Major and trace elements in suspended matter of western Siberian rivers: first
assessment across permafrost zones and landscape parameters of watersheds

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*Key words: trace metals, toxicant, micronutrient, season, river suspended matter, permafrost,
Siberia*

Submitted to *Geochim. Cosmochim. Acta*, after revision October 2019

Abstract

In contrast to good understanding of chemical composition of the river suspended matter (RSM) of large rivers, small rivers remain strongly understudied, despite the fact that they can provide valuable information on mechanisms of RSM generation and transport depending on key environmental parameters of the watershed. This is especially true for permafrost-affected boreal and subarctic territories, subjected to strong modification due to permafrost thaw and landscape changes under climate warming. We selected Earth's largest frozen peatland zone, the western Siberia Lowland (WSL) in order to test an impact of climate warming, permafrost thaw and landscape zone changes on riverine transport of particulate material from mainland to the Arctic Ocean. We sampled 33 small and medium size WSL rivers during spring flood, summer baseflow and autumn flood over a 1700 km gradient of climate and permafrost. Major and trace elements in particulate ($> 0.45 \mu\text{m}$) and dissolved ($< 0.45 \mu\text{m}$) fraction were analyzed. We hypothesize that future increase in active layer thickness and the change of dominant landscape from bogs and lakes to forest can be predicted via analyzing the actual pattern of RSM chemical composition across various permafrost zones and landscape parameters of WSL river watershed. We observed a minimum concentration of Li, Mg, Na, K, Rb, V, Cr, Zn, Cu, Co, Ni, Al, Ga, Y, REEs, Nb, W, Ti, Zr, Hf, Th and U in RSM collected from isolated and sporadic permafrost zones. Considering all seasons together, the presence of forest in the permafrost-bearing zone increased particulate concentrations of all alkalis and alkaline-earth elements, B, As, Nb, Mn, Co, Al, Ga, REEs, Ti, Zr, Hf, Th. This is consistent with element mobilization from mineral horizons that become available for interacting with soil fluids under forested regions. Lakes retained particulate alkaline-earths, Fe, Mn, Co, trivalent and tetravalent hydrolysates (TE^{3+} , TE^{4+}). The concentration of lithogenic low-soluble elements (TE^{3+} , TE^{4+}) in the RSM strongly increased with the river size (watershed area).

Compared to the world RSM average, the WSL rivers exhibited lower concentrations of all elements except Mn and P and a low share of suspended elements relative to total

(suspended+dissolved) forms of trace metals and of low-mobility (lithogenic) elements. Likely reasons for these features are: *i*) low runoff and low RSM concentration as there is no rock and mineral substrate exposed to physical weathering in WSL peatland; *ii*) organic, rather than mineral, nature of surrounding “solid” substrates and as a result, organic rather than silicate nature of RSM, and *iii*) high DOC and Fe concentration leading to high concentrations of typically low-solubility elements in the dissolved ($< 0.45 \mu\text{m}$) fraction due to colloids.

From a climate warming perspective, the increase in active layer thickness and involvement of mineral horizons into soil fluid migration in discontinuous to continuous permafrost zone will likely increase the share of particulate fraction in total element transport for many soluble (labile) elements and also lithogenic elements in WSL rivers. At the same time, permafrost boundary shift northward may decrease particulate concentrations of most major and TE in rivers of discontinuous permafrost zone. The lake drainage and forest colonization of tundra and bogs in the permafrost-affected part of WSL may increase the concentration of alkali and alkaline-earth elements, divalent metals and trivalent and tetravalent hydrolysates. As a result, export of particulate metal micronutrients and toxicants from the WSL territory to the Arctic Ocean may increase.

1. Introduction

The change of export of major and trace element, including macro- and micro-nutrients, from the land to the ocean in high latitude regions under various climate change scenarios is among the major scientific challenges of aquatic biogeochemistry (Hobbie et al., 1999; Holmes et al., 2000; Guo et al., 2004; Heinze et al., 2015; Toohey et al., 2016). The overwhelming number of studies in high latitudes dealt with dissolved rather than particulate fraction of the river load (Holmes et al., 2000; Cooper et al., 2008; Vonk et al., 2015; Tank et al., 2016; Kaiser et al., 2017), despite the fact that the majority of continental runoff to the ocean occurs in particulate rather than dissolved form (Meybeck, 1982; Schlesinger and Melack, 1981; Gislason

et al., 2006; Viers et al., 2009; Gordeev and Lisitzin, 2014). In contrast to numerous studies that have been devoted to the biogeochemistry of “dissolved” organic carbon and macro-nutrients in large rivers of the circumpolar zone (Gordeev, 2000; Lobbes et al., 2000; Stedmon et al., 2011; McClelland et al., 2016; Guo et al., 2004; Tank et al., 2012b, 2016; O'Donnell et al., 2016; Kaiser et al., 2017; Drake et al., 2018), very few works characterized major and trace elements other than C and nutrients in the particulate (> 0.22 or $0.45 \mu\text{m}$) fraction. Gordeev et al. (1996) and later Nikanorov et al. (2010) and Magritsky (2010) compiled the data from the Russian Hydrological Survey on suspended load of Arctic rivers, but no data for chemical composition was available. Gebhardt et al (2004) provided extensive data set for RSM concentration, C and N composition in the mixing zone of the Ob and Yenisey Rivers. Occasional data on elementary composition of RSM in boreal and subarctic rivers are available for European part of Russia (Morozov et al., 1974; Shevchenko et al., 2010; Savenko et al., 2004; Pokrovsky et al., 2010), Western Siberia (Gordeev et al., 2004), Central Siberian Plateau (Pokrovsky et al., 2015, 2016), Eastern Siberian Rivers (Kutscher et al., 2018), Canada (Gaillardet et al., 2003; Javed et al., 2018), the Mackenzie basin (Milot et al., 2010), and the 6 large Arctic rivers (data of PARTNERS and ARCTIC GRO; Holmes et al., 2002, 2012).

Moreover, one of the poorly studied aspects of RSM biogeochemistry is the impact of watershed size because small rivers remain strongly understudied in terms of their suspended load (Holmes et al., 2002). The reason for this is that, in anthropogenically-affected regions, the small rivers are subjected to strong modification by human activity; thus, the natural signal of RSM chemistry in these rivers is strongly blurred and does not allow assessment of mechanisms for suspended load formation. In pristine regions, the small rivers are hardly accessible because the human population and all field logistics are linked to large rivers. In addition to the paucity of data on RSM from small and medium-size rivers, there is another bias of seasonal aspect on RSM transfer by rivers: most available data represent easily collectable (dissolved) fraction of the river load, often sampled during summer baseflow on large rivers. This bias is especially

pronounced in high latitude boreal regions where the largest share of suspended flux occurs during spring freshet period, but the access to these sites during the full hydrological year is highly limited.

In contrast to many other regions in the world, western Siberia allows to overcome these aforementioned natural obstacles with RSM sampling. This relatively pristine peatland has a unique geographical setting and a sufficiently developed road infrastructure. Interest in the Western Siberia Lowland (WSL), the largest permafrost-affected peatland area, stems from: *i*) its storage of a sizeable amount of C in thawed and frozen peat (Krementski et al., 2003), *ii*) the fact that it is a significant reservoir of dissolved organic carbon in surface water (Polishchuk et al., 2017, 2018), *iii*) the fact that it supplies a large amount of freshwater and solutes to the Arctic Ocean (Frey et al., 2007a, b; Frappart et al. 2010), and *iv*) its emissions of high fluxes of greenhouse gases from the water area of bogs, lakes and rivers to the atmosphere (Shirokova et al., 2013; Sabrekov et al., 2017; Serikova et al., 2018, 2019). The permafrost in WSL is highly unstable and thaws faster than in other Siberian regions (Romanovsky et al., 2010). Due to the high fragility of permafrost in western Siberia, climate change is likely to have a profound influence on the magnitude of riverine fluxes through alteration of hydrological regimes in WSL rivers (Frey and McClelland 2009; Bring et al. 2016) and stimulation of element releases caused by widespread permafrost thawing (Vonk et al. 2015).

An important gap in our knowledge of RSM geochemistry is the role of landscape features of the watersheds, such as forest and bog coverage, as well as permafrost distribution. This information can be acquired from a sufficient number of small watersheds (i.e., < 10,000 km²) that cover a wide range of climate and physico-geographical zones on otherwise similar lithology. Among all global boreal and high latitude regions, only WSL offers possibility for testing the impact of landscape parameters and climatic conditions on RSM in rivers of various sizes that drain highly homogeneous rock substrates (peat overlaying silts and sands). Such a unique geographical situation of the WSL allows foreseeing the impacts of climate warming,

permafrost thaw and forest line migration to the north via analyzing ecosystem parameters across a climate and permafrost gradient at otherwise similar lithological and geomorphological environments. Such a substituting of “space for time” approach has been successfully used in western Siberia for the dissolved ($< 0.45 \mu\text{m}$) fraction of inorganic river load (Frey et al., 2007b), DOC (Frey and Smith, 2005; Pokrovsky et al., 2015), trace metals (Pokrovsky et al., 2016) and nutrients (Frey et al., 2007a; Vorobyev et al., 2017). On a broader context, this approach postulates that contemporary spatial phenomena can be used to understand and model temporal processes that are otherwise unobservable such as past and future events (Blois et al., 2013).

In this work, we studied chemical composition (major and trace elements) of RSM collected in small, medium and large rivers over 3 main hydrological seasons in the world’s largest frozen peatland. Within the substituting space for time scenario, that is well established in this part of Siberia, we hypothesized that the a) permafrost boundary shift northward, b) increase in the active (unfrozen) layer thickness (ALT) and drainage of lakes, and c) transformation of bogs into forest that are anticipated within climate warmings scenarios can all be approximated via comparing the current status of RSM geochemistry across rivers that drain various landscapes and permafrost zones. Specifically, we expected that thickening of the active layer and colonization of palsas bogs by forest would enhance the involvement of mineral horizons in particulate flux from the soil profile to the river via suprapermafrost flow. Alternatively, the disappearance of permafrost should bring about more active participation of underlying silt and sand deposits into RSM flux formation in both small and large rivers. The present work is aimed at testing these hypotheses via conducting a primary survey of chemical composition for river particles across a sizable permafrost and climate gradient in western Siberia.

2. Sampling and analyses

2.1. Study site

We sampled 33 rivers that belong to the Ob, Pur and Taz watersheds in the Western Siberia Lowland (WSL). WSL is a huge peatland (> 2 million km²) situated across taiga forest, forest-tundra and tundra zones (**Fig. 1**). The position of these biomes follows a decrease in mean annual air temperature (MAAT) from -0.5°C in the south (Tomskaya region) to -9.5°C in the north (Yamburg). Annual precipitation ranges from 550 mm at the latitude of Tomsk, 650-700 mm at latitudes for Nojabrsk and Siberian Uvaly, and 600 mm at the lower reaches of the Taz River. The annual river runoff gradually increases northward, from 160-220 mm y⁻¹ in the permafrost-free region to 280-320 mm y⁻¹ in the Pur and Taz river basins which are located in the discontinuous to continuous permafrost zone (Nikitin and Zemtsov, 1986). Permafrost distribution also follows the same latitudinal gradient of MAAT changing from absent through isolated and sporadic in the south to discontinuous and continuous in the north. The landscape parameters of sampled catchments were determined by digitizing available soil, vegetation, lithological and geocryological maps (Pokrovsky et al., 2016; Vorobyev et al., 2017) as listed in **Table S1** of Supplementary Material. Sampling was performed during spring flood (17 May – 15 June 2016), summer baseflow (1 – 29 August 2016), and autumn baseflow before ice (24 September – 13 October 2016) and covered three main hydrological seasons. Note that the collected data set of suspended (> 0.45 µm) and dissolved (< 0.45 µm) WSL river load is unique and independent from previous studies of dissolved river load assessed during several seasons (2013-2015) in WSL (Pokrovsky et al., 2015, 2016). Our previous work in this region was devoted to the biogeochemistry of dissolved (< 0.45 µm) carbon and major and trace elements in rivers sampled over 4 main seasons in 2014 (February, June, August and October) (Pokrovsky et al. 2015, 2016), and dissolved nutrients sampled during Spring and Summer 2015 (Vorobyev et

al., 2017). Transport of the particulate suspended ($> 0.45 \mu\text{m}$) fraction of river load has not been addressed before.

2.2. Sampling of RSM

During sampling we moved from south to north over a 2-3 week period collecting from all rivers in the transect at approximately the same time after ice off and before ice on. To assess inter-annual variations in RSM concentrations, we analyzed the RSM samples collected in WSL rivers across the same transect during previous campaigns in spring 2014, 2015 and 2016 and summer 2015 and 2016. Large water samples were collected from the middle of the river at 0.5 m depth in pre-cleaned polypropylene jars (30 to 50 L) and were allowed to decantate over 2-3 days. The water from the bottom layer of the barrels (approx. 30% of initial volume) was centrifuged on-site for 20 min at 3500 rpm using 50-mL Nalgene tubes. Sediment was frozen at -18°C and freeze-dried later in the laboratory. In addition to decantation and centrifugation, in several rivers, the RSM was collected via direct filtration of large volumes (20 to 30 L) of river water with an Inox (AISI 304) Teflon® PTFE-coated filtration unit (Fisher Bioblock) equipped with 142 mm acetate cellulose Sartorius membranes ($0.45 \mu\text{m}$) and operated at 5-7 bars. An average flow rate of 1-2 L/h was created by a peristaltic pump (MasterFlex B/T) with Teflon tubing. The agreement in elementary composition of RSM between two methods of collection was better than 20%. The total concentration of suspended material was determined in all samples. For this, smaller volumes of freshly collected river water (1-2 L) were filtered on-site (at the river bank or in the boat) with pre-weighted acetate cellulose filters (47 mm, $0.45 \mu\text{m}$) and Nalgene 250-mL polystyrene filtration units using a Mityvac® manual vacuum pump.

2.3. Analyses

Dissolved ($< 0.45 \mu\text{m}$) concentrations of major and trace elements in WSL river waters were analyzed by ICP-MS as described elsewhere (Pokrovsky et al., 2016a, b). Major and trace element concentrations in RSM collected from the large-volume separation procedure were

measured after full acid leaching in a clean room (class A 10,000) following ICP-MS (Agilent 7500 ce) analyses using methods for organic-rich natural samples employed in GET laboratory (Toulouse). The 100 mg dry weight powders were reacted for 30 min in an ultrasonic bath prior to full digestion using a Mars 5 microwave digestion system (CEM, France) using a mixture of 6.5 mL concentrated HNO₃, 3.5 mL concentrated HCl and 0.5 mL concentrated HF. HNO₃ and HCl were bi-distilled in the clean room and HF was of commercial ultra-pure quality (Fluka). For digestion, 10 samples of RSM, 1 certified 2711a Montana II Soil standard [or LKSD sediment] and 1 blank sample were loaded into Teflon reactors and were treated at 150°C for 20 min. After completing the digestion, contents of reactors were transferred into 30 mL Savilex vials and evaporated at 70°C. The residue was dissolved in 10 mL of 10% HNO₃ and diluted by 2% HNO₃ prior to analyses. The concentration of major and trace elements (TE) in filter digestion products was measured using an ICP-MS Agilent 7500ce with ~3 µg/L of In and Re as internal standards. Four in-house external standards were analyzed every 10 samples. The uncertainty for TE measurement ranged from 5 % at 0.1–100 µg/L to 10 % at 0.001–0.01 µg/L.

We interpreted the results for the elements that exhibited a good agreement between the certified or recommended values and our measurements within acceptable uncertainty levels (
$$\frac{([X]_{\text{recommended or certified}} - [X]_{\text{measured}})}{([X]_{\text{recommended or certified}} + [X]_{\text{measured}})/2} \times 100 \leq 10\%$$
), or for cases in which we obtain a good reproducibility (the relative standard deviation of our various measurements of standards lower than 10%), even if no certified or recommended data are available. All certified major (Ca, Mg, K, Na) and trace element (Al, As, B, Ba, Co, Cr, Cu, Fe, Ga, Li, Mn, Mo, Ni, Pb), all REEs, Sb, Sr, Th, Ti, U, V, Zn) concentrations of the SLRS-5 standard (e.g., Yeghicheyan et al., 2013) and the measured concentrations agreed with an uncertainty of 10-20%. Agreement for Cd, Cs and Hf was between 30 and 50%. For all major and most trace elements, concentrations in blanks were below analytical detection limits (≤ 0.1 -1 ng/L for Cd, Ba, Y, Zr, Nb, REE, Hf, Pb, Th, U; 1 ng/L for Ga, Ge, Rb, Sr, Sb; ≤ 10 ng/L for Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As).

In addition to total chemical analysis after HF+HNO₃ digestion, 11 RSM samples of small, medium and large rivers collected in May and August were processed for total Si concentration using wet chemical analysis with photometric detection (see Gurvich et al., 1995; Baturin and Gordeev, 2019 for methodology). Further, the mineralogical composition of particulate fraction on selected filters was studied by X-ray powder diffractometric method on a D8 ADVANCE (Bruker AXS) X-ray diffractometer equipped with a LYNXEYE linear detector (Lisitzin et al., 2015). The uncertainty of the relative proportion of mineral composition was 1–2% and the detection limit was 1%. Due to limited amount of RSM available for analyses, the latter could be performed only on 3 rivers (small, medium and large one) sampled in May and August.

2.4. Statistical treatment

Statistical analysis was used to quantify the relationship between major and trace element concentrations in RSM and % of permafrost, amount of wetlands/lake/forest coverage in the watershed, and the surface area of the watershed ($S_{\text{watershed}}$). For simplicity, we distinguished five zones of permafrost distribution in river watersheds: 1) permafrost-free zones located south of 61°N latitude, 2) isolated zones located between 61 and 63.5°N latitude; 3) sporadic zones located between 63.5 and 65°N latitude; 4) discontinuous zones located between 65 and 66°N latitude, and 5) continuous permafrost zones located north of 66°N latitude. Non-parametric statistics were used because, based on Shapiro-Wilk test of the normality of variables, data on major and trace element concentrations in RSM and the fraction of particulate elements were not normally distributed. For these reasons, we used the median, 1st and 3rd quartiles, to trace dependence of nutrient concentrations to the type of permafrost distribution. Correlations between element concentration in RSM and main parameters of the watershed (latitude, watershed area, runoff, percentage of bogs, forest and lakes and the permafrost coverage) were tested using both Pearson and Spearman coefficients at $p < 0.05$ for permafrost-bearing and

permafrost-free zones during each season as well as all 3 seasons simultaneously. However, because the data were not normally distributed (as verified by the Shapiro-Wilk test of the normality of variables) and due to the small number of samples in the permafrost-free zone (N=8) and possibly non-linear relationships, we preferably presented Spearman's rank correlation coefficient in Results and Discussion below. Further, the Spearman coefficients provided generally better description of element concentration dependence on watershed parameters. The differences in suspended element concentration between different seasons and between each of the two adjacent permafrost zones were tested using a Mann-Whitney U test for a paired data set with significance level at 0.05. For unpaired data, a non-parametric H-criterion Kruskal-Wallis test was performed for all watershed sizes and all permafrost zones.

Multiple regressions were performed for quantifying the relationship between particulate concentration of TE and watershed parameters. More thorough statistical treatment of both log-transformed and non-transformed major and TE concentration in RSM included a normed principal component analysis (PCA). To identify groups of elements that behaved in a similar way in river water particles, we applied a complementary hierarchical cluster analysis (HCA) with the Ward's method for the linkages rule.

3. Results

For convenience, the elements were divided into 5 groups according to their basic physiochemical properties, speciation in surface waters, affinity to colloids and dissolved organic matter, and behavior in peat soils of the region all of which were based on previous studies in WSL soils and waters (Stepanova et al., 2015; Raudina et al., 2017, 2018): 1) alkali and alkaline-earth metals, 2) oxyanions and neutral molecules (Si, B, V, Cr, Nb, W, As, Mo, Sb), 3) heavy metals (Fe, Mn, Cd, Pb, Zn, Cu, Co, Ni), 4) trivalent hydrolysates (Al, Ga, Y, REEs) and 5) tetravalent hydrolysates (Ti, Zr, Hf, Th).

The mineralogical composition of suspended matter (**Supplement A**) was strongly dominated by quartz (50-80%) and plagioclase (9-45%). The RSM of medium (Pyakopur, $S_{\text{watershed}} = 9881 \text{ km}^2$) and large (Pur, $S_{\text{watershed}} = 112,000 \text{ km}^2$) river exhibited small amount (< 10%) of K feldspar, amphibole, pyroxene, illite, chlorite and kaolinite which were however absent in small river (Vach-Yagun, $S_{\text{watershed}} = 99 \text{ km}^2$). We could not find any systematic difference in mineralogical composition of RSM related to season (spring flood versus summer baseflow). Note that the RSM of all WSL rivers has unusually high concentration of organic carbon ($15.3 \pm 9.7 \text{ wt.}\%$) as averaged over seasons (Krickov et al., 2018). Small rivers ($S_{\text{watershed}} < 100 \text{ km}^2$) have 2 to 3 times higher C_{org} (ca., 20-30%) compared to large ones (5-10% C_{org} in rivers with $S_{\text{watershed}} > 10,000 \text{ km}^2$).

3.1. Element concentration in RSM as a function of watershed size, latitude, permafrost, and landscape parameters

The chemical composition of RSM across all seasons in WSL territory is provided in **Table 1**, whereas mean ($\pm$ s.d.) concentrations during 3 seasons for each permafrost zone are listed in **Table S2**. Considering all seasons together, there was no significant difference (at $p < 0.05$) in element concentrations between permafrost-free and permafrost-bearing zone. The only exceptions are P, Ca, Mn, and Ba, which exhibited 2 x higher concentrations in the southern, permafrost-free rivers compared to northern rivers. The effect of permafrost type on major and TE in RSM is represented by box plots for the 5 groups of elements (**Fig. 2**). The overwhelming majority of elements yielded a U-shape dependence of RSM concentration on type of permafrost distribution. This dependence implied a minimum concentration in isolated to sporadic permafrost zone, and 3-5 times higher concentrations in permafrost-free and continuous permafrost zones compared to the beginning of permafrost disappearance (isolated and sporadic). These are elements in the 1st group (Li, Na, K, Rb, Mg), 2nd group (V, Cr, As, Nb, W, U), some elements of the 3rd group (Zn, Cu, Co, Ni), and all elements of the 4th and 5th groups

(TE³⁺, TE⁴⁺). As a result of this U-shape dependence of element concentration on the type of permafrost distribution, all the above mentioned elements exhibited a positive link to latitude and permafrost coverage in RSM of rivers draining through permafrost-bearing territories. Only a few elements did not follow this pattern: (i) Ca, Sr, and Ba were high in RSM of permafrost-free regions and demonstrated stable and low concentrations northward; (ii) B concentration increased northward, and (iii) Fe, Mn, Sb, Mo, Cd, Pb did not demonstrate any consistent (systematic) pattern for concentration dependence on type of permafrost.

Results of statistical treatment of watershed parameters (av. latitude, S_{watershed}, river runoff, % of bogs, forests, lakes and permafrost in the watershed) effect on element concentration in RSM (Spearman's rank correlation coefficient) are listed in Supplementary **Table S3** and analyzed below for separate groups of elements. Among the 1st group elements, alkali and Mg exhibited positive correlation with the watershed size ($R_{\text{Spearman}} = 0.5$ to 0.9 in permafrost-free zone) during spring and summer. In the permafrost-bearing zone, the correlation was lower and became visible only in summer and autumn ($R_{\text{Spearman}} = 0.3$ to 0.6). Latitude positively impacted all alkali and alkaline-earth elements in the permafrost-bearing zone during all three seasons. This is most likely linked to increase in these element concentration northward in the permafrost-bearing zone, as reflected in element box plots described above. In spring, lakes and bogs decreased the concentrations of Li, Na, K, Rb, Mg, Ca, Sr and Ba in the permafrost-bearing zone; this was also seen for Ca and Sr in summer and autumn. The effect of other watershed parameters on alkali and alkaline-earth element concentrations in RSM was not significant ($p < 0.05$). Among the 2nd group elements, V, Cr, Nb, and to a lesser degree W and U exhibited positive ($R_{\text{Spearman}} = 0.7$ to 0.95) correlations with S_{watershed} in permafrost-free regions in spring, summer and autumn. The effect however, was not pronounced in permafrost-bearing rivers. The concentrations of these elements in RSM were not affected by watershed landscape parameters. Statistical treatment of watershed size, permafrost, and landscape effect on Si concentration in RSM could not be performed due to low number of analyzed samples. There

was no clear relationship of Si with most environmental parameters of the watershed, except for a local minimum at 20 to 30% permafrost coverage (**Supplement A**).

Neither the size of the watershed nor its landscape parameters strongly affected the concentration of divalent 3rd group heavy metals. The exceptions are Ni and Cu, which positively correlated with watershed size in permafrost-free zone in spring and summer ($0.70 < R_{\text{Spearman}} < 0.93$). Mn and Fe stand apart from other transition metals as their concentrations were generally higher in small and medium watersheds ($S_{\text{watershed}} < 10,000 \text{ km}^2$) compared to larger ones (**Fig. 3 A, B**). Lakes exhibited a generally negative effect on Fe, Mn, and Co concentrations in the RSM and bogs and lakes negatively affected Mn, Co, Ni and Zn concentrations in the RSM of the permafrost-bearing zone during all seasons (**Table S3** and see **Fig. 3 C, D** as an example).

In the 4th and 5th groups, trivalent and tetravalent hydrolysates, $S_{\text{watershed}}$ significantly increased ($p < 0.05$) concentrations of Cr, V, Al, Ga, Y, all REEs, Ti, Zr, Hf and Th in RSM. This increase was mostly pronounced during summer and autumn (ca., a factor of 3 to 5 between the rivers with $S_{\text{watershed}} = 10\text{-}100 \text{ km}^2$ and rivers with $S_{\text{watershed}} > 100,000 \text{ km}^2$ as illustrated by Al, Y, Ga, Ti, Zr, and Th in **Fig. 4 A, B, C, D, E and F**, respectively). Trivalent and tetravalent hydrolysates were negatively impacted by the presence of bogs in the watershed, especially in permafrost-bearing rivers (**Table S3**). Permafrost and latitude positively impacted the 5th group (TE^{4+}) concentrations in RSM of rivers from the permafrost-bearing zone during all seasons.

Finally, we note that the inter-annual variations of major and TE concentrations for the same 7 rivers sampled in 2014, 2015 and 2016 were generally not significant (Mann-Whitney U-test $p > 0.05$). Several exceptions included Ti that was 20-30% lower in 2016 compared to spring 2014/2015 and summer 2015; Mn, Fe, Co, Y, Mo, Cd and Ba (enriched in spring 2015 compared to 2016); and Co, Ge, Zr, Mo, Sb, Ce and Tl (enriched in summer 2015 over 2016). However, most elements were not systematically different between years and further results are focused on the most complete data set from 2016.

379 3.2. *Suspended over total (dissolved+suspended) fraction as a function of latitude and landscape*
380 *parameters*

381 The suspended fractions of all elements in WSL rivers averaged over all seasons and
382 permafrost zones are listed in **Table 2**. Depending on the mean value of suspended fraction, 3
383 major categories of elements in WSL rivers could be distinguished: (i) soluble, highly mobile
384 elements appearing < 20% in particulate form and > 80% in dissolved (< 0.45 μm) forms: Li, B,
385 Si, Na, Mg, K, Ca, Ni, As, Rb, Sr, Mo, Sb and Ba; (ii) insoluble elements transported essentially
386 (> 60%) in particulate forms: Al, Ti, Fe, Ga, Zr, Nb, Cs, REEs, Hf, Pb, Th, and (iii) other
387 elements present in both the particulate and soluble fraction (20 to 60%): V, Cr, Mn, Co, Cu, Zn,
388 Cd, Y, U. The first group included soluble, highly mobile alkalis, alkaline-earth and some
389 oxyanion elements. The second group included typical low mobility elements, which are usually
390 transported as particles rather than solutes. The third group included mainly transition metals that
391 were equally present in soluble and particulate form.

392 Soluble elements decreased the particulate fraction with increase in $S_{\text{watershed}}$ and
393 increased particulate fraction northward (as illustrated for Ca and Sr in **Fig. S1** of Supplement).
394 Fe was present essentially (> 50%) in particulate form with a lower fraction of RSM_{Fe} in small
395 watersheds (< 100 km^2) compared to larger ones, and without clear relationship to bog, lake or
396 forest coverage in the watershed (**Fig. S2 A, B, C**). Mn exhibited lower particulate fraction in the
397 smallest rivers ($S_{\text{watershed}} < 100 \text{ km}^2$) compared to large rivers (**Fig. S2 D**) and did not show any
398 significant linkage ($p > 0.05$) to latitude, permafrost or landscape parameters (not shown).

399 The share of suspended Al increased with the increase in $S_{\text{watershed}}$ and forest coverage
400 (**Fig. 5 A and B**, respectively). This effect was not observed for other insoluble elements such as
401 Fe and Mn. Ti, Zr and REEs also increased the particulate fraction with increase of the
402 watershed size (**Fig. 5 C, D** for Ti and Zr, respectively). Cu and Ni decreased the share of their
403 suspended transport with increase in forest proportion in the watershed (**Fig. S3 A, B**,

respectively), but increased with bog coverage (**Fig. S3 C, D**). Watershed size and latitude weakly affected Cu suspended fraction (**Fig. S3 E**) but did not influence Ni (not shown).

3.3. Multiparametric statistics

The PCA treatment of element concentrations in RSM and watershed physiological parameters revealed two factors capable of describing only ~40% and 5-10% of overall variance. The F1 x F2 structure was highly similar and stable among seasons and permafrost zones for all rivers regardless of size. None of the factors were linked to landscape parameters. The 1st factor acted on most insoluble elements and divalent metals but also acted on alkalis and alkaline-earth metals. The 2nd factor acted on P, Ca, Sr, As, Ba, Mn and Fe (**Table S4, Fig. S4A**). It is important to note that 2nd factor was not pronounced in spring; during this high discharge period most elements (with exception of Mn, Sb, W) were controlled by the 1st factor and were merely linked to transport of silicate suspended material. The HCA yielded very strong links (linkage distance < 0.1) between insoluble elements (TE³⁺, TE⁴⁺) but also between some alkali and alkaline earth metals (Li, Na, Mg, K, Rb, Cs), V, and Ge. These alkali and alkaline earth metals were presumably hosted by silicate minerals (clays) dominating the RSM (**Table S4 and Fig. S4 B**).

4. Discussion

We will begin by discussing the RSM concentration and its chemical composition compared to other rivers of N. Eurasia and more generally the world. We then transition into analyzing the impact of watershed size and seasons on variability of major and trace element particulate

concentrations across a latitudinal and permafrost gradient while also taking into consideration the function of landscape parameters on the watershed. We conclude with discussion on the possible impact of a permafrost boundary shift northward and change in proportion of landscape components (bogs, forest and lakes) on major and trace element concentrations in suspended material of WSL rivers.

4.1. Chemical composition of western Siberia river particles in comparison to world's rivers.

In general, the average chemical composition of RSM across the world is comparable to that of the upper part of continental earth crust or shale (Savenko et al., 2006a, b; Viers et al., 2009). Taking the average values of non-permafrost + permafrost zones as a whole for Western Siberia, we calculated the ratio of element concentration in the RSM of WSL to the average elementary concentration in suspended sediments of world rivers (Viers et al., 2009) as illustrated in **Fig. 6**. Typically, WSL rivers are impoverished (the ratio $0.2 \leq \text{RSM}_{\text{WSL}}/\text{RSM}_{\text{World}} \leq 0.5$) with respect to Mg, Al, K, Ca, V, Cr, Ni, Cu, Zn, Ga, Ge, Rb, Y, Cd, Sb, Cs, REEs, Tl, Th and U. Stronger depletion ($\text{RSM}_{\text{WSL}}/\text{RSM}_{\text{World}} < 0.2$) has been observed for Zr and Mo in WSL rivers. We interpret this result as being due to the sizeable proportion of organic matter in RSM in western Siberia (Krickov et al., 2018), and the corresponding impoverishment of suspended matter in elements hosted by silicate (clay) materials. Note however that the world average value is essentially based on data from big rivers. These rivers are enriched in silicate mineral-dominated components because they carry higher proportions of suspended silicate material and smaller fractions of organic-rich particles. The WSL rivers are sizeably enriched relative to the world average only with respect to P and Mn (a factor of 2.5 and 4.8, respectively). Along with elevated C concentration in suspended matter of WSL rivers (ca., 15%, Krickov et al., 2018), this reflects presence of peat particles and vegetation debris as important components of RSM. Further, WSL rivers contain sizeably amount of Mn^{2+} oxidation products which are supplied from surrounding lakes and bogs, leading to enrichment in Mn hydroxide. It is important to note

that certain pristine C-rich rivers in N. Europe (i.e. Kalix River) also demonstrate high Mn_{RSM} concentrations due to formation of authigenic Mn oxides (i.e. Ponter et al., 1992; Andersson et al., 1998). In western Siberia, the high enrichment of RSM in Mn during summer and autumn may reflect biological removal of Mn^{2+} from lake and river water as well as immobilization of dissolved Mn on the surface of phytoplankton due to local pH rise during photosynthesis. This is consistent with laboratory microcosms (Shirokova et al., 2017) and the diurnal variation of Mn concentration during phytoplankton bloom (Pokrovsky and Shirokova, 2013).

Another explanation for elevated Mn and P in WSL rivers is the origin of these elements from an underground source. The 2nd PCA factor acted on Ca, Sr, Fe, Mn and P and was pronounced only in summer and autumn, when the groundwater influx in the hyporheic zone is highest. We hypothesize that anoxic conditions of the shallow groundwater create a favorable environment for generation of P, Mn and Fe-enriched particles due to oxidation of Fe^{2+} and Mn^{2+} and related to this P coprecipitation. However, the underground signal of Fe is offset (blurred) by the high concentration of this element in riverine mineral particles originating from bank abrasion and sedimentary rock physical weathering.

The REE upper-crust (UC) normalized pattern of average WSL rivers was rather flat with only a slight Eu-Gd anomaly (**Fig. 7**). Similar flat patterns of REE distribution were reported for many rivers across the world (Viers et al., 2009). In contrast to the majority of other rivers in the world which exhibit stronger enrichment in REE relative to UC, WSL rivers are impoverished compared to UC by a factor of ~2. Note that the lack of significant fractionation of REE in WSL river particles is reflected in PCA and HCA diagrams showing compact clusters of all REEs. The similarity of REE patterns in all WSL rivers and the lack of fractionation were presumably due to highly homogeneous sedimentary rock substrate (silt and sand) dominating the WSL territory. UC-normalized REE patterns for peat cores from WSL were also flat with Eu-Gd enrichment, reflecting a crustal origin for solid and liquid aerosols incorporated by mosses and preserved in the peat profile (Stepanova et al., 2015).

4.2. Role of landscape factors and permafrost in elementary composition of RSM

The present study allowed, for the first time in permafrost-affected territories, assessment of the role of watershed size on chemical composition of RSM during different seasons. Watershed size positively affected the concentration of many insoluble elements (TE^{3+} , TE^{4+}) in the RSM (**Fig. 4, Table S3**). These elements are typically linked to a relatively dense and insoluble (silicate) fraction of the suspended load. However, it is important to note that some elements of the 1st group could be linked to clay minerals via ion exchange interlayer sites within the clays. This is consistent with presence of illite and chlorite in RSM of large and medium size rivers and the absence of these minerals in a smaller river (Supplement A, Table A2). The positive link of $S_{\text{watershed}}$ to element concentrations in the RSM suggests that larger rivers have an enhanced capacity for physical erosion of river bank and remobilization of riparian zone clay sediments, especially pronounced during high flow. In contrast to large rivers, small rivers of the WSL often flow within peat zones with relatively little access to water flux of mineral substrate (Pokrovsky et al., 2015).

The forest coverage of the watershed was positively correlated with K, Rb, Sr, Mn, Co concentrations in the RSM collected in spring (**Table S3**). Furthermore, considering all seasons together, the presence of forest in the watershed positively acted on a number of elements but only in the permafrost-bearing zone (**Table S3**). These are all alkalis and alkaline-earth elements: B, As, Nb, Mn, Co, Al, Ga, REEs, Ti, Zr, Hf, Th. Such a long list of elements suggests that the forest mobilizes not only organic litter but also mineral particles from the soil to the river. This hypothesis is consistent with the following observations:

1) ALT strongly increases under forest growing in permafrost-affected territories of the WSL (Goncharova et al., 2015), 2) soils under forest cover are mineral-rich podzols unlike organic-rich histosols of palsa peat bog (Khrenov, 2011; Kulizhskiy et al., 2017a; Lim et al., 2017; Loiko et al., 2017), 3) mineral soils under forest exhibit stronger biological activity compared to peat

soils (Goncharova et al., 2016), and 4) the removal of fine particles from soil occurs more efficiently under well drained forest environment as it is known in various forest soils (Tonkonogov, 1999; Quénard et al., 2011) including those of Western Siberia (Loiko et al., 2015).

In reference to 1) the strong ALT increases under forests growing in permafrost-affected territories of the WSL lead to preferential water discharge to rivers through subsurface and shallow groundwater flow. This contrasts to shallow suprapermafrost flow within the peat horizons in tundra and bog zones (Raudina et al., 2018). Or in other words, in forest settings, thaw water flux over frozen horizons occurs through mineral layers in contrast to bog settings where this water flows to the river through organic horizons. Deep water flow paths increase the water travel time (Ala-aho et al., 2018) and lead to more efficient disintegration of mineral soil particles before their delivery to the river. In reference to 2), since soils under forest cover are mineral-rich podzols and not the organic-rich histosols of palsa peat bogs, forest soils are capable of supplying a larger amount of mineral particles due to physical erosion of soil mineral horizons. The potential of fine particles transport in some forest mineral soils of Western Siberia has been recently demonstrated (Kulizhskii et al., 2017b). As such, forest soils may act as sources for vertically and laterally moving C-rich colloids and suspensions. And finally in reference to 3), stronger biological activity in mineral soils under forests (when compared to peat soils) leads to stronger physical degradation of plant litter debris as well as mineral particles during local transport within the soil profile.

A striking result of the present study is the minimum concentrations of most major and TE in the sporadic to isolated permafrost zone belt (Li, Mg, K, Rb, V, Nb, U, Zn, Cu, Ni, Co, all trivalent and tetravalent hydrolysates as shown in **Fig. 2**). This can be explained as preferential retention of mineral components in thawing soils in the zone, and consequently, enhanced mobilization of particulate organic carbon rather than silicate minerals from soil to river. The later was demonstrated in a recent study of particulate nutrients across the WSL river gradient by

Krickov et al. (2018). This is also consistent with a local minimum of Si concentration in suspended matter of rivers having 20 to 30% of permafrost in their watersheds (**Fig. Supplement A**). The reason for the organic C maximum in the isolated to sporadic permafrost zone is that, at onset of permafrost appearance, soil water drains through the full depth of the unfrozen peat column which as a result provides mainly organic particles to the RSM.

In the northern, discontinuous and continuous permafrost zones, water travel time is much faster (Ala-aho et al., 2018) and runoff is higher (Nikitin and Zemtsov, 1986). Consequently, even small rivers exhibit a higher capacity for removal mineral sediments from soil horizons and, via bank abrasion, from former alluvial sediments within extended riparian zones. In this regard, the slower water flow in permafrost-free southern rivers is partially compensated by higher depth of active soil layer and possibility to mobilize mineral components by surface and shallow subsurface inflow to the river. As a result, both minimal capacity of surrounding soils to supply the mineral components to the river and the minimal ability of the river to mobilize mineral particles from riparian zone are encountered in rather narrow belt at the ‘permafrost thaw front’, in the isolated to sporadic zone.

4.3. Relative fraction of suspended over total (dissolved+suspended) elements in RSM of WSL

In permafrost-free watersheds, export of solid particles from the soil to the river occurs via lateral flow through the soil, oversurface flow in the forest floor, and by shallow groundwater discharge within the riparian or hyporheic zone. In the permafrost-affected territories, this transport is essentially controlled by suprapermfrost flow over the frozen layer via organic or mineral horizons. Although the mineral particles dominate the suspended load of all rivers regardless of size, the very small ones ($S_{\text{watershed}} < 100 \text{ km}^2$) are strongly influenced by plant litter and organic detritus (Krickov et al., 2018). Irregular spatial and temporal delivery of these C-rich particles from soil to river produces much higher scattering in the particulate fraction value. Note

here that for soluble highly mobile elements such as B, Na, Ca, Sr the effect is less pronounced in large rivers compared to small ones: large rivers are subjected more to effects of deep groundwaters feeding through taliks. These underground waters are rich in dissolved ($< 0.45 \mu\text{m}$) soluble elements and poor in suspended matter. Because the role of underground feeding strongly decreases in permafrost-bearing rivers (Frey et al., 2007b; Pokrovsky et al., 2015), these elements exhibited an increase in particulate form with both latitude and permafrost coverage (see **Fig. S1 B, C**). This feature can be interpreted as due to diminishing of the effect of groundwater (dissolved form input) and the appearance of minerals (clay horizons) due to maximal deepening of the active layer. There was a decrease in the particulate fraction of Mg, Ca, Sr in large rivers compared to smaller ones (see example for Ca and Sr in **Fig. S1 A and D**, respectively). The most likely reason for this is enhanced feeding of large rivers through deep underground water located within calcareous collectors, as evidenced from dissolved ($< 0.45 \mu\text{m}$) element patterns across the WSL riverine transect (Pokrovsky et al., 2015, 2016).

In contrast, there was an increase in particulate versus total (particulate dissolved) transport of Al, Ga, Cr, Co, Mn, Fe, REE, and Ti, Zr, Hf, Th with an increase in watershed area (**Fig. 5 A, C, D**). Such a pattern can be explained by efficient mobilization to the river, via abrasion of river banks, of fine clays containing these low soluble immobile elements. Al exhibited strong increase in particulate fraction northward and with an increase in $S_{\text{watershed}}$ during all seasons (**Fig. 5 A**). Enhanced mobilization of particulate Al in northern rivers in autumn, at the maximum of active layer thickness, may be due to involvement of mineral horizon to soil water paths occurring at the end of summer season. An additional reason for the low particulate fraction of Al in small rivers draining peatlands is enrichment of these rivers in dissolved ($< 0.45 \mu\text{m}$) Al due to high DOC and low pH. As a result, the ratio of particulate Al to total Al in these small streams is lower than that in large rivers.

Among divalent heavy metals, only Mn, Ni and Cu demonstrated certain correlations of particulate fraction with landscape and permafrost parameters. The trend of increasing the

particulate transport of Mn with $S_{\text{watershed}}$ increase (**Fig. S2 D**) is interpreted as due to an increase in residence time of this element in rivers. This would lead to transformation of dissolved $\text{Mn}^{2+}(\text{aq})$ into particulate forms of $\text{Mn}^{(\text{III}, \text{IV})}$ hydroxides via biotic and photochemical processes. Such processes were identified during the diurnal cycle of this element in boreal humic lakes (Pokrovsky and Shirokova, 2013) and also in boreal high latitude rivers (Ponter et al., 1992). Similarly, Ni and Cu exhibited an increase in suspended fraction with a decrease in watershed size (**Fig. S3 E**), especially visible in autumn for Cu ($R^2 = 0.32$, $p < 0.05$). This can be linked to Cu and Ni coprecipitation with/ adsorption onto Mn oxy(hydr)oxides. Additional point to consider is that this effect was consistent with an increase in C_{org} (RSM) in small rivers (Krickov et al., 2018) thereby demonstrating a close link between C and Cu. In autumn, there was an increase in particulate Cu share northward (**Fig. S3 F**) as well as an increase in lake and bog coverage of the watershed (**Fig. S3 C**). It could be linked to the coagulation of Cu-organic associates in lentic waters and their release into the river system during autumn floods rain.

A specific feature of WSL rivers is impoverishment of their RSM relative to world average suspended load values in a number of low-solubility low-mobility elements such as certain divalent heavy metals, all trivalent hydrolysates and all tetravalent hydrolysates (**Fig. 6**). Typically, these elements are transported in essentially the particulate fraction but this is not the case for WSL rivers which demonstrate a high colloidal load (Pokrovsky et al., 2016b). For example, the proportion of suspended over total Fe in WSL rivers ranges from 95 to 30% (**Fig. S2**) whereas the majority of world rivers exhibit values between 99 and 80%; furthermore, the share of particulate Fe decreases down to 40% only in some organic-rich rivers (Olivie –Lauquet et al., 1999). Our results corroborate the former observations that, depending on the size of the river and organic matter content, Fe may occur as Fe-OM colloidal associates and iron hydroxide particles (Olivie –Lauquet et al., 2000). In WSL streams and rivers there is a continuum of colloidal and particulate Fe that is stabilized by organic matter (Pokrovsky et al., 2016b). We hypothesize that these organic and organo-mineral colloids are responsible for the sizeable

decrease in RSM fraction of low-soluble elements with $S_{\text{watershed}}$ decrease. Overall, compared to the world average, WSL rivers exhibit relatively low amounts of suspended elements relative to the total (suspended+dissolved) load due to 3 factors: 1) low runoff and low RSM concentration as a result of no bare rocks and mineral substrates exposed to physical weathering, 2) the organic rather than mineral nature of surrounding “solid” substrates and the resulting high share of organic matter in the RSM and 3) high DOC and Fe concentrations leading to a high concentration of typically low-soluble elements in the dissolved ($< 0.45 \mu\text{m}$) fraction due to colloids. In reference to the 2nd factor it is important to note that in spring, when the highest RSM flux occurs, mineral soil horizons are fully frozen (Raudina et al., 2017).

4.4. Mechanisms of RSM enrichment and impoverishment in elements and perspectives for the permafrost thaw and climate change

A cartoon of possible processes generating the suspended load on WSL rivers and the RSM composition evolution under climate change and permafrost thaw is shown in **Fig. 8**. The enrichment of river water in mineral and organic suspended particles occurs at the main channel (via bank abrasion and resuspension of sediments at the floodplain) and in the thermokarst lakes connected to rivers. Mobilization of particles rich in lithogenic elements from deep mineral horizons and riparian sediments may occur via both bank erosion by flood and storm events and through suprapermfrost flow in summer and autumn. The latter process is enhanced in the presence of forests as trees increase the active layer thickness and allow soil fluids to reach the mineral horizon and export particles via lateral flow to the river.

Within the climate change context in WSL, there are four main processes capable of affecting RSM chemical composition as illustrated in **Fig. 8**: 1) a permafrost boundary shift northward, consisting in disappearance of continuous permafrost in the north and replacement of discontinuous permafrost by sporadic and isolated permafrost; 2) an increase in the ALT leading to involvement of a deeper soil/rock horizon in vertical and lateral water movement in the south

which would extend the duration of period when soil pore fluids can enter and come into contact with mineral layers under the peat horizon in the north; 3) a change of landscape environment such as northward migration of the forest line, colonization of bogs by forest and dwarf shrubs and thermokarst lake drainage; and 4) in the permafrost-affected part of WSL, the feeding of rivers by underground water through taliks can raise the winter discharge of the rivers. Although the 4th mechanism should not affect RSM chemical composition (except for Fe(III) oxy(hydr)oxide formation due to Fe²⁺ oxidation), it does influence the dissolved (< 0.45 μm) fraction of the river load (see discussion in Pokrovsky et al., 2015) and thereby controls the change in suspended fraction over total (dissolved+suspended) transport.

Results obtained here allow first-order foresight on the effect of climate warming and permafrost thaw on major and trace element concentrations in the suspended load of WSL rivers. The concept of “substituting space for time” in the WSL (Frey et al., 2007 a, b; Frey and Smith, 2005) implies a shift of the permafrost boundary to northward combined with simultaneous increase in ALT (**Fig. 8**). On a short-term scale (10 to 100 years) this may reconfigure permafrost distribution as following: continuous $\rightarrow$ discontinuous; discontinuous $\rightarrow$ sporadic; sporadic $\rightarrow$ isolated, isolated $\rightarrow$ absent. The U-shape dependences of most element concentration on permafrost type demonstrate a minimum at the beginning of permafrost thaw, in sporadic to discontinuous permafrost zones (**Fig. 2**). This concentration pattern implies that, upon a progressive shift of the permafrost boundary northward, there will be sizeable decrease in the concentration of alkalis, alkaline-earths, divalent heavy metals, and trivalent and tetravalent hydrolysates in northern rivers in currently discontinuous and continuous permafrost zones. This decrease may be a factor of 2 to 5 as follows from the position of the minimum elemental concentration in sporadic to discontinuous permafrost zones relative to the continuous permafrost zone (**Fig. 2**).

Moreover, an increase in the ALT will likely increase the particulate fraction in total element transport for many soluble (labile) and also lithogenic elements in WSL rivers, as more

mineral horizons (currently frozen under the peat layer) will be involved in water drainage and lateral export through soils. Specifically, if the current rate of soil warming persists, the active layer thickness may reach 4 m in the tundra of Yamal Peninsula, which is currently continuous permafrost zone, by the year 2100 (Sudakov et al., 2011). These changes will certainly produce much deeper water paths toward mineral soils and underlying sand, silt and clay deposits. As a result, the concentration of particulate lithogenic elements in the northern part of WSL may increase. On a long-term scale (100 to 1000 years), forests will progressively take over bogs and lakes and the permafrost-bearing territory will become a permafrost-free one. Regardless of season, an increase in forest proportion within the river watershed will inevitably increase concentrations of many elements (all alkalis and alkaline-earths, B, Mn, Co, As, Al, Ga, REEs, Nb, Ti, Zr, Hf, Th) in the permafrost-bearing zone. Although this increase is unlikely to offset the predicted decrease in concentration due to permafrost boundary shift northward, the overall impact of permafrost thaw and vegetation rise on element concentrations in RSM may be more complex than what follows from a mere shift in the permafrost boundary northward.

As for the evolution of particulate element fraction over total (dissolved + particulate) form, the increase in water connectivity between deep underground reservoirs and rivers due to permafrost thaw and the widespread appearance of taliks may increase the input of dissolved elements thereby further decreasing the already low share of particulate forms to total element export from the WSL territory to the Arctic Ocean. In this regard, peatlands of continental planes having low runoff may represent an exception compared to rivers of other mountainous subarctic regions. The latter will certainly increase their particulate flux following gradual increase in precipitation and ALT as well as abrupt permafrost thaw.

CONCLUSIONS

In order to resolve poorly known features of chemical composition of river suspended particles in the permafrost region, we measured major and trace elements in RSM of 33 western

Siberian rivers during different seasons. The concentration of all elements in the RSM followed the order “spring > summer ≥ autumn”. This order reflects the capacity of running water to mobilize relatively heavy (compared to peat) mineral particles via bank abrasion, resuspension in riparian zone, and lateral influx from soils via shallow subsurface and suprapermafrost flow.

The forest acted as an important source of elements in RSM as it enhanced the water path down to mineral horizons leading to physical erosion, breakdown of soil mineral particles via biological activity in the deep rooting zone thereby facilitating delivery of particles from deep soil horizons to subsurface inflow to the river. The lakes and bogs mainly retained mineral particles while generating C-rich RSM; however this was observed only for permafrost-bearing zone. The RSM enrichment in the soluble highly mobile elements (alkalis, alkaline earths) fraction for northern rivers is due to lower transport of the dissolved (< 0.45 μm) fraction for these elements in permafrost-bearing zones, where, compared to southern rivers, the underground feeding of rivers from carbonate-hosted deep rocks is not pronounced.

Compared to the other rivers of the world, the WSL rivers exhibited low suspended fraction of insoluble trace elements, presumably due to colloidal transport provided by high DOC and Fe concentration. We observed minimal concentrations of trace element in the RSM of isolated and sporadic permafrost zone. Using a “substituting space for time’ concept for predicting future changes in river chemistry, we foresee that the permafrost boundary shift may sizeably (2 to 5 times) decrease major and TE concentrations in RSM of northern rivers located in discontinuous to continuous permafrost zones; the forest line migration northward may only partially offset this decrease. At the same time, the increase in active layer thickness may enrich the RSM in lithogenic low soluble elements.

Acknowledgements:

We acknowledge the main support from an RSCF (RNF) grant No 18-17-00237 “Mechanisms of hydrochemical runoff of the Ob River...” and partial funding from RFFI (RFBR) grants No 16-

34-60203-mol_a_dk, 18-35-00563\18, and 19-55-15002. Chris Benker is thanked for English proofread corrections.

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Fig. 1. Sampling sites and physio-geographical context of WSL territory investigated in this work. The sampling numbers are explained in Table S1.

1st group

Fig. 2. Box plot of first and third quartiles (25 and 75%) of 5 groups of elements in the suspended matter of WSL rivers.

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2nd group

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1002 **Fig 2, continued**

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3rd group

Fig 2, continued

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4th group & 5th group

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1016 **Fig 2, continued**

Fig 3. Concentration of Fe (A) and Mn (B) in suspended matter of western Siebrian rivers as a function of watershed area and as a function of lake coverage of the watershed (C, D, respectively). The solid lines represent empirical, 2nd order polynom fit to the concentration dependence on lake percentage, with significant ($p < 0.05$) regression coefficients given in the graphs.

Fig 4. Concentration of Al (A), Ga (B), Y (C), Ti (D), Zr (E) and Th (F) in RSM of WSL as a function of watershed area. The solid lines represent empirical exponential fit to the concentration - watershed dependence with significant ($p < 0.05$) regression coefficients given in the graphs.

Fig. 5. Suspended fraction of Al in RSM total (suspended + dissolved) transport as a function of watershed area (A) and forest coverage of the watershed (B) and particulate fraction of Ti (C) and Zr (D) as a function of $S_{\text{watershed}}$. The solid lines represent 1st or 2nd polynomial empirical fit to the data, with significant ($p < 0.05$) regression coefficients given in the graph.

Fig. 6. The ratio of element concentration in RSM of WSL rivers (averaged over all seasons and permafrost zones) to the average element concentration in RSM of rivers worldwide (Viers et al., 2009).

Fig. 7. Upper-crust normalized pattern of WSL rivers suspended load (averaged over all seasons, river sizes and permafrost zones)

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1087 **Figure 8.** A scheme of element mobilization from the soil to the river in the form of suspended particles and provision for the change of element
 1088 concentrations in RSM and the share of suspended over total element transport under scenario of climate warming, permafrost thaw and landscape
 1089 evolution in western Siberia. The 4 relevant processes controlling the RSM delivery from the soil to the river are influenced by climate change in WSL
 1090 and impact element concentrations in WSL and the share of suspended fraction.

1091 **Table 1.** Mean ($\pm$ SD) concentrations (ppm dry weight) of elements in RSM of WSL averaged over
1092 all seasons and permafrost zones.

	All seasons permafrost-free N=24	All seasons permafrost-bearing N=68	All seasons All WSL N=92
Li	15.6 $\pm$ 10.7	10.2 $\pm$ 8.62	11.6 $\pm$ 9.46
B	9.76 $\pm$ 8.42	12.4 $\pm$ 14.0	11.7 $\pm$ 12.8
Na	3713 $\pm$ 2284	3760 $\pm$ 2856	3748 $\pm$ 2707
Mg	5481 $\pm$ 2846	4059 $\pm$ 2719	4430 $\pm$ 2808
Al	30930 $\pm$ 20812	24091 $\pm$ 17354	25875 $\pm$ 18450
P	7007 $\pm$ 6047	4187 $\pm$ 3004	4923 $\pm$ 4176
K	6995 $\pm$ 4539	6304 $\pm$ 4189	6484 $\pm$ 4269
Ca	17097 $\pm$ 12323	6048 $\pm$ 2917	8930 $\pm$ 8273
Ti	7756 $\pm$ 4773	8237 $\pm$ 6058	8112 $\pm$ 5729
V	61.4 $\pm$ 31.8	56.6 $\pm$ 34.6	57.9 $\pm$ 33.8
Cr	42.7 $\pm$ 25.3	41.1 $\pm$ 34.4	41.5 $\pm$ 32.2
Mn	14219 $\pm$ 19572	5829 $\pm$ 5909	8018 $\pm$ 11670
Fe	75641 $\pm$ 50000	67760 $\pm$ 42800	69816 $\pm$ 44700
Co	32.7 $\pm$ 44.2	21.8 $\pm$ 18.2	24.6 $\pm$ 27.6
Ni	26.9 $\pm$ 12.8	23.1 $\pm$ 20.4	24.1 $\pm$ 18.7
Cu	16.4 $\pm$ 8.71	14.0 $\pm$ 12.3	14.6 $\pm$ 11.5
Zn	112.8 $\pm$ 58.7	82.1 $\pm$ 65.6	90.1 $\pm$ 65.0
Ga	8.46 $\pm$ 3.74	6.01 $\pm$ 3.63	6.65 $\pm$ 3.80
Ge	0.42 $\pm$ 0.30	0.30 $\pm$ 0.25	0.33 $\pm$ 0.27
As	34.8 $\pm$ 28.7	13.9 $\pm$ 12.0	19.3 $\pm$ 20.0
Rb	36.3 $\pm$ 24.3	26.1 $\pm$ 18.9	28.8 $\pm$ 20.8
Sr	180 $\pm$ 117	115 $\pm$ 193	132 $\pm$ 178
Y	9.75 $\pm$ 4.85	8.75 $\pm$ 4.56	9.01 $\pm$ 4.63
Zr	34.8 $\pm$ 21.2	34.5 $\pm$ 22.1	34.6 $\pm$ 21.7
Nb	15.7 $\pm$ 9.69	14.9 $\pm$ 11.1	15.1 $\pm$ 10.7
Mo	0.49 $\pm$ 0.43	0.45 $\pm$ 0.31	0.46 $\pm$ 0.34
Cd	0.35 $\pm$ 0.22	0.31 $\pm$ 0.19	0.32 $\pm$ 0.19
Sb	0.73 $\pm$ 0.57	0.71 $\pm$ 1.33	0.72 $\pm$ 1.17
Cs	2.40 $\pm$ 1.74	1.39 $\pm$ 1.04	1.65 $\pm$ 1.33
Ba	617 $\pm$ 357	329 $\pm$ 181	404 $\pm$ 270
La	13.9 $\pm$ 6.29	12.2 $\pm$ 6.80	12.6 $\pm$ 6.68
Ce	28.9 $\pm$ 15.0	25.5 $\pm$ 14.6	26.4 $\pm$ 14.7
Pr	3.20 $\pm$ 1.68	2.88 $\pm$ 1.65	2.96 $\pm$ 1.66
Nd	12.4 $\pm$ 6.46	11.3 $\pm$ 6.37	11.6 $\pm$ 6.37
Sm	2.53 $\pm$ 1.31	2.24 $\pm$ 1.23	2.31 $\pm$ 1.25
Eu	0.59 $\pm$ 0.27	0.52 $\pm$ 0.28	0.54 $\pm$ 0.28
Gd	2.50 $\pm$ 1.25	2.20 $\pm$ 1.20	2.28 $\pm$ 1.21

Tb	0.34±0.17	0.30±0.16	0.31±0.17
Dy	1.92±0.99	1.73±0.94	1.78±0.95
Ho	0.36±0.18	0.33±0.17	0.33±0.18
Er	1.06±0.55	0.97±0.51	0.99±0.52
Tm	0.15±0.08	0.14±0.07	0.14±0.07
Yb	0.97±0.51	0.91±0.48	0.93±0.49
Lu	0.14±0.07	0.13±0.07	0.14±0.07
Hf	4.80±3.01	4.57±2.99	4.63±2.98
Ta	1.17±0.73	1.04±0.77	1.07±0.76
W	0.95±0.48	1.04±2.24	1.02±1.94
Tl	0.20±0.13	0.16±0.10	0.17±0.11
Pb	12.8±5.22	12.9±9.00	12.8±8.16
Th	3.78±2.38	2.75±1.77	3.02±1.98
U	0.81±0.49	0.68±0.42	0.72±0.44

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1110 **Table 2.** The percentage of particulate (> 0.45 µm) over total (particulate + dissolved (< 0.45 µm))
1111 concentration of elements in WSL rivers across three seasons and two permafrost zones (mean ± SD).

	Spring		Summer		Autumn	
	permafrost-free N=8	permafrost-bearing N=20	permafrost-free N=8	permafrost-bearing N=24	permafrost-free N=8	permafrost-bearing N=24
Li	8.76±8.69	11.3±8.4	4.45±3.08	2.45±2.36	1.20±0.77	5.22±4.61
B	0.61±0.55	1.89±1.12	0.55±0.55	0.71±0.94	0.10±0.09	2.17±2.67
Na	1.54±1.41	3.59±3.34	0.73±0.65	1.49±3.20	0.14±0.13	1.67±2.06
Mg	2.09±2.22	4.04±3.93	0.72±0.59	3.08±5.34	0.19±0.16	3.83±5.97
Al	66.8±32.8	70.2±22.0	81.6±24.0	82.2±21.4	81.8±22.1	81.3±16.1
K	6.44±6.19	19.8±14.2	6.19±5.54	8.17±9.39	1.47±1.48	15.8±14.8
Ca	0.46±0.46	2.61±2.47	0.41±0.21	1.52±1.76	0.17±0.13	2.08±2.37
Ti	79.9±20.1	88.1±16.2	83.9±21.0	79.3±17.8	90.3±19.2	98.4±1.68
V	42.7±26.8	54.3±17.2	45.3±19.0	48.3±19.4	27.1±18.7	54.1±16.1
Cr	49.8±34.6	32.5±21.3	59.1±22.8	51.4±21.2	29.9±17.2	36.8±14.4
Mn	59.8±19.6	32.9±21.7	83.8±21.8	56.0±36.0	93.8±10.0	46.5±27.8
Fe	49.4±28.5	51.3±18.5	79.1±21.0	71.1±23.3	71.1±19.6	72.8±17.6
Co	53.2±25.0	42.3±22.1	64.2±17.2	48.3±21.5	42.6±24.1	47.6±20.2
Ni	16.3±17.5	16.3±11.0	25.4±22.5	24.8±21.8	8.37±5.06	25.4±14.0
Cu	8.41±7.71	20.5±11.8	22.2±15.1	24.2±16.1	17.4±16.7	39.0±19.6
Zn	23.0±19.2	15.2±10.8	50.3±17.2	26.9±14.7	36.9±23.1	38.5±14.5
Ga	81.0±20.8	75.4±20.5	85.9±9.5	76.6±22.0	76.2±19.6	80.0±15.9
As	10.6±7.4	14.3±8.2	25.9±16.7	19.3±10.5	19.6±18.2	26.9±12.9
Rb	30.0±26.5	34.5±20.9	24.3±18.7	16.8±13.3	7.34±4.32	30.7±20.1
Sr	1.13±1.34	7.01±6.11	0.90±0.52	2.68±2.58	0.33±0.27	4.13±4.06
Y	31.6±28.7	29.6±17.7	68.8±22.5	48.6±17.7	52.2±23.8	48.3±18.4
Zr	52.9±33.7	66.6±21.2	74.0±27.0	66.7±20.4	71.6±28.4	70.8±16.7
Nb	77.5±26.4	89.6±15.8	87.0±20.9	90.2±10.7	84.5±26.4	95.6±5.8
Mo	1.64±1.07	22.5±17.8	4.29±3.8	17.5±15.7	2.07±2.73	27.6±19.3
Cd	19.8±11.8	22.3±13.5	41.5±26.7	28.1±19.0	32.7±19.1	44.4±21.5
Sb	6.35±4.19	12.0±9.54	9.51±6.5	13.1±10.6	13.4±11.7	23.6±16.7
Cs	76.2±28.4	72.5±30.1	80.8±26.8	60.8±25.9	68.8±27.1	71.2±26.0
Ba	11.6±9.08	31.0±20.1	15.7±6.7	24.8±14.3	6.95±5.27	28.1±17.4
La	39.4±31.0	34.1±18.8	83.4±17.4	60.4±22.2	73.1±27.6	55.5±22.2
Ce	47.3±30.9	42.6±18.9	87.4±18.4	66.9±21.6	82.0±24.5	67.1±20.1
Nd	39.6±32.0	39.2±18.3	80.2±23.8	61.6±21.4	74.5±25.2	61.6±20.8
Yb	31.8±29.6	30.2±15.8	65.7±24.4	44.1±17.5	53.0±25.6	43.3±16.1
Hf	54.8±33.8	64.5±21.5	77.3±25.1	66.6±22.9	74.2±28.1	76.5±15.5
Pb	54.6±29.6	57.8±24.0	85.0±14.1	56.3±21.8	79.8±22.6	79.8±11.4
Th	50.1±34.6	57.5±18.9	84.6±25.1	66.6±19.6	84.1±20.7	67.6±17.2
U	9.84±13.2	43.0±17.7	10.9±16.5	43.0±22.9	6.60±9.52	51.8±18.5

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