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Elemental composition of peat profiles in western Siberia: Effect of the micro-landscape, latitude position and permafrost coverage

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ABSTRACT

The concentrations of major and trace elements in the organic layer of peat soils across a 1800-km latitude profile of western Siberia were measured within various dominating ecosystems to evaluate the effect of landscape, latitude position and permafrost coverage on the peat chemical composition. In this study, peat core samples were collected every 10 cm along the entire length of the column, down to 3–4 m until the mineral horizon was reached. The peat samples were analyzed for major and trace elements using an ICP–MS technique following full acid digestion in a microwave oven. Depending on their concentration pattern along the peat column, several groups of elements were distinguished according to their general physico-chemical properties, mobility in soils, affinity to organic matter and plant biomass. Within similar ecosystems across various climate zones, there was a relatively weak variation in the TE concentration in the upper organic layer (green and brown parts of sphagnum mosses) with the latitude position. Within the intrinsic variability of the TE concentration over the peat column, the effects of climate, latitude position, and landscape location were not significantly pronounced. In different landscapes of the middle taiga, the peat columns collected in the fen zone, the low and mature forest, the ridge and the hollow did not demonstrate a statistically significant difference in most major and trace element concentrations over the full depth of the peat column. In live (green) parts and dead (brown) parts of sphagnum mosses from this climate zone, the concentrations of Mn, P, Ca and Cu decreased significantly with increasing moss net primary production (NPP) at various habitats, whereas the other elements exhibited no link with the NPP trends. The Al- and mineral horizon-normalized peat concentration profiles, allowing removal of the occasional contamination by the underlying mineral substrate and atmospheric dust, demonstrated a homogeneous distribution of TEs along the peat column among various climate zones in the non-permafrost regions but significantly non-conservative behavior in the discontinuous permafrost site. The peat deposits in the northern part of western Siberia potentially have very high release of metals to the surface waters and the riverine systems, depending on the persistence of the ongoing permafrost thaw and the increase in the thickness of the active layer.

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1. Introduction

The western Siberia Lowland (WSL), is the world's second largest lowland area after the Amazon basin (Aselmann and Crutzen, 1989), constituting 12.9% of the global peatlands (Matthews and Fung, 1987; Peregon et al., 2009). The WSL contains one of the largest peat resources on the planet, constituting a peat carbon pool of 70.2 Pg C (Sheng et al., 2004), which is more than 3% of all of the terrestrial carbon pool (Houghton et al., 1996) and 30% of the carbon pool of the former Soviet Union peatlands (Botch et al., 1995), an amount similar to the entire stock of the northern cryosphere vegetation (60–70 Pg C, McGuire et al., 2010). Approximately 40% of the total WSL peat C has accumulated since 2 ka, primarily in the southern, permafrost-free zone (Beilman et al., 2009).

Since the early 1970s, Soviet and Russian scientists (reviewed in Kremenetski et al. (2003)), and more recently, Western researchers (Botch et al., 1995; Peteet et al., 1998; Turunen et al., 2001; Frey and Smith, 2007; Sheng et al., 2004; Smith et al., 2004; Beilman et al., 2009) have devoted significant efforts to inventorying the

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western Siberia peat pool, characterizing its physical, botanical and hydrological properties and revealing its Late Quaternary history. These decades of research have yielded a comprehensive picture of the degree of peatland coverage in western Siberia, the peat relationship with vegetation and micro-landscapes and the peat role in CO_2 exchange with the atmosphere since the end of the last glacial cycle until the present time. Currently, the boreal and subarctic ecosystem response to the ongoing climate change is a major research focus (McGuire et al., 2009). The climate-driven changes in hydrology, such as drought, flooding and permafrost ice thawing, represent the major factors controlling the response of the peatlands to environmental changes (Limpens et al., 2005), which are notably important in western Siberia (Frey and Smith, 2003; Pokrovsky et al., 2013) and which may increase the occurrence of smouldering phenomena (Zaccone et al., 2014). The destabilization of frozen peatlands (Lawrence and Slater, 2005; Yi et al., 2007) represents a major environmental threat but also constitutes a very important (yet unknown) factor of nutrients (including metal micronutrients) and toxicants release to the hydrological network and their subsequent transport to the Arctic Ocean (Frey and Smith, 2003). The degree of nutrient release will be strongly dependent on the elemental composition of the soil (peat) column profile. The majority of relevant studies of peatlands have been devoted to cycles of CO_2, CH_4 and nutrients (Freeman et al., 2001; Macrae et al., 2012; Blodau, 2002; Blodau et al., 2004; Knorr et al., 2008), but there are only a few studies on trace elements and metal biogeochemistry related to the change in the hydrological conditions of the peat (cf., Tipping et al., 2003; Blodau et al., 2008; Szkokan-Emilson et al., 2013). The application of the available results to a prediction of the effect of peat thaw on the change in the water surface chemistry and element delivery to the ocean from the western Siberian wetlands is hindered by the lack of knowledge on the trace element concentration in the peat cores, related to specific microenvironments of the wetlands. This lack of information is in contrast to the situation with thermokarst lakes and thaw ponds of the WSL in which the biogeochemical parameters, such as the TE concentration and the speciation, are relatively well determined, and the effect of the lake drainage induced by the climate change on nutrient transport can be reasonably evaluated (Shirokova et al., 2013; Pokrovsky et al., 2011, 2013, 2014).

The WSL extends over 2000 km from south to north through taiga, forest–tundra and tundra zones of permafrost-free, sporadic, discontinuous and continuous permafrost and offers a unique site to test the effect of possible climate changes on the biogeochemistry of the landscapes using a well-established space-for-time substitution (e.g., Frey et al., 2007). This approach, which assumes that the contemporary difference in the local and global scales within the climate gradient created by latitude can serve as a proxy for future changes of a given system, was first developed for the western Siberian rivers (Frey et al., 2007) and recently has been applied to thermokarst lakes (Manasypov et al., 2014). In these studies, it has been concluded that following the climate warming, the increase in the thickness of the active layer and the permafrost thaw will increase the effect of the deep soil and groundwaters on the chemical composition of the rivers. These deep subsurface waters are often in contact with the deep peat horizons, whose influence on the element delivery to the ocean will presumably increase with time. To quantify this effect, information on the TE concentration over the full length of the peat profile from various climate and permafrost zones of western Siberia is required. Therefore, ground-based studies in western Siberia are crucial for the incorporation of the currently available land cover products into terrestrial ecosystem models in northern wetland environments (Frey and Smith, 2007). Moreover, given the dominance of micro-landscapes within the western Siberia peatlands (Glagolev et al., 2011; Sabrekov et al., 2014), studies of peat cores from different adjacent microenvironments of the same climate zone are also required.

The goal of the present study is to fill this information gap by providing a thorough analysis of 11 peat cores collected over a 1800 km latitudinal profile in western Siberia. To date, the majority of studies on peat geochemistry have been focused on tracing the atmospheric pollution, the local environmental history or revealing the mechanisms of TE enrichment in the peat profiles (Benoit et al., 1998; Bindler, 2006; Cloy et al., 2009; Pratte et al., 2013; Shotyk et al., 1992, 2001, 2002; Shotyk, 1996a,b). There are also several punctual analyses of *Sphagnum* peat cores from Central Siberia, which were performed to trace specific catastrophic events (Tostitti et al., 2006) or the local pollution around large industrial centers (Yakovlev et al., 2008). The present study is novel because it covers a significant geographic region with and without permafrost on various micro-landscapes using the same analytical method and in this study, we analyzed mostly unpolluted, pristine zones. In addition to peat cores, we collected and analyzed surface moss samples at each location corresponding to the substrate of contemporary peat. We attempted to address the following specific questions:

(1) Is the concentration of TEs in the green and brown parts of sphagnum mosses (the upper part of the peat column) sensitive to the latitude position?
(2) How variable are the element concentrations in different landscapes of the middle taiga peat profile, such as the fen, ryam, ridge and hollow?
(3) Is the concentration profile of TEs in the peat column different between the permafrost-bearing and the permafrost-free zones?

We anticipate that answering these questions will aid the quantification of a possible change in the active (unfrozen) stock of trace elements in the peat and the prediction of the consequences of the soil temperature change on the surface water composition in this region.

2. Study sites, sampling, analyses, and statistics

A map of the sampled sites is presented in Fig. 1A, and their description is given in Table 1. The study sites cover all of the major landscape zones of the WSL, from the forest–steppe in the south to the forest–tundra/tundra in the north. The sample IDs in Fig. 1A correspond to those given in Table 1 following their geographical names: PM and PB for Pangody mound and Pangody trough, respectively; ML, MR, MGG, MGM and MT for Mukhrino tall ryam, low ryam, ridge, hollow and fen, respectively; KO, PR, UR and NR for Kondakovskie lakes, Plotnikovo ryam, Ubinskoe ryam and Nikolaevka ryam, respectively.

The depth of sampling at each site was restricted by the position of the mineral layer and varied from 170 to 400 cm. The two northern sites of the forest–tundra, developed on the permafrost ground, could be sampled only over the depth of the active (thawed) layer close to 35 cm. Generally, the sampling setting of the present study is highly representative of the western Siberia peatlands. According to the general setting of peat deposits in western Siberia (Krementski et al., 2003), the mean peat depth in the WSL is 256 ± 166 cm, and there is no statistically significant latitudinal trend in the peatland depths or in the radiocarbon age across the WSL from 55 to 70°N.

A landscape profile in the middle taiga zone of western Siberia showing different type of micro-landscapes and corresponding peat deposits is shown in Fig. 1B. Eight general types of mire

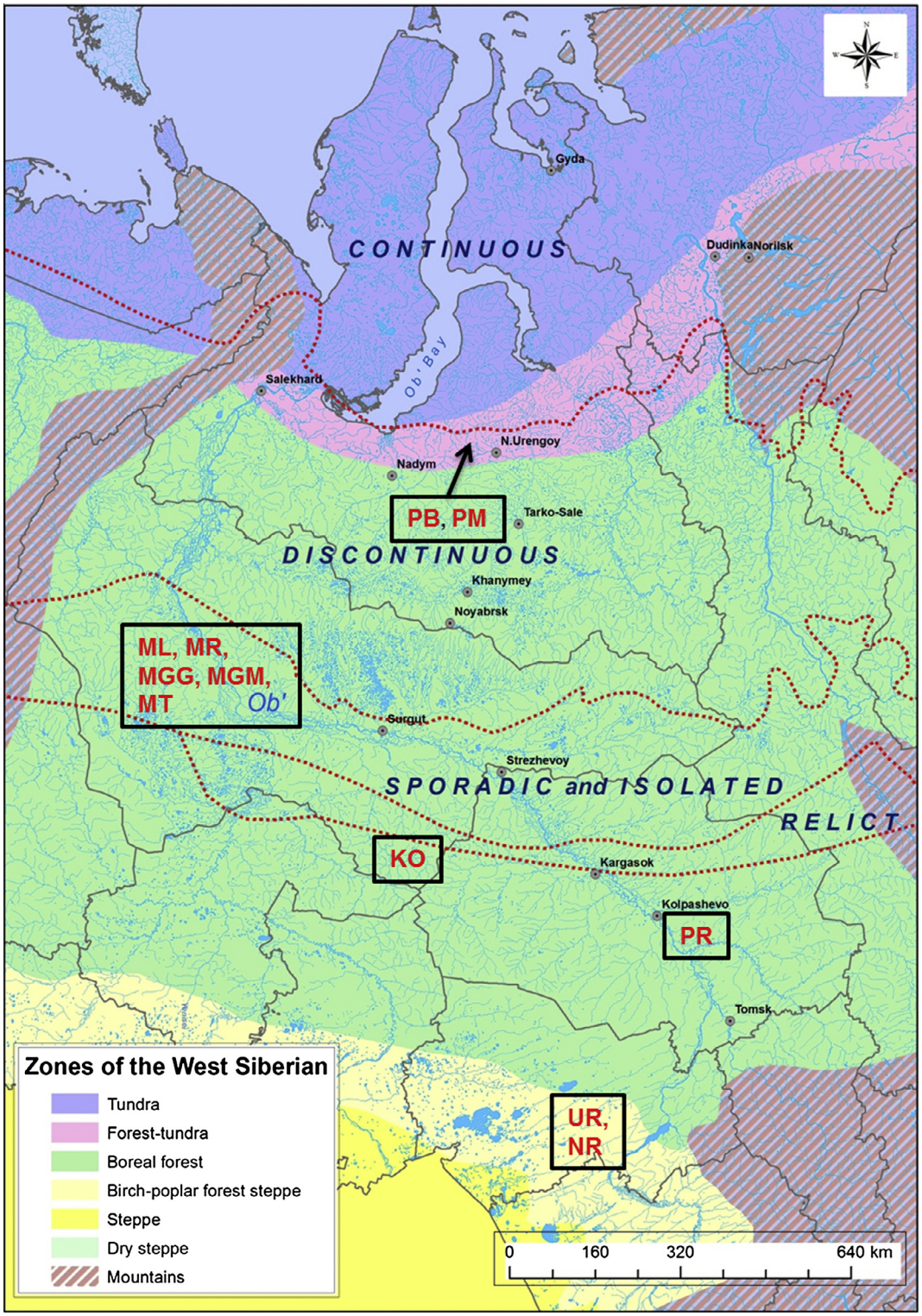

Fig. 1A. Study site of western Siberia. See Table 1 for abbreviations. Seven dominant physico-geographical zones are shown by different color whereas the borders of continuous, discontinuous, sporadic and isolated and relict permafrost are shown by red dotted line. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

micro-landscapes are identified in western Siberia (Peregon et al., 2008) and are briefly described in the ESM-1. In this study, the majority of the peat profiles were collected on raised bogs and, more specifically, on wooded bog represented by a pine-shrub-sphagnum community, called "ryam". Other typical settings included ridges and oligotrophic hollows in the middle taiga zone and mound and trough micro-environments on the palsa (frozen flat mound peatland, most similar to the ryam site in the south) in the permafrost zone. The majority of our sampling points corresponded to key sites in the Siberian Mire Landscapes Study, as described in the systematic survey of western Siberia productivity and greenhouse gas exchange with the atmosphere (Glagolev et al., 2011; Peregon et al., 2008, 2009; Repo et al., 2007; Maksyutov et al., 1999; Bleuten and Filippov, 2008). The peat deposits in these

Table 1
Sampling sites, ecosystem position, sample abbreviation and their description. MAT and *P* stand for mean annual temperature and precipitation, respectively.

Sampling site	Ecosystem	Abbreviation	Botanical composition	Depth, fraction, horizon
Pangody (palsa peat bog in forest–tundra, equivalent to low ryam); 63°52′N, 74°58′E	Trough	PM 1	*S. fuscum*	Green moss + brown parts
		PM 2–PM 4	*Cladonia*	Peat, each 10 cm
MAT = −7.4 °C	Mound	PB 1	*S. fuscum* + *Cladonia*	Green + brown parts
P = 458 mm		PB 2–PB 4		Peat, each 10 cm
Khanty-Mansiisk (Mukhrino, middle taiga); N 60°54′; E 68°40′	Tall ryam	ML 1	*S. fuscum*, *S. angustifolium*, *S. papilosium*	Green parts of moss
MAT = −1.2 °C,		ML 2	*S. fuscum*	Brown parts of moss
P = 522 mm		ML 3–ML 15	*S. fuscum*	Peat, each 10 cm
		ML 16 (min)		Mineral horizon
	Low ryam	MR 1	*S. fuscum*	Green parts of moss
		MR 2	*S. angustifolium*	Brown parts of moss
		MR 3–MR 33		Peat, each 10 cm
	Ridge	MGG 1	*S. fuscum*	Green parts of moss
		MGG 2	*S. papilosium*	Brown parts of moss
		MGG 3–MGG 37	*S. angustifolium*	Peat, each 10 cm
		MGG 38 (min)		Mineral horizon
	Hollow	MGM 1	*S. balticum*	Green parts of moss
		MGM 2	*S. balticum* +*Scheuchzeria*	Brown parts of moss
		MGM 3–MGM 35		Peat, each 10 cm
		MGM 36 (min)		Mineral horizon
	Fen	MT 1	*S. fuscum*	Green parts of moss
		MT 2	*S. papilosium*	Brown parts of moss
		MT 3–MT 33	*S. balticum*	Peat, each 10 cm
		MT 34 (min)		Mineral horizon
Kondakovskie lakes (middle taiga) N 60°51′; E 63°30′	Low ryam	KO 1	*S. fuscum*	Green parts of moss
		KO 2		Brown parts of moss
MAT = −0.9 °C		KO 3–KO 29	*S. fuscum* and *S. balticum*	Peat, each 10 cm
P = 470 mm		KO 30		Mineral horizon
Plotnikovo (southern taiga) N 56°51′; E 82°51′	Low ryam	PR 1	*S. fuscum*	Green parts of moss
		PR 2		Brown parts of moss
MAT = −0.4 °C		PR 3–PR 14	*S. fuscum* + *S. fallax*	Peat, each 10 cm
P = 408 mm		PR 15		Mineral horizon
Ubinskoe (forest–steppe) N 55°19′; E 79°42′	Low ryam	UR 1	*S. fuscum*	Green + brown part of moss
		UR 2–UR 9	*S. fuscum*	Peat, each 10 cm
MAT = −0.1 °C		UR 10		Mineral horizon
P = 347 mm				
Nikolaevka (forest–steppe) N 55°09′; E 79°03′	Low ryam	NR 1	*S. fuscum*	Green + brown part of moss
MAT = −0.1 °C		NR 2–NR 16	*S. fuscum*	Peat, each 10 cm
P = 347 mm		NR 17		Mineral horizon

sites are generally well dated; for a more general context of the peat age across the latitude profile in western Siberia see Kremenetski et al. (2003).

The geochemical profile of various landscapes, following their latitude position as shown in Fig. 1A, included the low ryam (MR) occupying the eluvial position, the tall ryam (ML) corresponding to the accumulative position, the ridge (MGG) located at the eluvial position, the hollow (MGM) of the transient position, and the fen (MT) of the accumulative positions. In our study, the low ryam and the ridge in the ridge–hollow complex are considered as autonomous primary geochemical landscapes (Fig. 1B and Electronic Supplementary Material 1, Figs. ESM-1.1, 1.2). The tall ryam, the hollow in the ridge–hollow complex, and the fen are geochemically subordinate landscapes. Peat deposits of ecosystems of low ryam (MR, KO, PR, UR and NR), ridge (MGG), hollow (MGM), and fen (MT) are formed by oligotrophic peat of *Sphagnum* mosses. Therefore, the *Sphagnum* mosses are the dominant components of the peat columns considered in the present study, with primarily *Sphagnum fuscum* in ecosystems of tall ryam, low ryam, and ridge and *S. fuscum* with *Sphagnum balticum* in hollow and fen ecosystems.

The most diverse landscape positions can be found at the middle taiga (Khanty-Mansiisk, Mukhrino) site (ML, MR, MGG, MGM, and MT). The other sites exhibited much less variable micro-landscapes and as such were not tested. Instead, only dominant micro-landscapes (low ryam) were sampled south of 60°54′ latitude. The forest–tundra (palsa) permafrost site of Pangody (65°52′ N) was most close to low ryam of the other sites although it exhibited two contrasting micro-environments, the mound (PB) and the trough (PM). In this regard, the most representative N–S latitude profile of the peat core could be obtained from the southern low ryam sites (MR, KO, PR, UR and NR) combined with the most northern permafrost sites (PB and PM).

The sampling was performed in August–September at the end of the active season at all of the sites. A Russian peat corer with Ti blades and a holder was used to extract the peat column from the surface to the mineral layer (or the permafrost ice). The column was cut at the site using a ceramic knife and was bulked at each 10 cm horizon. Similar to previous studies, we present the average depth of each horizon, corresponding to the middle position (Zaccone et al., 2007). Note that the alternative way of sampling would be cutting the cores into 1 cm slices in order to maximize

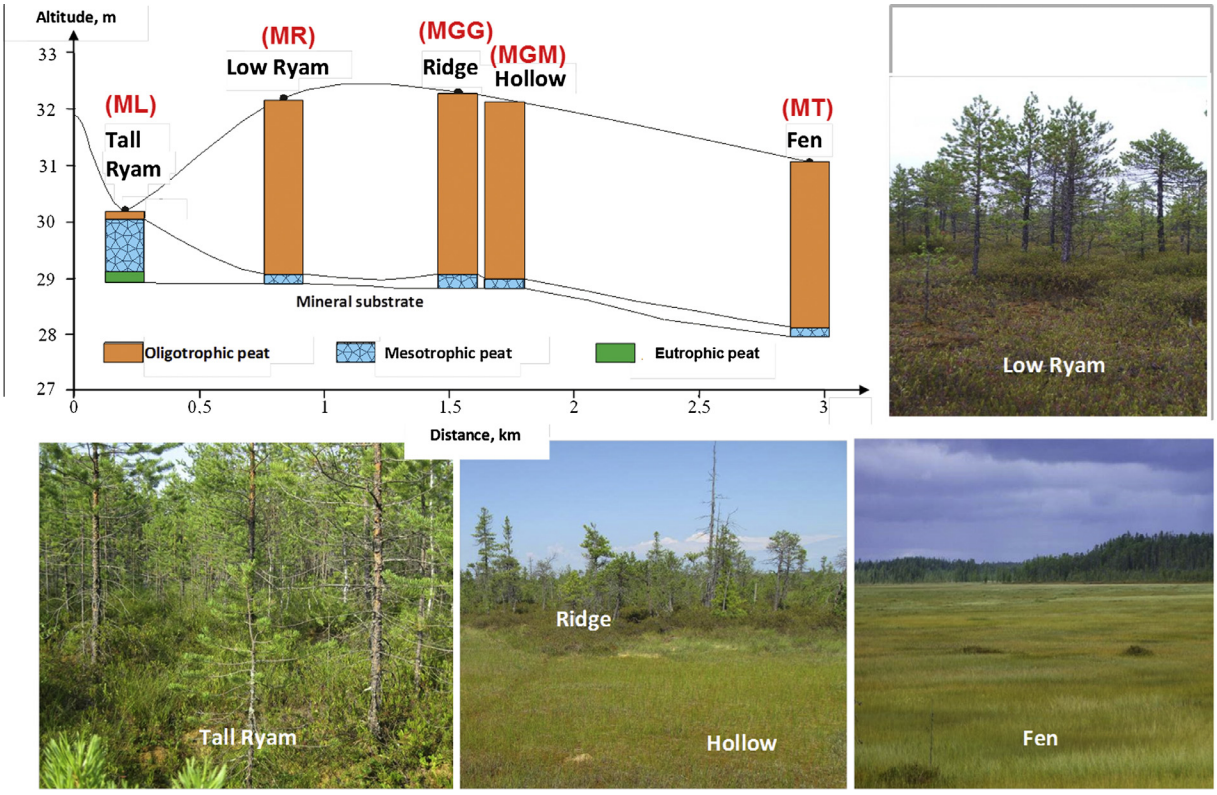

Fig. 1B. A landscape profile in the middle taiga zone of western Siberia showing different type of micro-landscapes and corresponding peat deposits. The oligotrophic (*Sphagnum*), mesotrophic (*Sphagnum* and green mosses) and eutrophic (*Sphagnum*) peat sustain the pH of 2.5–3.5, 3.5–5.5, and 5.1–6.5, respectively.

the signal/noise ratio of the peaks in trace element concentrations, used to improve the accuracy, reproducibility and reliability of peat cores from bog as archives (Givelet et al., 2004; Zaccone et al., 2012). However, the present study is aimed at assessing the first-order concentrations of major and trace element in western Siberian peat for which such a resolution was not necessary.

For the measurement of the element concentrations, the samples were first processed in a clean room (class A 10,000). Approximately 100 mg of peat or moss, previously ground with an agate mortar and pestle to the <1 mm fraction, was placed in Teflon (Savilex®) reactors with 6 mL bi-distilled HNO_3, 0.2 mL ultrapure HF and 1 mL ultrapure H_2O_2. The HF attack was necessary to dissolve the silicate admixture in peat and to provide the full digestion of the sample. Twelve reactors were loaded into a Mars 5 microwave digestion system (CEM, France) and exposed for 20 min at 150 °C. Each series of reactors was composed of 10 samples of mosses or peat/moss, 1 certified lichen standard CRM 482 sample (from BCR, Belgium) or other NIST standards and 1 blank sample. After cooling, the samples were transferred to 30 mL Savilex® vials and evaporated at 70 °C for 24 h. The dry residue was dissolved in 10 mL of 10% HNO_3 and further diluted by a factor 10 using 2% HNO_3 prior to the analyses. Nitrogen and carbon concentration in dry peat samples was measured by Cu–O catalysed dry combustion at 900 °C with ⩽0.5% precision for standard substances (Elementar Vario Maxi CHNS Analyser).

The major and trace element concentrations were measured by ICP–MS (Agilent 7500 ce) using a three-point calibration against a standard solution of known concentration. Indium and rhenium were used as the internal standards to correct for instrumental drift and eventual matrix effects. The appropriate corrections for oxide and hydroxide isobaric interferences were applied for the Rare Earth Elements (REE) (Ariés et al., 2000). In addition to BCR CRM-482 lichen, the international geostandards of basaltic rock BE-N (from CRPG, France), Apple Leaves SRM 1515 (from NIST, USA), and Pine Needles SRM 1575a (from NIST, USA) were routinely run with each of the 10 samples and were used to check the efficiency of the acid digestion protocol and the analysis. The data tables present the results for the elements, exhibiting a good agreement between the certified or recommended values and our measurements (the relative difference is expressed as $([X]_{\text{recommended or certified}} - [X]_{\text{measured}})/(([X]_{\text{recommended or certified}} + [X]_{\text{measured}})/2) * 100$, lower than 10%), or for cases in which we obtain a good reproducibility (the relative standard deviation of our various measurements of standards lower than 10%), even if no certified or recommended data are available. During ICP MS analysis, SLRS-5 international standard was measured routinely each 10 samples to assess the external accuracy and sensitivity of the instrument. All certified major (Ca, Mg, K, Na, Si) and trace element (Al, As, B, Ba, Co, Cr, Cu, Fe, Ga, Li, Mn, Mo, Ni, Pb, all naturally-occurring REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu), Sb, Sr, Th, Ti, U, V, Zn) concentrations of the SLRS-5 standard (e.g., Heimburger et al., 2012) and the measured concentrations agreed with an uncertainty of 10–20%. The agreement for Cd, Cs and Hf was between 30% and 50%. For all major and most trace elements, the concentrations in the blanks were below analytical detection limits (⩽0.1–1 ng/L for Cd, Ba, Y, Zr, Nb, REE, Hf, Pb, Th, U; 1 ng/L for Ga, Ge, Rb, Sr, Sb; ⩽10 ng/L for Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As). Some rare elements such as Sn, Nb, W, Tl, Ta, Bi could not be measured in diluted samples of the upper part of peat core including mosses and as such were not used in the interpretation. More details about the entire analytical procedure of organic-rich soils and plants are available in Viers et al. (2007, 2013).

The data on the element concentrations were analyzed with best fit functions based on the least squares method, the Pearson correlation and one-way ANOVA with the STATISTICA version 8 software (StatSoft Inc., Tulsa, OK). Regressions and power functions were used to examine the relationships among the element concentrations, the latitude and the depth of the peat column.

The correlation coefficients were calculated to elucidate the relationships between the organic carbon/Fe and the TE concentrations within the same column and between the major and TE over the full dataset, in organic and mineral horizons separately. A criterion for a significant correlation between elements was that the Pearson coefficients were higher than 0.5 ($R^2 \geqslant 0.5$). The ANOVA method was used to test the differences in the average TE concentrations and the concentration – depth regression slopes for different sites and landscapes. The ANOVA test was performed with a one-way analysis of variance using Dunn's method due to the different number of sampled peat horizons for each geographic zone and for the different landscapes within the same zone (SigmaPlot version 11.0/Systat Software, Inc). In this method, a value of $P < 0.05$ indicates that the differences in the median values are important and are statistically significant. In contrast, a value of $P > 0.05$ indicates that the differences in the median values are not statistically significant and that these differences may stem from random sampling variability. A similar statistical approach has been applied to treat the TE concentration in thermokarst lakes developed on peat soils from various climates and permafrost zones of western Siberia (Manasypov et al., 2014). Note that, given the low number of sampling site and highly composite character of analyzed long peat columns together with mosses, advanced geochemical methods like Exploratory Data Analyses (EDA, see Reimann et al., 1997a,b, 2012 for application to mosses and soils, respectively) could not be employed.

3. Results and discussion

3.1. Organic carbon and major elements (K, P, Na, Ca, Mg)

The major and trace element chemical composition of the sampled peat columns is listed in Table ESM-2 of the Electronic Supporting Information 2. Altogether, 235 samples were measured. The average content of the total carbon in the peat deposits of the studied bog ecosystems ranged from 52% to 55% for low ryam and fen, respectively. This value varied slightly (~3%) within the vertical profile and did not significantly depend on the chosen ecosystem. The beginning of the mineral horizon was clearly marked by a decrease in the C_{org} value and an increase in the ash content (Table ESM-2); thus, these trends were used to distinguish the organic (peat) and the mineral substrate.

The magnesium, phosphorus, calcium, and aluminum concentrations exhibited a relatively constant vertical profile in the peat deposits, with concentrations variation coefficients in the upper part of the peat core lower than 70%. The highest uniformity of the element concentrations over the peat column was observed for the tall ryam of the middle taiga zone (ML), characterized by an accumulative landscape position, which is illustrated in Fig. 2 for Fe and Ca and further detailed in Fig ESM-1.3A and B. The distributions of potassium, sodium, and phosphorus are correlated ($0.6 \leqslant r^2 \leqslant 0.85$) in peat cores of dominant landscapes (for low ryam MR and ridge MGG), and the concentration of potassium and sodium are highly correlated ($r^2 = 0.8–0.9$) in the peat column of the subordinate landscapes (hollow MGM and fen MT). The general trend was a decrease in the sodium and potassium concentrations in all of the studied peat deposits from the upper to the lower horizons. The presence of the maxima in these element concentrations was often observed in the upper part of the peat deposit profile. Apparently, this trend reflects the high mobility of potassium and sodium due to their leachability from the biological peat matrix (Shotyk et al., 1990) and due to the plant/mycorrhizae uptake from the peat (Wang et al., 2014). The role of atmospheric deposition of Na on the moss layer, transferred to the upper part of the peat profile, and removed subsequently via washing by surface

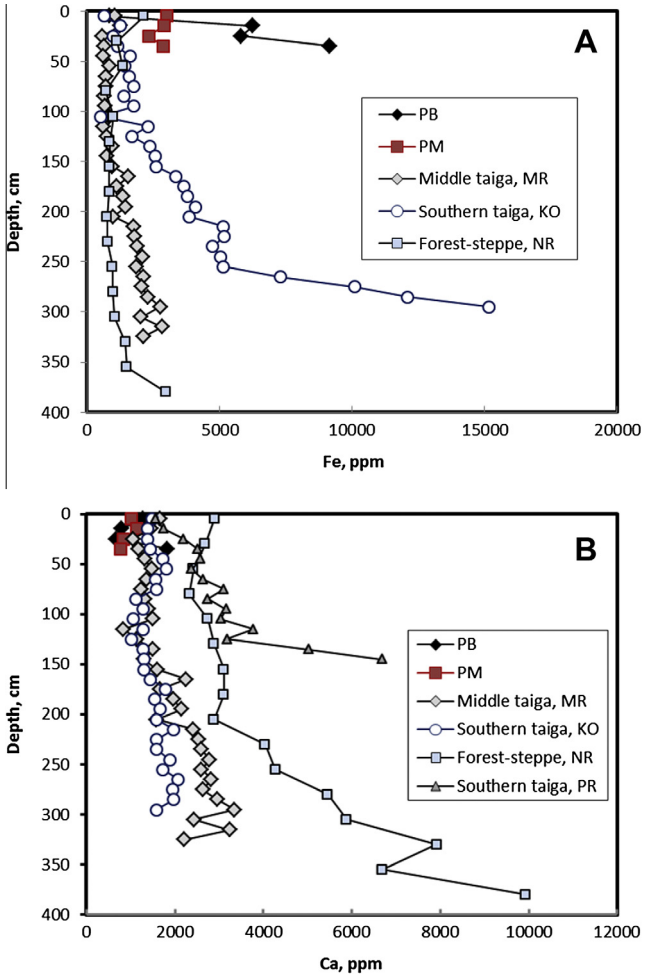

Fig. 2. Fe (A) and Ca (B) concentrations in the peat profile of two permafrost-bearing sites (PB, PM), the middle and southern taiga zone (MR and KO), and the forest–steppe (NR). Refer to Table 1 for terminology used and to Fig. 1A for geographical location.

flow, should also be taken into account. In contrast, the removal of K is mostly via plant uptake, given its high affinity to the vegetation.

Close relationships among the distribution of magnesium, calcium, and iron were detected within thick oligotrophic peat deposits (low ryam MR, ridge MGG, hollow MGM and fen MT). The similarity in the accumulation of these elements within the peat column profile indicates their stability and simultaneous supply to the peat deposits. A downward increase of the magnesium, calcium, and iron concentrations was observed within all of the profiles of the *Sphagnum* deposits. The calcium and strontium concentrations were highly correlated ($r^2 \geqslant 0.9$) over the peat profiles, except for the mound site of the permafrost zone (PB series). The progressive downward increase of the Ca and Sr concentrations in the majority of the studied peat profiles corroborates the previous data from the *Sphagnum* peat bog of Central Siberia (Tostitti et al., 2006). Note that this increase is significantly less evident in the permafrost zone (the Pangody site PB, PM) compared with the non-permafrost zone (samples of the middle taiga and the forest–steppe). The increase of Ca concentration in the bottom part of the peat column by a factor of ~2 is mostly visible in the southern taiga (PR) and forest–steppe zone (NR, UR). In these sites, a likely cause of Ca enrichment may be the presence of rich soil containing Ca-bearing sedimentary minerals and upward migration of Ca under rather humid environment. In the last third

part of the peat cores, Ca concentration increases ~1.5–2 times in all sites of the middle taiga zone (low ryam MR, tall ryam ML, ridge MGG, hollow MGM, and fen MT) as illustrated in Fig. ESM-1.3A. One cannot detect statistically significant difference between sites containing trees (tall ryam, low ryam and ridge) and open sites containing only mosses and dwarf shrubs (hollow, fen). As such, the contemporary element cycling by trees cannot significantly modify Ca concentration in the deeper peat profiles.

3.2. Trace element distribution along the peat column

The majority of the trace elements were evenly distributed in the organic portion of the peat columns collected in permafrost-free sites, with a slight (<30%) to significant (a factor of 2–3) increase in their content at the bottom of the peat profile. This increase can be explained by the release of these elements from the bottom layers of the underlying horizon into the bog water, their further transfer to the top of the profile due to diffusion, and the subsequent accumulation due to adsorption of dissolved metals on the organic matrix or their binding within the matrix (Gorham and Janssens, 2005; Hill and Siegel, 1991; Steinmann and Shotyk, 1997). A good correlation ($0.7 \leqslant r^2 \leqslant 0.95$) between the concentrations of nickel, cobalt, and barium was observed over the full length of the peat columns, which may be linked to the simultaneous accumulation of these elements in various hydrous Mn oxides, similar to the lake sediments of western Siberia (Audry et al., 2011).

The distribution of the concentration of divalent metals within the peat profiles may be associated with specific biogeochemical processes, active or passive element uptake by the biomass, and local or remote pollution. The accumulation of lead and cadmium in the upper part of the peat columns is often attributed to atmospheric deposition (Shotyk et al., 1990). For example, an increase in the concentration of Pb and Ni in mosses and lichens sampled within the proximity of large industrial centers in the southern part of western Siberia has been reported in previous studies (Valeeva and Moskovchenko, 2002; Moskovchenko, 2006). The increase in the Pb loading southward in the Canadian Arctic produced an increase of this element concentration with increasing latitude (France and Coquery, 1996). The last result contrasts that from the essentially pristine monitoring sites of the present study that do not demonstrate any statistically significant trend ($P > 0.05$) with the latitude of heavy metal (Cd, Pb, Ni, Cu, and Zn) concentrations in green and brown parts of mosses sampled above the peat profiles, from most northern PB to most southern NR sites (Fig. 3 and Table ESM-2). This is especially pronounced for Pb whose concentration profile remains quite similar along the transect from forest–tundra (permafrost site PB/PM) to forest–steppe (UR, NR, Fig. 3C). Therefore, rather than originated from short- or long-range industrial pollution, two alternative sources of Cd and Pb can be considered: (i) the dust input from the Gobi desert of Mongolia and Kazakhstan steppes and (ii) local geogenic background sources, delivered to the moss surface in the form of aerosols.

Moreover, the homogeneity of the Cu and Ni distribution over the full depth of the studied peat columns under low ryam (MR, KO, PR, UR) and permafrost palsa bog (PB, PM) ecosystems suggests the lack of deposition of industrially-originated metal-bearing solid phases from Cu–Ni smelters, such as the Norilsk factory, located c.a. 700 km NE of the most northern site in this study, with their subsequent migration along the peat column. This result contrasts the case of the peat sphagnum from a contaminated ombrotrophic bog in Finland (cf. Rausch et al., 2005a). Although Cu does not show any statistically significant enrichment ($P > 0.05$) at the surface horizons of all of the studied peat columns (except, most likely, the KO site), Pb, Zn and Cd in the western Siberian peat columns from the bogs and ryams behave very similarly to what

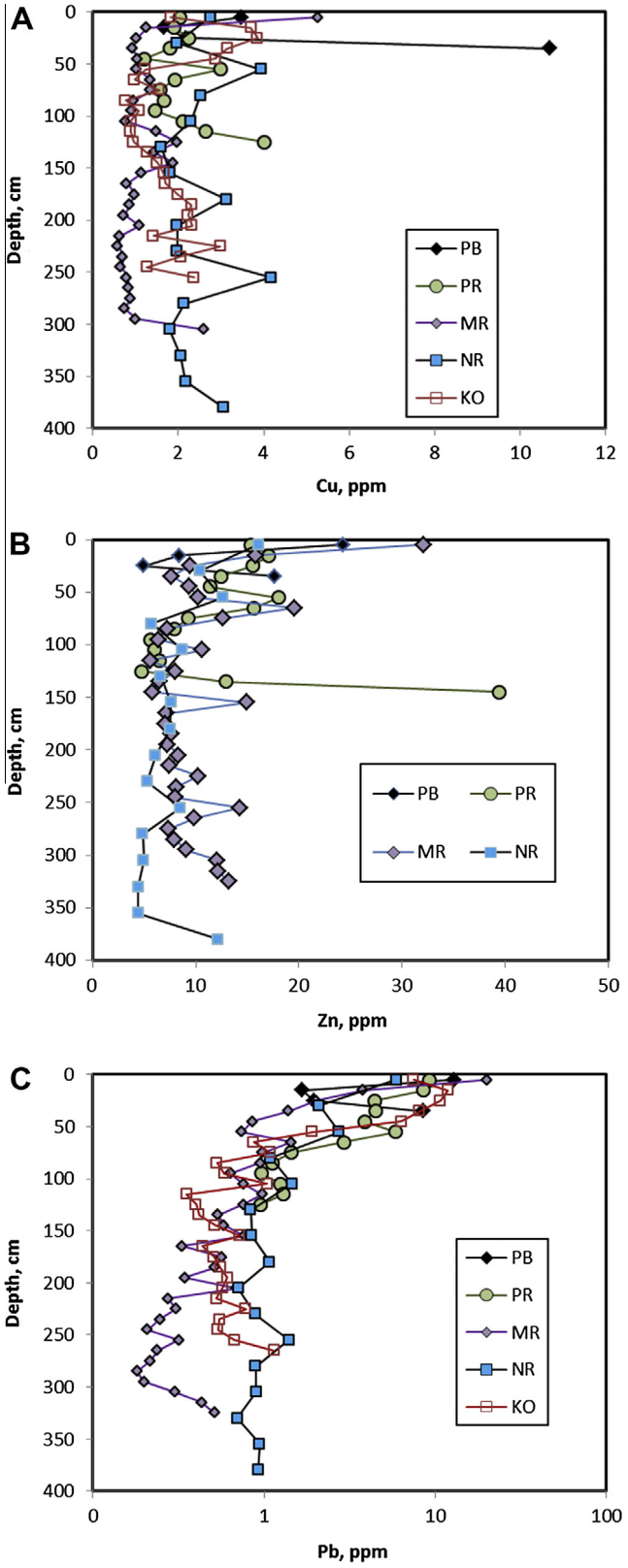

Fig. 3. Cu (A), Zn (B) and Pb (C) concentrations in the peat profile of the permafrost site (PB), the middle and southern taiga zone (MR, PR and KO), and the forest–steppe (NR). Note log scale for Pb (C) and low variability of metal concentration in the main part of the peat profile. Refer to Table 1 for terminology used and to Fig. 1A for geographical location.

is reported in European peat bogs (cf., Shotyk et al., 2002), with a notable accumulation in the surface horizon at 10–40 cm and a

relatively smooth decrease down the mineral horizon. While this type of enrichment of the surface horizon in metals in Europe is interpreted as resulting from industrial atmospheric pollution (Shotyk et al., 1992), highly pristine environment of the western Siberian profile refutes the local industrial origin in this study. Rather, the enrichment of divalent metals in the upper peat profile may reflect significant accumulation of these metals in mosses (Reimann et al., 2001). This accumulation is linked to high adsorption capacities of divalent metals on Sphagnum (Gstoettner and Fisher, 1997; Gonzalez and Pokrovsky, 2014). This enrichment exhibits a universal character since it is detected at the northern and southern sites of western Siberia and thus could reflect biological control of metal distribution in the organogenic horizons as it known for other regions (Reimann and de Caritat, 2005). To which degree the metal delivery to the mosses may be controlled by worldwide, long-range atmospheric transfer versus local geogenic background is not possible to quantify. Note that, despite the increase of population and traffic density southward, the southern sites (UR, NR) do not demonstrate statistically significant enrichment in divalent metals and metalloids. Therefore, in contrast to regional atmospheric deposition patterns of trace elements in more industrialized parts of the European Arctic (Reimann et al., 1997a,b), this may suggest the negligible impact of local pollution on element accumulation in mosses and the upper peat profile. At the same time the profile of the most northern, permafrost sites PB and PM is too short to quantitatively evaluate the degree of atmospheric deposition in the permafrost zone compared with the non-permafrost regions.

Vanadium and chromium exhibit a relatively constant distribution in all studied peat cores, with concentration variation coefficients within the vertical profile lower than 70%. These elements are often considered as tracers of atmospheric dust deposition and industrially related contaminations with a strong enrichment after the industrial revolution from the beginning of the 20th century (Shotyk et al., 2002; Krachler et al., 2003). In the most complete peat profile of central Europe, a clear enrichment in the first 10 cm of the peat column is linked to this contamination. However, 8 out of 11 peat profiles sampled in western Siberia did not demonstrate a statistically significant ($P > 0.05$) accumulation of Cr and V in the surficial (0–40 cm) horizons, with only a slight enrichment of V and Cr in the taiga zone (MR). Therefore, the industrial pollution by dust deposits should be minimal in western Siberia, and the long-range atmospheric transfer of these contaminants is not pronounced in this region.

Similar to other ombrotrophic peat bog profiles (i.e., Krachler and Shotyk, 2004), K, Rb and Cs were highly correlated with each other ($r^2_{Rb,K} > 0.9$; $r^2_{Cs,K} \geqslant 0.8$–0.9) and strongly enriched in the living layers of peat bog surfaces compared with the deeper zones (Table ESM-2). This correlation is observed in all of the studied columns regardless of the landscape and latitudinal position and indicates a strong biological uptake (K and Rb) or silicate dust deposits (Cs) on the moss surfaces followed by intensive leaching of these highly mobile elements during moss transformation to the peat.

In addition to concomitant deposition of clay dust containing alkali metals notably Cs in the interfoliar space, strong biological uptake of K, Rb and Cs by live mosses, inherited in the peat, is also possible as it was evidenced in various parts of western Siberian vegetation growing in the middle taiga zone (ML, MR, MGG, MGM and MT, see Stepanova and Pokrovsky, 2011).

Al, Ga, Ti, Zr, Hf, Th and U exhibited a relatively homogeneous distribution along the peat profile of the middle taiga sites (ML, MR, MGG, MGM and MT, see Fig. ESM-1.3), which is in contrast to the bogs located within the mountain regions (Krachler and Shotyk, 2004). Unlike the latter setting that has historically received various mineral inputs, Siberian peat bogs are located within a flat, pristine, industrial–free (on a century scale) area with minimal lateral runoff. These bogs receive the majority of the elements from the atmosphere, except for the ridge of the middle taiga zone (column MGG), demonstrating a maximum amount of lithogenic elements (Al, Ti, Sc, Zr, Ga, REEs, and Th) at a 100–120 cm depth (Fig. ESM-1.3E, F for Al and Ti and Table ESM-2 for the other elements). The lateral input of these elements from adjacent hills could cause this mineral-rich layer to have the highest ash proportion within the column. The coincidence of mineral (ash) enrichment and Ti local enrichment on the same horizons is well established in peat column studies in other ombrotrophic bogs (Zaccone et al., 2007).

The depth distribution profile of As is significantly different between permafrost (PM, PB) and permafrost-free environments of the middle taiga and forest–steppe zone (MR, NR, Fig. 4). All of the non-permafrost settings exhibit a maximum As concentration within the first (surface) peat horizons and a high concentration in the mineral horizon, whereas the permafrost site demonstrates a progressive accumulation of As with depth without any surface enrichment. The reason for this contrast may be linked to the following: (1) the specificity of moss and vegetation controlling As accumulation during peat formation at the surface, and/or (2) the rapid accumulation of Fe oxy(hydr)oxide down the peat profile, observed only at the permafrost site PB and PM (cf. Fig. 2A), which is capable of sequestering significant amounts of As in the adsorbed/coprecipitated form.

The Sb concentration pattern in Siberian peat of this study does not follow that of As. This decoupling is recorded for all studied columns and it is in contrast to the contaminated European peat records (i.e., Shotyk et al., 1996). In the permafrost palsa site PM, the vertical distribution of As and Sb was completely different, with As increasing down the profile and Sb accumulating mostly in the surface layer, which is similar to that in non-permafrost settings (not shown). Although both As and Sb are enriched in the mineral horizons, no correlation with the ash distribution along the peat column could be evidenced ($P > 0.05$). This strongly suggests that for these metals, the effect of long-range atmospheric dust pollution, including anthropogenic sources starting from the Roman times that are, according to Shotyk et al. (1996), easily detectable in Europe, is not pronounced in the western Siberia.

3.3. Variation of the TE concentration over the climate gradient and among various landscapes within the same climate zone

As a first approximation over the dominant and representative landscape in each zone, we could assess the average peat

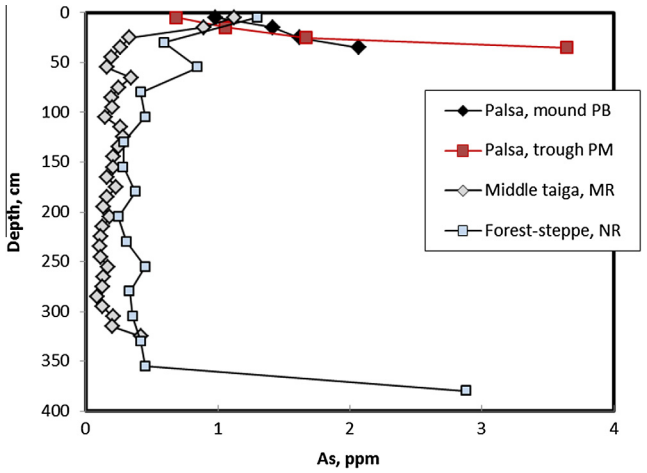

Fig. 4. As concentrations in the peat profile of two permafrost sites (PB and PM), the ryam of the middle taiga zone (MR), and the forest–steppe (NR). Refer to Table 1 for terminology used and to Fig. 1A for geographical location.

composition across almost 1800 km profile from north to south. For this transect, the dominant landscape type, low ryam, was selected in all forested sites (MR, KO, PR, UR and NR). The low ryam is closest, in terms of ground vegetation and peat drainage conditions, to the permafrost site of the forest–tundra (PB and PM).

The following four primary sites can be considered comparable in terms of geographical position and landscape context: forest–tundra (palsa), middle taiga (MT), southern taiga (ST) and forest–steppe (FS). The order of element abundance throughout the depth profile in these sites follows the sequences: for Al, Palsa < ST < MT < FS; for Zr, Palsa ⩽ ST < MT < FS; and for Ca, Palsa < MT < ST ⩽ FS. The accumulation of many major and trace elements in the southern part of the study region may be linked to extensive evaporation and the proximity of mineral horizons.

A detailed analysis of major and trace element distribution in the peat cores of western Siberia along a latitudal profile becomes possible based on average element concentration in the major (central), moss- and mineral-free part of the peat column (Table 2). According to their behavior over the latitude gradient, the elements can be distributed among 3 groups:

(i) B, Mg, Ca, Sr and U, exhibiting stable concentration north of 60°N and ~2 to 3-fold increase from 60°N to 54°N (Fig. 5A–D);
(ii) the majority of elements showing no any statistically significant correlation with latitudal position with typically less than a factor of 2 variation between different sites: Na, K, Rb, Cs, Al, Sc, Ga, Y, REEs, Ti, Hf, Th, V, Cr, Mn, Cu, Zn, Ba, Sb, Tl, W, Nb, Bi (not shown);
(iii) elements increasing their concentration north of 60°N and exhibiting a variation a factor of 2 in the concentration south of 60°N: P, Fe, Co, Ni, As, Cd and Pb (Fig. 5E–H).

In most cases, however, significant intrinsic variation over the peat core layers producing large 2 s.d. error bars (Fig. 5) does not allow for establishing of statistically significant trend. This is the case of Cd and Pb (Fig. 5G, H), Co, Ni, As, U (not shown). The elevated concentration of B and alkaline-earth metals in the southern sites may be linked to evaporation and/or biological immobilization. A decreasing trend of Ca northward (Fig. 5C) reflects the decrease of soil fertility and plant biomass capable of delivering this element to the topsoil horizon. A concomitant increase of P and Fe in the permafrost site PB/PM (66°N) compared to all permafrost-free sites (south of 62°N) may reflect the presence of shallow, Fe-rich waters capable to enrich the unfrozen peat layer during the active season. As a result, P could be fixed in the peat column together with Fe in the form of iron phosphate.

The striking difference of the permafrost palsa site (mound and trough, PM and PB, respectively) compared with the other, permafrost-free zones (MR, and KO of middle taiga, PR of southern taiga and UR + NR of forest–steppe) regarding the TE distribution as a function of depth required a special evaluation. According to their differentiation along the peat profile of the permafrost sites PB and PM, three groups of elements can be distinguished. The relative enrichment coefficient (K_e) of the deep layer can be defined as the ratio of the element concentration in the deepest horizon (30–35 cm) to the average concentration in the surface horizon (0–30 cm) and is illustrated in Fig. 6.

The use of 0–10 cm layer and 10–20 cm layers instead of the average of the three surface horizons (0–30 cm) provided similar results. As such, the discussion of element differentiation in the permafrost sites (PB and PM) is not appreciably affected by the method of coefficient calculation. Divalent metals (Zn, Co, Ni, and Pb), Mo, As, Cd and P exhibit values of $K_e < 2$. This result may be explained by the enrichment of live moss parts and consequently, the surface-most layer of the peat, by micronutrients such as Zn, Co, Ni, Mo. A passive assimilation of atmospherically deposited dust linked to long-range transfer from the Kazakhstan steppe and the Gobi desert together with local geochemical background for Cd, Pb and As cannot be excluded. Alkaline-earth metals (Mg, Ca, Sr, and Ba), Mn, Cu, Fe, B, Sb, REEs, U and Th have K_e values ranging from 2 to 10. Finally, alkali metals (Na, K, Rb, and Cs) and trivalent (Al, Ga, and Cr) and tetravalent hydrolysates (Ti, Zr, and Hf) exhibit K_e values higher than 10. The low proportion of highly mobile alkali metals in the surface layers may be due to their extensive leaching to the surrounding rivers and lakes with an abundant surface and shallow subsurface flow in this water-saturated zone. In contrast, the enrichment of the deep horizon by low solubility, low mobility elements is due to their possible presence as refractory mineral phases in the deeper peat horizons.

The variations in the element concentrations in the peat profiles collected at different sites of the middle taiga zone (tall and low ryams, hollow, ridge and fen) are illustrated in ESM-1.3. For this analysis, we selected two major mineral elements (Fe and Ca), two micronutrient metals (Cu and Zn) and two geochemical tracers of low mobility (Al and Ti). These figures show that Ca and Fe exhibited a constant concentration up to the depth of 200 cm followed by a gradual increase by a factor of 3–4 towards the mineral horizon. Divalent metals, such as Cu and Ni, demonstrated a quasi-constant concentration to a depth of 300 cm followed by an abrupt increase close to the mineral horizon. Presumably, these elements exhibiting high affinity to organic matter, and forming strong organic complexes, are not subjected to significant re-translocation within the peat profile. In contrast, Zn, Mn, and Pb showed a significant enrichment at the surface moss layers and surface peat at a depth of 0–50 cm for all of the habitats. These elements could be actively (Mn, Zn) and passively (Zn, Pb) accumulated, via adsorption and intracellular assimilation, by the mosses from the atmospheric aerosol deposition of natural origin and preserved in the upper part of the peat layers.

Finally, the lithogenic elements (Al, Ti, and Zr) demonstrated a local increase at ~100 cm followed by their progressive decrease with depth before the rise in the mineral horizon. The primary result obtained is that the variations of these elements within each individual site of the middle taiga zone (ridge MGG, ryams ML/MR, fen MT and hollow MGM) are clearly larger than the difference among the sites at the $P > 0.05$ level.

3.4. Average TE concentrations in western Siberian peat cores and comparison with other boreal regions

The average concentrations of major and trace elements were calculated for each studied peat profile, excluding the surface (green and brown parts of mosses) and the mineral horizons (Table 2). The non-systematic variation of element concentration within the moss- and mineral-free peat column could not justify distinguishing two parts of the peat core, upper and bottom, to calculate the average values. Indeed, statistical tests did not demonstrate significant difference in average TE concentration in the first 50% length of the peat core and the second 50% length of the peat core.

The background values of the metal concentrations in western Siberian peat have been calculated following the approach developed in Finish peat cores (Rausch et al., 2005a). Deeper layers of peat profiles not influenced by contemporary atmospheric deposition (typically, from a depth of 30 to 50 cm to the beginning of the mineral layer) were averaged, and the values within 2 s.d. were compared with the available data from other peat profiles. Calculating the median value instead of arithmetic average did not provide significantly different results and the median values were, in most cores, within the uncertainty of the averages.

Table 2
Average concentrations (ppm) of major and trace element in peat profiles of western Siberia. The median values for all elements and all profiles are within the 2 s.d. uncertainties of the average. The latitudinal profile of similar landscapes comprise the columns PB, PM, MR, KO, PR, UR and NR (labelled with *). See Table 1 and Fig. 1A for sample location and description.

Without green moss and without mineral part, major part of the peat column													
	PB*	PM*	MT	MR*	ML	MGG	MGM	KO*	PR*	UR*	NR*	AVERAGE	2 s.d.
Macro-nutrients													
P	917	532	287	142	250	166	193	324	289	298	151	323	226
K	578	532	188	146	1080	196	460	248	631	360	359	434	271
Alkali metals													
Na	295	160	149	90	567	126	207	76	575	289	169	246	175
Rb	2.30	3.30	1.04	0.662	2.71	0.725	1.825	1.06	3.10	1.62	1.33	1.79	0.95
Cs	0.111	0.072	0.066	0.040	0.154	0.043	0.122	0.052	0.240	0.112	0.114	0.102	0.059
Alkaline-earth metals													
Mg	249	356	232	283	248	297	195	331	459	670	844	379	204
Ca	728	937	1787	1877	1454	2159	1666	1477	3101	3534	4276	2091	1103
Sr	14.2	10.6	15.9	16.5	15.9	14.0	12.1	12.0	21.8	48.8	51.5	21.2	14.6
Ba	44.0	20.6	29.6	26.5	55.5	22.5	30.7	27.4	28.0	22.7	25.7	30.3	10.4
Micro-nutrients													
Mn	17	17	16	23	24	26	23	34	88	21	21	28.1	20.6
Fe	6035	2775	1003	1266	1604	1020	952	3130	2554	835	973	2013	1569
Co	3.10	1.50	0.710	0.869	1.10	0.673	0.676	3.06	1.37	0.502	0.414	1.27	0.96
Ni	6.64	4.31	1.967	1.33	3.92	1.28	1.98	5.24	2.90	1.77	1.54	2.99	1.80
Cu	1.92	2.096	1.236	1.04	2.73	1.21	2.70	1.61	2.64	1.82	2.30	1.94	0.62
Zn	6.69	17.3	7.022	9.07	10.6	9.83	8.97	5.81	10.05	7.79	6.22	9.03	3.20
Oxyanions													
B	4.9	5.9	2.1	4.6	3.9	8.6	2.2	4.0	5.5	10.0	9.2	5.5	2.7
V	4.72	2.86	3.01	1.85	5.28	1.90	4.86	2.265	3.970	3.389	3.195	3.39	1.19
Cr	4.15	2.43	2.72	1.51	5.05	1.63	3.70	2.002	3.200	2.967	2.282	2.88	1.09
Mo	0.295	0.222	0.215	0.130	0.415	0.235	0.241	0.153	1.402	0.424	0.407	0.38	0.36
As	1.52	1.76	0.526	0.187	0.575	0.196	0.668	0.399	1.496	0.579	0.365	0.75	0.56
Sb	0.072	0.244	0.094	0.177	0.085	0.185	0.077	0.113	0.176	0.126	N.D.	0.13	0.06
W	0.076	0.062	0.040	0.043	0.097	0.048	0.048	0.043	0.086	0.052	0.064	0.06	0.02
*Immobile tri-valent and tetravalent hydrolysates**													
Al	3674	1397	1883	1469	3296	1565	2657	1674	2750	1901	2362	2239	771
Sc	0.670	0.305	0.281	0.228	N.D.	0.285	N.D.	0.385	0.537	0.281	0.386	0.37	0.14
Ga	0.622	0.335	0.506	0.319	1.03	0.348	0.754	0.339	0.731	0.517	0.527	0.55	0.22
Y	1.343	0.795	0.579	0.397	0.906	0.430	0.805	0.569	0.745	0.612	0.697	0.72	0.26
La	1.883	0.741	0.886	0.685	1.72	0.690	1.291	0.710	1.322	0.988	1.071	1.09	0.42
Ce	3.975	1.694	1.787	1.367	3.24	1.37	2.59	1.444	2.683	2.016	2.151	2.21	0.84
Pr	0.430	0.205	0.199	0.154	0.360	0.154	0.295	0.162	0.298	0.225	0.236	0.247	0.090
Nd	1.737	0.842	0.762	0.586	1.36	0.582	1.120	0.651	1.199	0.850	0.895	0.962	0.360
Sm	0.339	0.172	0.149	0.108	0.254	0.109	0.218	0.124	0.212	0.164	0.179	0.184	0.069
Eu	0.082	0.040	0.034	0.025	0.057	0.025	0.048	0.031	0.047	0.037	0.041	0.042	0.016
Gd	0.351	0.188	0.150	0.109	0.217	0.107	0.195	0.129	0.207	0.170	0.177	0.182	0.067
Tb	0.049	0.023	0.020	0.014	0.031	0.013	0.028	0.017	0.027	0.022	0.023	0.024	0.010
Dy	0.278	0.147	0.120	0.081	0.180	0.081	0.160	0.103	0.158	0.134	0.141	0.144	0.055
Ho	0.050	0.030	0.023	0.014	0.003	0.015	0.002	0.020	0.029	0.023	0.025	0.021	0.013
Er	0.146	0.091	0.066	0.043	0.105	0.045	0.089	0.058	0.085	0.070	0.074	0.079	0.030
Yb	0.116	0.095	0.060	0.042	0.103	0.045	0.084	0.055	0.078	0.068	0.068	0.074	0.024
Lu	0.020	0.013	0.008	0.006	0.015	0.006	0.012	0.008	0.012	0.017	0.010	0.012	0.004
Ti	208	86	109	98	352	108	183	84	162	121	140	150	78
Zr	5.38	3.75	3.033	2.31	7.07	2.65	3.65	1.96	3.72	3.45	3.020	3.64	1.45
Hf	0.16	0.134	0.098	0.16	0.201	0.185	0.111	0.086	0.136	0.110	0.210	0.14	0.04
Th	0.466	0.215	0.187	0.12	0.460	0.133	0.333	0.173	0.376	0.199	0.186	0.26	0.13
Other trace elements													
Nb	0.541	0.326	0.328	0.324	0.924	0.370	0.518	0.273	0.520	0.425	0.499	0.46	0.18
Cd	0.549	0.748	0.320	0.339	0.098	0.205	0.125	1.04	0.141	0.320	0.223	0.37	0.29
Sn	0.092	0.135	N.D.	0.090	0.178	0.076	0.133	0.065	0.097	0.056	0.312	0.12	0.08
Pb	1.81	3.76	1.233	0.645	2.10	0.541	1.17	0.614	2.75	1.75	0.979	1.58	1.00
Bi	0.017	0.031	0.015	0.008	N.D.	0.008	N.D.	0.008	0.018	0.017	0.013	0.015	0.007
U	0.158	0.072	0.084	0.068	0.218	0.076	0.124	0.078	0.183	0.213	0.166	0.13	0.06

The geochemistry of the major and certain trace elements in European peat profiles is relatively well known (i.e., see the review by Shotyk (1988)). Significant research efforts have also been devoted to deciphering the signature of metal deposition in peat profiles within various sources of pollution, notably in Finland (Rausch et al., 2005a,b), Scotland (Shotyk, 1997; MacKenzie et al., 1998), Switzerland (Shotyk et al., 2001, 2002) and Canada (Pratte et al., 2013). However, these results cannot be directly applied to western Siberian sites due to the presence of the permafrost and the significant variations of the peat nature and ground vegetation within the micro-landscapes encountered in this region.

The western Siberia regional background values of peat are similar to those of northern Europe (Rausch et al., 2005a,b) for Cu (1.9 ± 0.6 and 1.3 ± 0.2 ppm, respectively) but different from those for Co (1.3 ± 1.0 and 0.25 ± 0.04 ppm, respectively), Cd (0.37 ± 0.29 and 0.08 ± 0.01 ppm, respectively) and Zn (9.0 ± 3.2 and 4 ± 2 ppm, respectively). Although this difference is detectable, it remains within the variability of the points within each individual profile.

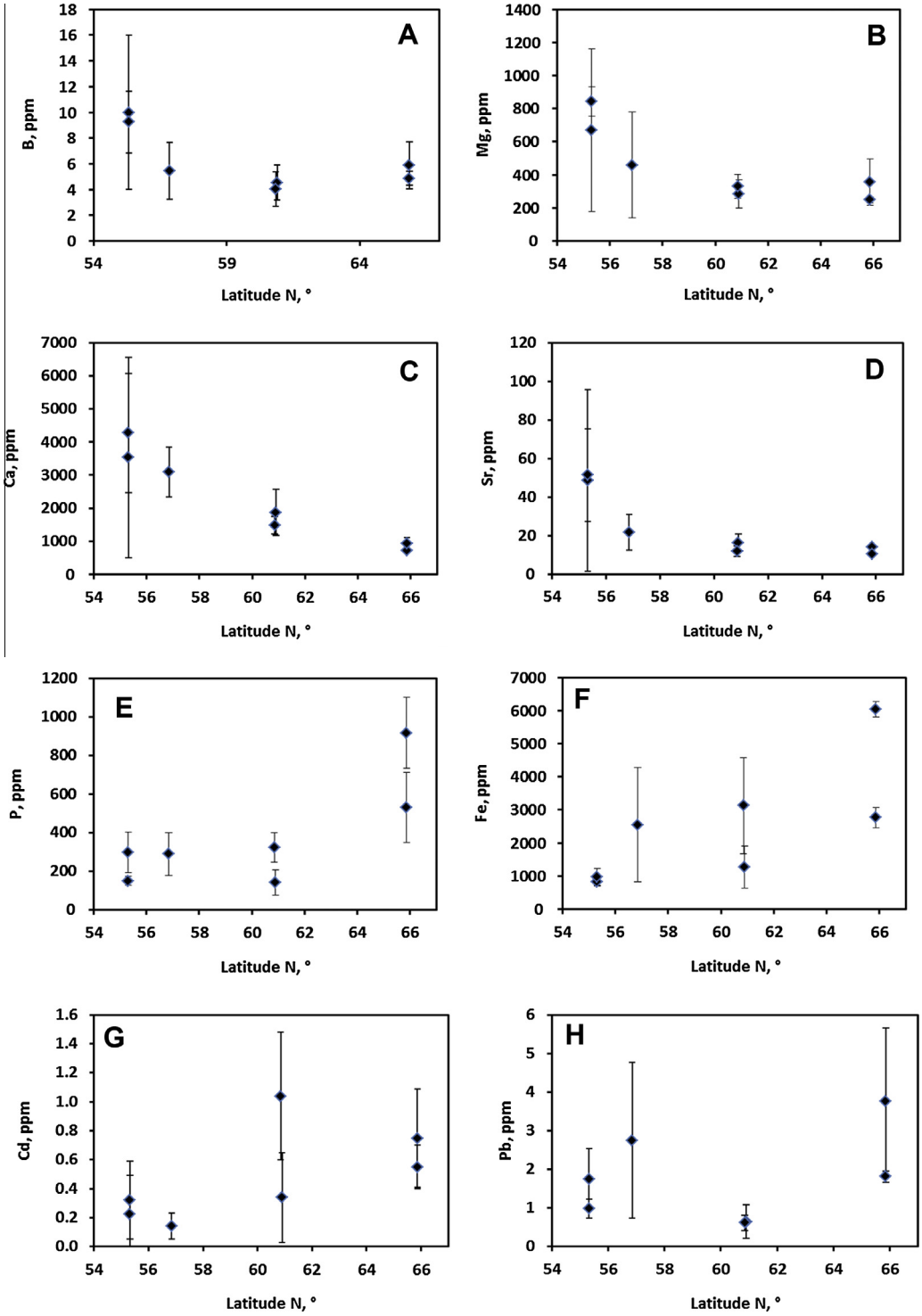

Fig. 5. Average, moss- and mineral-free concentration of B (A), Mg (B), Ca (C), Sr (D), P (E), Fe (F), Cd (G) and Pb (H) in peat cores of western Siberia as a function of latitude. Error bars represent 2 s.d.

Given the significant geographic spread of the samples in this study, this agreement is remarkable and may suggest a universal feature of the chemical composition of boreal and subarctic peat deposits. Another important conclusion that can be drawn from such highly homogeneous concentrations is the lack of punctual pollution sources in the form of industrial activity and dispersed local pollution originated from roads and towns in the south. A uniform impact of long-range dust originated from desert regions across the 1800 km transect is also unlikely given significant geographical coverage and drastically different distance from the sampling sites to the dust provenances. However, local geochemical background is highly homogeneous in western Siberia and thus the observed similarity in the peat cores may well reflect the similarity in the active or passive processes of element uptake by moss following the moss-to-peat transformation.

The average background concentration of trace metals in the western Siberia peat profile can also be compared with the pristine metal concentration in terrestrial ecosystems across the Russian

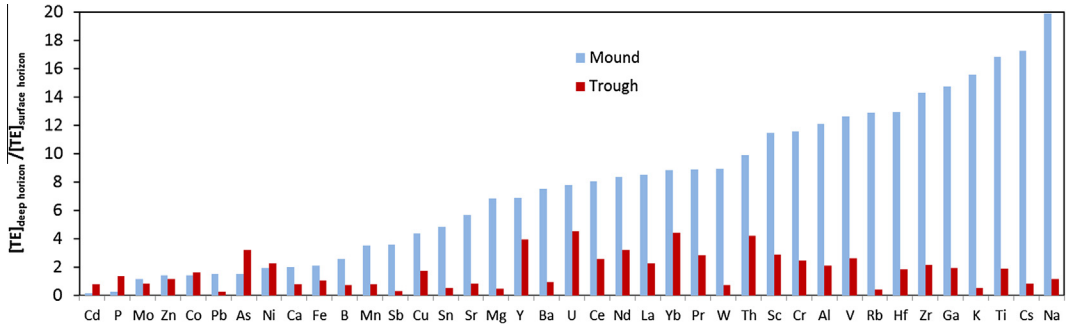

Fig. 6. The ratio of element concentration in the deepest horizon (30–35 cm) to the average concentration in the three surface horizons (0–30 cm) measured at the micro-mound (blue) and micro-trough (red) of the permafrost site (PB and PM, see Table 1 and Fig. 1A for location and description). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

Arctic (Zhulidov et al., 1997). The concentrations of Cd and Zn measured in this study are within the range reported for the surface peat horizons, whereas the concentrations of Pb and Cu are a factor of 5 and 10, respectively, lower in western Siberian peat compared with the north of Siberia and the Arctic islands, as reported by Zhulidov et al. (1997). Two possible causes of this difference are as follows: (1) the difference in methodology of sampling and analysis and (2) the preferential enrichment of the surface peat at the northern sites in these metals compared with deeper horizons. Currently, distinguishing between these two reasons is difficult. It is also important to note that over the past few decades, metal emissions in Europe have decreased but those in Asia have increased (Pacyna and Pacyna, 2001). Although this difference is likely to only slightly affect the peat concentration, the mosses, both the green and the brown parts, will definitely experience a significant shift in atmospheric metal loading. Therefore, a straightforward comparison of the trace metal concentration of the peat surface and mosses from different regions collected during different periods (on a decadal scale) is unwarranted.

The concentrations of the major and trace elements measured in sphagnum mosses were assessed at each site. For this calculation, we used the live (green) parts or both the green and brown parts at certain sites (Table 3). The average concentrations of Co, V, Cr and Zn in mosses of western Siberia (0.51 ± 0.32, 2.4 ± 2.0, 2.2 ± 1.4, and 27.9 ± 11.1 ppm, respectively) were similar, within uncertainty, to those reported in the European subarctic (0.87, 2.6, 0.91 and 34 ppm, respectively, Äyräs et al., 1997) and Finland (Poikolainen et al., 2004). The Co, V and Cr concentrations in European mosses are presumably affected by contamination from the smelters in Monchegorsk and Zapolyarnij (Äyräs et al., 1997). Presumably, the concentration of these elements in western Siberian mosses represents the background values and any possible effect of industrial pollution cannot be distinguished. Rather, these concentrations reflect the similarity of biological concentration factors of trace metals in mosses in the boreal zone, despite certain differences in the dominant moss species at the two sites (*Hylocomium splendens* or *Pleurozium schreberi* in Europe and *Sphagnum* sp. in Siberia). The green and the brown parts of Sphagnum mosses of the surface are distinctly enriched in As relative to the underlying peat, which may be linked to the contemporary atmospheric input. A possible mechanisms of As enrichment in the surface horizons of mosses and peat columns in the pristine regions may be co-precipitation with and adsorption onto amorphous iron (oxyhydr) oxides originated from coagulation of surface water colloids.

The enrichment of the peat surface horizons by Mn and Zn compared with the deeper peat horizons is a relatively well established fact, most likely linked to a significant biological accumulation of these bio-essential micronutrients (cf., Zaccone et al., 2007). The concentrations of Cu and Ni are an order of magnitude higher in the moss coverage of the European boreal zone (15.8 and 18.3 ppm, respectively, Äyräs et al., 1997) compared with those in western Siberia (2.7 ± 1.4 and 1.77 ± 1.0 ppm, respectively, Table 3). This difference likely reflects the presence of Kola's smelters in the subarctic European zone in which the maximal contamination is typically reflected (de Caritat et al., 2001; Reimann et al., 2000a, 2000b). The variations in the Cu and Ni concentrations in the mosses of Finland are extremely high and exhibit a significant time trend due to the modification of the degree of atmospheric pollution (Poikolainen et al., 2004). The lower concentrations of these metals in western Siberia mosses and upper peat horizons likely reflect rather pristine environment of this region where the metals are accumulated, according to their requirements by mosses and plants, from available atmospheric aerosols. These atmospheric depositions, while not reflecting any specific local contamination, likely reflect the long-range natural dust transfer.

Supporting this hypothesis, Fe and Pb exhibit significantly higher concentrations in mosses of western Siberia (1224 ± 98 and 8.6 ± 4.7 ppb, respectively) compared with those in subarctic Europe (385 and 3.3 ppb, respectively). This result suggests the dominance of natural rather than anthropogenic factors regulating metal accumulation in terrestrial vegetation and peats of western Siberia. The boggy context of western Siberia with significant Fe deposits and Fe concentration in surface waters may potentially explain this difference. Pb could be either linked to Fe-organic colloids and taken up by mosses during flooding from surrounding surface waters or deposited by dust via long-range atmospheric transfer from southern districts, such as the Gobi Desert of Mongolia. The higher concentration of Pb in more pristine western Siberian sites compared to subarctic Europe calls into question the widely accepted local industries and long-range transport of anthropogenic emissions as the only mechanisms of Pb enrichment in upper peat profiles. Rather, local and surrounding dust provenances and local biogeochemical processes controlling the atmospheric aerosols interaction of precipitated metals with the main constituents of peat, the mosses, should be considered as the main factors of Pb accumulation in the pristine boreal environments.

3.5. The TE concentration in peat cores normalized to mineral admixtures

To consider the differences in the mineral matter contents of the underlying sediments, such as clays and sands, the element enrichment and depletion through the peat profile were calculated for each stratigraphic layer relative to the average composition of the underlying sediments, i.e., the last (mineral) horizon. Examples for Ca, Fe, Cu, Zn, Ni, Cr, Al, Zr, Pb, and U are shown in Fig. ESM-1.4. Some elements are depleted in the upper part

Table 3
Average major and TE concentrations in mosses of western Siberia peatlands (ppm). The median values for all elements and all profiles are within the 2 s.d. uncertainties of the average. The latitudal profile of low ryam and palsa site comprise the columns PB, PM, MR, KO, PR, UR and NR (labelled as *). See Table 1 and Fig. 1A for sample location and description.

	PB*[a]	PM*[a]	MT	MR*	ML	MGG	MGM	KO*	PR*	UR*[a]	NR*[a]	AVERAGE	2 s.d.
Macro-nutrients													
P	333	371	330	577	232	240	166	361	295	493	557	360	133
K	917	1073	2914	2185	2224	840	3204	4703	1032	790	1212	1917	1265
Alkali metals													
Na	287	229	431	321.6	126	206.1	251	458.9	239.2	532.0	629.3	337	155
Rb	4.15	6.69	13.97	7.58	5.28	2.85	10.66	13.32	3.96	1.50	3.60	6.69	4.25
Cs	0.14	0.112	0.40	0.319	0.173	0.126	0.267	0.217	0.210	0.265	0.247	0.23	0.1
Alkaline-earth metals													
Mg	411	527	602	487	629	527	621	859	458	273	898	572	183
Ca	1276	1011	1355	1656	2398	1326	696	1482	1555	3005	2895	1696	749
Sr	9.5	11.1	6.4	7.2	3.6	7.2	3.4	5.7	10.7	32.0	26.7	11.2	9.4
Ba	33.2	22.1	18.8	34.8	17.2	15.7	10.6	12.6	17.3	36.2	30.9	22.7	9.4
Micronutrients													
B	5.10	8.4	6.85	5.9	3.0	15.1	0	3.3	7.3	10.6	11.4	7.0	4.3
V	3.13	1.7	0.87	3.291	0.853	1.25	0.773	0.837	2.532	6.737	4.962	2.4	2.0
Cr	2.13	1.6	0.82	3.665	1.22	1.21	0.999	0.954	2.383	4.879	4.091	2.2	1.4
Mn	54.83	29.0	78.1	90.7	283	107	42.8	108.3	60.6	31.2	23.9	82.7	73.0
Fe	860	3007	455	1045	248	1091	398	658	1118	2444	2137	1224	908
Co	0.57	1.14	0.20	0.430	0.154	0.500	0.157	0.304	0.477	0.967	0.688	0.51	0.32
Ni	2.24	2.81	0.75	2.534	0.857	1.33	0.473	0.905	1.553	3.379	2.60	1.77	1.0
Cu	3.48	1.69	0.48	5.29	3.06	2.70	1.50	1.825	2.04	4.48	2.75	2.66	1.4
Zn	24.3	21.8	26.9	32.1	40.2	27.1	34.3	51.5	15.4	17.4	16.1	27.9	11.1
Mo	0.10	0.192	0.21	0.250	0.045	0.125	0.062	0.086	0.283	0.609	0.646	0.24	0.2
Trivalent and tetravalent hydrolysates													
Al	1720	1155	377	1747	382	690	372	362	1692	2046	4156	1336	1143
Sc	0.23	0.210	0.19	0.306	N.D.	0.224	N.D.	0.288	0.296	0.292	1.274	0.37	0.34
Ga	0.49	0.277	0.13	0.623	0.128	0.180	0.118	0.168	0.462	1.10	0.798	0.41	0.3
Y	0.51	0.359	0.11	0.477	0.112	0.214	0.112	0.108	0.488	0.439	1.128	0.37	0.3
La	0.82	0.589	0.18	0.778	0.213	0.271	0.211	0.139	0.702	0.561	1.672	0.56	0.4
Ce	1.77	1.188	0.33	1.565	0.351	0.552	0.327	0.290	1.415	1.611	3.341	1.16	0.93
Pr	0.20	0.136	0.03	0.182	0.040	0.066	0.036	0.034	0.161	0.185	0.347	0.13	0.10
Nd	0.77	0.519	0.16	0.652	0.152	0.249	0.122	0.118	0.749	0.791	1.364	0.51	0.40
Sm	0.16	0.087	0.02	0.118	0.028	0.054	0.026	0.019	0.115	0.167	0.279	0.10	0.08
Eu	0.04	0.017	0.01	0.027	0.007	0.011	0.006	0.007	0.025	0.053	0.061	0.02	0.02
Gd	0.14	0.100	0.02	0.123	0.024	0.056	0.021	0.020	0.114	0.165	0.251	0.09	0.07
Tb	0.02	0.011	0.00	0.016	0.004	0.007	0.003	0.003	0.018	0.028	0.038	0.01	0.01
Dy	0.09	0.078	0.02	0.094	0.021	0.044	0.020	0.018	0.142	0.157	0.207	0.08	0.06
Ho	0.02	0.015	0.00	0.018	0.000	0.007	0.000	0.003	0.018	0.031	0.041	0.01	0.01
Er	0.05	0.037	0.01	0.058	0.012	0.020	0.011	0.010	0.059	0.087	0.114	0.04	0.04
Tm	0.01	0.006	0.00	0.009	0.002	0.003	0.002	0.003	0.007	0.018	0.016	0.01	0.01
Yb	0.05	0.033	0.01	0.057	0.012	0.021	0.012	0.008	0.050	0.085	0.100	0.04	0.03
Lu	0.01	0.005	0.00	0.008	0.002	0.003	0.002	0.002	0.007	0.019	0.015	0.01	0.01
Ti	143	90	16.9	132	24.5	36.1	19.2	17.0	95.2	188	217	89.0	72.9
Zr	2.93	2.48	0.60	3.288	0.538	1.326	0.493	0.496	2.825	5.619	4.813	2.31	1.8
Hf	0.09	0.129	0.03	0.244	0.014	0.321	0.014	0.072	0.141	0.203	0.520	0.16	0.15
Th	0.17	0.089	0.01	0.080	0.026	0.074	0.039	0.018	0.124	0.112	0.177	0.08	0.06
Other trace elements													
As	0.98	0.684	0.85	1.13	0.700	1.54	0.812	0.772	1.43	2.03	1.300	1.11	0.4
Sb	0.18	0.463	0.51	0.662	0.247	0.499	0.283	0.148	0.667	0.630	0.432	0.43	0.2
Cd	0.51	1.254	0.64	0.547	0.232	0.616	0.170	1.332	0.236	0.389	0.200	0.56	0.4
W	0.10	0.070	0.04	0.133	0.001	0.065	0.009	0.023	0.107	0.093	0.123	0.07	0.05
Tl	0.06	0.028	0.03	0.080	0.071	0.060	0.009	0.012	0.025	0.035	0.019	0.04	0.02
Pb	12.9	3.9	4.6	20.1	5.5	8.4	5.8	7.5	9.2	10.5	5.9	8.6	4.7
U	0.06	0.034	0.01	0.065	0.016	0.026	0.016	0.013	0.064	0.209	0.170	0.06	0.07

[a] Green + brown parts of *Sphagnum* moss, the other samples are green parts of the *Sphagnum* moss only.

of the column (the green and brown parts of the Sphagnum mosses) and in the peat column itself; these are alkaline and alkaline-earth elements (Ca, Sr, and Ba, Fig. ESM-1.4A) and Fe (Fig. ESM-1.4B). Many elements, such as trivalent and tetravalent hydrolysates (Al, Y, REEs, Ti, Zr, Hf, and Th) and U, are highly conservative within the peat column, exhibiting a quasi-constant concentration from the surface to the beginning of the mineral horizon. In agreement with the results on the European peat column (Shotyk et al., 1992), V and Cr are also highly conservative (Fig. ESM-1.4F), but Ni exhibits a dynamic behavior with progressive accumulation from the surface to the bottom of the peat profile (Fig. ESM-1.4E). Zn and Pb are clearly enriched in the upper horizons relative to the local mineral substrate (Fig. ESM-1.4D, I). The micro-nutrient Zn is assimilated by upper parts of mosses following its deposition in the form of liquid and solid aerosols. In contrast, indifferent to plants Pb may be passively absorbed by moss surfaces (i.e., Gonzalez and Pokrovsky, 2014) both from liquid aerosols or from surface waters in case of flooding. Given the remote context of studied sites, for both metals, the likely sources of metals in the atmospheric fluids are natural (geogenic) dust and silicate suspended particles dissolution rather than their release from anthropogenic particulate matter.

Interestingly, all of the sites demonstrated a depletion in As in the majority of the peat column relative to the mineral horizon (Fig. ESM-1.4H). This result illustrates the elevated mobility of As in the peat environment, most likely linked to its mobilization from the mineral layers in the form of organic and organo-ferric colloids (Bauer and Blodau, 2009). The coefficient of depletion that can be defined as the ratio of the bottom (mineral) to the depth-average peat horizon decreases from south to north in the following order: NR ~ UR ~ PR (5–10) > KO (5) > MGM ~ ML (3) ⩾ MR (2) > 1.5 (PB). This order may reflect the increase in the As concentration in the mineral layers from north to south most likely linked to the different lithological substrates (sands versus clays).

To account for admixtures of mineral fractions and to evaluate the relative enrichment of the peat compared with the underlying mineral substrate and atmospheric silicate dust, normalization to supposedly inert components (Sc, Al, Ti, and Zr) is often used (see Shotyk et al., 2001). Although the majority of trivalent and tetravalent hydrolysates are quite mobile in Siberian soil solutions and surface waters (Pokrovsky et al., 2012), such normalization allows attenuation of the variations of TE concentration linked to the presence of silicate admixtures of non-biological origin. In this study, we chose to normalize to aluminum because it is often used for the Siberian soil weathering index (Pokrovsky et al., 2005b, 2006) and for normalizing the fractionation of major and trace elements between soil substrate and plants in Siberia (Viers et al., 2013). Besides, using Al allows us to normalize in the presence of both silicate dust (the Gobi and Kazakhstan Desert Provinces are most likely to contribute to the solid aerosols in Siberia) and the clay mineral substrate encountered in the majority of the studied sites. We observed a relative enrichment in Fe of the permafrost site and enrichment in Ca with depth of the ryams (ML, MR) in southern taiga (Fig. ESM-1.5). These trends likely reflect the typical Fe-rich surface water and topsoil environment of the north of the boreal zone and the accumulation of biogenic Ca, due to the elevated primary plant productivity, which causes an enhanced input of the plant litter to the topsoil horizons in the southern boreal zone.

The depth patterns of Al-normalized divalent metals (Cu, Zn, Ni, Co, Mn, and Cd) are in general agreement with a previous analysis of mineral-layer normalization (Fig. 7), with a relatively conservative behavior of these elements over the full depth of the peat profile in all of the permafrost-free sites, including the mineral horizon. The ratios of Cu, Zn, Ni, Mn and Co to Al exhibit homogeneous distribution in the first half length of the peat core including the upper (moss) layer with variation coefficient lower than 2, followed by downward increase of the ratio by less than a factor of 3. The similarities of these element variation between different remote sites and between mosses and peat strongly suggest that (i) either there are some "universal" biological regulation mechanisms of element incorporation in the moss tissue or, (ii) in case of passive uptake of metals from atmospheric aerosols, the local geochemical source of these metals is similar over 1800 km latitudinal profile in western Siberia.

Pb is drastically different from the other metals as its Al-normalized concentration decreases from the top to the bottom peat profile by factor of 2–5 with high (a factor of 3–10) enrichment in the moss layer. The homogeneity of this pattern across all studied long latitudinal transect strongly suggests the lack of long-range transport of Pb-bearing silicate dust and its incorporation in the moss tissue; rather, Pb is passively absorbed from the liquid

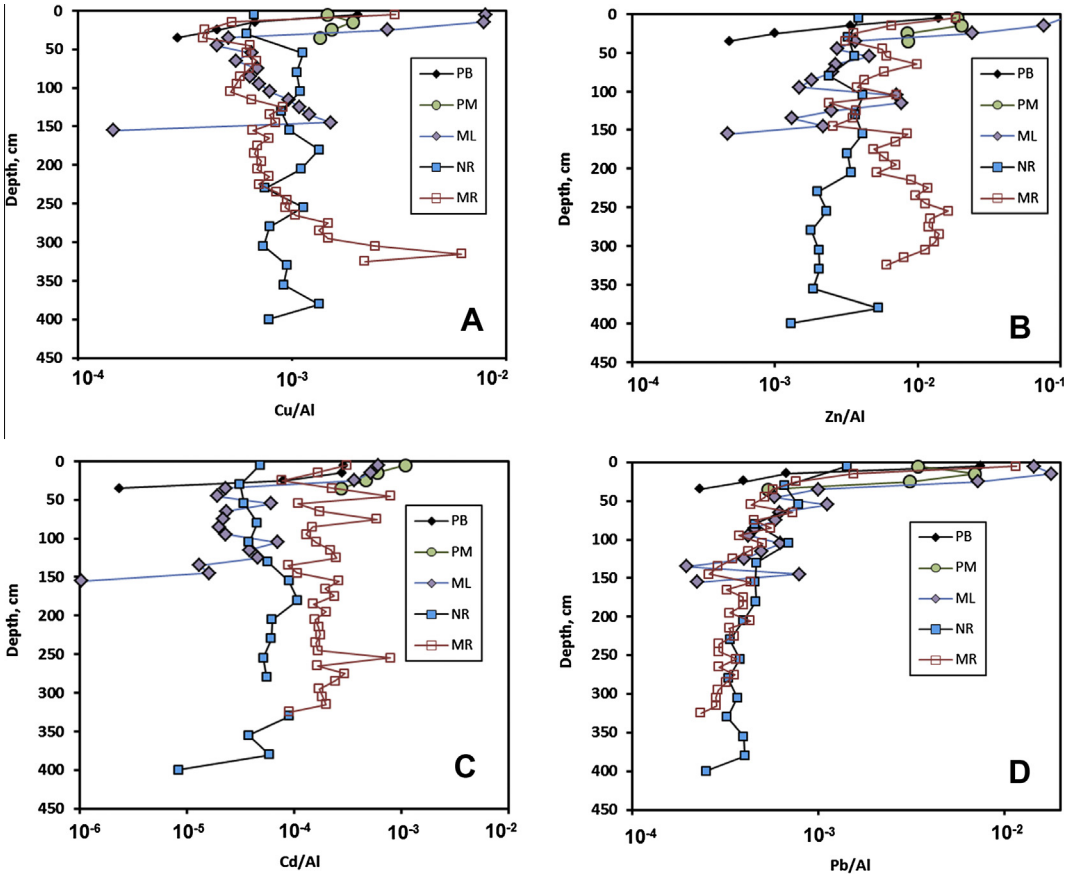

Fig. 7. Plot of Cu (A), Zn (B), Cd (C) and Pb (D) to Al ratios in peat column and mosses of several WSL zones. PB, palsa, mound (permafrost); PM, palsa, trough (permafrost); ML, low ryam, middle taiga; NR, low ryam, forest–steppe; MR, low ryam, middle taiga. Refer to Table 1 for terminology used and to Fig. 1A for geographical location.

atmospheric aerosols and, during peat formation, being leached from the peat column by downward penetrating fluids. The striking difference between indifferent Pb and micronutrient Zn possibly reflects the moss demand for Zn and passive accumulation of Pb from the environment following the geochemical background received in the form of atmospheric deposition or surface water contact with the moss surface. Both elements however are subjected to re-distribution along the peat column due to their migration in the form of organic and inorganic low molecular weight complexes (Zn) and large-size Fe-rich colloids (Pb) as shown in another boreal peat soil solutions (Pokrovsky et al., 2005a).

The Al-normalized divalent metal profile in the permafrost site (PB/PM) was drastically different from the other sites with respect to the following: (1) it demonstrates a systematic increase in the Me^{2+}/Al ratio from the deep to the surface horizon, typically more than an order of magnitude and (2) although the surface horizon ratio is similar to that of the other site, the deepest sampled horizon (i.e., 35 cm) exhibited a significantly lower Me^{2+}/Al ratio compared with all of the other studied peat columns. Therefore, the seasonal thawing/freezing of the active 30–50 cm layer in the forest–tundra site can produce a significant variation in the Al-normalized divalent metal concentration patterns, thus affecting the potential metal bioavailability and their migration along the peat column and to the surrounding surface water bodies. The palsa sites PB and PM are the only ones affected by permafrost and seasonal thawing/freezing of the active layer. Therefore, we hypothesize that the freezing front migration can drastically modify the pattern of element distribution in the peat subjected to seasonal thaw/freeze cycle and this effect will be significantly more pronounced at the northern site of the WSL compared with the southern, permafrost-free sites.

Normalization to Al removes the difference between the different peat horizons for the distribution of the insoluble (lithogenic) elements (Ti, Y, Zr, Hf, and REE), as shown in Fig. ESM-1.5. Via removing possible contribution of geogenic (silicate) dust, we could evidence rather similar profile of many trace elements over the peat columns collected in various climate zones of western Siberia. A number of lithogenic elements, such as Sc, Ti, Y, REEs, Zr, and Hf, can be used to indicate the changes in the concentrations and fluxes in the soil dust (i.e., Shotyk et al., 2001). Despite the possibility of preferential uptake of LREE by vegetation (i.e., Stille et al., 2006), the REEs patterns of peat potentially allow the identification of an atmospheric signal (Aubert et al., 2006). For REE normalization, we used the average values of the REE concentration calculated over the full depth of the peat column at each site, excluding the green/brown parts of the sphagnum mosses and the mineral horizon (Table 2). The upper-crust normalized (McLennan, 2001) REE patterns of the studied peat profiles are generally flat with a clear MREE maximum corresponding to Eu and Gd enrichment relative to the upper crust (Fig. 8).

This pattern likely reflects an essentially crustal origin for the solid and liquid aerosols incorporated by mosses and preserved in the peat profile. The calculation of the REE pattern for the green and brown parts of mosses and for the peat column, normalized to the underlying mineral horizon, yielded a similar result to the UC normalization pattern, with a relatively flat pattern, a slight Eu anomaly and an occasional MREE enrichment (primarily Sm, Eu and Gd), which is typical for ground vegetation (Aubert et al., 2006). Because the MREE enrichment is observed for both the UC and mineral horizon-normalized patterns, it reflects the atmospheric accumulation of REE rather than the geochemical specificity of the mineral substrate.

3.6. Behavior of TE in peat cores under ongoing environmental changes

According to the results of the detailed study of western Siberian rivers along a 2000 km latitudinal gradient with climate warming and consequent permafrost thaw, this region may shift from a surface water-dominated system to a groundwater-dominated system (Frey et al., 2007). With continuous warming of the western Siberian soil, the thickness of the active layer will increase, and deep peat horizons will be involved in the element supply to surface waters via leaching from the mineral and organic substrates. Therefore, with time, increasingly deeper peat horizons will release trace elements to the surface waters. These TEs are present in the form of organic and organo-ferric complexes in the adjacent surface waters, such as thermokarst lakes, and will be delivered in the form of colloids to the rivers (Pokrovsky et al., 2014). For the majority of the studied sites in the middle taiga within the permafrost-free zone, the major and trace element concentration in the peat cores changes insignificantly, within a factor of <2 down to 1.5–2.5 m (see Section 3.2, Table ESM-2 and Figs. 2–4). Therefore, the increase in the thaw layer thickness in the sporadic/discontinuous permafrost zone from 60 to 62°N will not appreciably affect the chemical composition of the surface waters in the central part of western Siberia. In contrast, in the northern part of western Siberia, within the discontinuous/continuous permafrost zone, the effect of the increase of the mean depth of the active layer may produce significant changes in the chemical composition of the surface waters. At the most northern site in this study (Pangody, PB and PM), the peat profile sampled at the mound micro-landscape demonstrated a systematic increase in the major

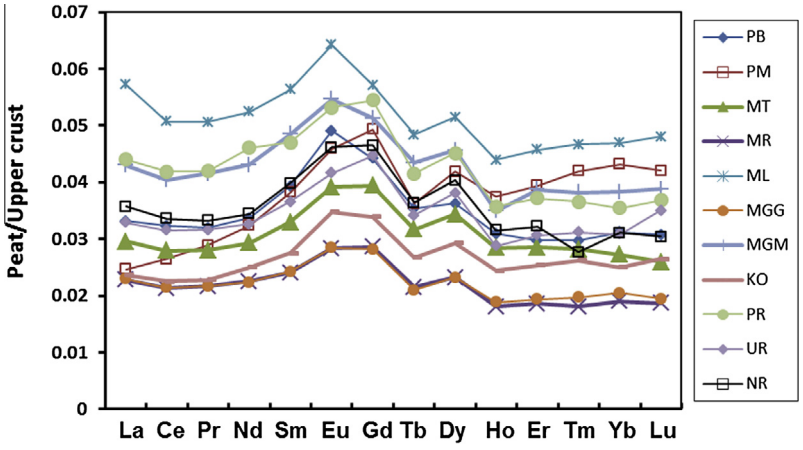

Fig. 8. Upper crust-normalized REE pattern of the average values of the peat column (mineral- and moss-free) of all sites. See Table 1 for site abbreviations. Note generally flat pattern without significant differentiation between sites and weak MREE anomaly, typical for atmospheric precipitates.

and trace elements with the depth, with a maximal concentration achieved within the mineral-bearing layer (Fig. 6).

The proportion of the mineral (ash) fraction in the deep layer of the peat profile at the mound was a factor of 3–6 times higher than that in the surface horizons. Simultaneously, the deep/surface enrichment coefficient of alkali metals and trivalent and tetravalent hydrolysates was higher than 10 (Section 3.3, Fig. 6). Therefore, the enrichment by low-solubility elements and alkali metals of the deep layer is significant, and their mobilization during the permafrost thaw may significantly affect the chemical composition of the surface waters. Upon thawing of the frozen mounds, the water draining these micro-environments will be significantly enriched in soluble alkali metals and slightly soluble trivalent and tetravalent hydrolysates. However, in the case of thawing of the trough (hollow), the effects will be significantly smaller. In these settings, the maximal enrichment of the deep peat horizons relative to the surface horizons (by a factor of ~4) was detected only for heavy REE, Th and U, whereas LREE and As exhibited an enrichment coefficient ranging from 3 to 4. The other trace and major elements did not exhibit any statistically significant enrichment between the deep and surface horizon. Overall, given that the surface of lake-free palsa is covered by an equal amount of troughs and mounds (Peregon et al., 2009; Mironicheva-Tokareva et al., 2007), the global effect of the increasing thawing depth will mobilize a high concentration of major and trace elements in the surface waters. Therefore, the total dissolved solids (Ca, Mg, Na, etc.) migrating in essentially ionic form and low-mobility hydrolysates (Fe, Al, Ti, REEs, etc.) migrating in the form of Fe-rich and organic-rich colloids will increase their concentration by at least a factor of 2–5. A similar degree of element concentration increase is anticipated due to thawed ponds and the formation of small lakes induced by the permafrost thaw in the northern part of western Siberia (Pokrovsky et al., 2013; Shirokova et al., 2013). However, it is clear that the present study provided a first-order approximation of the chemical composition of the peat profiles over a large range of climate and landscape conditions. A detailed study of peat profiles located in sporadic, discontinuous and continuous permafrost zones coupled with a surface stream analysis is required to quantitatively evaluate the effect of permafrost thaw on element mobilization from the peat soil to the Arctic rivers and the Arctic Ocean.

4. Conclusions

The measurement of major and trace element concentrations in peat columns collected over a 2000-km latitude gradient in the western Siberia Lowland allowed an evaluation of the effect of latitude and permafrost coverage on element concentration in peat. We demonstrated a relatively homogeneous distribution of the majority of the trace elements along the permafrost gradient, from permafrost-free peat in the south to the northern border of discontinuous permafrost in the north. The peat bog ecosystems of the WSL are characterized by a similar elemental profile in all of the permafrost-free zones, in contrast to the micro-environments of the discontinuous/continuous permafrost site. Simultaneously, characterization of the elemental chemical composition in various contrasting but highly representative habitats (low and tall ryam, hollow and ridge representing the dominant landscapes) within a permafrost-free/sporadic permafrost zone of the middle taiga demonstrated that the variations within the column profile are larger than the difference between landscapes. The average concentrations of most major and trace elements in peat columns from western Siberia are comparable with those from other regions, notably industrial Europe. The upper part of the peat column, primarily represented by green and live *Sphagnum*, was enriched in divalent metals relative to the bulk peat. Given the pristine aspect of the sampled sites, we argue that the element distribution in moss layers and peat cores reflects general features of geochemical background with possible input of natural dust from adjacent deserts rather than the effect of local industries and anthropogenically-induced long-range transport.

Within various contrasting landscape of the middle taiga permafrost-free/sporadic zone, there was a systematic decrease in the Mn and Cu concentrations and an increase in Na, K, and Rb with increasing moss productivity. The moss mineralization intensity correlated with the accumulation of low-mobility Fe, Al, Ti, divalent metals and metalloids. Within the permafrost-free and sporadic permafrost zones of western Siberia, many elements are highly conservative over the peat column, exhibiting a quasi-constant concentration from the surface to the beginning of the mineral horizon. Within the permafrost region, the bottom horizon of the sampled peat column is significantly enriched in alkali metals and trivalent and tetravalent insoluble elements relative to the upper unfrozen horizons. Climate warming in western Siberia has been speculated to increase the proportion of groundwater and deep peat horizon water feeding in overall riverine fluxes in the permafrost-free zone and to increase the thawed (unfrozen) layer thickness in the permafrost environments. Therefore, continuous climate change will not appreciably affect the chemistry of the soil/subsoil waters in the permafrost-free environment, whereas it might significantly enrich in soluble and colloidal elements the surface waters by draining the deeper peat horizons in the permafrost environments.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apgeochem.2014.12.004.

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