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

3

4 Ivan V. KRICKOV¹, Artem G. LIM¹, Rinat M. MANASYPOV^{1,2},

5 Sergey V. LOIKO¹, Sergey N. VOROBYEV¹, Vladimir P. SHEVCHENKO³, Olga M. DARA³,

6 Vyacheslav V. GORDEEV³, Oleg S. POKROVSKY^{1,2,4*}

7

8 ¹ *BIO-GEO-CLIM Laboratory, Tomsk State University, Tomsk, Russia*

9 ² *Institute of Ecological Problems of the North, N. Laverov Federal Center for Integrated Arctic
10 Research, Arkhangelsk, Russian Academy of Science, Russia*

11 ³ *Shirshov Institute of Oceanology, Russian Academy of Science, Moscow, Russia*

12 ⁴ *Geosciences and Environment Toulouse, UMR 5563 CNRS, 14 Avenue Edouard Belin 31400
13 Toulouse, France*

14

15 **Email: oleg.pokrovsky@get.omp.eu*

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42 **Abstract**

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

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

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

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

84

85 **1. Introduction**

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

94 et al., 2006; Viers et al., 2009; Gordeev and Lisitzin, 2014). In contrast to numerous studies that
95 have been devoted to the biogeochemistry of “dissolved” organic carbon and macro-nutrients in
96 large rivers of the circumpolar zone (Gordeev, 2000; Lobbes et al., 2000; Stedmon et al., 2011;
97 McClelland et al., 2016; Guo et al., 2004; Tank et al., 2012b, 2016; O'Donnell et al., 2016;
98 Kaiser et al., 2017; Drake et al., 2018), very few works characterized major and trace elements
99 other than C and nutrients in the particulate (> 0.22 or $0.45 \mu\text{m}$) fraction. Gordeev et al. (1996)
100 and later Nikanorov et al. (2010) and Magritsky (2010) compiled the data from the Russian
101 Hydrological Survey on suspended load of Arctic rivers, but no data for chemical composition
102 was available. Gebhardt et al (2004) provided extensive data set for RSM concentration, C and N
103 composition in the mixing zone of the Ob and Yenisey Rivers. Occasional data on elementary
104 composition of RSM in boreal and subarctic rivers are available for European part of Russia
105 (Morozov et al., 1974; Shevchenko et al., 2010; Savenko et al., 2004; Pokrovsky et al., 2010),
106 Western Siberia (Gordeev et al., 2004), Central Siberian Plateau (Pokrovsky et al., 2015, 2016),
107 Eastern Siberian Rivers (Kutscher et al., 2018), Canada (Gaillardet et al., 2003; Javed et al.,
108 2018), the Mackenzie basin (Milot et al., 2010), and the 6 large Arctic rivers (data of
109 PARTNERS and ARCTIC GRO; Holmes et al., 2002, 2012).

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

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

123 In contrast to many other regions in the world, western Siberia allows to overcome these
124 aforementioned natural obstacles with RSM sampling. This relatively pristine peatland has a
125 unique geographical setting and a sufficiently developed road infrastructure. Interest in the
126 Western Siberia Lowland (WSL), the largest permafrost-affected peatland area, stems from: *i*) its
127 storage of a sizeable amount of C in thawed and frozen peat (Krementski et al., 2003), *ii*) the fact
128 that it is a significant reservoir of dissolved organic carbon in surface water (Polishchuk et al.,
129 2017, 2018), *iii*) the fact that it supplies a large amount of freshwater and solutes to the Arctic
130 Ocean (Frey et al., 2007a, b; Frappart et al. 2010), and *iv*) its emissions of high fluxes of
131 greenhouse gases from the water area of bogs, lakes and rivers to the atmosphere (Shirokova et
132 al., 2013; Sabrekov et al., 2017; Serikova et al., 2018, 2019). The permafrost in WSL is highly
133 unstable and thaws faster than in other Siberian regions (Romanovsky et al., 2010). Due to the
134 high fragility of permafrost in western Siberia, climate change is likely to have a profound
135 influence on the magnitude of riverine fluxes through alteration of hydrological regimes in WSL
136 rivers (Frey and McClelland 2009; Bring et al. 2016) and stimulation of element releases caused
137 by widespread permafrost thawing (Vonk et al. 2015).

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

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

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

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174 **2. Sampling and analyses**

175 *2.1. Study site*

176 We sampled 33 rivers that belong to the Ob, Pur and Taz watersheds in the Western
177 Siberia Lowland (WSL). WSL is a huge peatland (> 2 million km²) situated across taiga forest,
178 forest-tundra and tundra zones (**Fig. 1**). The position of these biomes follows a decrease in mean
179 annual air temperature (MAAT) from -0.5°C in the south (Tomskaya region) to -9.5°C in the
180 north (Yamburg). Annual precipitation ranges from 550 mm at the latitude of Tomsk, 650-700
181 mm at latitudes for Nojabrsk and Siberian Uvaly, and 600 mm at the lower reaches of the Taz
182 River. The annual river runoff gradually increases northward, from 160-220 mm y⁻¹ in the
183 permafrost-free region to 280-320 mm y⁻¹ in the Pur and Taz river basins which are located in
184 the discontinuous to continuous permafrost zone (Nikitin and Zemtsov, 1986). Permafrost
185 distribution also follows the same latitudinal gradient of MAAT changing from absent through
186 isolated and sporadic in the south to discontinuous and continuous in the north. The landscape
187 parameters of sampled catchments were determined by digitizing available soil, vegetation,
188 lithological and geocryological maps (Pokrovsky et al., 2016; Vorobyev et al., 2017) as listed in
189 **Table S1** of Supplementary Material. Sampling was performed during spring flood (17 May – 15
190 June 2016), summer baseflow (1 – 29 August 2016), and autumn baseflow before ice (24
191 September – 13 October 2016) and covered three main hydrological seasons. Note that the
192 collected data set of suspended (> 0.45 μm) and dissolved (< 0.45 μm) WSL river load is unique
193 and independent from previous studies of dissolved river load assessed during several seasons
194 (2013-2015) in WSL (Pokrovsky et al., 2015, 2016). Our previous work in this region was
195 devoted to the biogeochemistry of dissolved (< 0.45 μm) carbon and major and trace elements in
196 rivers sampled over 4 main seasons in 2014 (February, June, August and October) (Pokrovsky et
197 al. 2015, 2016), and dissolved nutrients sampled during Spring and Summer 2015 (Vorobyev et

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

200 *2.2. Sampling of RSM*

201 During sampling we moved from south to north over a 2-3 week period collecting from
202 all rivers in the transect at approximately the same time after ice off and before ice on. To assess
203 inter-annual variations in RSM concentrations, we analyzed the RSM samples collected in WSL
204 rivers across the same transect during previous campaigns in spring 2014, 2015 and 2016 and
205 summer 2015 and 2016. Large water samples were collected from the middle of the river at 0.5
206 m depth in pre-cleaned polypropylene jars (30 to 50 L) and were allowed to decantate over 2-3
207 days. The water from the bottom layer of the barrels (approx. 30% of initial volume) was
208 centrifuged on-site for 20 min at 3500 rpm using 50-mL Nalgene tubes. Sediment was frozen at
209 -18°C and freeze-dried later in the laboratory. In addition to decantation and centrifugation, in
210 several rivers, the RSM was collected via direct filtration of large volumes (20 to 30 L) of river
211 water with an Inox (AISI 304) Teflon® PTFE-coated filtration unit (Fisher Bioblock) equipped
212 with 142 mm acetate cellulose Sartorius membranes ($0.45 \mu\text{m}$) and operated at 5-7 bars. An
213 average flow rate of 1-2 L/h was created by a peristaltic pump (MasterFlex B/T) with Teflon
214 tubing. The agreement in elementary composition of RSM between two methods of collection
215 was better than 20%. The total concentration of suspended material was determined in all
216 samples. For this, smaller volumes of freshly collected river water (1-2 L) were filtered on-site
217 (at the river bank or in the boat) with pre-weighted acetate cellulose filters (47 mm, $0.45 \mu\text{m}$)
218 and Nalgene 250-mL polystyrene filtration units using a Mityvac® manual vacuum pump.

219

220 *2.3. Analyses*

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

224 measured after full acid leaching in a clean room (class A 10,000) following ICP-MS (Agilent
225 7500 ce) analyses using methods for organic-rich natural samples employed in GET laboratory
226 (Toulouse). The 100 mg dry weight powders were reacted for 30 min in an ultrasonic bath prior
227 to full digestion using a Mars 5 microwave digestion system (CEM, France) using a mixture of
228 6.5 mL concentrated HNO₃, 3.5 mL concentrated HCl and 0.5 mL concentrated HF. HNO₃ and
229 HCl were bi-distilled in the clean room and HF was of commercial ultra-pure quality (Fluka).
230 For digestion, 10 samples of RSM, 1 certified 2711a Montana II Soil standard [or LKSD
231 sediment] and 1 blank sample were loaded into Teflon reactors and were treated at 150°C for 20
232 min. After completing the digestion, contents of reactors were transferred into 30 mL Savilex
233 vials and evaporated at 70°C. The residue was dissolved in 10 mL of 10% HNO₃ and diluted by
234 2% HNO₃ prior to analyses. The concentration of major and trace elements (TE) in filter
235 digestion products was measured using an ICP-MS Agilent 7500ce with ~3 µg/L of In and Re as
236 internal standards. Four in-house external standards were analyzed every 10 samples. The
237 uncertainty for TE measurement ranged from 5 % at 0.1–100 µg/L to 10 % at 0.001–0.01 µg/L.

238 We interpreted the results for the elements that exhibited a good agreement between the
239 certified or recommended values and our measurements within acceptable uncertainty levels
240 ($([X]_{\text{recommended or certified}} - [X]_{\text{measured}}) / (([X]_{\text{recommended or certified}} + [X]_{\text{measured}})/2) \times 100 \leq 10\%$), or for
241 cases in which we obtain a good reproducibility (the relative standard deviation of our various
242 measurements of standards lower than 10%), even if no certified or recommended data are
243 available. All certified major (Ca, Mg, K, Na) and trace element (Al, As, B, Ba, Co, Cr, Cu, Fe,
244 Ga, Li, Mn, Mo, Ni, Pb), all REEs, Sb, Sr, Th, Ti, U, V, Zn) concentrations of the SLRS-5
245 standard (e.g., Yeghicheyan et al., 2013) and the measured concentrations agreed with an
246 uncertainty of 10-20%. Agreement for Cd, Cs and Hf was between 30 and 50%. For all major
247 and most trace elements, concentrations in blanks were below analytical detection limits (≤ 0.1 -
248 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,
249 V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As).

250 In addition to total chemical analysis after HF+HNO₃ digestion, 11 RSM samples of
251 small, medium and large rivers collected in May and August were processed for total Si
252 concentration using wet chemical analysis with photometric detection (see Gurvich et al., 1995;
253 Baturin and Gordeev, 2019 for methodology). Further, the mineralogical composition of
254 particulate fraction on selected filters was studied by X-ray powder diffractometric method on a
255 D8 ADVANCE (Bruker AXS) X-ray diffractometer equipped with a LYNXEYE linear detector
256 (Lisitzin et al., 2015). The uncertainty of the relative proportion of mineral composition was 1–
257 2% and the detection limit was 1%. Due to limited amount of RSM available for analyses, the
258 latter could be performed only on 3 rivers (small, medium and large one) sampled in May and
259 August.

260

261 *2.4. Statistical treatment*

262 Statistical analysis was used to quantify the relationship between major and trace element
263 concentrations in RSM and % of permafrost, amount of wetlands/lake/forest coverage in the
264 watershed, and the surface area of the watershed ($S_{\text{watershed}}$). For simplicity, we distinguished five
265 zones of permafrost distribution in river watersheds: 1) permafrost-free zones located south of
266 61°N latitude, 2) isolated zones located between 61 and 63.5°N latitude; 3) sporadic zones
267 located between 63.5 and 65°N latitude; 4) discontinuous zones located between 65 and 66°N
268 latitude, and 5) continuous permafrost zones located north of 66°N latitude. Non-parametric
269 statistics were used because, based on Shapiro-Wilk test of the normality of variables, data on
270 major and trace element concentrations in RSM and the fraction of particulate elements were not
271 normally distributed. For these reasons, we used the median, 1st and 3rd quartiles, to trace
272 dependence of nutrient concentrations to the type of permafrost distribution. Correlations
273 between element concentration in RSM and main parameters of the watershed (latitude,
274 watershed area, runoff, percentage of bogs, forest and lakes and the permafrost coverage) were
275 tested using both Pearson and Spearman coefficients at $p < 0.05$ for permafrost-bearing and

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

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

292

293 **3. Results**

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

301 The mineralogical composition of suspended matter (**Supplement A**) was strongly
302 dominated by quartz (50-80%) and plagioclase (9-45%). The RSM of medium (Pyakopur,
303 $S_{\text{watershed}} = 9881 \text{ km}^2$) and large (Pur, $S_{\text{watershed}} = 112,000 \text{ km}^2$) river exhibited small amount (<
304 10%) of K feldspar, amphibole, pyroxene, illite, chlorite and kaolinite which were however
305 absent in small river (Vach-Yagun, $S_{\text{watershed}} = 99 \text{ km}^2$). We could not find any systematic
306 difference in mineralogical composition of RSM related to season (spring flood versus summer
307 baseflow). Note that the RSM of all WSL rivers has unusually high concentration of organic
308 carbon ($15.3 \pm 9.7 \text{ wt.}\%$) as averaged over seasons (Krickov et al., 2018). Small rivers ($S_{\text{watershed}} <$
309 100 km^2) have 2 to 3 times higher C_{org} (ca., 20-30%) compared to large ones (5-10% C_{org} in
310 rivers with $S_{\text{watershed}} > 10,000 \text{ km}^2$).

311

312 *3.1. Element concentration in RSM as a function of watershed size, latitude, permafrost,* 313 *and landscape parameters*

314 The chemical composition of RSM across all seasons in WSL territory is provided in
315 **Table 1**, whereas mean (\pm s.d.) concentrations during 3 seasons for each permafrost zone are
316 listed in **Table S2**. Considering all seasons together, there was no significant difference (at $p <$
317 0.05) in element concentrations between permafrost-free and permafrost-bearing zone. The only
318 exceptions are P, Ca, Mn, and Ba, which exhibited 2 x higher concentrations in the southern,
319 permafrost-free rivers compared to northern rivers. The effect of permafrost type on major and
320 TE in RSM is represented by box plots for the 5 groups of elements (**Fig. 2**). The overwhelming
321 majority of elements yielded a U-shape dependence of RSM concentration on type of permafrost
322 distribution. This dependence implied a minimum concentration in isolated to sporadic
323 permafrost zone, and 3-5 times higher concentrations in permafrost-free and continuous
324 permafrost zones compared to the beginning of permafrost disappearance (isolated and
325 sporadic). These are elements in the 1st group (Li, Na, K, Rb, Mg), 2nd group (V, Cr, As, Nb, W,
326 U), some elements of the 3rd group (Zn, Cu, Co, Ni), and all elements of the 4th and 5th groups

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

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

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

355 Neither the size of the watershed nor its landscape parameters strongly affected the
356 concentration of divalent 3rd group heavy metals. The exceptions are Ni and Cu, which positively
357 correlated with watershed size in permafrost-free zone in spring and summer ($0.70 < R_{\text{Spearman}} <$
358 0.93). Mn and Fe stand apart from other transition metals as their concentrations were generally
359 higher in small and medium watersheds ($S_{\text{watershed}} < 10,000 \text{ km}^2$) compared to larger ones (**Fig. 3**
360 **A, B**). Lakes exhibited a generally negative effect on Fe, Mn, and Co concentrations in the RSM
361 and bogs and lakes negatively affected Mn, Co, Ni and Zn concentrations in the RSM of the
362 permafrost-bearing zone during all seasons (**Table S3** and see **Fig. 3 C, D** as an example).

363 In the 4th and 5th groups, trivalent and tetravalent hydrolysates, $S_{\text{watershed}}$ significantly
364 increased ($p < 0.05$) concentrations of Cr, V, Al, Ga, Y, all REEs, Ti, Zr, Hf and Th in RSM.
365 This increase was mostly pronounced during summer and autumn (ca., a factor of 3 to 5 between
366 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
367 Al, Y, Ga, Ti, Zr, and Th in **Fig. 4 A, B, C, D, E and F**, respectively). Trivalent and tetravalent
368 hydrolysates were negatively impacted by the presence of bogs in the watershed, especially in
369 permafrost-bearing rivers (**Table S3**). Permafrost and latitude positively impacted the 5th group
370 (TE^{4+}) concentrations in RSM of rivers from the permafrost-bearing zone during all seasons.

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

378

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**,

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

406

407

408

409 *3.3. Multiparametric statistics*

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

423

424

425

426 **4. Discussion**

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

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

435

436 *4.1. Chemical composition of western Siberia river particles in comparison to world's rivers.*

437 In general, the average chemical composition of RSM across the world is comparable to
438 that of the upper part of continental earth crust or shale (Savenko et al., 2006a, b; Viers et al.,
439 2009). Taking the average values of non-permafrost + permafrost zones as a whole for Western
440 Siberia, we calculated the ratio of element concentration in the RSM of WSL to the average
441 elementary concentration in suspended sediments of world rivers (Viers et al., 2009) as
442 illustrated in **Fig. 6**. Typically, WSL rivers are impoverished (the ratio $0.2 \leq \text{RSM}_{\text{WSL}}/\text{RSM}_{\text{World}} \leq 0.5$)
443 with respect to Mg, Al, K, Ca, V, Cr, Ni, Cu, Zn, Ga, Ge, Rb, Y, Cd, Sb, Cs, REEs, Tl, Th
444 and U. Stronger depletion ($\text{RSM}_{\text{WSL}}/\text{RSM}_{\text{World}} < 0.2$) has been observed for Zr and Mo in WSL
445 rivers. We interpret this result as being due to the sizeable proportion of organic matter in RSM
446 in western Siberia (Krickov et al., 2018), and the corresponding impoverishment of suspended
447 matter in elements hosted by silicate (clay) materials. Note however that the world average
448 value is essentially based on data from big rivers. These rivers are enriched in silicate mineral-
449 dominated components because they carry higher proportions of suspended silicate material and
450 smaller fractions of organic-rich particles. The WSL rivers are sizeably enriched relative to the
451 world average only with respect to P and Mn (a factor of 2.5 and 4.8, respectively). Along with
452 elevated C concentration in suspended matter of WSL rivers (ca., 15%, Krickov et al., 2018), this
453 reflects presence of peat particles and vegetation debris as important components of RSM.
454 Further, WSL rivers contain sizeably amount of Mn^{2+} oxidation products which are supplied
455 from surrounding lakes and bogs, leading to enrichment in Mn hydroxide. It is important to note

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

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

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

482

483 *4.2. Role of landscape factors and permafrost in elementary composition of RSM*

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

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

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

508 soils (Goncharova et al., 2016), and 4) the removal of fine particles from soil occurs more
509 efficiently under well drained forest environment as it is known in various forest soils
510 (Tonkonogov, 1999; Quénard et al., 2011) including those of Western Siberia (Loiko et al.,
511 2015).

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

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

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

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

549

550 *4.3. Relative fraction of suspended over total (dissolved+suspended) elements in RSM of*

551 *WSL*

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

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

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

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

586 particulate transport of Mn with $S_{\text{watershed}}$ increase (**Fig. S2 D**) is interpreted as due to an increase
587 in residence time of this element in rivers. This would lead to transformation of dissolved
588 $\text{Mn}^{2+}(\text{aq})$ into particulate forms of $\text{Mn}^{(\text{III}, \text{IV})}$ hydroxides via biotic and photochemical processes.
589 Such processes were identified during the diurnal cycle of this element in boreal humic lakes
590 (Pokrovsky and Shirokova, 2013) and also in boreal high latitude rivers (Ponter et al., 1992).
591 Similarly, Ni and Cu exhibited an increase in suspended fraction with a decrease in watershed
592 size (**Fig. S3 E**), especially visible in autumn for Cu ($R^2 = 0.32$, $p < 0.05$). This can be linked to
593 Cu and Ni coprecipitation with/ adsorption onto Mn oxy(hydr)oxides. Additional point to
594 consider is that this effect was consistent with an increase in C_{org} (RSM) in small rivers (Krickov
595 et al., 2018) thereby demonstrating a close link between C and Cu. In autumn, there was an
596 increase in particulate Cu share northward (**Fig. S3 F**) as well as an increase in lake and bog
597 coverage of the watershed (**Fig. S3 C**). It could be linked to the coagulation of Cu-organic
598 associates in lentic waters and their release into the river system during autumn floods rain.

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

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

621

622 *4.4. Mechanisms of RSM enrichment and impoverishment in elements and prospectives*
623 *for the permafrost thaw and climate change*

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

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

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

647 Results obtained here allow first-order foresight on the effect of climate warming and
648 permafrost thaw on major and trace element concentrations in the suspended load of WSL rivers.
649 The concept of “substituting space for time” in the WSL (Frey et al., 2007 a, b; Frey and Smith,
650 2005) implies a shift of the permafrost boundary to northward combined with simultaneous increase
651 in ALT (**Fig. 8**). On a short-term scale (10 to 100 years) this may reconfigure permafrost
652 distribution as following: continuous → discontinuous; discontinuous → sporadic; sporadic →
653 isolated, isolated → absent. The U-shape dependences of most element concentration on
654 permafrost type demonstrate a minimum at the beginning of permafrost thaw, in sporadic to
655 discontinuous permafrost zones (**Fig. 2**). This concentration pattern implies that, upon a
656 progressive shift of the permafrost boundary northward, there will be sizeable decrease in the
657 concentration of alkalis, alkaline-earths, divalent heavy metals, and trivalent and tetravalent
658 hydrolysates in northern rivers in currently discontinuous and continuous permafrost zones. This
659 decrease may be a factor of 2 to 5 as follows from the position of the minimum elemental
660 concentration in sporadic to discontinuous permafrost zones relative to the continuous
661 permafrost zone (**Fig. 2**).

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

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

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

686

687 **CONCLUSIONS**

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

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

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

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

712

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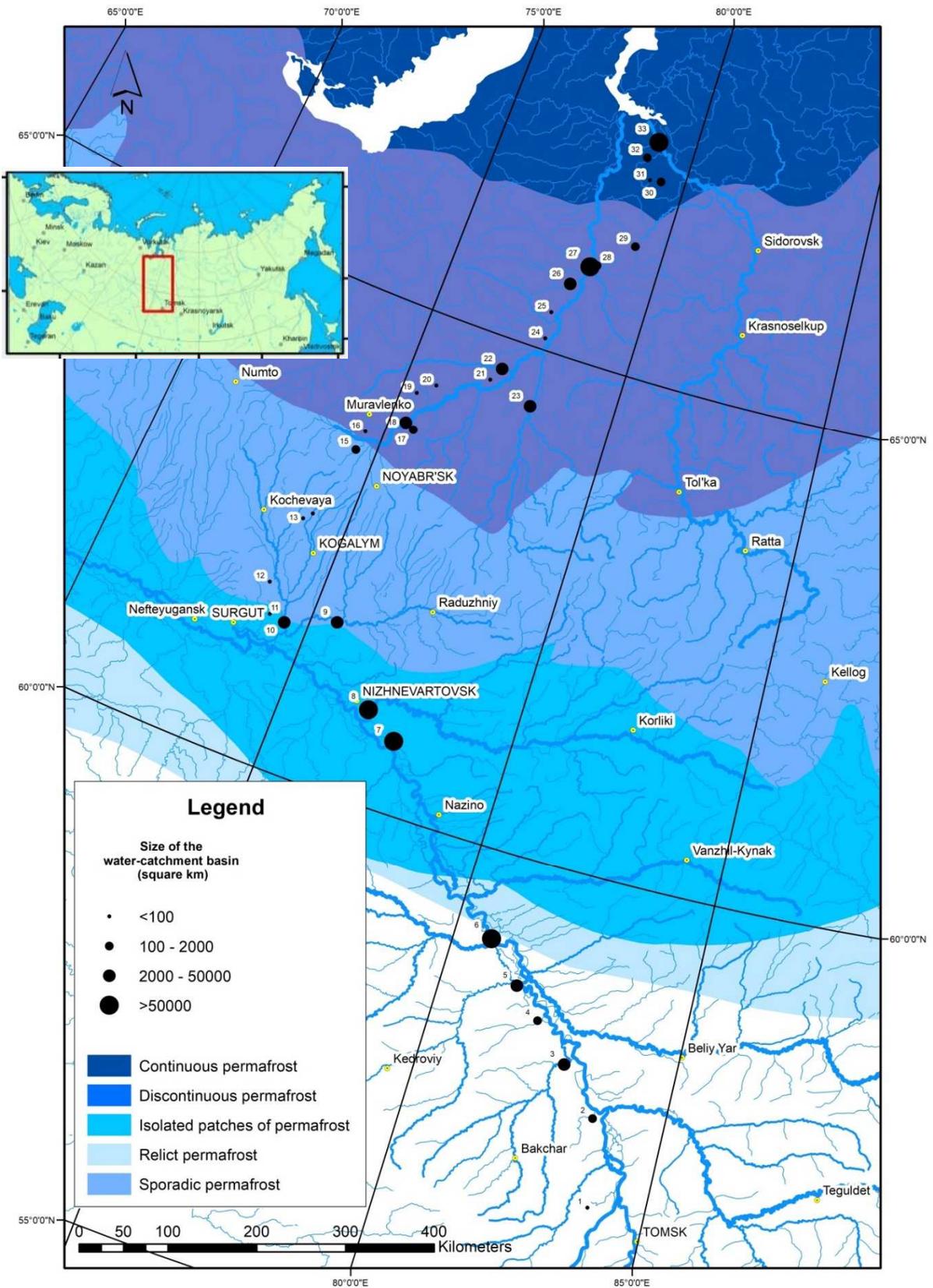
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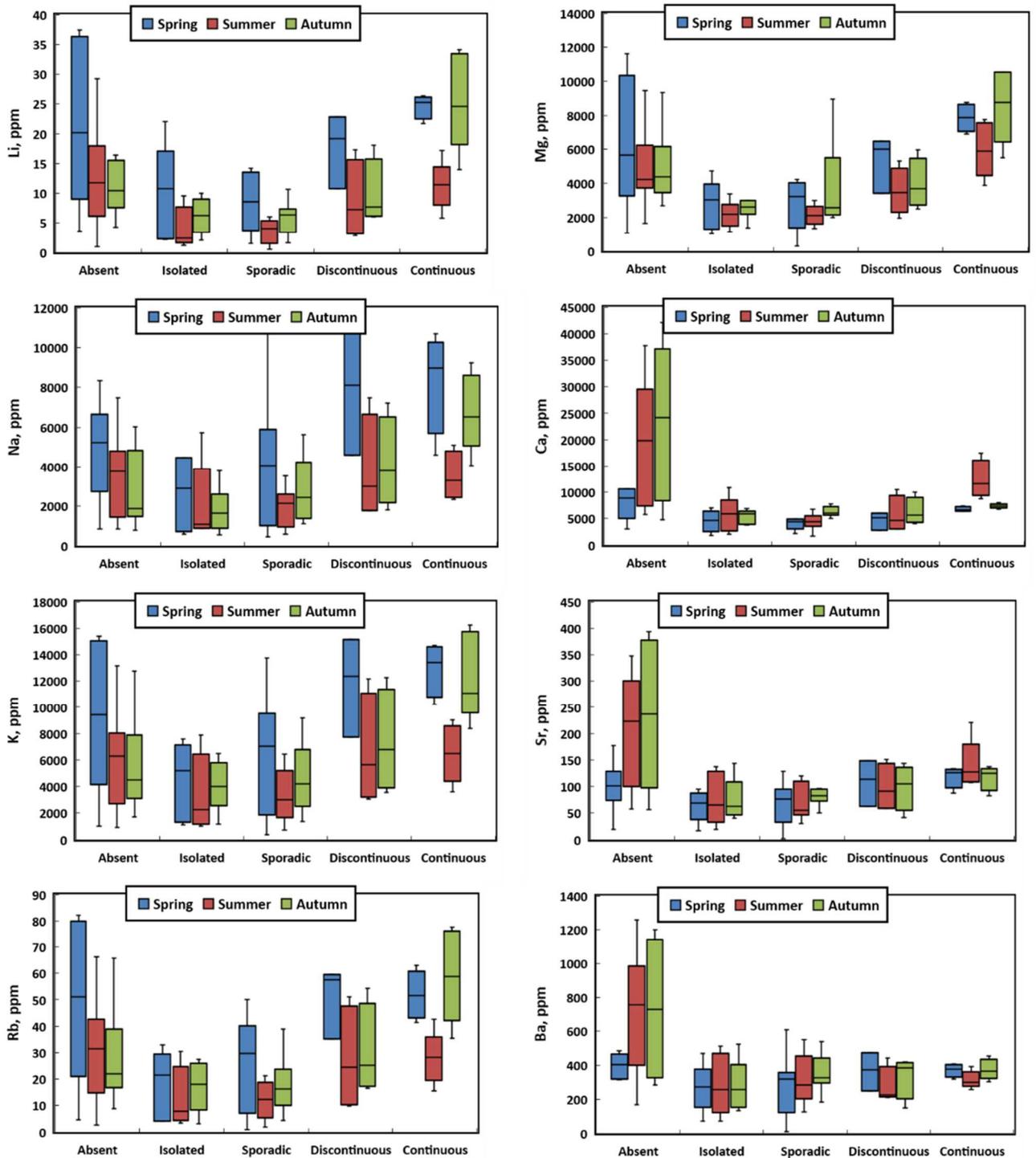
988 **Fig. 1.** Sampling sites and physio-geographical context of WSL territory investigated in this
 989 work. The sampling numbers are explained in Table S1.

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1st group



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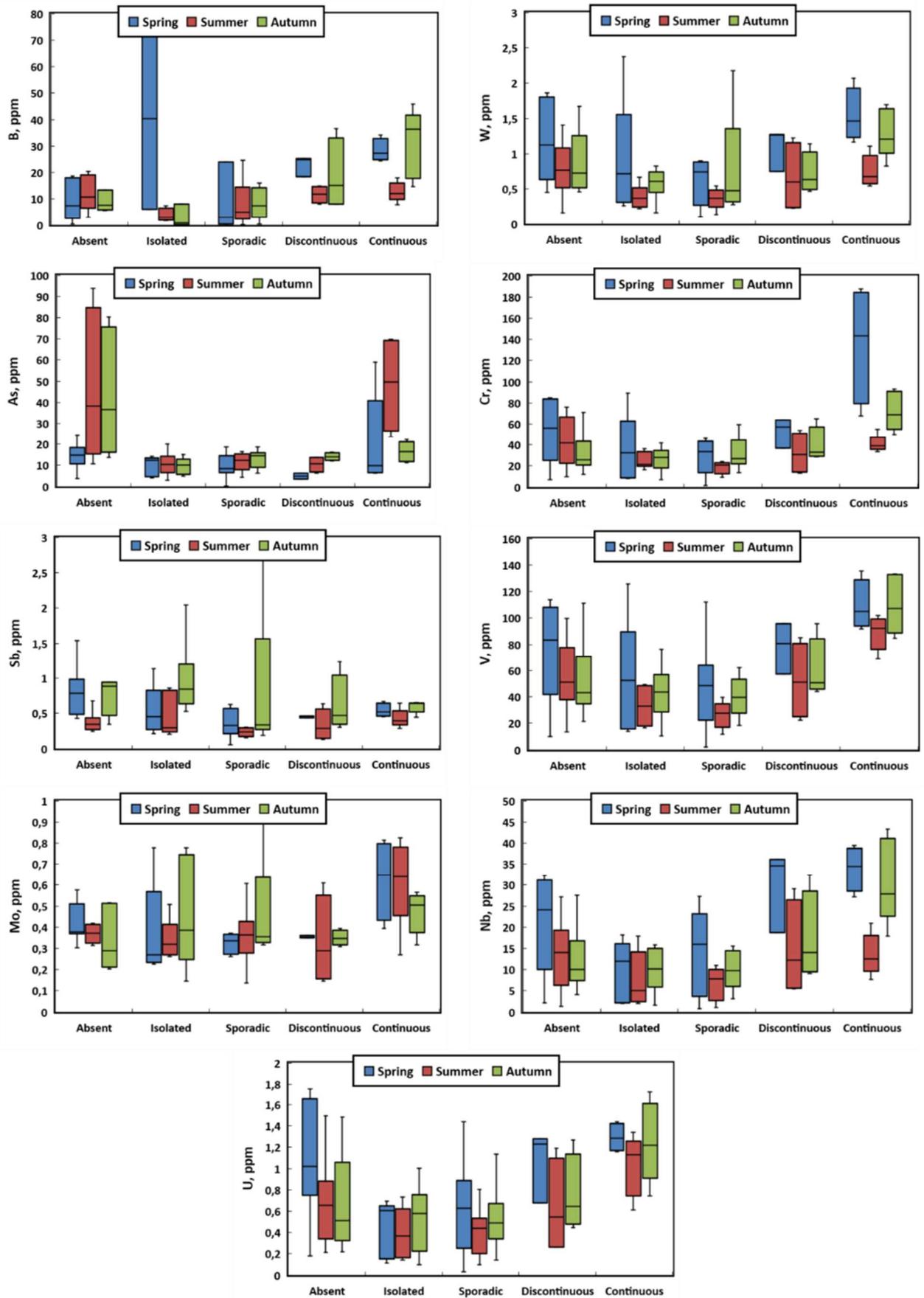
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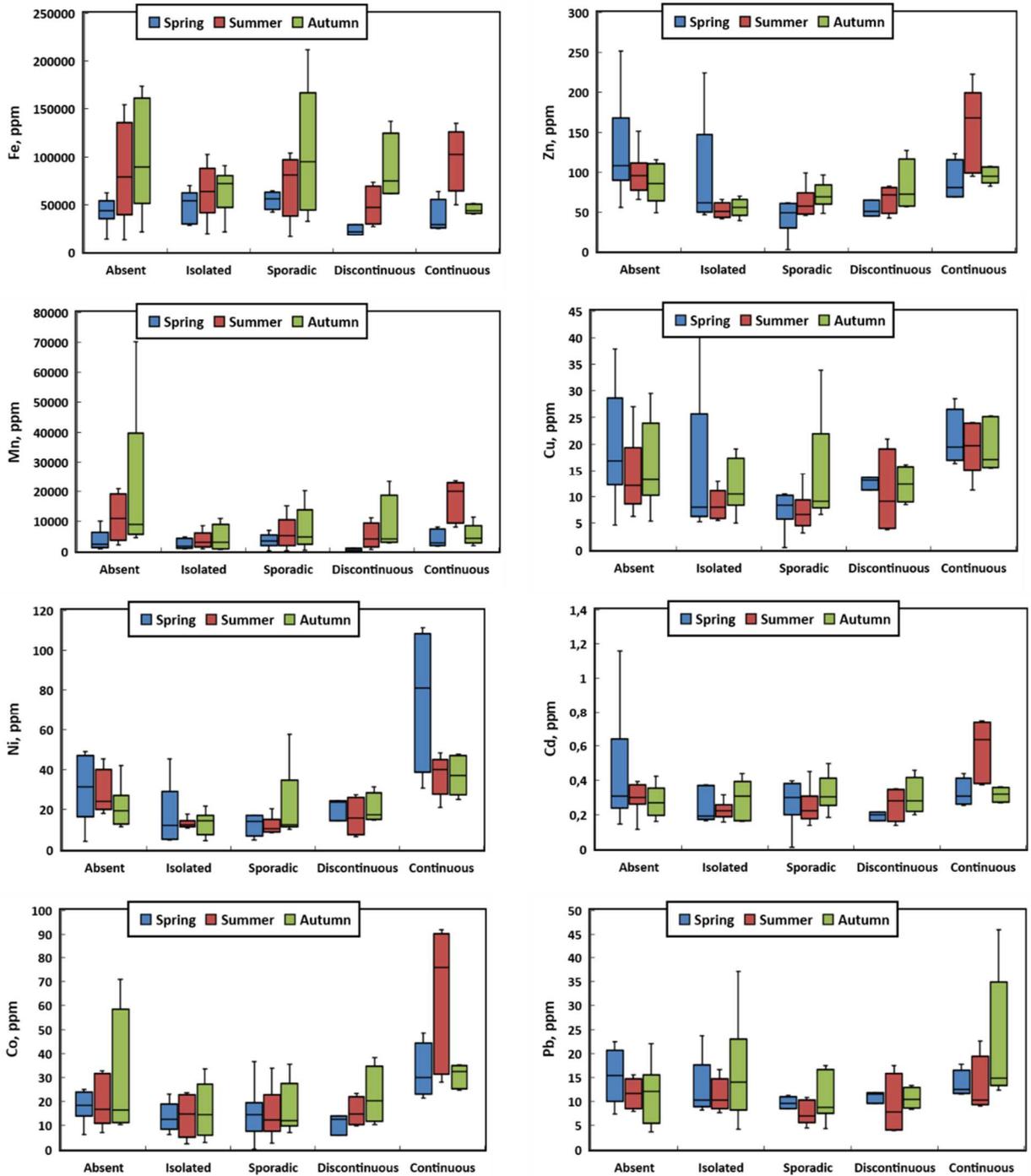
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997 **Fig. 2.** Box plot of first and third quartiles (25 and 75%) of 5 groups of elements in the
998 suspended matter of WSL rivers.

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1006 **Fig 2**, continued

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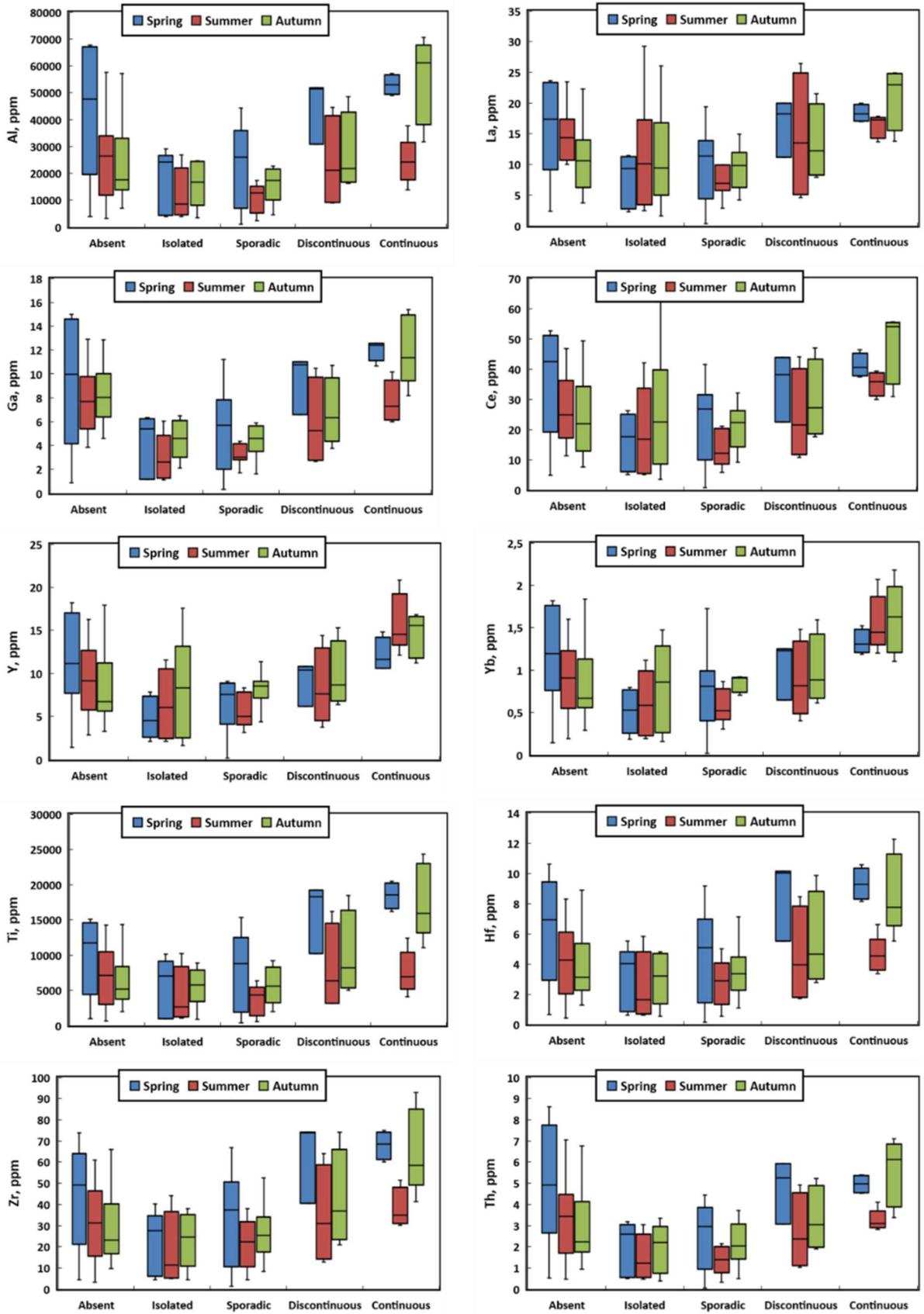
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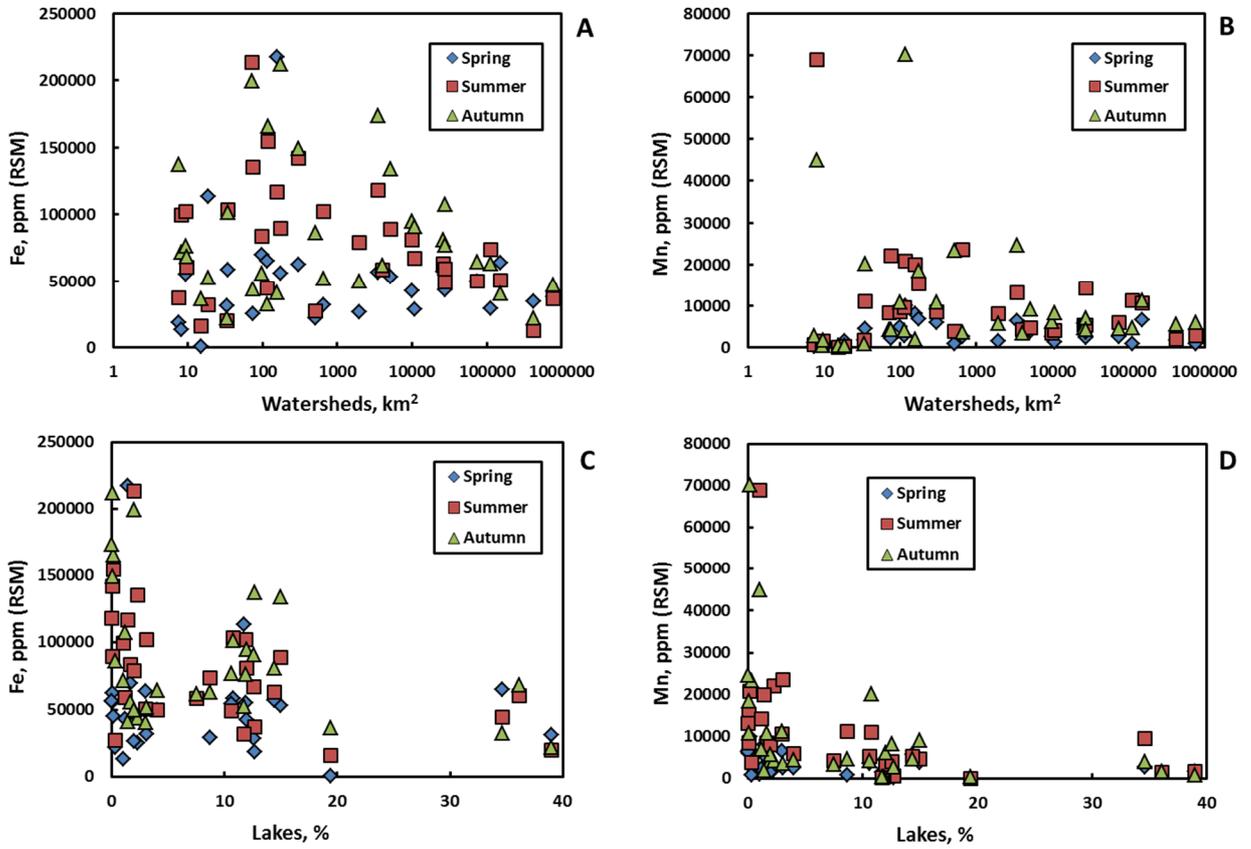
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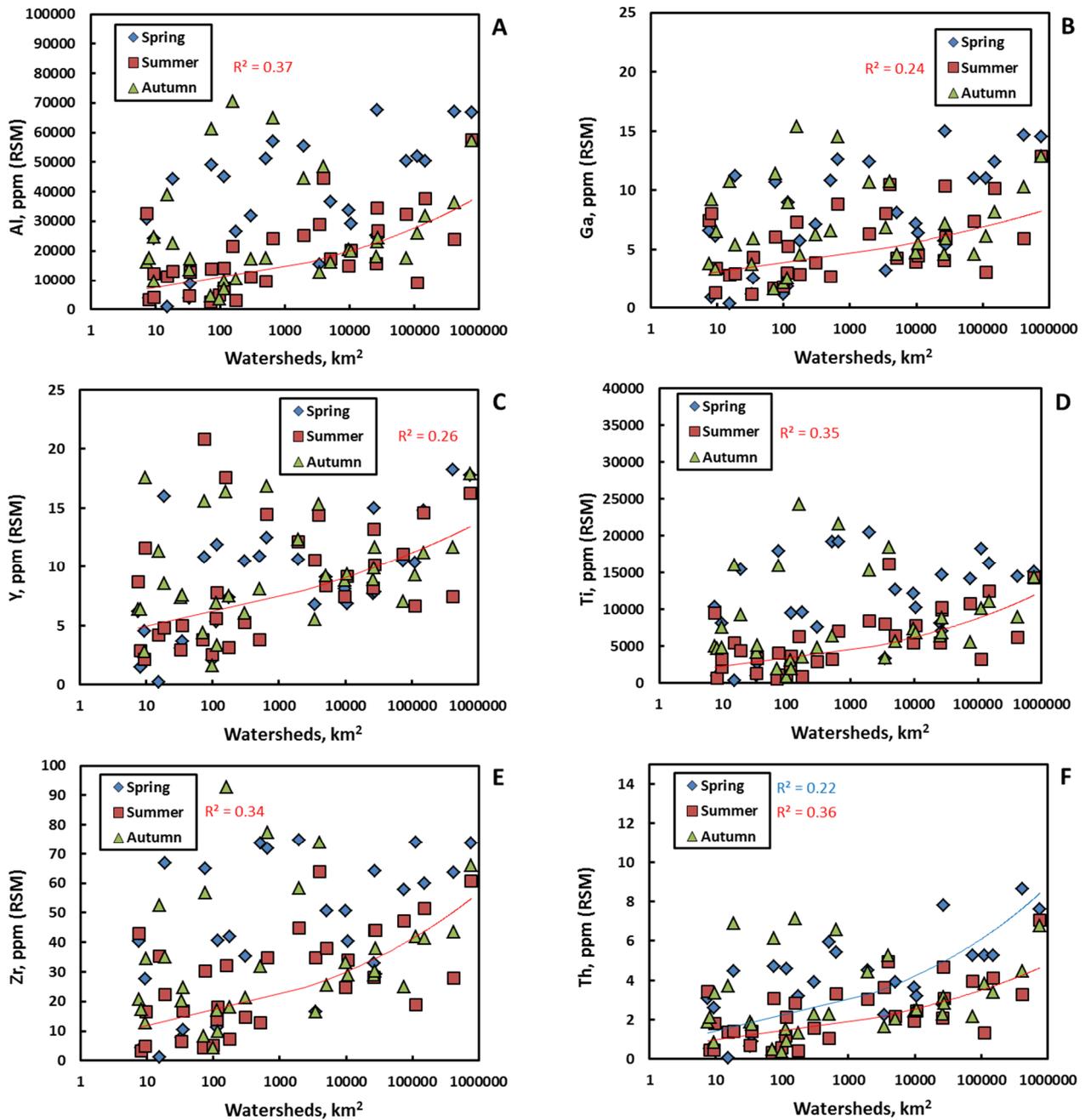


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1024 **Fig 3.** Concentration of Fe (A) and Mn (B) in suspended matter of western Siebrian rivers as a
1025 function of watershed area and as a function of lake coverage of the watershed (C, D,
1026 respectively). The solid lines represent empirical, 2nd order polynom fit to the concentration
1027 dependence on lake percentage, with significant ($p < 0.05$) regression coefficients given in the
1028 graphs.

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1042 **Fig 4.** Concentration of Al (A), Ga (B), Y (C), Ti (D), Zr (E) and Th (F) in RSM of WSL as a
1043 function of watershed area. The solid lines represent empirical exponential fit to the
1044 concentration - watershed dependence with significant ($p < 0.05$) regression coefficients given in
1045 the graphs.

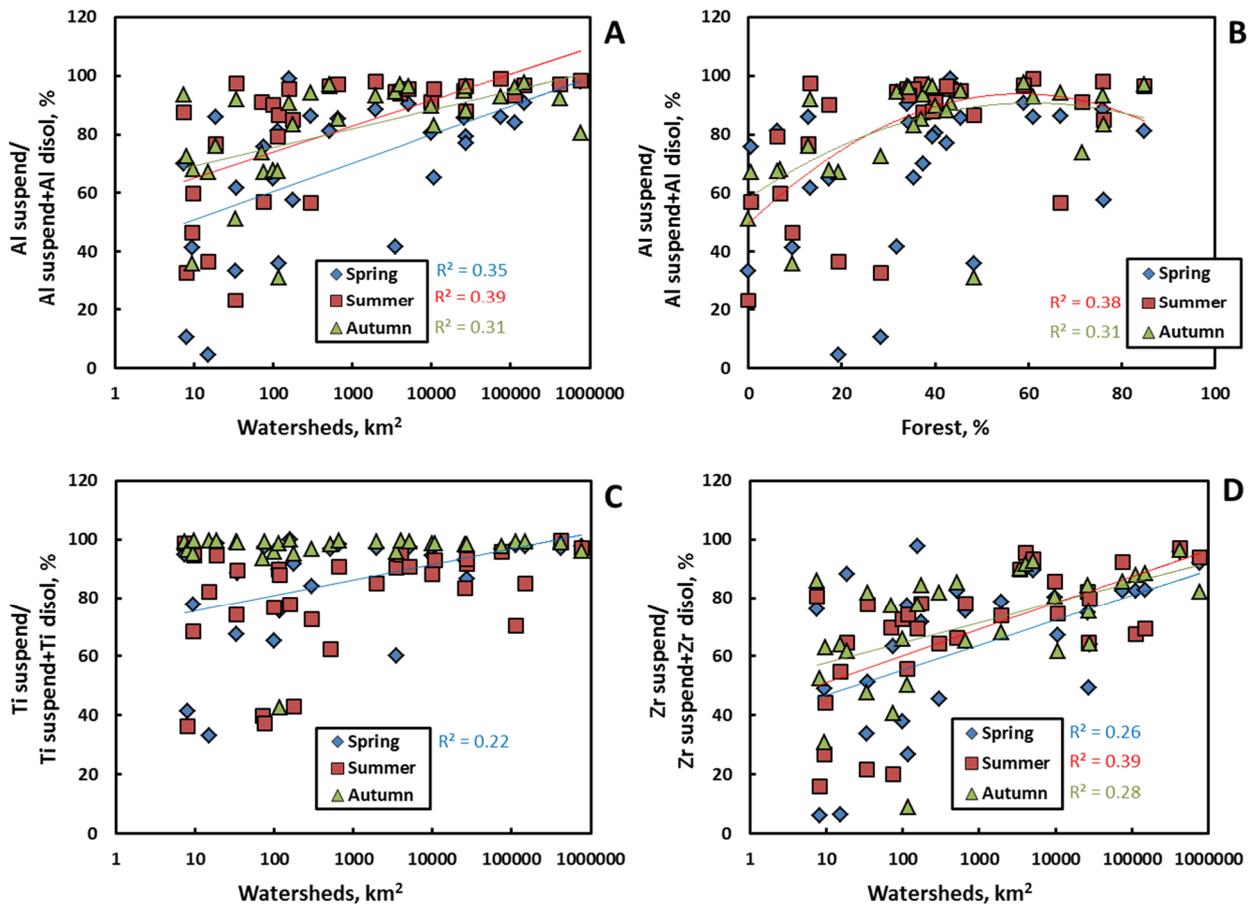
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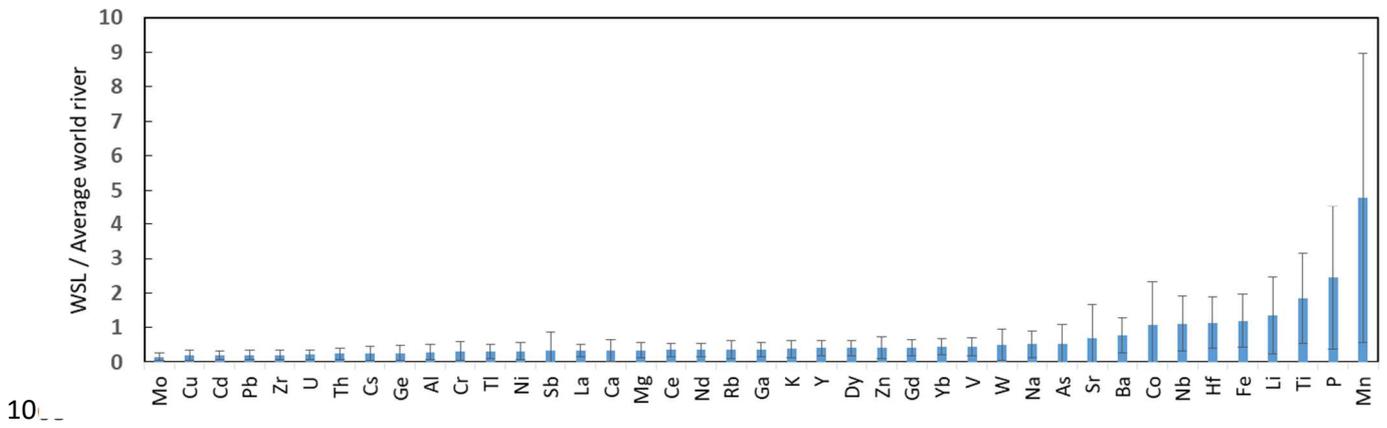
1053 **Fig. 5.** Suspended fraction of Al in RSM total (suspended + dissolved) transport as a function of
1054 watershed area (A) and forest coverage of the watershed (B) and particulate fraction of Ti (C)
1055 and Zr (D) as a function of $S_{\text{watershed}}$. The solid lines represent 1st or 2nd polynomial empirical fit to
1056 the data, with significant ($p < 0.05$) regression coefficients given in the graph.

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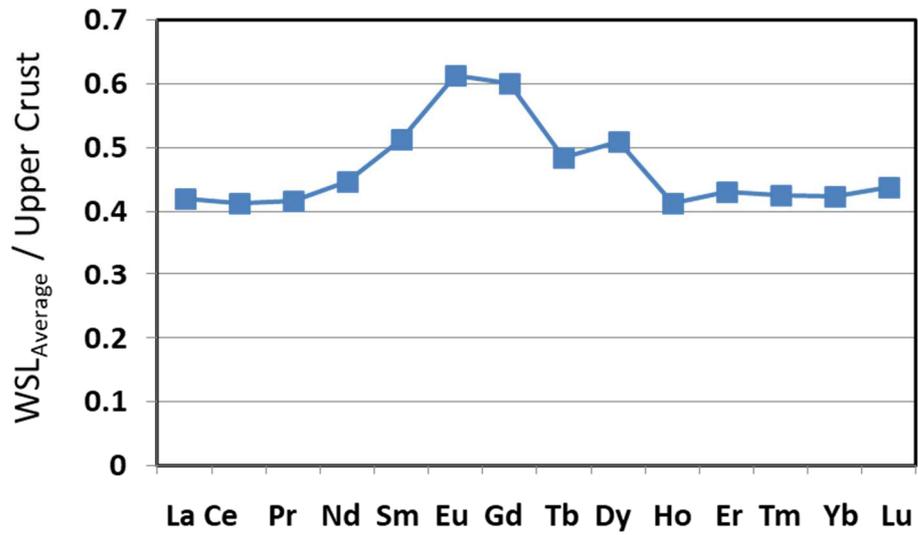
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1070 **Fig. 6.** The ratio of element concentration in RSM of WSL rivers (averaged over all seasons and
1071 permafrost zones) to the average element concentration in RSM of rivers worldwide (Viers et al.,
1072 2009).

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1077 **Fig. 7.** Upper-crust normalized pattern of WSL rivers suspended load (averaged over all seasons,
 1078 river sizes and permafrost zones)

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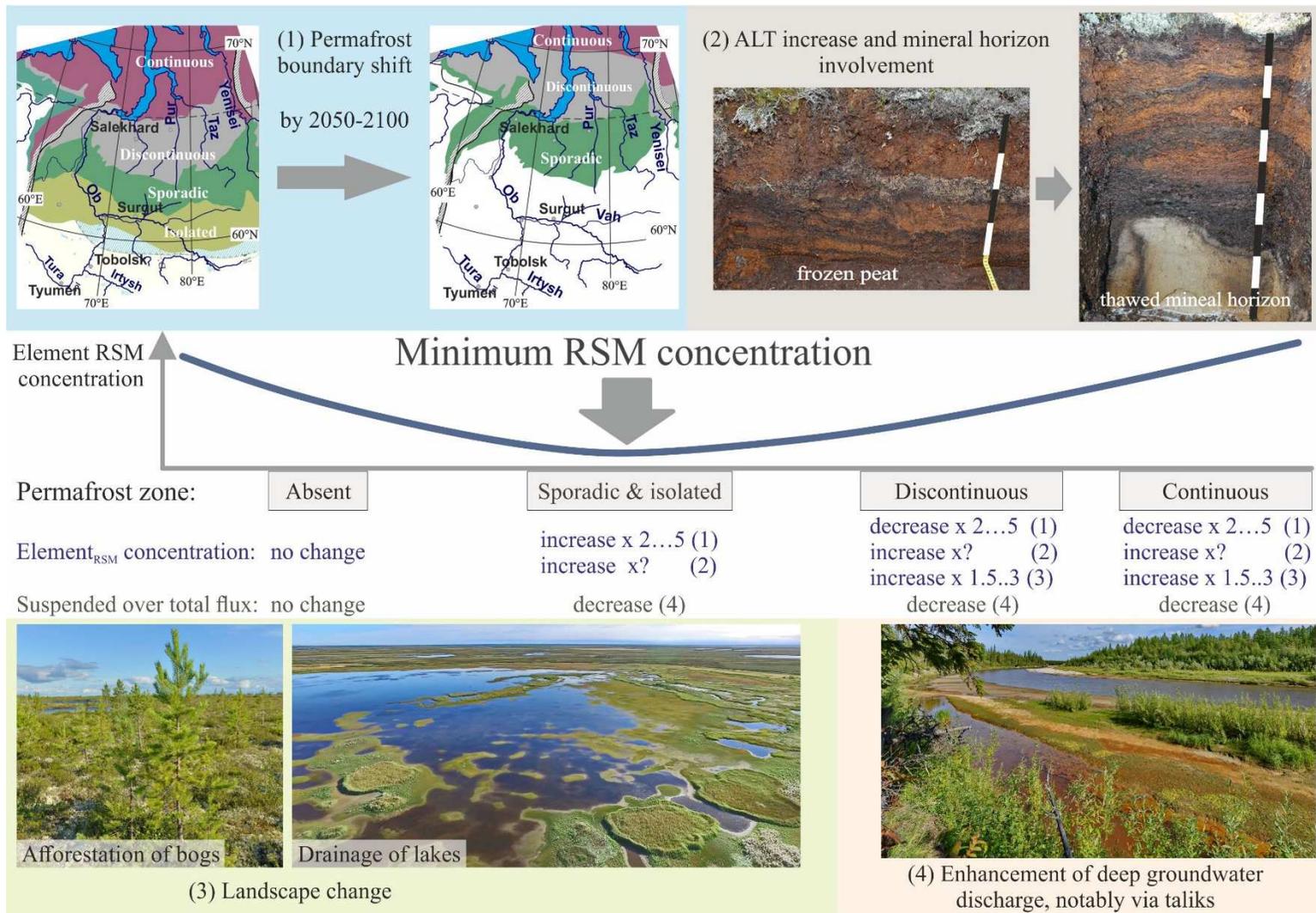
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1087 **Figure 8.** A scheme of element mobilization from the soil to the river in the form of suspended particles and provision for the change of element
 1088 concentrations in RSM and the share of suspended over total element transport under scenario 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	All seasons	All seasons
	permafrost-free N=24	permafrost-bearing N=68	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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