Impact of snow deposition on major and trace element concentrations and elementary fluxes in surface waters of Western Siberian Lowland across a 1700-km latitudinal gradient

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Abstract. Towards a better understanding of chemical composition of snow and its impact on surface water hydrochemistry in poorly studied Western Siberia Lowland (WSL), the surface layer of snow was sampled in February 2014 across a 1700-km latitudinal gradient (c.a. 56.5 to 68°N). We aimed at assessing the latitudinal effect on both dissolved and particulate forms of element in snow and quantifying the impact atmospheric input to element storage and export fluxes in inland waters of the WSL. The concentration of dissolved+colloidal (< 0.45 µm) Fe, Co, Cu, As, La increased by a factor of 2 to 5 north of 63°N compared to southern regions. The pH and dissolved Ca, Mg, Sr, Mo and U in snow water increased with the increase in concentration of particulate fraction (PF). Principal Component Analyses of major and trace element concentration in both dissolved and particulate fractions revealed 2 factors not linked to the latitude. A hierarchical cluster analysis yielded several group of elements originated from alumino-silicate mineral matrix, carbonate minerals and marine aerosols or belonging to volatile atmospheric heavy metals, labile elements from weatherable minerals and nutrients. The main sources of mineral components in PF are desert and semi-desert regions of central Asia.

The snow water concentration of DIC, Cl, SO_4, Mg, Ca, Cr, Co, Ni, Cu, Mo, Cd, Sb, Cs, W, Pb and U exceeded or were comparable with spring-time concentration in thermokarst lakes of the permafrost-affected WSL zone. The spring-time river fluxes of DIC, Cl, SO_4, Na, Mg, Ca, Rb, Cs, metals (Cr, Co, Ni, Cu, Zn, Cd, Pb), metalloids (As, Sb), Mo and U in the discontinuous to continuous permafrost zone (64-68°N) can be explained solely by melting of accumulated snow. The impact of snow deposition on riverine fluxes of elements strongly increased northward, in discontinuous and continuous permafrost zones of frozen peat bogs. This was consistent with the decrease of the impact of rock lithology on river chemical composition in the permafrost zone of WSL, relative to the permafrost-free regions. Therefore, the present study demonstrates significant and previously underestimated atmospheric input of many major and trace elements to their riverine fluxes during spring flood. A broader impact of this result is that current estimations of river water fluxes response to the climate warming in high latitudes may be unwarranted without detailed analysis of winter precipitation.

1 Introduction

The snow cover exhibits a number of properties making it unique natural archive and indicator of the ecosystem status (Baltrėnaitė et al., 2014; Bokhorst et al., 2016; Callaghan et al., 2011; Caritat et al., 1998, 2005; Garbarino et al., 2002; Guéguen et al., 2016; Kashulina et al., 2014; Lisitzin, 2002; Niu et al., 2016; Ross and Granat, 1986; Singh et al., 2011; Siudek et al., 2015; Van de Velde et al., 1999; Walker et al., 2003). The snow washes out insoluble aerosols particles from the atmosphere as well as soluble compounds, including various pollutants (Telmer et al., 2004; Barrie, 1986; Tranter et al., 1986, 1987). Unlike rain, the snow remains at the soil surface and thus records all atmospheric input during the glacial period of the year. In boreal and subarctic regions, both dissolved and particulate fraction of snow water reflect the air chemistry in winter, when the land is covered by snow and the water surfaces are covered by ice. During winter, the input of mineral compounds from adjacent regions is minimal and the main factor controlling chemical composition of snow is long-range, hundred and thousand km, atmospheric transport (Franzén et al., 1994; Huang et al., 2015; Shevchenko, 2003, Shevchenko et al., 2000, 2010, 2016; Welch et al., 1991; Zdanowicz et al., 1998, 2006; Krachler et al., 2005; Zhang et al., 2015).

Several studies of major elements and some trace metals in particulate fraction of snow have been conducted in western Siberia (Boyarkina et al., 1993; Ermolov et al., 2014; Kashulina et al., 2014; Moskovchenko and Babushkin, 2012; Shevchenko et al., 2015; Talovskaya et al., 2014). The dissolved (< 0.45 µm or < 0.22 µm) fraction of snow was traditionally studied in European subarctic (Caritat et al., 1998; Chekushin et al., 1998; Kashulina et al., 2014; Reimann et al., 1999; Reinosdotter and Viklander, 2005) but the data on trace elements in snow water collected in boreal, arctic and subarctic regions are limited. This is especially true for large and geographically homogeneous territories of western Siberia, presenting relatively similar level of snow deposition during winter seasons (i.e., from 100 mm of water in the south to 140–150 mm of water in the north) without any pronounced influence of large industrial centers, mountain regions and marine aerosols over the territory close to 1.5 million km² (Resources, 1972, 1973; Boyarkina et al., 2013).

The originality of the present study consists in *i*) sampling of substantial (~1700 km) latitudinal transect in relatively pristine zones comprising forest, forest tundra and tundra within the permafrost-free, discontinuous and continuous permafrost regions; *ii*) assessment of both dissolved+colloidal and particulate forms of major and trace elements in snow samples. Given the scarcity of available measurements of snow chemical and particulate composition in Western Siberia, we aimed at addressing the following specific issues: (1) characterizing the effect of the latitude on major and trace element concentration in dissolved (< 0.45 µm) and particulate (> 0.45 µm) fractions of snow; (2) testing the link between dissolved and particulate fractions of elements and the impact of particle mineralogy on snow chemical composition; (3) comparing dissolved concentrations of major and trace elements in snow to those in lakes and rivers across the latitudinal gradient of WSL and (4) assessing the share of snow deposition on seasonal and annual export of dissolved elements by western Siberian rivers. Via addressing quantitatively the abovementioned issues using unified methodology in quite large geographical coverage (56 to 68°N) of orographically flat low populated terrain, we anticipate to enhance our knowledge of the winter atmospheric deposition in western Siberia, in the absence of direct influence of marine aerosols and large industrial centers. This should eventually allow to evaluate the impact of snow deposition on chemical composition and elementary fluxes of subarctic inland waters across a large latitudinal gradient of climate and permafrost parameters.

2. Study site, materials and methods

2.1. Geographic settings

Western Siberia Lowland, located between the Ural mountains and the Yenisei River, extends over 2000 km from south to north and presents highly homogeneous, from physico-geographical point of view, taiga, forest-tundra and tundra landscapes comprising bogs and mires in the permafrost-free zone and thermokarst lakes developed on flat peat bogs (palsa) in the permafrost-bearing zone. Detailed physico-geographical description, hydrology, lithology and soils can be found in earlier works (Botch et al., 1995; Smith et al., 2004; Frey and Smith, 2007; Beilman et al., 2009) and in our recent geochemical studies (Manasypov et al., 2014; Stepanova et al., 2015; Pokrovsky et al., 2015). Because of its flat orographic context, extensive vegetation cover and relative remoteness from the Arctic Coast (except the north of the Gyda and the Yamal peninsulas), the atmospheric precipitates in winter are likely to bear the signature of remote desert and semi-desert regions of Central Asia. The anthropogenic impact is not expected to be strongly pronounced because of *i*) low population density (average 6 people/km^2 but only 0.5–2 people/km^2 in the northern half of WSL) and *ii*) moderate local pollution from the gas burning in oil wells mostly in the permafrost-free zone, south of the Surgut town. The part of WSL north of 64°N contains essentially gas exploration facilities (no gas burning) and minimally impacts the environment. Taken together, the latitudinal profile of the WSL presents a unique opportunity to study the chemistry of atmospheric deposits within highly homogeneous physico-geographical context and relatively low local anthropogenic impact.

2.2. Snow sampling

The snow of the WSL was sampled along the latitudinal transect S → N, from the vicinity of the Tomsk city (zone of southern taiga) to the eastern coast of the Ob estuary (tundra zone) from 19.02.2014 to 5.03.2014 (**Fig. 1**). The possible sources of snow deposition and the pathways of aerosols transport to the WSL were reconstructed by analyzing meteorological maps and by calculating back trajectories of air transport to the observation points using NOAA's HYSPLIT model (Draxler and Rolf, 2003). In order to assess a snapshot of snow deposition across 1700-km latitudinal profile and collect the freshest snow that was subjected to minimal transformation, we chose to sample only the upper layer of the snow cover. This technique, in contrast to traditional sampling of full snow column (i.e., Guéguen et al., 2016; Niu et al., 2017) allows adequate representation of the upper fresh snow layer that had minimal transformation at the soil, and frequently used in remote regions (Kang et al., 2007; Zhang et al., 2013). The isotope composition of collected snow proved its fresh character, not subjected to any metamorphism (Vasil'chuk et al., 2016).

The upper 0–5 cm of snow was sampled in 39 locations (**Fig. 1**). All sampling points were located more than 500 m from the winter road. The sampling was performed using metal-free technique, in protected environment, using pre-cleaned plastic shovel and vinyl single-used gloves. Approximately 30 L of snow was collected into single-used polyethylene bags. These polyethylene bags were thoroughly washed with 1 M HCl and abundant MilliQ water in the clean room class A 10,000. In the laboratory, the snow was melted at ambient temperature, and filtered through pre-weighted acetate cellulose filters (Millipore, 47 mm diameter) of 0.45 µm poresize. The storage of unfiltered snow water samples was less than 1 h at 4°C.

2.3. Particle analyses

The sizes and morphology of particles on filters and elemental composition of individual particles were studied using scanning electron microscope VEGA 3 SEM (Tescan) with a microprobe attachment INCA Energy (Oxford Instruments). The mineralogical composition of particulate fraction on selected filters was studied by X-ray powder diffractometric method on the D8 ADVANCE (Bruker AXS) X-ray diffractometer equipped with the 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%.

Freshly melted snow water was filtered through pre-weighted 0.45 µm acetate cellulose (Millipore) filters. These filters were placed in the Petri dishes, dried at 60°C in an oven and digested using microwave acid attack which comprised 6.5 mL concentrated HNO_3, 3.5 mL concentrated HCl and 0.5 mL concentrated HF. HNO_3 and HCl were bi-distilled in the clean room and HF was commercial ultra-pure quality (Fluka). The filters were reacted 30 min in ultrasonic bath prior full digestion using Mars 5 microwave digestion system (CEM, France). For this, 10 samples of filters, 1 certified 2711a Montana II Soil standard and 1 blank filter sample were loaded into Teflon reactors subjected to treating at 150°C during 20 min. After completing the digestion, the content of reactors was transferred to 30 mL Savilex vials and evaporated at 70°C. The residue was dissolved in 10 mL of 10% HNO_3 and dilutes by 2% HNO_3 prior to the analyses. For the analysis of snow particles on filters, the blanks (digestion of initial filters) were a factor of 10 to 100 lower than the filters with particles after 0.5-1.0 L of snow water filtration. The concentration of major and trace elements (TE) in filter digestion products was measured using an ICP-MS Agilent 7500 ce with ~3 µg/L of indium and rhenium as internal standards. 4 in-house external standards were analyzed every 10 samples. Necessary corrections for oxide and hydroxide ion interferences were made for rare earth elements (REE) and metals (Ariés et al., 2000). Based on replicate analyses of in-house standards and certified materials, the uncertainty for TE measurement ranged from 5 % at 0.1–100 µg/L to 10 % at 0.001–0.01 µg/L. Analyses of low concentrations of Hf, Ge, Cs, Ga, and W (e.g., on the order of 0.001 µg/L, comparable with detection limits) was possible with a minimal estimated uncertainty of 20%.

2.4. Melted snow analyses

The pH and specific conductivity were measured on unfiltered snow water samples using Hanna portable instruments. The dissolved (< 0.45 µm) fraction of snow water was obtained via filtration using a polycarbonate Nalgene vacuum filter unit, and a PVC-made Mityvac hand vacuum pump. This fraction included colloidal and truly dissolved (ionic) forms. Blanks of MilliQ water were also placed in polyethylene bags for the same time as melting snow (≤ 1 h at 4°C) and processed via filtration similar to snow samples. The filtrates were divided into two parts; one was acidified with double distilled HNO_3 acid and stored in pre-cleaned HDPE vials for ICP MS analysis, the second part was stored in HDPE bottles without acidification, for dissolved organic and inorganic carbon analysis (DOC and DIC), respectively, and anion analysis.

The major anion concentrations (Cl^-, SO_4^{2-}) in the < 0.45 µm fraction were measured using ion chromatography (HPLC, Dionex ICS 2000i), with an uncertainty of 2%, estimated from the replicate analyses of PERADE and RAIN international certified materials. The DOC and DIC in this fraction were analyzed using a Carbon Total Analyzer (Shimadzu TOC-VSCN) with an uncertainty of 5% and a detection limit of 0.1 and 0.05 mg/L, respectively.

Filtered snow water samples were analyzed with an Element XR ICP MS allowing for much better precision of the analyses of highly diluted samples and avoiding many interferences compared to Agilent 7500 ce. The uncertainty of the Element XR analysis was ± 5%, while its detection limit was a factor of 100 lower than the traditional (Agilent) instrument. The Element XR operated in three modes depending on the elements measured: low resolution for B, Rb, Sr, Zr, Mo, Cd, Sb, Cs, Ba, REEs, Hf, W, Pb, Th, U; medium resolution for Na, Mg, Al, Si, P, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, and high resolution for K and As. The agreement between two instruments for most elements was within 10 %. The international geostandards SLRS-5 (Riverine Water References Material for Trace Metals certified by the National Research Council of Canada) was used to assess the validity and reproducibility of the analyses.

2.5. River fluxes and snow storage

The mass balance calculation of the degree of snow melt influence on element fluxes in WSL rivers was performed, taking into account of *i*) the water stock in snow (in mm snow water accumulated during winter), fairly well known for Western Siberia (Karnatzevitch and Khruschev, 2014; Resources, 1972, 1973; Zakharova et al., 2011) and *ii*) the spring-time river runoff (in mm during May and June) calculated from hydrological parameters. For water stock calculation, we used the available mean multi-annual daily and monthly discharges of WSL rivers across the latitudinal profile (Resources, 1972 and 1972 and recently complied in the database R-AcricNET (www.r-arcticnet.sr.unh.edu). The WSL territory is covered by Russian Hydrological Survey (RHS) gauging stations which allowed to calculate the discharge during May-June as described elsewhere (Pokrovsky et al., 2015). The most recent complete hydrological data of small and medium size rivers in permafrost – affected area of WSL (Novikov et al., 2009) were used together with RHS database to calculate the spring flood fluxes of individual rivers and snow water stock for three latitudinal zones, 56-60°N, 60-64° and 64-68°N. Note that a comparison between the elementary snow stock and the river elementary discharge could not be performed for individual river watersheds, since no snow water chemical data are available with necessary spatial resolution. Therefore, we compared the winter snow stock with riverine spring flood fluxes of major and trace element for three latitudinal zones. For this, both spring flood flux of individual rivers and snow water stock were averaged for each latitudinal zone.

2.6. Statistical methods

Statistical analysis of the average, median and geometric mean values and the link between element concentration in suspended and dissolved fraction as well as comparison of different sampling sets (snow water and snow particles) included ANOVA, H-criterion of the Kruskal–Wallis and Mann–Whitney U tests. These tests allowed evaluating the difference between two sets of data separately for each TE following the approaches developed for lakes and rivers of western Siberia (Manasypov et al., 2014, 2015; Pokrovsky et al., 2015, 2016). The multiple regressions were performed for quantifying the relationship between dissolved and particulate concentration of TE and the latitudinal trends of concentrations and enrichment factors. More thorough statistical treatment of both log-transformed and non-transformed major and TE concentration in dissolved and particulate fraction of snow samples in each location included a normed PCA analysis using the ADE-4 R package (Thioulouse et al., 1997; Chessel et al., 2004) using the methods for scores and variables (De la Cruz and Holmes, 2011).

To identify the group of elements that behaved in a similar way in snow water and snow particles, we applied a complementary hierarchical cluster analysis (HCA) (e.g. Hartigan, 1975; Kaufman and Rousseeuw, 2005) which is widely adopted in geochemical interpretations of element concentration data (e.g. Bini et al., 2011; Levitan et al., 2015; Schot and van der Wal,1992; Moragues-Quiroga (2017). We used the Ward's method (Ward, 1963) for the linkages rule, following previous studies (Gourdol etal., 2013; Lin et al., 2014). The Pearson correlation distance was used for the linkage distance, which is frequently used for cluster variables (Reimann et al., 2008). These choices are in agreement with the group search of the PCA loadings.

In order to assess the degree of element fractionation in snow particles, Al-normalized TE enrichment factor (EF) with respect to the average upper part of continental earth crust (Rudnick and Gao, 2003) was calculated according to:

$$\mathrm{EF} = \frac{[TE]/[Al]_{sample}}{[TE]/[Al]_{crust}}$$

For the assessment of element enrichment factor in snow particles, a normalization to both general upper Earth crust and the local geological background (soil, peat and moss) was used. The reason for this is that, unlike in studies of the local pollution tracing in the European arctic (e.g., within the Kola Ecogeochemistry project, see de Caritat et al., 1997; Reimann and de Caritat, 2000; Reimann et al., 2000) or small-scale stream bed sediments or soils (N'guessan et al., 2009; Moragues-Quiroga et al., 2017; Levitan et al., 2015) where the normalization to the local soil or bedrock was necessary, the present study essentially deals with winter-period long-range atmospheric transport of soluble and mineral forms of elements. As such, following the common practice in this field, the normalization to upper Earth crust allowed assessing the true enrichment/depletion of the atmospheric aerosols. However, in order to better represent the elementary features of snow particles, the concentration of elements in PF was also compared with western Siberian mineral soils, peat and moss.

3. Results

3.1. Soluble fraction of the snow water

For all major and most trace elements, the concentrations in the blanks were below or comparable with analytical detection limits (≤ 0.1 ng/L for Cd, Ba, Y, Zr, REEs, 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). These values were at least 5 times lower than the average concentration of trace elements in snow samples. Most TE presented in this work exhibited ≤ 15%-agreement between the certified or recommended values and our measurements. The TE for which certified or recommended data were not available were considered only for the cases where we obtained good analytical reproducibility (i.e., the relative standard deviation based on our standard measurements was ≤ 10%).

The latitude-averaged concentrations of dissolved and particulate fraction of snow samples are listed in **Table 1.** A full data set of major and TE concentration in snow water is given in the "Data availability" section. Examples of the effect of latitude on dissolved (< 0.45 µm) element concentrations are shown in **Fig. 2.** Fe and Cu demonstrated a 2 to 5-fold increase in dissolved concentration north of 63°N (at $p < 0.05$). Zn and Pb did not exhibit any systematic effect of latitude, and Sb, Cd and Ni demonstrated a single maximum at c.a. 63-65°N. As exhibited two maxima, at 63.5 and 67.5°N with overall 2 to 3-fold decreasing trend northward. All other major and trace elements demonstrated a lack of systematic variation of concentrations as a function of latitude (not shown).

The PCA treatment of soluble fraction suggested that at least two factors are interpretable. The PC1 x PC2 correlation circle revealed two large groups of variables (**Fig. 3A**). The first group is composed of Al, Fe, Cr, Zr, Pb, REEs corresponding to lithogenic, poorly soluble trace elements. The second large group is composed of DOC, K, Rb, Cs, Mn, Co, Ba, Sb, Co, Mo, Mg, Si, Sr, Na, Ca, pH. These highly mobile elements presumably reflect the marine aerosols and leaching from soluble soil minerals such as carbonates as well as plant biomass. Similar factors determine chemical composition of snow water regardless of the latitude of the sampling and no specific conditions or limiting factors depended on geographical location.

The HCA analysis was conducted on the basis of first two factors of the PCA. The criterion of non-intersection between the groups allowed partitioning the chemical elements of the dissolved part into 6 specific groups presented in **Fig. 3B**. These groups characterize the elements according to their general chemical properties, ability to mobilize in aqueous solution from the solid minerals, affinity to the biota or their presence in the contaminated particles of industrial activity. Thus, the first two group of the dissolved fraction shown in **Fig. 3B** and encircled in **Fig. 3A** comprise low mobile elements likely originated from alumino-silicate mineral matrix (Al, Cr, REE, Ti, Zr, Fe, V) as well as some volatile heavy metals typically present in the solid aerosol particles (Cu, Cd, Pb). The 4th group includes major constituents of carbonate or marine aerosols matrix (elevated pH, Mg, Ca and Na). The 5th group is represented by typical macro- and micronutrients (K, Rb, Mn, Co, Ba). Finally, the last 6th group of elements comprises both labile elements linked to weatherable minerals (Sr, Sb, Si, Ni) and nutrients such as Sr, Ni, Si, DOC and Mo. Three of these elements are strongly enriched in snow particles relative to the Earth crust (Sr, Sb, Mo, see section 3.3 below), thus suggesting their possible leaching from atmospheric dust into the soluble fraction of snow. We could not find a straightforward explication of the common group of Zn and U in soluble snow fraction (**Fig. 3 B**)

The effect of particulate fraction on dissolved element composition in snow is illustrated in **Fig. 4** where the value of pH (**4 A**), Sr (**4 B**), Al (**4 C**) and Pb (**4 D**) in dissolved fraction are plotted as a function of total particle concentration in snow water. The elements of 4th and 5th group (Ca, Mg, Sr, Mn, and Co) increase their concentration in snow water by ca. an order of magnitude with the increase in particle concentration by 2 orders of magnitude. The insoluble hydrolysates (Fe, Al, light REEs, Zr, Cu and Pb) belonging to 1st and 2nd HCA group decrease their concentration (less than a factor 10) when the particle concentration increases by 2 orders of magnitude. Other elements in < 0.45 µm fraction exhibit the variations within an order of magnitude (DOC, DIC, Na, Cl, SO_4, K, Si, Cr, V, Ni, Cu, Zn, As, Sb, Rb, Cd, Cs, Ba, heavy REE and U) or two orders of magnitude (Ti, Ga, Mo, W) and do not demonstrate any significant (at $p < 0.05$) link with particle concentration.

3.2. Particle concentration and TE in particulate fraction of snow

Concentration of particulate fraction (PF) of snow and its elementary composition are available in the “Data availability” section. The mineralogical composition of most representative snow samples is given in **Table S1** of the Supplement. The dominant minerals are quartz (37%), albite (13%), K-feldspar (13%), phlogopite (10%), chrysotile (8%), illite (7%), and chlorite (5%). The concentration of dolomite and calcite ranges from 1 to 48 and 1 to 19%, respectively. Although mineral components dominated the composition of particulate fraction, the PF also contained organic fibers, diatom frustules, pollens and particles produced during fuel burning (fly ash and black carbon). The concentration of particles in snow water ranged from 0.4 to 67 mg/L. The highest values are encountered in the vicinity of the Tomsk city (No SF 1) and around towns of Surgut (No SF 54, 14), Nojabrsk (SF 36, SF 38) and Gubkinsky (SF 33). Although the proportion of fly ash and black carbon in these samples is significant and higher than in the rest of samples as follows from SEM observation, the mineral particles (1-25 µm size) still dominate. Note that high content of fly ash and fuel burning spheres was not linked ($p > 0.05$) to high particulate and dissolved elements. The lowest concentrations of particles (< 5-10 mg/L) were recorded north of 65°N, the region of gas industry, and between 58 and 61°N corresponding to the winter road along the Ob River with very low population density.

The enrichment coefficient ranged from ~1–5 (Ga, REEs, Fe) to > 100 (Mo, W, As, Sb, Ni, Cu, Pb, Mg, Ca, Na) as illustrated in **Fig. 5 A.** The highest enrichment (EF ≥ 1000) is observed of Sb, Zn and Cd. The variation of the enrichment factor as a function of latitude is shown for elements most enriched in particulate fraction in **Fig. S1 of Supplement.** For Mg, Ca, Sr, Ba, Fe, Mn, Co, Ni, K, Rb, Cs, V, Cr, As, Cd, W the EF exhibits a maximum around 63-64.5°N. This maximum coincides with the maximum of particulate fraction concentration (not shown).

The majority of chemical elements are present in particulate rather than dissolved form in snow meltwater samples. This is illustrated by a histogram of the ratios averaged over full latitudinal profile (**Fig. 5 B**). Although the variations of this ratio for different snow water samples across the WSL achieve ±0.5 order of magnitude, the average values shown in this figure illustrate the importance of particulate deposition of Al, Fe, Ga, REEs, Cr, V, Ti, Zr, Mo and W. For other elements, particulate and dissolved inputs in the form of snow are within the same order of magnitude. Some soluble elements such as Na, Cd, Ca, Sr, Ba, K, As and Zn exhibit the dominance of dissolved transport in snow.

Although the use of average crust for assessment of element enrichment in snow particles is justified by long-range transfer of snow components, it is known since the works of group of Reimann and de Caritat in NW Europe that the "average crust" is unlikely to represent the local background and the use of the "upper crust" average value can introduce a 2 to 3 order of magnitude uncertainty to any calculated EF (de Caritat et al., 1997; Reimann and de Caritat, 2000; Reimann et al., 2000). As such, western Siberia moss, peat and clay/loam horizons were used to assess relative enrichment of elements in snow particles. It can be assumed that the leaching of soluble forms of elements from these solid phases in winter is highly unlikely. The specificity of western Siberia is that the mineral ("geological") local substrate is completely frozen, even in summer, since the active (unfrozen) layer depth does not exceed the peat thickness, and in that case, the use of "organic" substrates is most relevant. All three WSL reference substances ("local" moss, peat and clays) represent latitudinal-averaged values based on large (> 50) number of samples collected in previous studies across the 1700-km latitudinal gradient.

The elementary ratios of snow particles to that in mineral soil, peat and moss of the WSL are illustrated in **Fig. 6 A, B, and C**, respectively. Given significant variation on the latitude-averaged values of element concentration in snow particles, mineral, peat and moss of soil column, the deviation of the ratios from unity is significant if it exceeds a factor of 2 to 3. Compared to mineral soil of WSL, the snow particles are strongly (≥ 10×) enriched in Sb, Zn, Ni and Cd and in a lesser degree (≥ 5×) in Mg, Ca, Pb, Mo, and As (**Fig. 6 A**). Note that western Siberian soils, developed on sand and clay (silt) deposits (Vasil'evskaya et al., 1986), are quite poor in Ca and Mg, especially in the permafrost-bearing zone north of 62°N. The enrichment of snow particles relative to peat is observed for all elements, being particularly high (> 50×) for Ni, Cr, Pb, Cu, Zn, Mg, Na and Sb (**Fig. 6 B**). Only P, Ge and Cd, exhibiting high affinity to peat (Shotyk et al., 1990, 1992), are not significantly ($p > 0.05$) higher in snow particles compared to the peat column. Finally, the mosses are most depleted by all elements relative to snow PF with only biogenic elements (P, K, Rb, Mn and Cd) known to be concentrated in bryophytes being non-significantly higher in snow particles relative to mosses (**Fig. 6 C**).

The PCA of elementary composition of particulate fraction demonstrated the F1 x F2 structure (**Fig. S2** A of the Supplement). Here, two groups can be distinguished: highly mobile elements (Na, Ca, V, Ni, Mg, Mn) and low mobile elements (REE, Zr, Pb, Cd, Ga, P). For the particulate fraction, the HCA attributed the elements to 5 formal groups shown in **Fig. S2 B** and encircled in **Fig. S2 A.** This distinction, however, is less certain than that of the dissolved fraction and does not allow establishing a clear link between the selected groups and physico-chemical properties of elements or their possible sources in the snow particles. Thus, in the 1st group, among three labile elements (Mg, Na and Ca) we identified V, which may exhibit elevated mobility in the form of anion in carbonate-bearing mineral particles. Divalent metals (Co, Ni, Mn) and Sr constitute the 2nd labile group of elements, yet this group also comprises low-mobile Fe and Cr. The 3rd group of insoluble low mobile elements is marked by the presence of phosphates (REE and P), refractory Zr and volatile Pb. The 4th group of elements revealed by HCA of particles is composed of Sb, Cu and Zn. All these elements are strongly enriched in snow particles over the soil minerals (see **Fig. 6 A**). The last group of elements in snow particles comprises both labile (Li) and biologically-important Mo, K, Rb, Ba, toxic volatile elements which could bear the signature of anthropogenic pollution (As, Cd) but also low mobile Ti and Ga. We could not identify the link of elements in this group to the degree of snow particles enrichment relative to main "local" substrates of the WSL (moss, peat and clays), shown in **Fig. 6.**

3.3. Possible impact of snow deposition on major and TE in lakes and rivers.

3.3.1. Snow water in comparison to lake and river water

The concentrations of dissolved major and trace element in snow water fraction can be compared with those in thermokarst (thaw) lakes of western Siberia measured in 2013-2014. These lakes are shallow (0.5-1.5 m depth) water bodies representing the largest reservoir of surface waters in western Siberia, north of 62°N (Polishchuk et al., 2017).

The average concentration of major and TE in thermokarst lakes of various size (Manasypov et al., 2014) can be compared with those in snow water collected in this study across the same latitudinal gradient. Because the size of thermokarst lakes of WSL ranges from few m² to several km², 4 representative ranges of lake diameters are used for this comparison (0-10, 11-100, 101-500 and > 500 m). Given that the spring-time lake concentrations across the latitudinal gradient are not available, the summer-time elementary compositions of lakes were taken as most representative for the open water period of the year. The concentrations of low-soluble elements such as Fe, Al, trivalent and tetravalent hydrolysates in lakes are 1 to 2 order of magnitude above their concentrations in snow (not shown). At the same time, Zn, Cu, Cd, Pb, Sb and Mo exhibited snow-water concentrations that were comparable or significantly higher ($p < 0.05$) than the concentrations in lakes.

Because the main source of water in shallow lakes of WSL in spring is melted snow (Manasypov et al., 2015), we could compare the mean concentrations of snow water with spring-period lake water concentration for one particular region of discontinuous permafrost zone (town of Nojabrsk, Khanymey site) for which high-resolution seasonal observations on lakes of various size are available. For two classes of lake size (< 0.5 km² and > 0.5 km²), the following three groups of elements could be distinguished. The concentrations of dissolved Na, Mn, Zn, As, Rb and Sr in snow water are similar (within a factor of 2) to lake water concentrations. Concentrations of DIC, Cl, SO_4, Mg, Ca, Cr, Co, Ni, Cu, Mo, Cd, Sb, Cs, W, Pb and U in snow are close or higher ($p < 0.05$) than those in lakes. And finally, concentrations of DOC, Al, Si, K, Ti, V, Fe, Ga, Zr, Ba, and REEs in snow water are significantly lower than the lakes' concentrations. There was no distinction of elements belonging to individual groups of the HCA and this classification.

The concentrations of elements in snow water could be also compared with river water concentrations measured during spring flood 2014 across the full latitudinal profile, since such data for rivers of different size are available (Pokrovsky et al., 2015, 2016a). Examples of elements whose concentrations in snow water are higher or comparable with those in rivers during spring flood are illustrated in **Fig. S3**. Generally, the effect of snow melt is mostly pronounced north of 64°N. During this period, when the rivers are essentially fed by melted snow, the atmospheric deposition exhibited comparable or higher ($p < 0.05$) concentrations of SO_4, Cr, Co, Ni, Cu, Zn, Mo, Cd, Sb, Cs, W and Pb than those in rivers. These elements belonged to 5 dominant groups of HCA treatment. The concentrations of all other elements in WSL rivers cannot be explained by solely snow water concentration.

Note that, by filtering the snow and the lake/river water to 0.45 µm, the dissolved fraction includes a colloidal load, which can play a crucial role in the concentration of trace elements (Pokrovsky et al., 2016b). However, with typical concentration of DOC in snow water around 1-2 mg/L, the share of colloidal forms of metals will be an order of magnitude lower than that in river and lakes of the WSL having 10 to 30 mg/L of DOC.

3.3.2. Comparison of river fluxes in spring and snow water stock

Considering the mass balance calculation of snow melt influence on element fluxes in WSL rivers, the ratios of river fluxes in May-June to snow stock can be presented in the form of histograms for 3 latitudinal zones (**Fig. 7**). These ratios systematically decrease with the increase in the latitude. In the southern, permafrost-free zone, Zn, Cd, Pb, Ga, Cs, W, Sb and Cl fluxes in rivers can be provided essentially by snow melt. The riverine fluxes of DIC, Cl^-, SO_4^{2-}, Na, Mg, Ca, Sr, Rb, Cs, Zn, Cu, Cr, Ni, Cu, Pb, As, Sb, Mo, W and U are strongly (i.e., ≥ 50% at $p < 0.05$) affected by snow melt in the discontinuous and continuous permafrost zones, north of 60-62°N.

According to the evolution of the ratio [river flux] / [snow stock] with the latitude, three group of element can be distinguished: (*i*) elements that steadily decrease this ratio suggesting an increase in the impact of snowmelt northward: DOC, SO_4, Al, Ti, V, Cr, Rb, Sr, Cd, Sb, Cs, La, Ce, W, Pb; (*ii*) elements for which this ratio decreases abruptly to 62±2°N and then remains constant further northward: DIC, Na, Mg, Si, K, Ca, Ni, Cu, As, Mo and U; (*iii*) elements exhibiting non-systematic variation of the ratio with latitude but having strong (> 50%) impact of snowmelt on river fluxes (Cl, Co, Zn, Ga) and (*iv*) elements having negligible (< 10 %) impact of snowmelt on river fluxes (Mn, Fe, Zr and Ba). Overall, the impact of snow melt on river export fluxes in spring strongly increases northward for DIC, Cl^-, SO_4^{2-}, Na, Mg, Ca, Cd, Pb, Sb, Cr, Cu, Ni, As, Mo, Rb, U. Although these elements belong to all 5 major groups of cluster analysis (**Fig. 3 B**), they can be characterized as soluble (highly labile) elements, originated either from marine aerosols or from leaching from soluble minerals such as carbonates, and also include volatile constituents of the atmospheric aerosols (Cd, Pb, Sb, As).

4. Discussion

4.1. Dissolved major and trace elements in Siberian snow

In accord with general knowledge of the Arctic aerosol chemistry (Barrie, 1986; Barrie and Barrie, 1990; Laing et al., 2014, 2015; Nguyen et al., 2013; Pacyna and Ottar, 1989; Shevchenko et al., 2003; Weinbruch et al., 2012), the principal component structure of snow water chemistry identified the combination of lithogenic source (dust and soil particles dissolution, providing low-mobile, insoluble elements such as Al, Fe, Cr, Zr, REEs) and marine aerosols (soluble forms, providing high concentration of mobile elements such as Ca, Mg, Na, Mo, Ni). The latter may also originate from aeolian transport of carbonate-rich soils. The biogenic component may include Mn, Zn, K, Rb, DOC, Si whereas the anthropogenic pollution originates from coal combustion (Sb, Co) and heating systems, gas flaring at the gas oil production site as well as non-ferrous metal-smelter industry (Sb, Zn, Vinogradova et al., 1993) and ground transportation (Pb, Cu, Zn, Cr, Ni, As, Rossini Oliva and Fernández Espinosa, 2007; Sutherland et al., 2000).

The soluble highly mobile elements such as alkali and especially alkaline-earth elements, Sb, Mo, W and U demonstrated an increase in their dissolved (< 0.45 µm) concentration with the increase in the total particulate fraction (**Fig. 4 B**). We interpret this increase in concentration, also correlated with $\text{pH}_{\text{snow water}}$ increase (**Fig. 4 A**), as a result of element leaching from soluble minerals such as calcite and dolomite. There was a positive ($R^2 = 0.53$, $p < 0.05$) correlation between % of calcite in the particulate fraction of snow and Ca concentration in snow meltwater (not shown). Therefore, we hypothesize that simultaneous mobilization of carbonate minerals and soluble elements from the soil and rocks to the atmosphere occurs in southern, carbonate-rock bearing provinces where the winter aerosols are generated. The generation of insoluble elements such as trivalent and tetravalent hydrolysates in dissolved fraction of snow occurs independently of snow enrichment in solid particles. Indeed, the decrease, and not increase in insoluble elements dissolved concentration with the increase in particle concentration (**Fig. 4 C, D**) suggests that these elements are not desorbed or leached from mineral particles, either within the origin of aerosol formation or during snow melting and filtration in the laboratory.

Regional background concentrations of dissolved metals in snow of Quebec, Canada are reported to be 1.1, 1.7, and 1.6 мg/$\text{L}_{\text{meltwater}}$ for Cu, Pb, and Zn, respectively (Telmer et al., 2004). The values for Cu and Pb are comparable with average snow water concentration across the WSL (0.83 and 0.68, respectively) but the concentration of Zn in the WSL snow is significantly higher (10.1±5.0 µg/L, excluding 3 contaminated samples near the Tomsk city). Background concentrations of dissolved Cu, Pb, and Zn in snow of Alaskan Arctic are much lower (0.08, 0.09 and 1.2, respectively, Snyder-Conn et al., 1997). In snow from background areas of north-eastern European Russia, the concentrations of dissolved Cu are near at the same level as in snow from the WSL, whereas the concentrations of dissolved Pb and Zn are 2 times lower (Walker et al., 2003). Concentrations of dissolved Cu and Zn in snow of NW Finland are few times lower than in snow of WSL; concentrations of dissolved Pb are at the same level (Caritat et al., 1998).

Significant enrichment in Ni is known for the aerosols of the Arctic Ocean (Shevchenko et al., 2003). It may be linked both to Ni transport from Norilsk and Kola smelters but also with Ni fractionation at the sea surface (Duce et al., 1976). Ni concentration in snow water of the northern part of WSL significantly exceeds that in the thermokarst lakes. The winter snow stock of dissolved Ni is several times higher than the river export of this element during spring flood in the permafrost-bearing zone of the WSL, north of 60°N, and Ni concentration in snow particles exceeds up to 2 orders of magnitude its concentration in moss and peat of the territory.

The winter-time deposition of dissolved (< 0.45 µm) metals on the surface of northern part of the WSL can be calculated taking into account the mean multi-annual volume of accumulated snow during 8 winter months (in mm of snow water) and the average concentration of elements in February snow collected north of 64°N. The monthly depositions of selected metals (µg m^{-2} $month^{-1}$) on the north of the WSL in the form of snow are equal to 2.8, 12, 15, 210 and 0.9 for As, Ni, Pb, Zn, and Cd which is significantly higher than the values for winter deposition of insoluble aerosols into the Russian Arctic (0.22, 0.74, 2.7, 1.3 and 0.056, respectively, Shevchenko et al., 2003). Only V exhibited similar values of Arctic aerosol and snow deposition (0.71 and 0.96 µg m^{-2} month, respectively).

4.2. Particulate forms of elements in the snow across the latitudinal profile: the effect of mineralogical substrate, industrial centers, local pollution and long-range transport.

The majority of elements are transported in particulate rather than dissolved fraction in the snow water (**Fig. 5 B**). This is in general agreement with the results of other studies in Scandinavia and Kola Peninsula (Reimann et al., 1996), north-eastern European Russia (Walker et al., 2003) and on drifting ice in the northern Barents Sea (Gordeev and Lisitzin, 2005). The enrichment of snow particulate fraction relative to the earth crust as shown by Al-normalized enrichment coefficient (**Figs. 5 A, S1**) can be understood via taking into account the particle concentration in snow and microscopic observations. We suggest that the clays supply most trace elements in the PF. The atmospheric particles are known to exert significant impact on soils and ground vegetation (Kabata-Pendias and Pendias, 1984; Rasmussen, 1998; Steinnes and Friedland, 2006). In the case of WSL, the elementary composition of snow particulate fraction was compared with three main reservoirs of elements within the soil, sampled over significant latitudinal profile, from 55°N to 68°N (Stepanova et al., 2015). These reservoirs are averaged over full latitudinal range and include *i*) mineral fraction from the bottom of the peat column; *ii*) depth-averaged peat column composition, and *iii*) *Sphagnum* mosses, collected in ombrotrophic bogs, which receive their constituents essentially from the atmosphere (e.g., Santelman and Gorham, 1988).

The particularity of the northern part of western Siberia lowland is that the active (seasonally unfrozen) soil layer is located within the organic (moss+peat) rather than mineral horizon; the latter is represented by poorly reactive sands and clays (Baulin et al., 1967; Baulin, 1985; Tyrtikov, 1973, 1979). As a result, the surface waters drain essentially organic part of the column which is very poor in lithogenic elements (Pokrovsky et al., 2015, 2016a). The supply of mineral particles from the snow therefore may significantly enrich the rivers and lakes in dissolved alkaline earths, metal micronutrients, phosphorus and other elements given high reactivity of incoming silicate and carbonate grains in acidic (pH < 3-4), organic-rich (10 < DOC < 50 mg/L) surface waters of Western Siberia. The degree to which such a supply can lead to overestimation of the calculated chemical weathering export fluxes of cations in the permafrost zone is not possible to quantify. Therefore, in view of the importance of atmospheric input of solid particles for mineral-poor, peat bogs of western Siberia, the seasonal, year-round measurements of particulate atmospheric deposition in this region are necessary.

The main source of mineral particles in the southern part of latitudinal profile (56–58°N) may be soils of steppe and forest-steppe regions south of WSL, where the land is cultivated and the snow cover is relatively thin. The aeolian transport of soil particles under these conditions may be efficient even in winter (Evseeva et al., 2003). The main source of ash particles in southern part of the profile is the industry and transport of the city of Tomsk (Boyarkina et al., 1993; Yazikov et al., 2000; Talovskaya et al., 2014). The concentration of particles in snow collected from 58°N to 61°N ranged between 0.85 and 5.72 mg/L which is comparable or slightly higher than the values reported for the Arctic snow cover (Darby et al., 1974; Mullen et al., 1972; Nürnberg et al., 1994; Shevchenko et al., 2002, 2010). It is important that in this zone of low PF concentration, combustion spheres, fly ash and black carbon of few µm diameters were dominating. This can explain relatively low concentration of all TE at low PF concentration, as carbon compounds likely contain very low proportion of trace metals. The most important sources of fly ash and black carbon are gas flaring, land transport, heating plants, residential combustion, forest fires (mainly in summer) and industrial plants (Moskovchenko and Babushkin, 2012; Quinn et al., 2008; Stohl et al., 2013). Chemical pollution of atmosphere during gas flaring associated with oil industry is known for the WSL (Raputa, 2013; Yashchenko et al., 2014). The black carbon produced during gas burning is detected not only in western Siberia but in the Russian sector of the Arctic Ocean in high latitudes (Stohl et al., 2013).

In the zone 62–64.5°N, where some impact of oil industry is possible, the concentration of insoluble particles in snow were above 10 mg/L, achieving the value of 66.6 mg/L in sample SF36. Backward trajectories to this site using Draxler and Rolf (2003) approach show that, during last few days before sampling, the air masses arrived from south-western direction. Accordingly, the particulate fraction in these samples contained mostly mineral particles 1–25 µm size with some fly ash (burning spheres). It is possible that mineral particles are supplied here via long-range transport from forest-steppe, steppe and semi-desert regions south and south-west from the study site. Indeed, during winter snow coverage period, the dominant winds in this zone have S, SW and W directions (Moskovchenko and Babushkin, 2012). The events of mineral dust transport over large distances are well known in the boreal zone (Lisitzin, 1978, 2011; Shevchenko et al., 2010).

Further north of studied latitudinal profile, from 65 to 68°N, the concentration of snow particles ranged from 0.8 to 9.2 mg/L. These values are within the background in the Arctic and subarctic (Darby et al., 1974; Mullen et al., 1972; Nürnberg et al., 1994; Shevchenko et al., 2002). The particulate fraction was represented by mineral debris of 1 to 15 µm in size, with frequent but not significant presence of spherical ash particles, biogenic strains and porous carbon particles. Because the main source of mineral particles is long-range transport from southern desert and steppe regions, moving to the north decrease the influence of these provinces.

We believe that the elevated concentrations of divalent metals, As and Sb in snow particles (**Fig. 5 A, S1**) should not be interpreted as necessarily pollution from the industrial centers. Rather, volatile Pb, Cd, As may originate from long-range transport of desert material. Therefore, we attempted to distinguish the well-known refractory, non-volatile heavy metals such as Cu, Ni and Co and more volatile elements such as Pb, Cd and As (i.e., Reimann et al., 2000) based on the HCA treatment. For both particulate and dissolved fraction, these elements are located in three or two different groups but never belong to one single group of inter-correlated elements. As such the available data do not evidence similar origin of Cu, Ni and Co, or Pb, Cd, and As in the snapshot of WSL snow sampled in this work.

4.3. Impact of snow on hydrochemistry of inland waters and riverine elementary fluxes.

Quantitative comparison of element input to the land surface with winter snow and element concentration and fluxes in the WSL inland waters provided the assessment of minimal atmospheric contribution to lake storage and river export. The concentrations of Pb, Zn, Cu, Cd, Sb and Mo in lakes are significantly lower than those in snow. However, these elements belong to 4 various group of elements in dissolved snow fraction, identified by the HCA (**Fig. 3 B**). In rivers, SO_4, Cr, Co, Ni, Cu, Zn, Mo, Cd, Sb, Cs, W and Pb are dominated by snow input. These elements also belong to 4 various group of the HCA. It thus can be concluded that there is no direct link between the group of elements identified by cluster dendrogram in the snow water and the elements whose concentration in rivers or lakes are significantly affected by snow deposition. We believe that a natural cause of this apparent inconsistency is different mechanisms controlling the element distribution in the aerosols (local sources of pollution, remote desert provinces, leaching of soluble elements from particulate fraction) and surface waters (interaction of melted snow with upper peat and moss/lichen horizons; underground feeding, release of elements from silicate river suspended matter due to abrasion in spring flood).

Overall, the impact of the snowmelt on chemical composition of western Siberian thermokarst lakes may be very high. This will be further accentuated by reported increase in the proportion of meltwater that does not reach the main rivers but is stored by the wetlands (i.e., from 20-30% in early 1990s to 50-60% in the mid-2000s, Zakharova et al., 2011). A comparison of snow stock/river water fluxes demonstrates the increase in the influence of atmospheric deposition northward (**Fig. 7**). At the same time, the chemical composition of the snow water, although subjected to significant variation, does not exhibit any systematic trend with the latitude (**Fig. 2**) as also follows from the PCA (section 3.1). The reason for this difference may be relatively low fluxes and concentrations in rivers of the northern, permafrost-affected territory of the WSL compared to the southern, permafrost-free zone (Pokrovsky et al., 2015, 2016a). As a result, the impact of atmospheric deposition on the riverine transport is more pronounced in the permafrost zone than in the permafrost-free zone. We expect this effect to be quite general for flat bog tundra areas of northern Eurasia, including, in addition to northern part of western Siberia (~400,000 km²) studied in this work, the Yamal and Gyda Peninsula (122,000 and 160,000 km², respectively), the North-Siberian Lowland (~700,000 km²), the Kolyma Lowland (170,000 km²), and the Yana-Indigirka Lowland (180,000km²) with overall territory close to 1.7 million km². The impact of snow deposition on river elementary fluxes should be much lower in permafrost-bearing mountainous terrain such as Central and Eastern Siberia, the Alaskan slopes, north of Scandinavian shield and the Canadian High Arctic. In those territories, two factors may decrease the contribution of snow deposition to river fluxes: 1) the impact of local mineral dust for aerosols generation may be well pronounced and 2) the chemical weathering occurs within the mineral seasonally unfrozen layer producing higher fluxes of inorganic components.

In contrast, in the lowlands of Northern Eurasia, the rivers drain essentially organic layer (peat bog) terrain, thus mineral feeding of rivers is really low. As it is demonstrated in section 3.3.2 of this study, low chemical (cationic) weathering in the north of the WSL during spring suggests that total dissolved cationic and DIC fluxes in May-June in this and other similar regions are essentially controlled by snowmelt, rather than by weathering. It follows that during the spring period, the intensity of chemical weathering in these latitudes can be a factor of 2 (major cations) to 5 (TE) lower than that deduced from riverine fluxes. However, given that the shares of spring flood period (May-June) in the annual export fluxes are only 5 to 10% for major cations and 10 to 20% for TE (Pokrovsky et al., 2015, 2016), the overall impact of atmospheric deposits on element export fluxes will be strongly pronounced (i.e., ≥ 50% of total measured river flux value) only for elements which have the ratio of the spring-time river export to snow stock less than 0.2, i.e., SO_4, Cu, Mo, Cd, Sb, Cs, W and Pb. With further increase of winter precipitation in western Siberia (i.e., Bulygina et al., 2009), the impact of snowmelt on element transport to the Arctic Ocean by rivers may increase thus enriching the surface waters in many elements such as Cd, Pb, Sb, Cr, Cu, Ni, As, Mo, Rb, U.

Conclusions

The chemical composition of surface layer of snow cover was studied across a 1700-km latitudinal gradient in western Siberia Lowland. The particulate fraction ranged from 0.4 to 66 $mg/L_{meltwater}$ and increased in the regions of enhanced dust deposition from southern steppe and desert provenances, in the proximity of industrial centers and due to fly ash production from gas burning of the oil exploration sites. There was an increase in concentration of soluble elements (Ca, Mg, Sr, Mn, Co) and pH in snow water with the increase in mineral (calcite, dolomite) fraction. The elementary composition of PF demonstrated its significant enrichment in most elements relative to mineral soil horizon, peat and moss across full latitudinal profile (~1700 km) of WSL. As such, solid atmospheric aerosols may be important factor of insoluble element delivery to the soil surface. The supply of mineral particles from the snow may also significantly enrich the rivers and lakes in dissolved alkaline earths, metal micronutrients, phosphorus and other elements given high reactivity of incoming silicate and carbonate grains in acidic ($pH < 3$-4), organic-rich ($10 < DOC < 50$ mg/L) surface waters of Western Siberia.

Concentrations of Na, Mn, Zn, As, Rb and Sr in winter aerosols are similar (within a factor of 2) to lake water concentrations during spring period. Concentrations of DIC, Cl, SO_4, Mg, Ca, Cr, Co, Ni, Cu, Mo, Cd, Sb, Cs, Pb and U in filtered snow water are close or higher than those in lakes. In the southern, permafrost-free zone, only Zn, Cd, W, Pb, Cs and Sb fluxes in rivers during May-June period can be provided by dissolved fraction of the snow melt. However, the impact of snow melt on river export fluxes in spring strongly increases northward for DIC, Cl, SO_4, Na, Mg, Ca, Cd, Pb, Sb, Cr, Cu, Ni, As, Mo, Rb, U. In the permafrost zone, ≥ 50% of riverine fluxes of these elements during spring flood can be provided by the snowmelt. The reason for such high sensitivity of WSL surface reservoirs to atmospheric deposition is feeding of surface waters by essentially organic (moss, peat) soil profiles.

Data availability

Full data set of major and trace element concentration in snow water (< 0.45 µm) and snow particles sampled across the latitudinal profile of Western Siberia Lowland is available at the Research Gate, https://www.researchgate.net/publication/309666956; DOI: 10.13140/RG.2.2.12156.54408.

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Table 1. Minimal, maximal, median and geometric mean concentration of dissolved (µg L$^{-1}_{\text{snow water}}$), n=35, and particulate (µg g$^{-1}_{\text{particles}}$), n=34 snow components. The data for upper continental crust (UPC) are from Rudnick and Gao (2003). N.A. stands for non analyzed.

	Dissolved				Particulate				UPC
Element	Min	Max	Median	Geometric mean	Min	Max	Median	Geometric mean	
pH	4.38	8.73	5.11	5.44	N.A.	N.A.	N.A.	N.A.	N.A.
SC, µS cm^{-1}	9	35	15.5	16.3	N.A.	N.A.	N.A.	N.A.	N.A.
DIC, mg/L	0.26	2.12	0.37	0.47	N.A.	N.A.	N.A.	N.A.	N.A.
DOC, mg/L	0.46	1.87	0.84	0.85	N.A.	N.A.	N.A.	N.A.	N.A.
Cl, mg/L	0.07	2.94	0.51	0.48	N.A.	N.A.	N.A.	N.A.	N.A.
SO_4, mg/L	0.41	2.01	0.71	0.72	N.A.	N.A.	N.A.	N.A.	N.A.
Li	N.A.	N.A.	N.A.	N.A.	2.6	32.2	10.8	10.7	24
Be	N.A.	N.A.	N.A.	N.A.	0.12	2.11	0.59	0.59	2.1
Na	47	1982	295	303	1452	39156	6717	7314	24200
Mg	19	862	114	114	3492	156712	19089	21411	14900
Al	1.6	35.2	15.5	12.3	6444	138267	31079	31565	81500
P	N.A.	N.A.	N.A.	N.A.	70	1928	481	503	660
Si	3.5	180	64.6	33.2	N.A.	N.A.	N.A.	N.A.	N.A.
K	39.2	120	55.5	63.0	1682	38395	5895	6023	23200
Ca	57	2266	267	296	3944	159272	17331	17775	25600
Ti	0.001	0.338	0.032	0.018	194	5762	674	689	3800
V	0.007	0.221	0.051	0.049	23.8	322	67.4	69.7	97
Cr	0.027	0.340	0.111	0.117	43.8	841	138	156	92
Mn	0.62	9.54	3.06	2.99	180	1242	400	404	780
Fe	1.8	62.2	14.6	12.0	7206	41255	15873	16488	39100
Co	0.006	0.418	0.097	0.094	5.9	60.7	19.4	18.6	17.3
Ni	0.04	5.66	0.36	0.36	28.1	1067	149	145	47
Cu	0.16	2.51	0.57	0.63	13.1	273	63.4	75.1	28
Zn	1.7	31.0	8.3	8.3	70.7	3832	202	255	67
Ga	0.0001	0.0185	0.0023	0.0014	1.8	26.7	8.32	7.73	17.5
Ge	N.A.	N.A.	N.A.	N.A.	0.36	3.18	0.88	0.91	1.4
As	0.02	0.46	0.19	0.15	3.8	67.2	16.1	16.0	4.8
Rb	0.033	0.262	0.066	0.075	6.1	124	24.1	23.4	84
Sr	0.26	10.2	1.04	1.23	26.2	580	117	115	320
Y	N.A.	N.A.	N.A.	N.A.	1.52	40.2	7.1	7.5	21
Zr	0.0001	0.0403	0.0024	0.0015	7.7	383	36.8	38.5	193
Nb	N.A.	N.A.	N.A.	N.A.	0.80	25.5	3.54	3.72	12
Mo	0.0001	0.059	0.010	0.005	0.55	10.4	2.12	2.24	1.1
Cd	0.015	0.180	0.047	0.046	0.11	3.37	0.71	0.71	0.09

Sn	N.D.	N.D.	N.D.	N.D.	1.13	29.3	7.76	7.36	2.1
Sb	0.009	0.132	0.036	0.038	1.67	27.2	5.96	6.15	0.4
Cs	0.0015	0.0105	0.0034	0.0036	0.32	4.78	1.35	1.24	4.9
Ba	0.74	13.6	3.35	3.32	88	1664	374	391	628
La	0.001	0.049	0.012	0.011	2.0	60.2	10.3	10.8	31
Ce	0.003	0.095	0.022	0.019	4.05	128	19.0	20.6	63
Pr	0.0001	0.0084	0.0022	0.0019	0.50	15.5	2.30	2.35	7.1
Nd	0.0013	0.0275	0.0085	0.0067	1.86	58.6	8.32	8.70	27
Sm	0.0001	0.0072	0.0020	0.0016	0.39	11.8	1.78	1.79	4.7
Eu	0.00010	0.00253	0.00096	0.00083	0.11	2.56	0.45	0.47	1.0
Gd	0.0004	0.0082	0.0022	0.0022	0.40	10.3	1.71	1.77	4.0
Dy	0.00002	0.0041	0.0016	0.0008	0.32	7.83	1.35	1.42	3.9
Ho	0.00006	0.00123	0.00061	0.00054	0.06	1.51	0.26	0.27	0.83
Er	0.0002	0.0029	0.0010	0.0010	0.18	4.71	0.77	0.80	2.3
Tm	0.00002	0.00088	0.00011	0.00009	0.03	0.72	0.11	0.11	0.3
Yb	0.00000	0.00289	0.00089	0.00049	0.16	4.91	0.73	0.73	1.96
Lu	N.A.	N.A.	N.A.	N.A.	0.024	0.76	0.11	0.11	0.31
Hf	N.A.	N.A.	N.A.	N.A.	0.25	13.2	1.10	1.18	5.3
Ta	N.A.	N.A.	N.A.	N.A.	0.18	4.35	0.62	0.62	0.9
W	0.002	0.108	0.020	0.017	2.0	102	35.9	28.8	1.9
Tl	N.A.	N.A.	N.A.	N.A.	0.04	0.73	0.23	0.23	0.90
Pb	0.02	3.67	0.51	0.38	13.2	703	71.9	67.9	17
Th	N.A.	N.A.	N.A.	N.A.	0.43	17.1	2.22	2.33	10.5
U	0.0007	0.0063	0.0031	0.0028	0.19	4.69	0.92	0.93	2.7

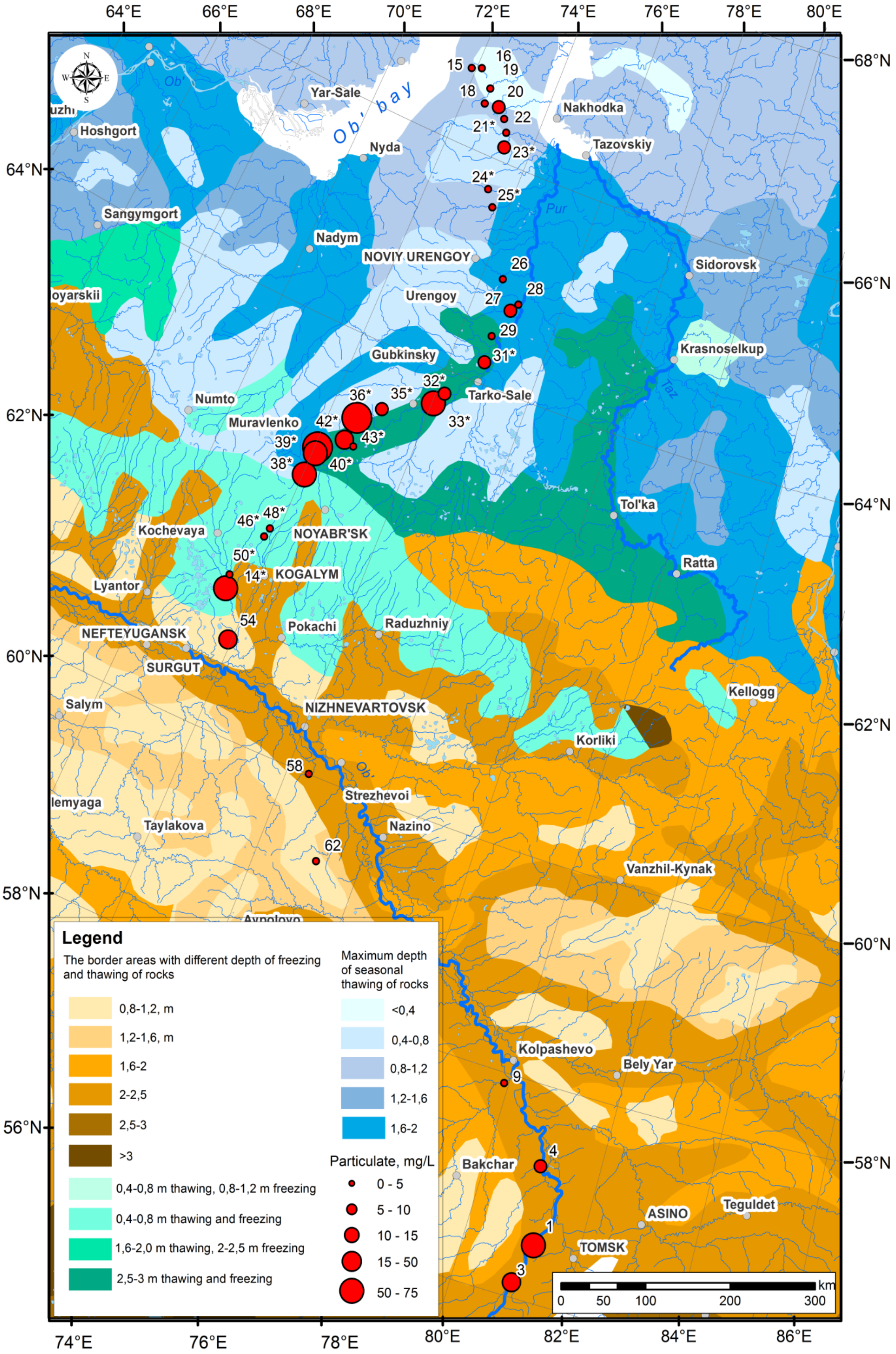

Figure 1. Map of the study site. The size of the sampling points reflects the concentration of particulate fraction (mg/$L_{\text{snow water}}$)

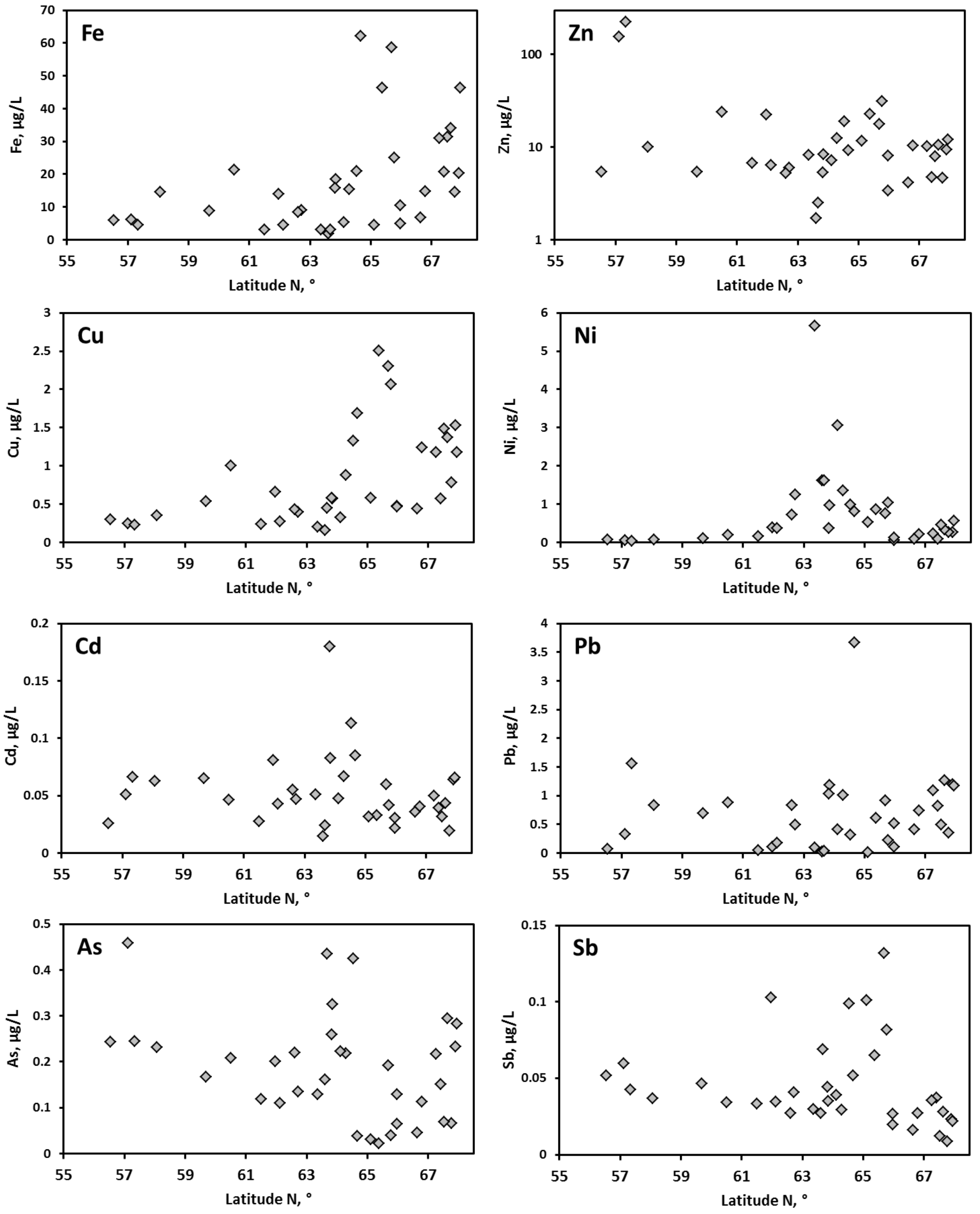

Fig. 2. Examples of dissolved (< 0.45 µm) metal concentrations in snow water as a function of latitude. The cause for the elevated concentrations of Ni, Cd and Sb at ca. 64-65°N is most likely industrial impact, but given relatively low number of data points around industrial centers it is hard to prove it unambiguously.

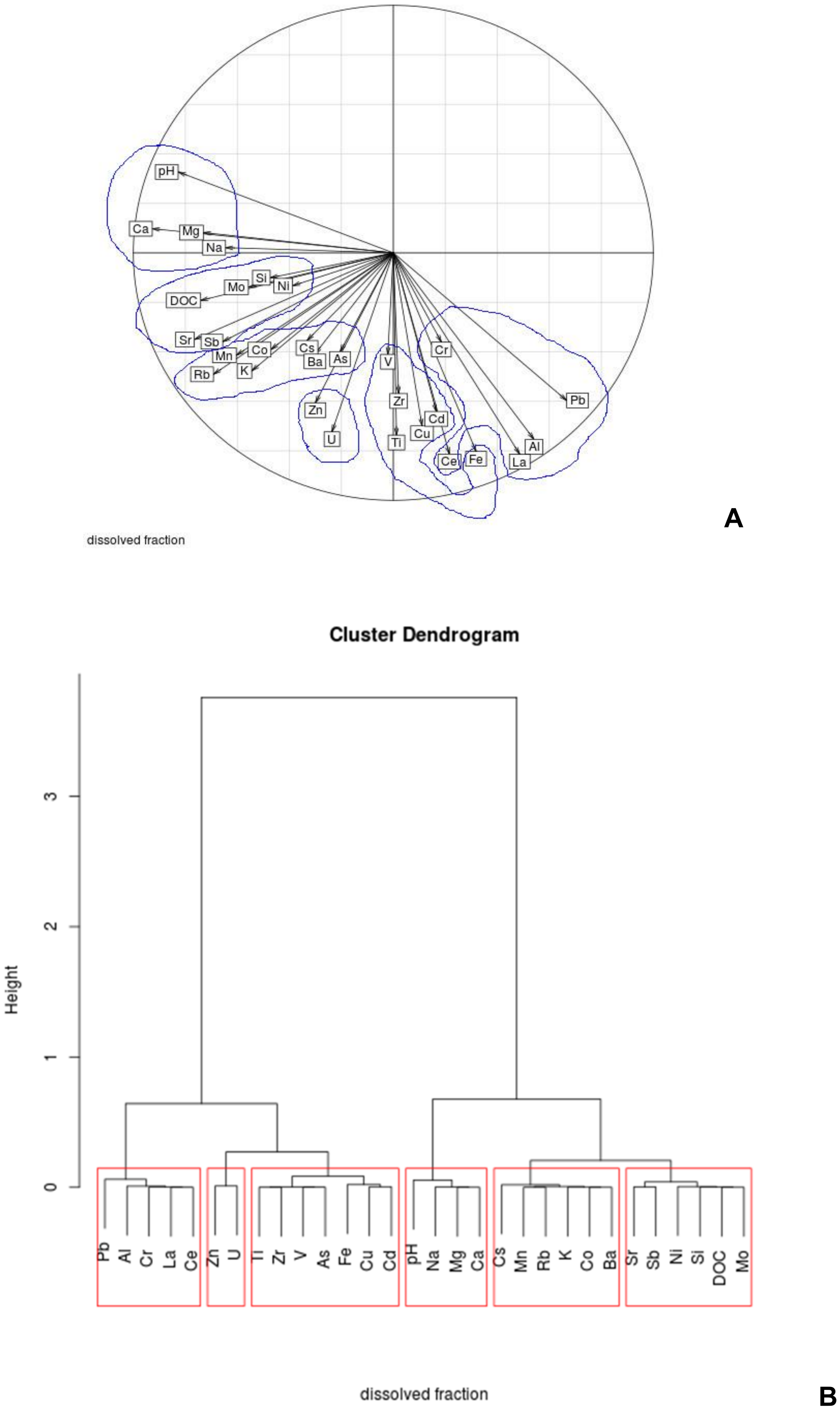

Fig. 3 A: PCA Factorial map F1xF2 of elements of a reconstructed table for the dissolved fraction. Partition of elements into 6 groups revealed by HCA is shown by a contour line. **B:** Dendrogram of a hierarchical cluster analysis (HCA) performed on variables of a reconstructed table for the dissolved fraction using the Pearson correlation as a distance measure and Ward's method for the linkage rule.

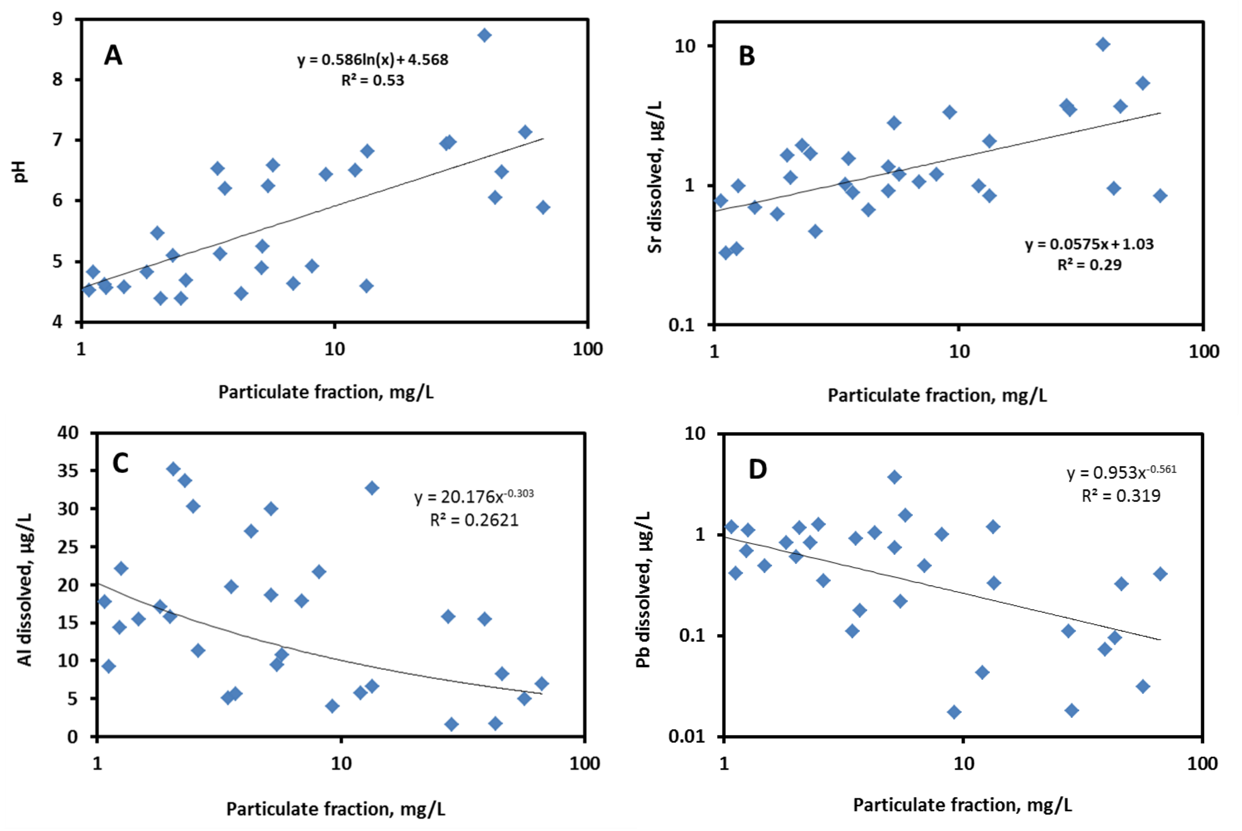

Fig. 4. pH value (A) and Sr (B), Al (C) and Pb (D) concentration in dissolved fraction of snow as a function of concentration of particles. Note log X scale for Sr and Pb.

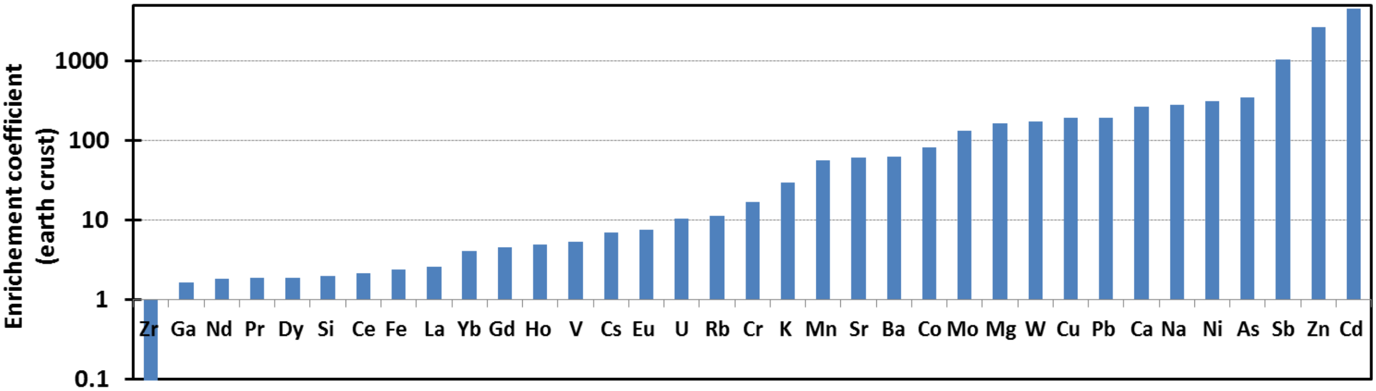

Fig. 5 A. The latitude-averaged Al-normalized enrichment coefficient of snow particles with respect to the earth crust.

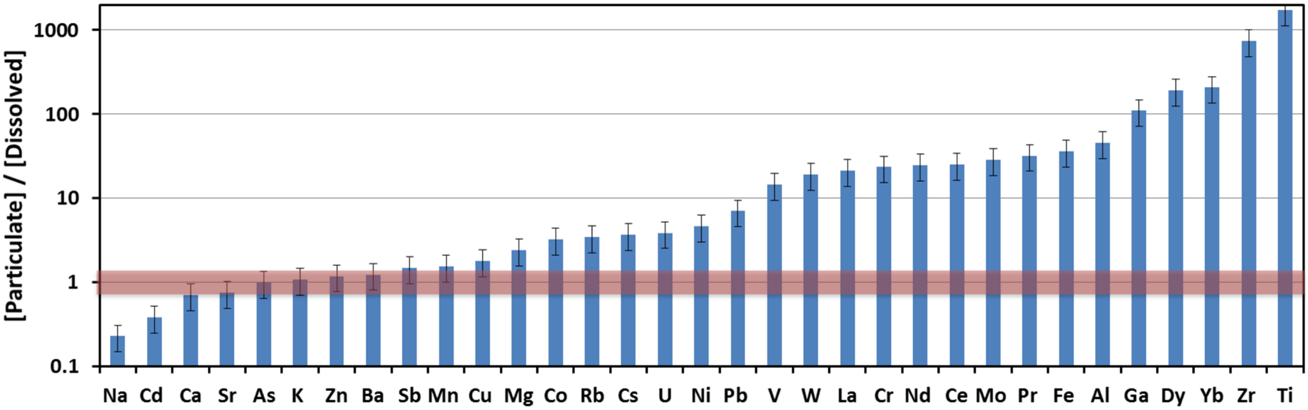

Fig. 5 B. The average values (56 to 68°N) of the ratio of particulate to dissolved element concentration in snow water of western Siberia. Bold red line indicates statistically non-significant deviation from 1.

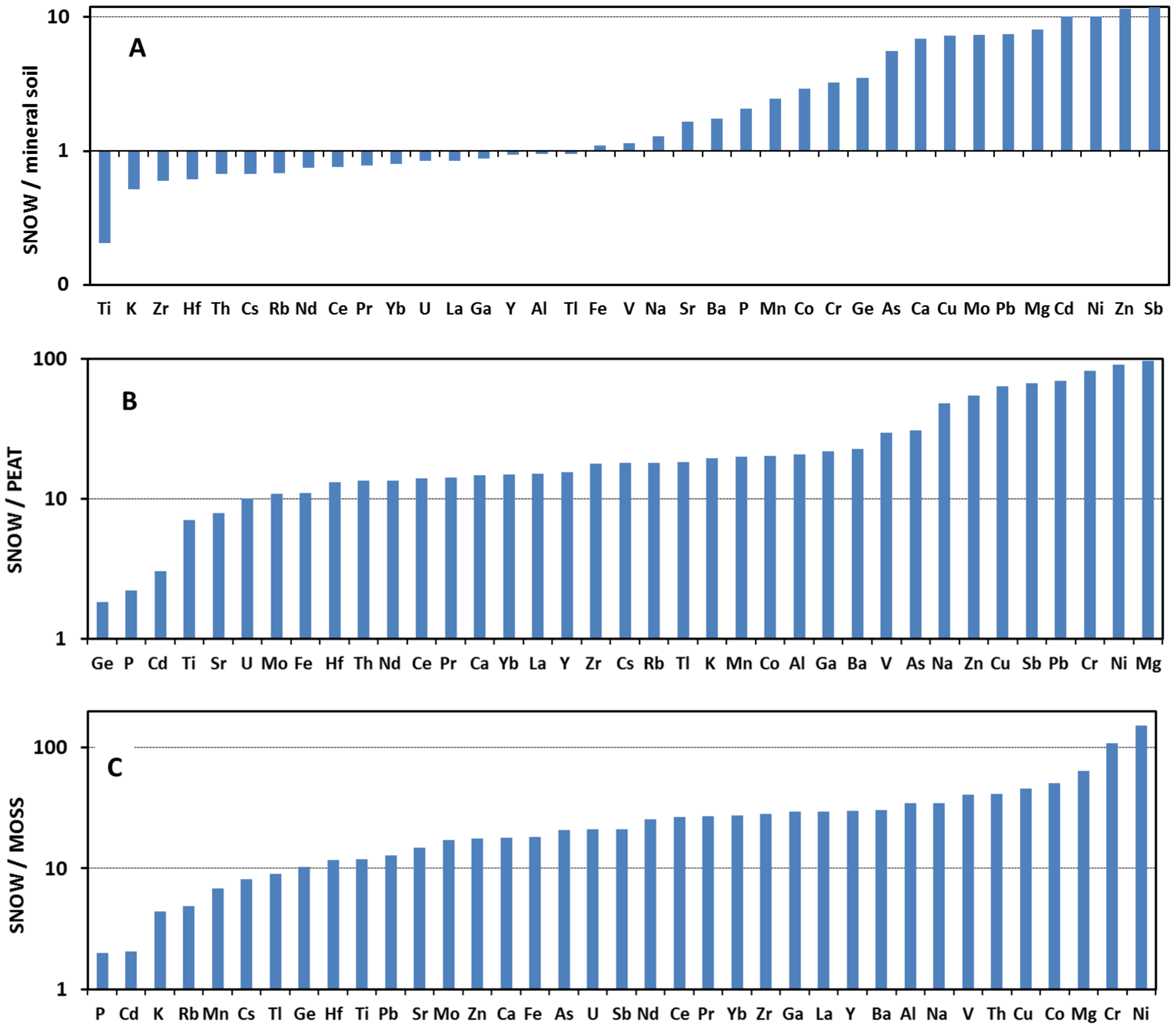

Fig. 6. The ratios of the average concentrations of elements in snow particles (neglecting sample SF22) to those in mineral soil (A), peat (B) and mosses (C) of WSL. The peat, moss, and underlying mineral horizons data are averaged over the latitude of 55 to 68°N as described in Stepanova et al (2015). Note normal Y scale for mineral soil (A) and log Y scale for peat and moss (B, C).

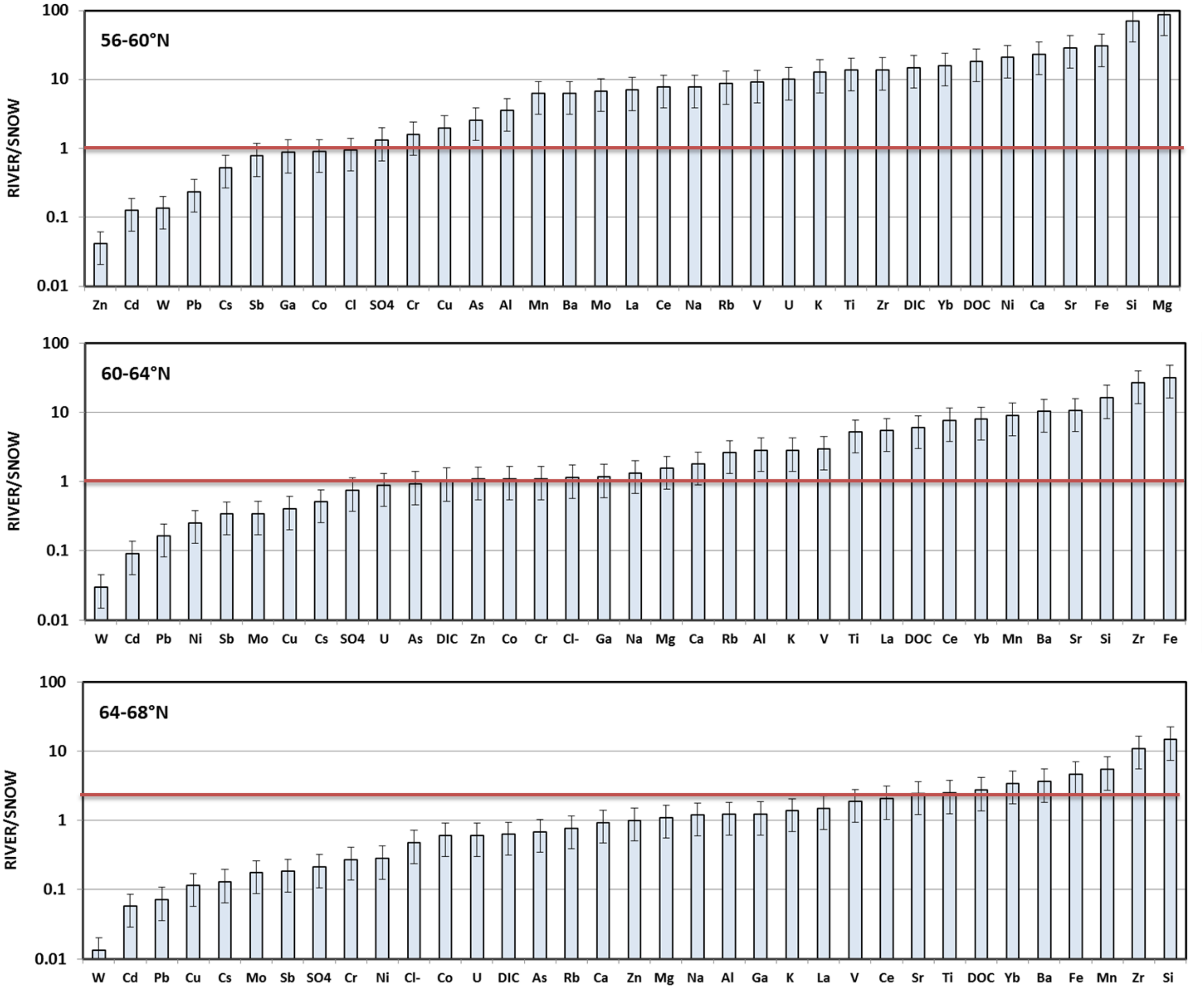

Fig. 7. The ratio of mean dissolved flux of rivers in three latitudinal zones (56-60°N, 60-64°N, and 64-68°N) of WSL to the stock of dissolved fraction of snow. For this calculation, the snow volume (in mm of water) accumulated over full winter and mean river runoff over May and June were used.

SUPPLEMENTARY INFORMATION

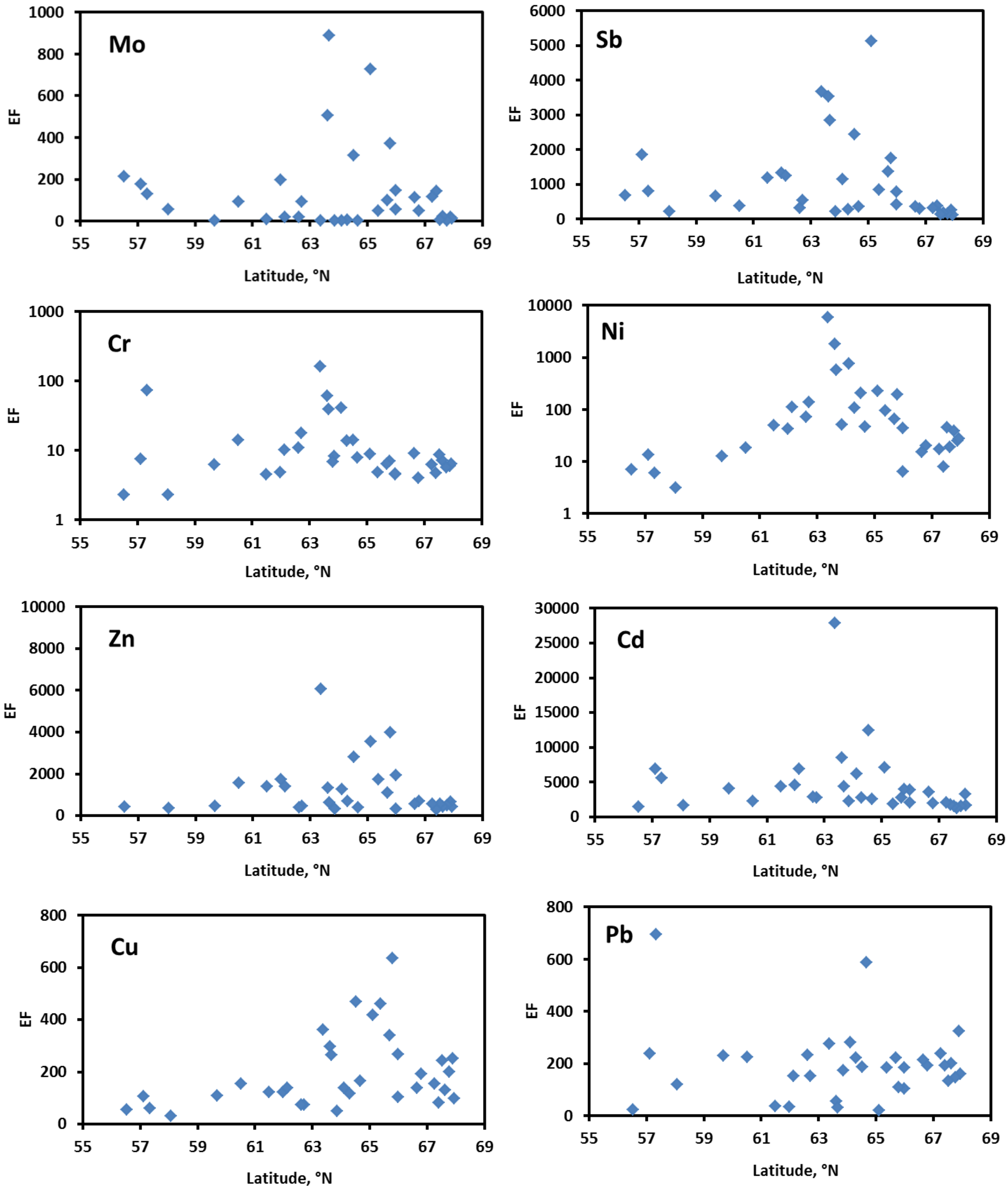

Fig. S1. The Al-based enrichment factor (relative to the upper part of continental earth crust) of particulate fraction of snow for Mo, Sb, Cr, Ni, Zn, Cd, Cu and Pb as a function of latitude.

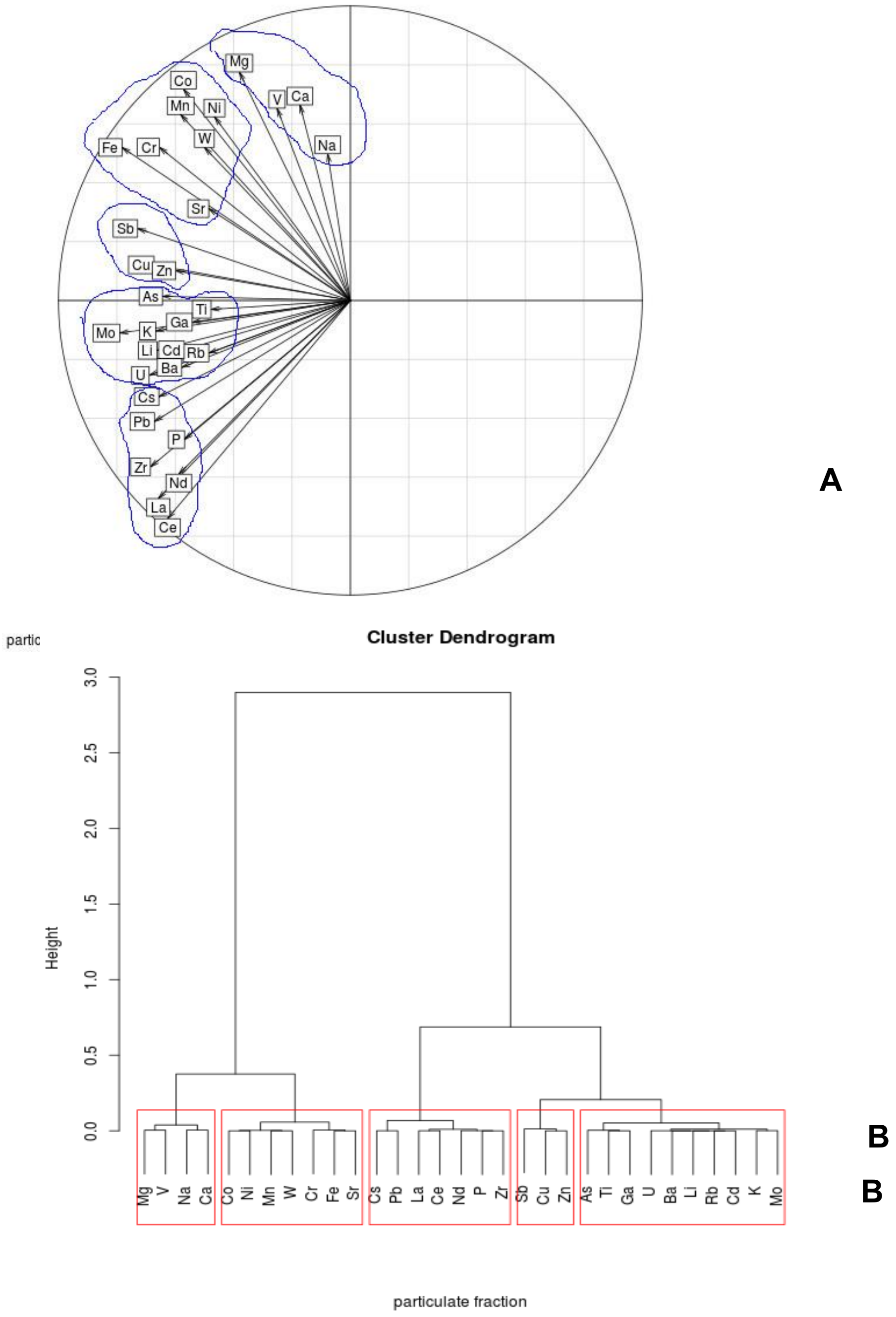

Fig. S2 A. PCA Factorial map F1xF2 of variables (elements) of a reconstructed table for the particulate fraction. Partition of elements into 5 groups revealed by HCA is reported by a contour line. **B**: Dendrogram of a hierarchical cluster analysis (HCA) performed on variables of a reconstructed table for the particulate fraction using Pearson correlation distance as distance measure and Ward's method for the linkage rule.

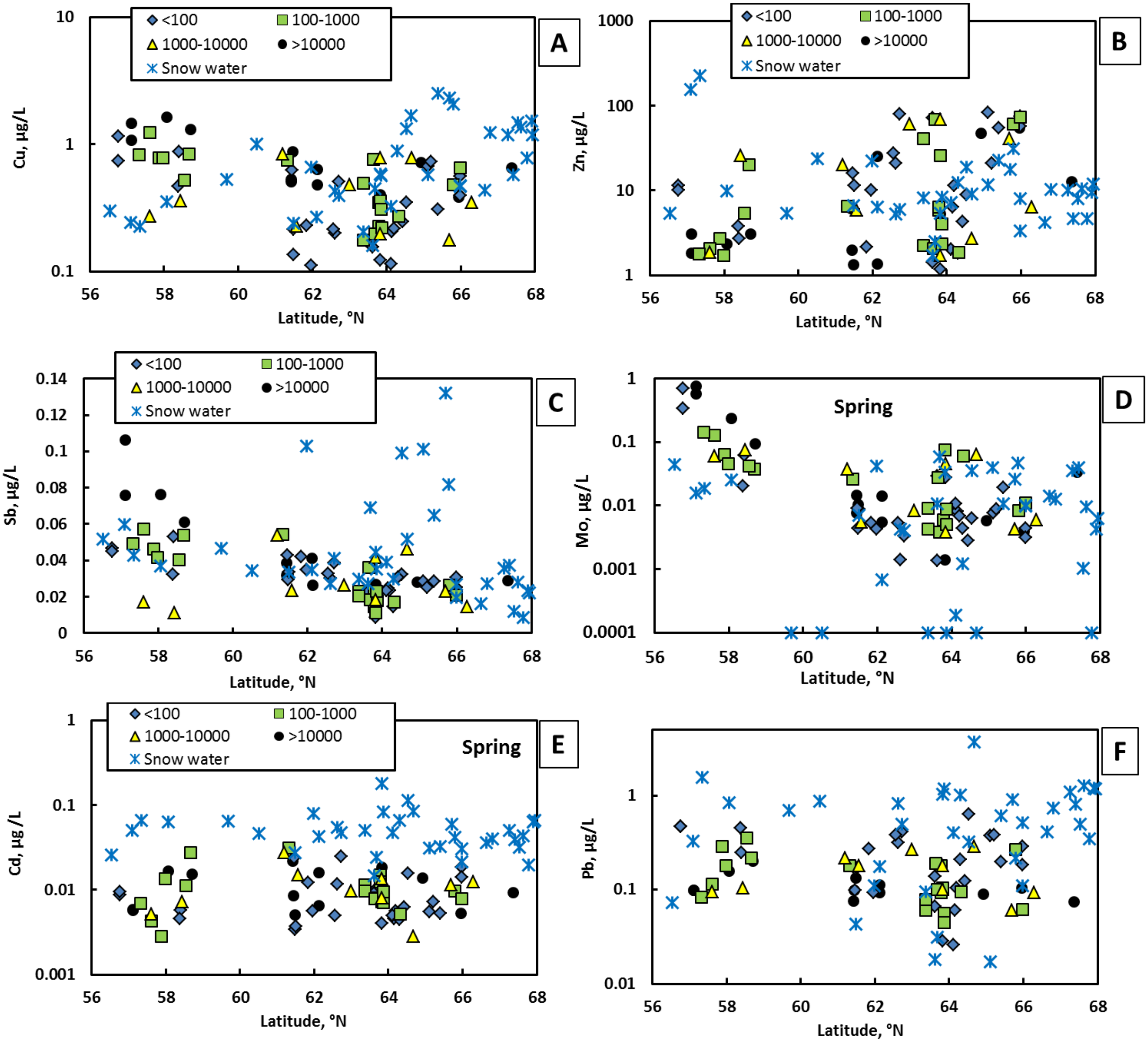

Fig. S3. Snow water soluble (< 0.45 µm) of Zn (A), Cu (B), Cd (C), Pb (D), Sb (E) and Mo (F) (blue asterisk) compared with actual concentrations in rivers during spring flood (May-June) of different size of the watershed (closed diamonds, squares, triangles and circles correspond to < 100, 100-1000, 1000-10,000 and > 10,000 km² surface area, respectively) in western Siberia along the latitudinal gradient.

Table S1. Mineralogical composition of selected snow particles.

No	Quartz	Albite	K-Fs	Calcite	Dolomite	Chlorite	Illite	Phlogopite	Amphibole	Pyroxyne	Chrisotyle	Magnesite	Forsterite	Talc	Magnetite
SF-1	37	20	11	19	< 1	4	7		2						
SF-3	38	27	9	3		10	9		3						
SF-14	20	8	6	1	48	5	4		3	1	2			1	
SF-31	30	20	12		8	8		12	6		3				
SF-33	35	16	9		10	3		16	4		3	4			
SF-36	47	7	11		1	4		5	3	3	12		4	3	
SF-38	48	3	6		1	6		4	3		16		6	4	3
SF-39	41	8	6	4	8	5		12	2	2	8		2	2	
SF-40	35	12	9	6	3	4		8	4	3	10		4	2	