseflow (Yang et al., 2004; Ye et al., 2009; Serreze et al., 2000) due to the increase of the groundwater feeding (Frey et al., 2007a, b) is likely to

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increase the export of Fe during winter period. Transport of TE, linked to Fe during winter baseflow (Al, Ga, REEs, V, Zr, Th) whose concentration increases northward, may also increase; however, the low share of winter flux in the annual transport for these elements will not allow significant (i.e., $> 50\,\%$) annual flux modification. In contrast, export of Mn, depicting an order of magnitude higher concentration in winter compared to other seasons, may turn out to be significantly, by a factor of 2 to 3, affected by the rise of winter flow, equally in the northern and southern regions of the WSL.

The last and most uncertain factor capable modifying TE fluxes in WSL rivers is the increase of the vegetation productivity reported for Arctic river basins (Sturm et al., 2001; Tape et al., 2006; Kirdyanov et al., 2012). From the one hand, this should rise the short-term release of micronutrients from plant litter, notably during spring flood (Zn, Mn, Co, Ba). A spring-time increase of these element concentration northward illustrates the importance of organic matter leaching in the topsoil horizon and transport to the river via suprapermafrost flow. From the other hand, the increase of the plant biomass stock will lead to transient uptake of micronutrients from organic soil horizons and their storage in the aboveground vegetation. As a result, overall modification of TE fluxes in discontinuous/continuous permafrost zone may be smaller than those projected by simple latitudinal shift.

5 Conclusions

Seasonal analysis of dissolved ($< 0.45\,\mu m$) trace elements in ~ 60 rivers of Western Siberia Lowland sampled over 1500 km gradient of permafrost, climate and vegetation during three main hydrological seasons, demonstrated rather low sensitivity of element concentration and fluxes to the size of the watershed. The season also played a secondary role in determining element concentration pattern and variations among the rivers. The PCA analyses revealed two main factors contributing to the observed variability of elements in rivers and persisting during all sampled seasons. The first is the DOM controlling TE^{3+}, TE^{4+} migration in the form of organic and organo-mineral

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colloids. The second is the latitude of the watershed translated to the effect of underground water-rock interaction and river feeding via groundwater influx or taliks. This factor was most visible for labile soluble elements such as Li, B, Ca, Mg, DIC, Sr, Mo, As, Sb, W and U. Overall, the major environmental parameters controlling trace elements concentration in western Siberian rivers can be ranked as following: watershed size < seasons < latitude. Mn was an exception demonstrating an order of magnitude increase in rivers during winter regardless of the latitude, which was presumably linked to the change of redox conditions. Insoluble elements however (Fe, Al, and other trivalent hydrolysates) demonstrated significant, up to an order of magnitude, increase of concentration northward during winter, which was probably linked to their DOM-promoted leaching (Al) from silicate minerals followed by organo-mineral colloid formation.

Within the soil – bedrock profile, the four main reservoirs supplying trace elements to the river are the following: (I) plant litter, soil O_e horizons, moss and lichen cover, releasing metal micronutrients (Mn, Zn, Cu, Co, Ni, Ba, Rb) and atmospherically-deposited toxicants (Cd, Pb) mostly in the form of organic complexes via surface flow, especially visible during spring flood; soil horizon leaching including both (II) peat organic layer and (III) underlying mineral (clay) layer, providing Fe, Al, TE^{3+}, TE^{4+}, V, Cr, mostly as organic complexes and organo-ferric colloids; and finally (IV) underground water reservoirs bearing the signature of water-rock interaction at depth, mostly visible during winter baseflow and connected to the river through taliks (in the permafrost-bearing region) and supplying Li, B, Sr, Mo, V, As, Sb, W, U. Significant, > a factor of 10, decrease of Sr, Mo and U concentration northward, detectable during all seasons, stems from the decrease of these element concentration in both peat and underlying mineral horizons as well as the decrease of the underground feeding along the 1500 km latitudinal profile of WSL. Under climate warming scenarios, comprising active layer thickening and permafrost boundary shift northward, the surface (I) and underground (IV) contributions to the river are unlikely to be modified. From the other hand, the change of the relative degree of the peat (II) and mineral (III) soil leaching to the river may cause the

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decrease of divalent metal organic complexes and increase of organo-ferric colloids of TE^{3+}, TE^{4+} delivery to the river via suprapermafrost flow and hyporheic influx.

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Author contributions. O. S. Pokrovsky designed the study, performed analyses and wrote the paper; R. M. Manasypov and I. A. Krickov performed sampling and their interpretation; S. N. Vorobyev and S. N. Kirpotin was responsible for the choice of sampling objects and statistical treatment; S. Loiko provided conceptual scheme of element mobilization from the soil to the river; L. G. Kolesnichenko supplied the background information on soil, peat, and permafrost active layer; S. G. Kopysov provided hydrological information and water and element flux calculation, analysis and interpretation. All authors participated in field expeditions. Each co-author have seen and approved the final paper and contributed to writing the manuscript.

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Table 1. Latitude-averaged (56–67° N) export fluxes (±2 SD) of TE by rivers of the WSL.

Element	Flux, $kg\,km^{-2}\,yr^{-1}$	Flux, $kg\,km^{-2}\,yr^{-1}$ [a]
B	4.3 ± 1.9	4.1 ± 1.8
Al	8.5 ± 2.2	8.1 ± 2.3
Ti	0.20 ± 0.06	0.19 ± 0.06
V	0.12 ± 0.07	0.12 ± 0.05
Cr	0.083 ± 0.022	0.077 ± 0.014
Mn	49.2 ± 30.0	33.8 ± 8.7
Fe	211 ± 124	165 ± 84
Cu	0.12 ± 0.07	0.108 ± 0.046
Zn	4.2 ± 2.6	3.2 ± 1.7
Co	0.17 ± 0.24	0.074 ± 0.029
Ni	0.26 ± 0.17	0.23 ± 0.10
Rb	0.14 ± 0.06	0.12 ± 0.05
Sr[b]	26–3.6[b]	14.0 ± 9.8
Zr	0.033 ± 0.014	0.030 ± 0.009
Mo[b]	0.034–0.0025[b]	0.012 ± 0.012
Cd	0.0028 ± 0.0012	0.0023 ± 0.0009
Sb	0.0067 ± 0.0017	0.0062 ± 0.0014
As	0.19 ± 0.12	0.173 ± 0.097
Ba	10.2 ± 5.2	9.2 ± 5.6
La	0.025 ± 0.014	0.020 ± 0.004
Ce	0.055 ± 0.031	0.044 ± 0.008
Nd	0.029 ± 0.017	0.024 ± 0.006
Pb	0.033 ± 0.012	0.032 ± 0.014
Th	0.0036 ± 0.0014	0.0031 ± 0.0009
U[b]	0.017–0.0011[b]	0.0057 ± 0.0062

[a] 56–66° N, neglecting r. Khadutte in winter.
[b] Average value cannot be recommended.

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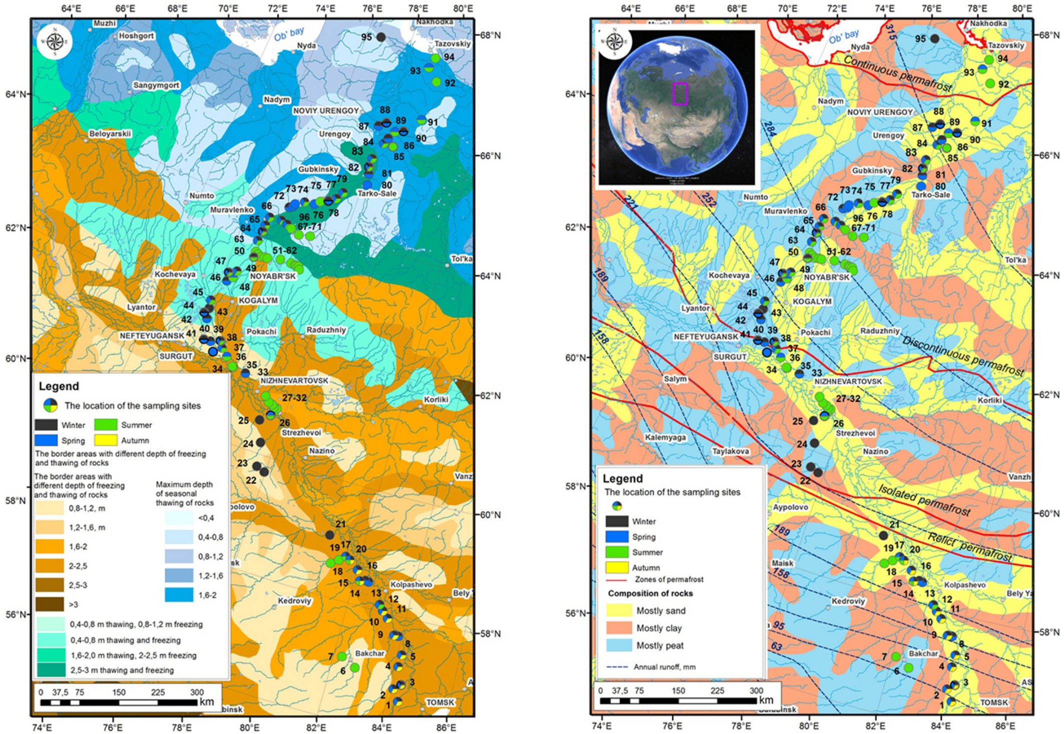

Figure 1. Scheme of sampled rivers in the Western Siberia Lowland (WSL) together with lithological information and thawing soil depth.

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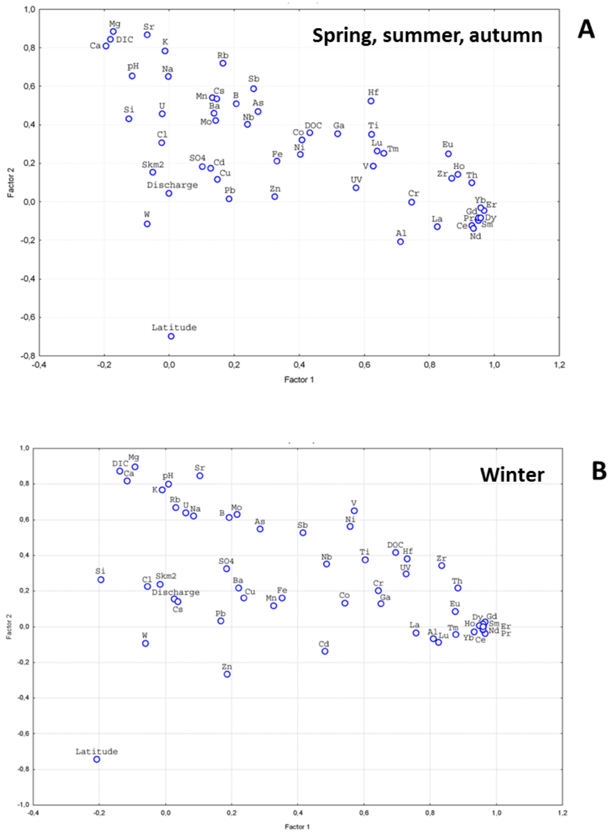

Figure 2. PCA analysis of ∼ 50 variables in ∼ 60 rivers sampled during open-water period **(a)** and in winter **(b)**. The first factor comprises DOC and insoluble trivalent and tetravalent hydrolysates. The second factor is latitude which is inversely correlated with soluble major and trace elements, alkali and alkaline earth metals, oxyanions and U whose concentration decreases with increasing latitude.

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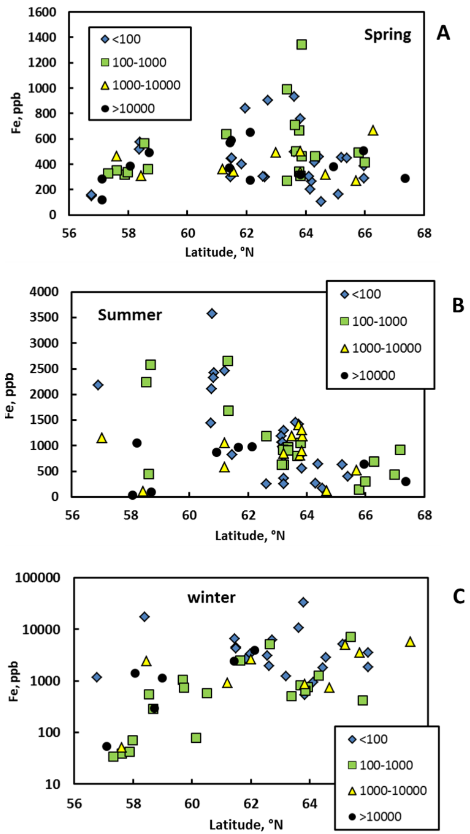

Figure 3. Variation of river water dissolved Fe with the increase of the latitude during spring **(a)**, summer **(b)** and winter **(c)**. The variability among different watershed size is smaller than that between the seasons and within the latitude gradient. Diamonds, squares, triangles and circles represent watershed of size < 100 km^2, 100 to 1000 km^2, 1000 to 10 000 km^2, and > 10 000 km^2, respectively.

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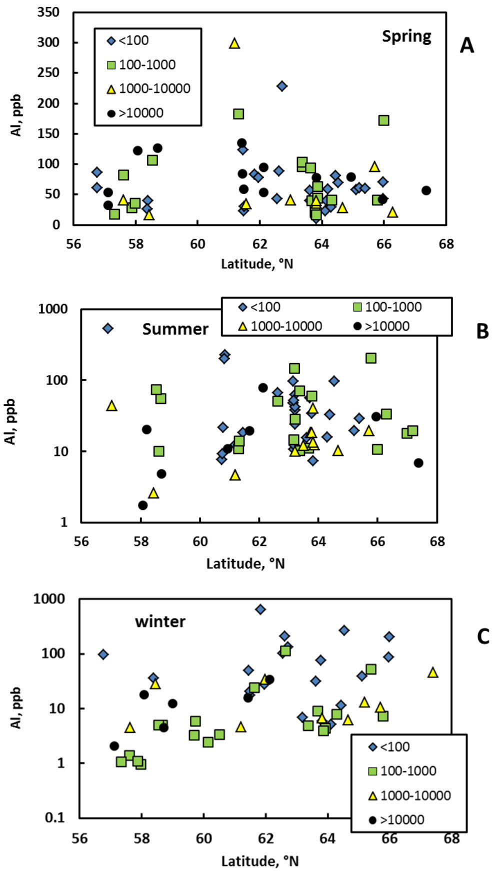

Figure 4. Variation of Al concentration on the latitude during spring **(a)** and summer **(b)** and an increase of Al concentration northward in winter **(c)**. The latitudinal trend in winter is significant at $p < 0.05$. Considering all seasons together, the differences between different watershed sizes are not statistically significant ($p > 0.05$). The symbols are the same as in Fig. 2.

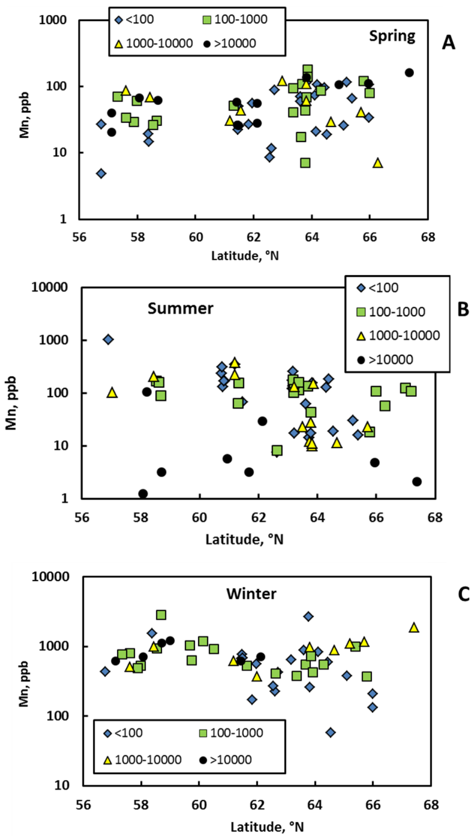

Figure 5. The variation of Mn concentration with latitude during spring **(a)**, summer **(b)** and winter **(c)** for watershed of different size. The symbols are the same as in Fig. 2. Note a factor of 10 higher Mn concentrations in winter compared to spring and summer, presumably linked to Mn reduction in anoxic waters. The latitudinal trends and the differences between different watershed size are not statistically significant ($p > 0.05$).

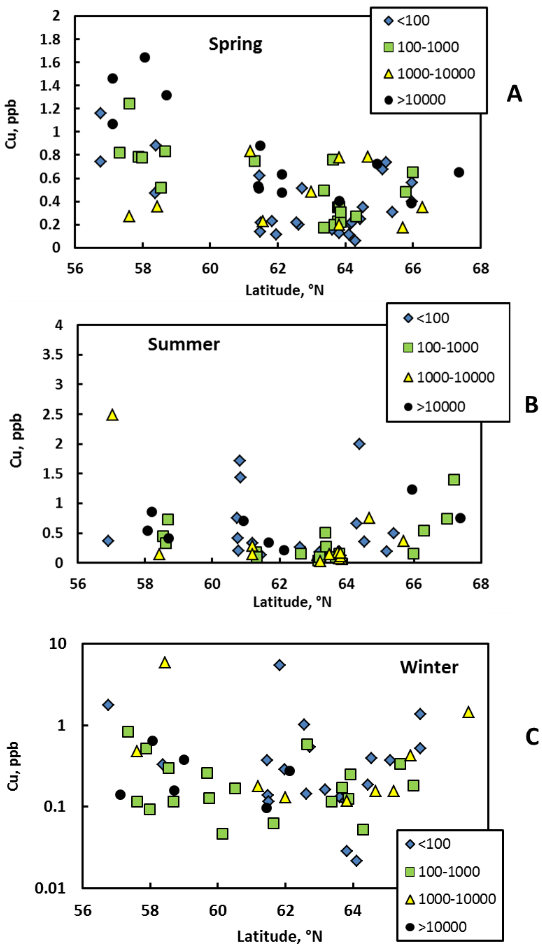

Figure 6. The variation of Cu concentration with latitude during spring **(a)**, summer **(b)** and winter **(c)** for watershed of different size. The symbols are the same as in Fig. 2.

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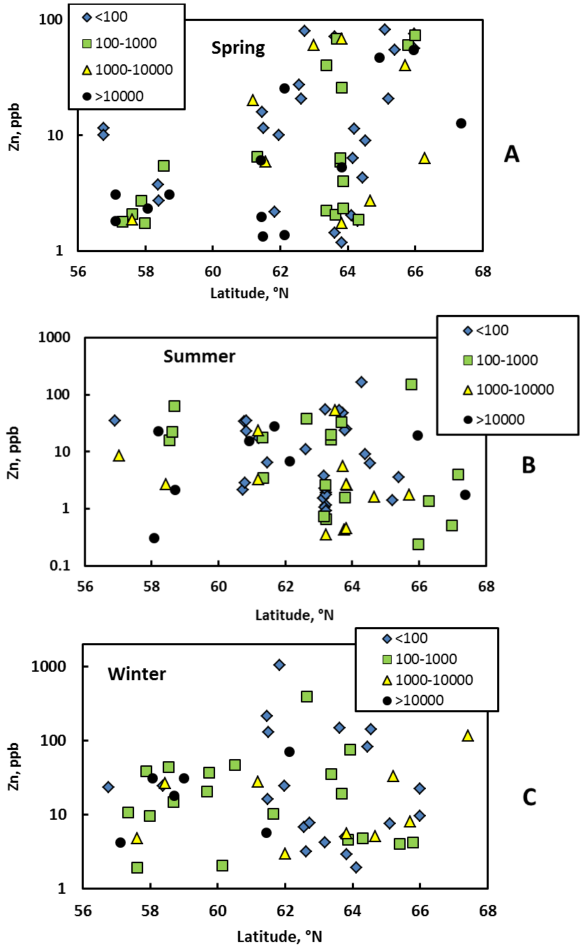

Figure 7. The variation of Zn concentration with latitude during spring **(a)**, summer **(b)** and winter **(c)** for watershed of different size. The symbols are the same as in Fig. 2.

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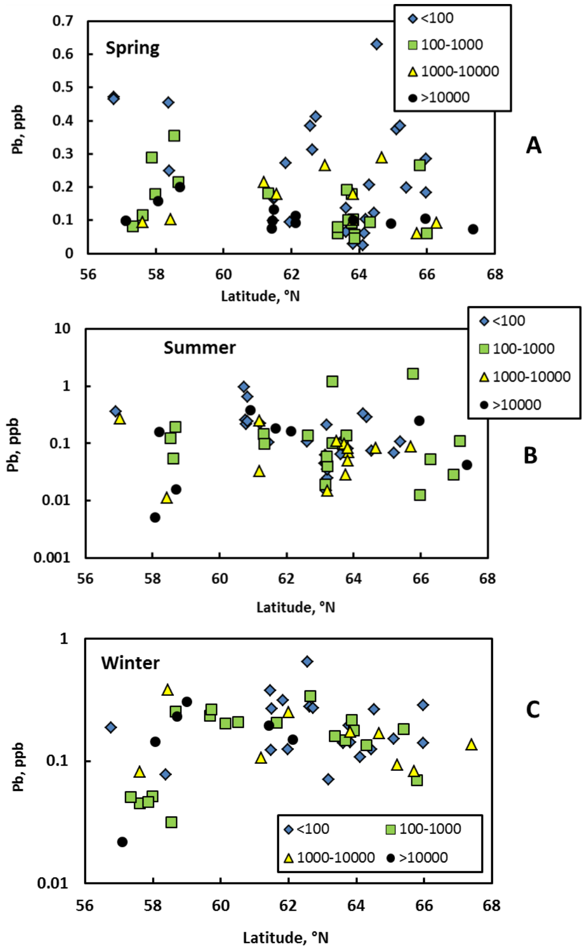

Figure 8. The variation of Pb concentration with latitude during spring **(a)**, summer **(b)** and winter **(c)** for watershed of different size. The symbols are the same as in Fig. 2.

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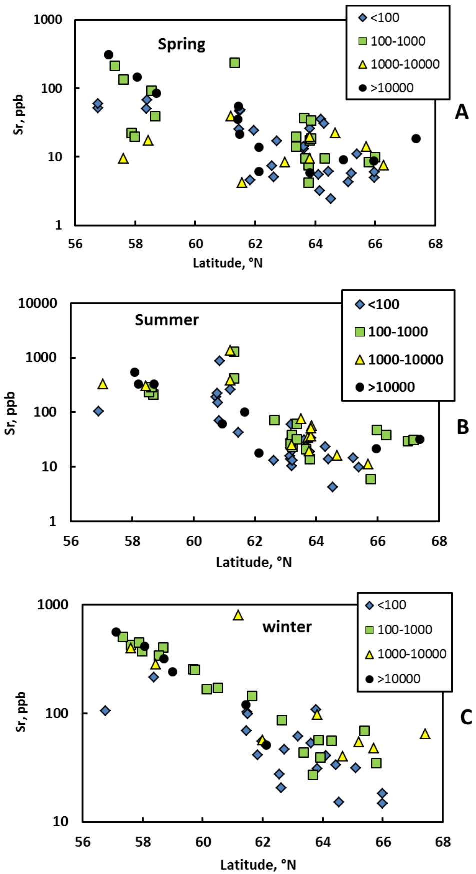

Figure 9. The variation of Sr concentration with latitude during spring **(a)**, summer **(b)** and winter **(c)** for watershed of different size. The symbols are the same as in Fig. 2. Clear groundwater effect consists in gradual decrease of concentration northwards, most visible during winter baseflow.

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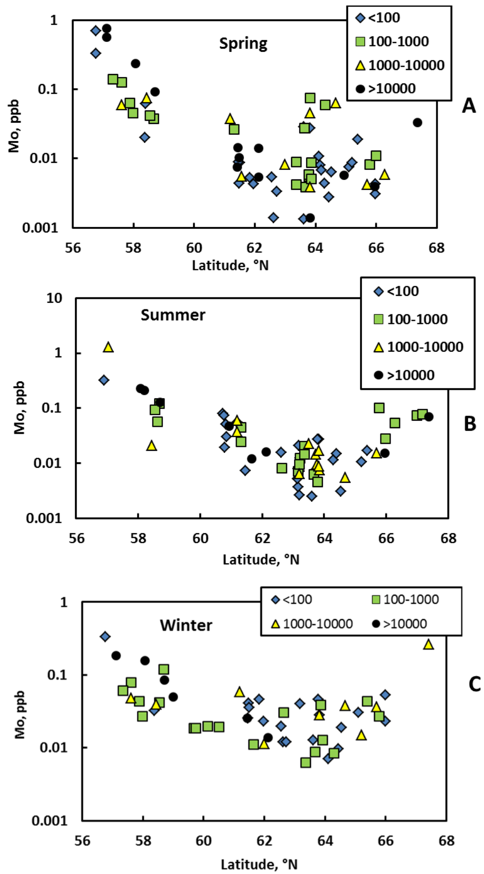

Figure 10. The variation of Mo concentration with latitude during spring **(a)**, summer **(b)** and winter **(c)** for watershed of different size. The symbols are the same as in Fig. 2. Clear groundwater effect consists in gradual decrease of concentration northwards, most visible during winter baseflow.

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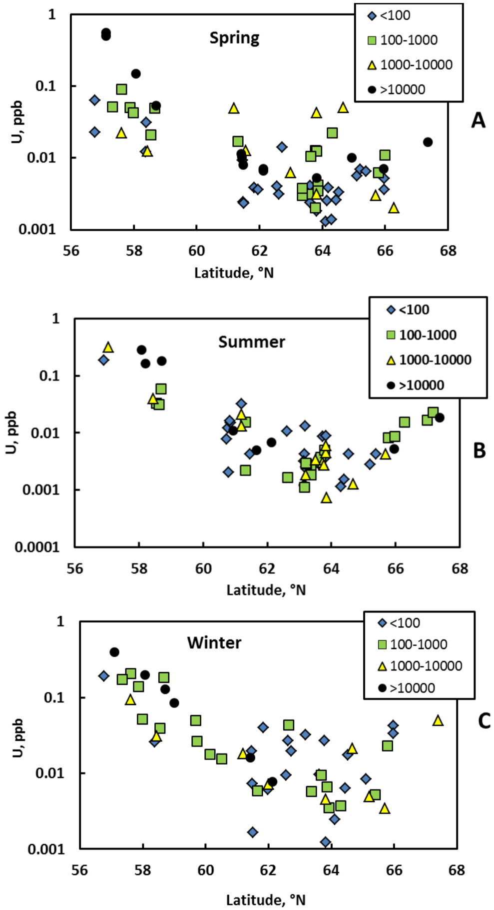

Figure 11. The variation of U concentration with latitude during spring **(a)**, summer **(b)** and winter **(c)** for watershed of different size. The symbols are the same as in Fig. 2. Clear groundwater effect consists in gradual decrease of concentration northwards, isible during all seasons.

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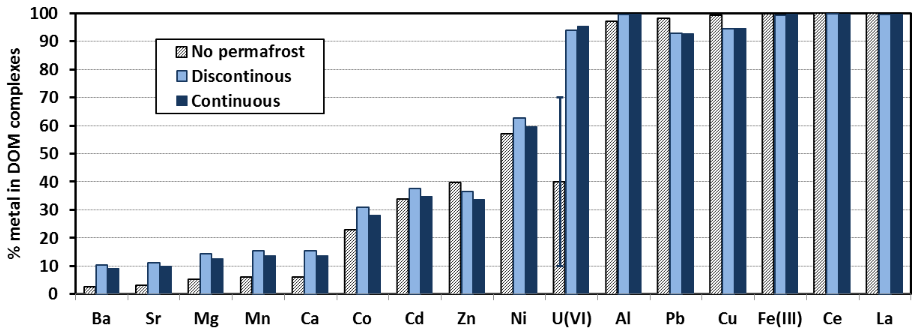

Figure 12. Percentage of organic complexes in western Siberian rivers (< 0.45 µm fraction) calculated using Stockholm Humic Model (vMinteq, version 3.1, Gustafsson, 2014). The values of major and trace elements measured in 66 rivers in permafrost-free zone, 110 rivers in discontinuous permafrost and 39 rivers in continuous permafrost zone averaged over all seasons were used.

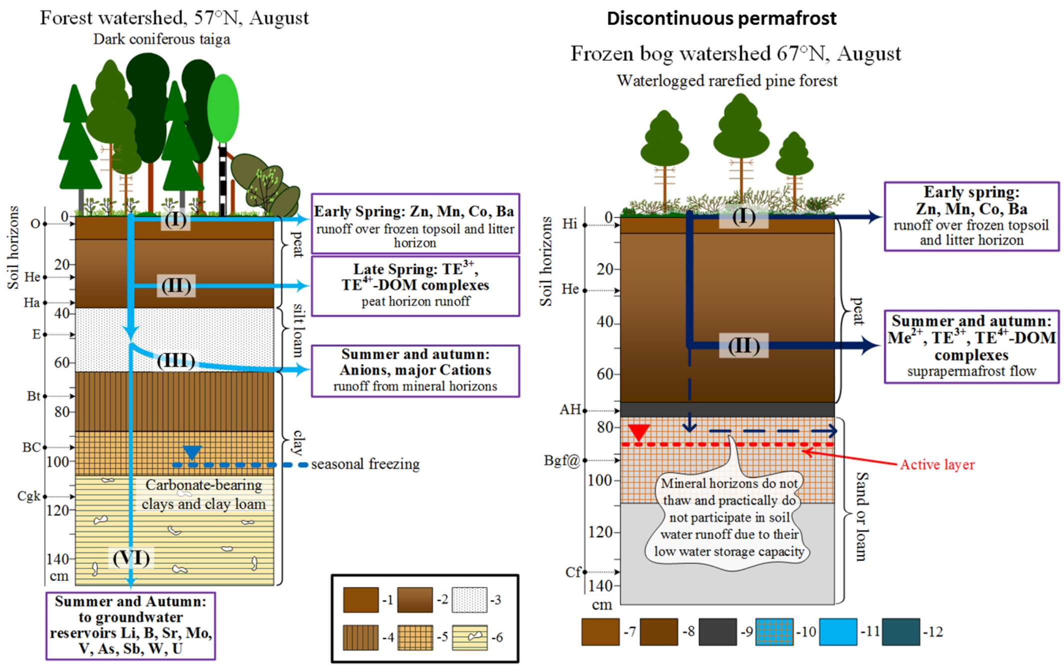

Figure 13.

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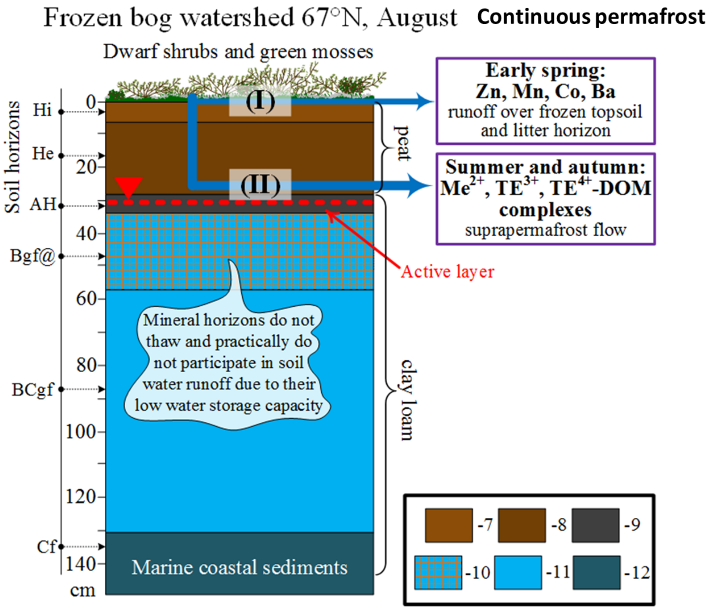

Figure 13. Scheme of TE pathways within the soil profile and to the river, (**a**, left): in forest watershed of the south, permafrost-free zone (57° N) and (**b**, right), discontinuous permafrost forest-tundra zone. Soil horizons (FAO, 2006): 1, O (Mor, forest litter); 2, Medium-decomposed peat (He) transforming into strongly decomposed peat (Ha) in the bottom layer; 3, Mollic humic horizon (E); 4, ABg surface horizons with stagnic properties; 5, Bg middle stagnic horizon; 6, Cgk carbonate-bearing clays and clay loam. **(c)** TE pathways in frozen bog peatlands of continuous permafrost (67° N). Soil horizons (FAO, 2006); 7, weakly decomposed peat (Hi); 8, partially decomposed peat (He); 9, humic horizons (AH); 10, cryoturbated frozen stagnic horizon (Bgf@); 11, frozen stagnic horizon (BÑgf); 12 sedimentary deposits (Cf). In the south, Me^{2+}-DOM complexes is retained by clay and deep in the soil profile, by clay loam with carbonates. In the north, the active layer depth does not exceed the overall thickness of the peat and thus the leachate of ground vegetation and peat layer do not meet mineral horizons during their transit to the river.