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Influence of Anthropogenic Activities on Metals in Arctic Permafrost: A Characterization of Benchmark Soils on the Yamal and Gydan Peninsulas in Russia

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Abstract

Permafrost-affected region in Russian Arctic is an important study area for investigating fate of trace metals in soils by geological processes and human-induced trace metals through atmospheric deposition. Two plots of soils in Yamal region were selected: Northern Trans-Urals area (PU1, PU2, PU3) adjacent to urban areas and Gydan Peninsula representing reference groups as natural landscapes (Yavai, Gyda, Enysei). The levels of most metals in Urals area were more than those in Gydan Peninsula. In soil profile, Histic horizon revealed the accumulation of most metals. Cd and Pb were classified as metals, which were transported by atmosphere from urban areas and accumulated in surficial organic layers. Gleying processes and cryogenic mass exchanges transported metals from bottom to top layers in mineral horizons. Moreover, gleying horizon functioned as a geochemical barrier for metal transporting below permafrost table. The levels of As, Mn, and Fe were obliviously higher than threshold limit values of Russian Siberia. However, these values cannot represent the natural hydromorphic soils in Arctic tundra. The Geoaccumulation Index (I_{geo}) were determined for assessing surface soil samples regarding to metals' pollution. The results suggested local geology pollution for Gydan Peninsula and atmospheric transport pollution for Urals area. More investigations with respect to trace metals behavior in permafrost-affected soil profile needed to be studied for understanding levels of trace metals with changes of active layer depth due to climate changing.

The Russian Arctic is characterized as cryogenic landscapes and permafrost-affected environments with sparse population. However, the exploration of hydrocarbon and development of industry in Russia Arctic have increased the localized environmental pollution (Abakumov et al. 2015; Pryde 1991; Ryaboshapko et al. 1998; Walker et al. 2003). In the meantime, pronouncedly climatic changes may change main soil properties, such as redox potential and carbon, which leads to a migration of pollutants (Balbus et al. 2013; Dube et al. 2001). Both human-induced impacts and predicted climatic changes may result in a substantial and irreversible degradation in the Arctic ecosystem (ACIA 2005; Johnsen et al. 2005).

Permafrost is defined as soil or bedrock layer which has temperature below 0° for at least two consecutive years (Harris et al. 1988). Soils underlaid by permafrost are widely distributed in Russian Siberia (Goryachkin and Targulian 1990). Approximately 60% of Russian territory is covered by permafrost-affected soils (Murton 2018). Permafrost has an important effect on the physical and chemical processes of soil functioning in changing environments (Catt 2005). Permafrost-affected soils have the great amounts of stored organic matter (Tarnocai et al. 2009). Zubrzycki et al. (2013) reported that the average soil organic carbon stock of upper 1-m soils of the Holocene terrace in the Lena River delta (East Russian Siberia) was estimated to be 29 kg $m^{-2} \pm 10$ kg m^{-2}. Organic matter can bind the majority of trace metals by forming organo-mineral associations (Davranche et al. 2011; Dube et al. 2001; Hofle et al. 2013). However, Permafrost thaw caused by climatic changing is related to increases of active layer thickness, which may result in mobilization of soil organic matter (Desyatkin and

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Desyatkin 2006). This may lead to intensify biogeochemical cycling within the large amount of carbon involving bound trace metals in upper layers of permafrost-affected soils.

In Russia, the Ural Mountains keep numerous minerals. The most northern mining factory of chromite in the world is located in the polar Urals (Yamal region) (Perevozchikov et al. 2005). Besides, the extraction industries of oil and gas are active in this region, including Yamal and Gydan Peninsula and on the shelf of Kara Sea. However, the data with respect to soil contaminations in Russian Arctic is limited. Soils polluted by metals were observed (Pb, Zn, Ba, and Sr) in well drilling on the Yamal Peninsula (Moskovchenko 1998). Pollution of Ba, Mn, Zn, Co, Ni, Pb, Cr, and V were identified in the bottom sediments from oil extraction areas of Russian Arctic (Opekunov 2008). The anthropogenic sources of trace metals reported in Russian Arctic were Norilsk industry area in western Siberia and nickel mining industries in the Kola Peninsula (town of Monchegorsk and Zapolyrny) (Boyd et al. 2009; Jaffe et al. 1995; Niskavaara et al. 1997; Reimann et al. 1997, 1999; Zhulidov et al. 2011). These industrial activities caused sustaining contamination in the Arctic ecosystem across several 100 km (Zhulidov et al. 2011). Therefore, soils in Yamal region play an important role of stabilizing the pollutants resulting from exploration and mining activities. The Arctic ecosystem is highly vulnerable to contamination relevant to the oil and gas industries.

Trace metals are naturally appearing in soils and parent rocks, which are present in the form of oxides, sulfides, carbonates, and silicates (Antcibor et al. 2014). Conversely, trace metals are considered as a main group of anthropogenic pollutants in soils. The problems of west Siberian Arctic environments are currently significantly related with the exploration of oil and gas fields. Yamal region is one of the most actively developing areas in Russian Arctic. The new settlements in this area are exposed by enhancing pollution risk of trace metals. However, the knowledge of the background concentration of the major trace metals is lacked for environmental decision makers in this region. The problem of environmental management and restoration has sharply risen in Yamal, Taz, and southeast Gydan Peninsula (Koptseva and Sumina 2001; Rebristaya and Khitun 1997). Therefore, it is urgently needed to calculate the contamination indexes and evaluation of contamination levels. The objectives of present study are (1) to assess the background volumetric concentrations in selected benchmark soils in Yamal region, and (2) to investigate the geochemical status of Yamal soils.

Materials and Methods

Study Area

Soil investigations were conducted in Yamal-Nenets Autonomous district, which includes two study areas (Fig. 1): the northern Trans-Urals and Gydan Peninsula. The wind direction and speed of these two areas are given in Table 1.

The area of northern Trans-Urals is situated in vicinity to the eastern foothills of the Polar Urals, which belongs to the Sub-Arctic climatic zone. Terraced lowlands are dominant landscapes, which represent Ob' River-southern Yamal

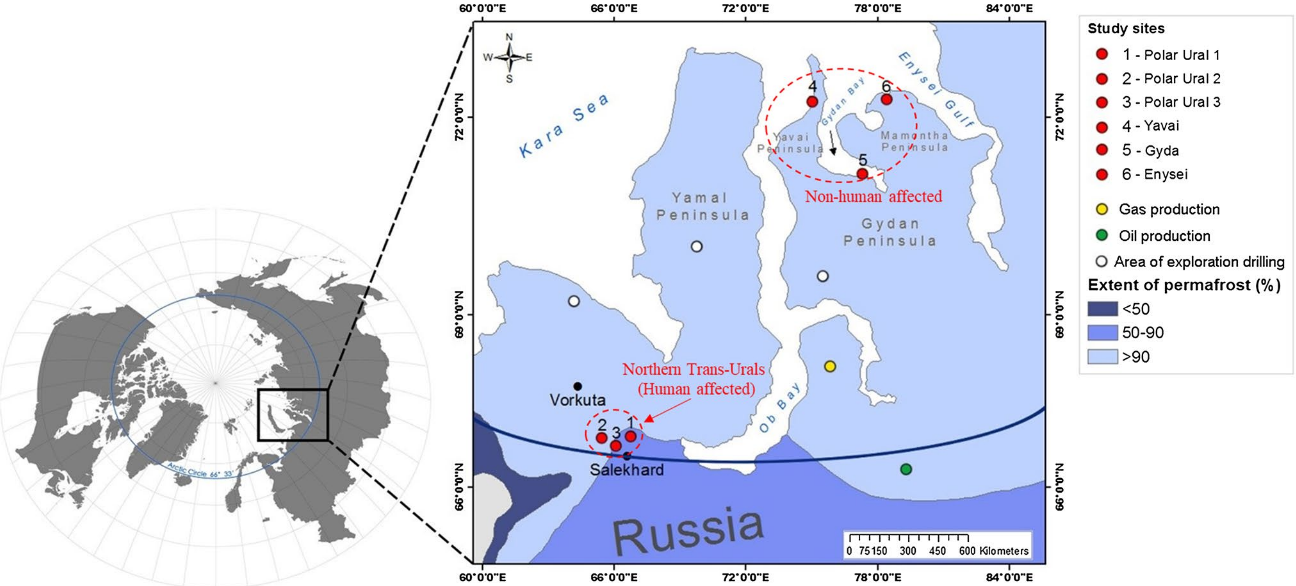

Fig. 1 The locations of investigated sites (studied soil benchmark plots)

Table 1 The average wind direction relative to the cardinal directions

	Weed speed (m/s)	Wind direction
Jan	3.84	180
Feb	3.95	205
Mar	4.07	215
Apr	4.04	228
May	3.89	242
Jun	3.87	264
Jul	3.82	275
Aug	3.87	286
Sept	4.05	284
Oct	3.85	278
Nov	3.85	270
Dec	3.87	259
Annually average	3.91	248

flat depression plains, foothill (so-called small Ural ridge), and low mountains composing of metamorphic and effusive rocks. According to the meteorological station in Salekhard, the annual air temperature and precipitation on average is – .4 °C and 450 mm, respectively. The parent rocks in this region originate from Quaternary deposits comprising marine and glacial-marine sediments of late Pleistocene. Watersheds of the study are mainly characterized by shrub, dwarf willow-shrub, and lichen-moss hummocky tundra.

Gydan Peninsula is located between the Ob' River and Enysei Gulf and extends into the Kara Sea. This area belongs to the Arctic climatic zone with the average annual air temperature and precipitation of – 10.9 °C and 250–300 mm, respectively. The northern coast of Gydan Peninsula has two subpeninsulas divided by the Gydan Bay (Fig. 1): Yavai Peninsula and Mamontha Peninsula. This area is predominant by flat relief. Soils of Gydan Peninsula were developed on the Pleistocene sands underlaid by deposited marine clays and alluvial sediments during the late Quaternary period. Grass, moss, and lichen are the dominant vegetation in this region. Shrubs are also sparsely distributed.

Soil Sampling

The soil profiles were investigated during the summer field expeditions in July, 2016–2017. The sampling sites of Trans-Ural area (Polar Ural 1, 2, and 3) were selected to evaluate the benchmark concentration of trace metals in soils adjacent to the urban areas. PU1 (Polar Ural 1) is an alluvial terrace located on the bank of the Ob's River, which is nearby the rail road. PU2 is located on the bank of Ob's River, which is in vicinity to the city Labytnangi. PU3 is a lake terrace close to the city Salekhard. Conversely, sampling sites of Gydan Peninsula were designed to characterize metals' concentrations in well-developed soils in different latitudes, which are far from human activities. Sampling sites in Gydan Peninsula were located in the coastline, including in Yavai (Yavai Peninsula), Gyda (interior of Gydan Bay), and Enysei (close to Enysei Gulf in Mamontha Peninsula).

Soil samples were taken from each genetic horizon in the thawing layer for total six soil profiles and stored in polyethylene bags covered with aluminum foil. All samples were dried at room temperature (around 24 °C) in a laboratory fuming cupboard (St. Petersburg State University, Russia). Once the weights of soil samples were stable (± 0.001 g), the soils were sieved through a 2-mm mesh screen (plant roots and coarse rocks were removed). Afterwards, sieved samples were kept in the refrigerator (– 15 °C) before the extraction. All soil types were determined by World Reference Base for Soil Resources (WRB 2015). The general information of landscapes, soil physicochemical properties and qualitative data is shown in Table 2.

Chemical Analysis

Pretreatment

Trace metals were extracted with 65% v/v HNO_3. For organic soils, 500 mg of sample was weighed and extracted with 5 mL of 65% v/v HNO_3. For mineral soils, 300 mg of sample was extracted with 10 mL of 65% v/v HNO_3. The extraction was conducted in hermetically closed Teflon vessels. Pre-extraction of samples lasted for 5 h at room temperature, followed by 5 h at 80 °C in microwave (Mars Xpress, CEM GmbH, Kamp-Lintfort, Germany). As soon as the samples cooled down, the solutions were filtered and diluted to 25 mL with deionized water and transferred to a 15 mL of polypropylene vial. The extracts were kept at – 15 °C before Atomic absorption spectroscopy (AAS) analysis. Triplicates from each soil sample were analyzed separately. Three blanks (Metals & Cyanide Blank Soil, Waters ERA, Golden, CO), which contains only iron and aluminum were run parallel to extraction procedures of organic and mineral soils, respectively.

Atomic Absorption Spectrometry

The contents of cadmium (Cd), lead (Pb), zinc (Zn), manganese (Mn), iron (Fe), arsenic (As), and cobalt (Co) were analyzed by graphite furnace AAS (SpectrAA 220G, Varian, Palo Alto, CA). Reagent blank values were used for collecting the results. Soil certified reference material SQC-001 (Sigma-Aldrich, Saint Louis, MO) was used to check stability of instrument. The relative standard deviation of all detected metals was less than 10%. The measured metal composition of the reference soil material was compared with the corresponding standard values for the accuracy of the method. The accuracy for method is < 10% for Cd, Pb,

Table 2 The general information of landscapes, soil physicochemical properties, and qualitative data in investigation sites

	GPS coordinates	Landscape description	Soil type	Soil horizon	Depth (cm)	Munsell color	pH-H_2O	pH-KCl	$C_{organic}$ (%)	N_{total} (%)	C/N ratio	Basal respiration (mg CO_2 100 g^{-1} 24 h^{-1})	Texture class
Northern Trans-Urals area													
PU1	66° 89.552′N 66° 72.777′E	Hummock tundra	Turbic Cryosols	O_i	3–7	2.5 YR 3/3	4.22	3.55	4.22	0.46	24.5	29.8	Silty loam
				O_e	7–41	2.5 YR 3/2	6.47	5.21	6.47	0.12	14.4	83.2	Silty loam
				CR_s	41–56	5 YR 8/1	6.95	5.81	6.95	0.08	11.0	83.6	Silty loam
PU2	66° 86.075′N 65° 45.322′E	Shrub/carex/moss tundra	Subaquatic Cryosols	O_i	4–12	2.5 YR 3/4	6.20	5.21	15.60	0.98	15.9	65.5	ND
				CR_s	12–29	5 YR 8/1	7.53	6.42	0.64	0.05	11.9	82.8	Sandy loam
				C_g	29–46	5 YR 8/1	7.47	6.50	0.98	0.09	10.1	97.1	Clay loam
				C	46–63	7.5 YR 2/1	7.40	6.41	0.44	0.06	7.36	84.9	Silty clay
PU3	66° 72.138′N 66° 08.378′E	Shrub/carex/moss/lichen tundra	Fibric Histosols	O_i	0–3	2.5 YR 2.5/1	3.23	2.45	36.9	0.88	4.21	84.5	Silty loam
				O_e	3–12	2.5 YR 2.5/1	3.93	3.13	44.1	0.91	48.5	362.0	Silty loam
				O_a	12–23	2.5 YR 3/1	4.35	3.37	32.3	1.66	19.4	82.9	Sandy loam
				C_g	23–27	2.5 YR 8/3	4.91	3.75	1.58	0.07	23.0	84.5	Sand
Gydan Peninsula													
Yavai	72° 21.753′N 75° 05.016′E	Shrub/moss/lichen tundra	Turbic Cryosols	O_i	0–10	10.5 YR 6/3	6.07	5.92	4.29	0.27	15.9	38.8	Sandy loam
				CR	10–20	5 Y 5/1	7.82	7.13	0.90	0.09	10.0	33.6	Loam
				CR	20–30	5 Y 5/1	7.89	7.09	1.29	0.11	11.7	27.2	Loam
				CR	30–55	5 Y 5/1	7.59	6.85	2.32	0.11	21.1	22.2	Loam
				CR_s	55–70	5 YR 8/1	7.30	7.21	2.61	0.13	20.1	15.4	Loam
				C_g	70–83	5 YR 8/1	6.33	6.12	1.88	0.11	17.1	38.9	Loam
				C_f	>83	7.5 YR 2/1	7.51	6.69	2.19	0.11	19.9	41.5	ND
Gyda	71° 18.812′N 77° 33.245′E	Moss/lichen tundra	Oxyaquic Cryosols	O_i	0–7	10 YR 6/4	5.73	4.53	24.5	1.86	13.2	66.0	ND
				C_g	7–25	10 YR 6/4	6.46	4.14	1.24	0.10	12.4	30.2	Loam
				CR_g	20–40	10 YR 5	6.45	5.53	1.08	0.09	12.0	35.1	Loam
				C_g	40–60	5 YR 2/2	7.48	ND	0.92	0.09	10.2	33.9	Loam
				C_f	60–65	5YR 2/2	7.37	ND	0.96	0.1	9.60	42.7	Clay loam
Enysei	72° 22.451N 78° 38.586E	Lichen/moss tundra	Histic Cryosols	O_i	0–6	10 YR 6/4	5.70	4.82	11.1	0.79	14.1	35.6	ND
				C_s	6–9	5 YR 8/1	5.22	3.55	2.19	0.13	16.9	26.4	Loam
				C_g	9–18	7.5 YR 4/3	5.70	4.11	2.19	0.14	15.6	33.9	Loam
				C_s	18–35	5 YR 8/1	6.46	4.22	2.61	0.17	15.4	49.0	Clay loam
				C_{gh}	35–40	7.5 YR 4/2	5.38	4.30	3.24	0.22	14.7	52.1	Clay loam
				C_f	> 40	7.5 YR 4/3	5.54	4.62	2.71	0.19	14.3	32.5	ND

ND not determined. Main horizon: O organic matter; *A* surface layer; *C* parent rock; *R* the layer of partially weathered bedrock. Suffixes of a horizon: *i* slightly decomposed organic matter; *e* organic material of intermediate decomposition; *a* highly decomposed organic material; *s* sesquioxide accumulation (Al_2O_3 and Fe_2O_3); *g* strong gleying in which iron has been reduced and removed during soil formation or in which iron has been preserved in a reduced state because of saturation with stagnant water; *h* accumulation of organic matter; *f* permafrost

Zn, Mn, and As and 10–15% for Co and Fe. The recoveries of all measured metals were ranged between 83 and 94%. The detection limits of the machine for measured metals were in range of 0.03 to 0.1 mg kg^{-1}.

Soil Physicochemical Parameters

For determining soil pH, 1 g of organic soil and 8 g of mineral soil were taken, respectively. The pH of soil samples was potentiometrically determined with a pH meter (Ekotest-2000, Moscow, Russia) in the supernatant suspension of a 1:2.5 soil:liquid mixture. The liquid is a 1 M KCl solution (unbuffered). The total carbon content (TOC) and total nitrogen (TN) were measured by C/N analyzer (vario MAX CNS Element Analyzer, Elementar, Germany).

Basal respiration were determined by the method of Anderson and Ineson (1982). Five grams of fresh soil were adjusted to a moisture content (60% of the water-holding capacity) and were incubated at 25 °C in the sealed plastic bottles with 1 M of NaOH in duplicate. The amount of CO_2 trapped in the alkaline solution was measured by titration after 7 days incubation.

Data Processing

Boxplot was performed with SPSS package version 21.0 (IBM, Armonk, NY). Bar chart was generated by GraphPad Prism 5.0 software (San Diego, CA). Before plotting, the concentrations of metals were long-transformed due to the data were strongly left-skewed for most of the metals. Spearman correlation coefficient ($p < 0.05$) was used for statistical association between metal concentrations and soil physiochemical properties by SPSS 21.0.

Geoaccumulation index (I_{geo}) was used to understand present environmental status and pollution status of trace metal regarding natural background values (Muller 1969). The calculation is according to the following equation:

$$I_{geo} = \log_2 \left[\frac{C_m}{1.5B_m} \right]$$

C_m represents the detected concentration of the metal. B_m is geochemistry background value of the metal, which was taken from the background values of the topsoil from Russian Siberia by Abakumov et al. (2017). For the background value of Co and As, the values of the crust of earth were taken (Meharg 2011). The constant 1.5 is used to minimize possible variations due to lithogenic variations (Taylor and McLennan 1995). Seven grades of soil pollution levels are shown Table 3.

One-way ANOVA was applied to evaluate the significant different in metal concentrations in the two investigated sites using Duncan's post hoc test. Rotated component matrix was applied to possible sources of metals in the same sampling sites. Analysis was conducted by IBM SPSS 25 for windows.

Table 3 Seven grades of geoaccumulation index (I_{geo}) for soil pollution levels

Grade I_{geo}	Pollution level
1 (< 1)	Unpolluted
2	Slightly polluted
3	Moderately polluted
4	Moderately to highly polluted
5	Highly polluted
6	Highly to extremely polluted
7 (> 7)	Extremely polluted

Results and Discussion

Soil Diagnostics and Physicochemical Characteristics

Soils of the Northern Trans-Ural area were classified as Turbic Cryosols (PU1), Subaquatic Cryosols (PU2), and Fibric Cryosols (PU3). The soil diversity in the permafrost region is directly related to the forms of relief. Turbic Cryosols are typical for the cryogenic hummock tundra with the processes of cryoturbation. Subaquatic Cryosols were observed on the over-moist gentle slope and Fibric Histosols were formed under low-center polygon of alluvial terrace.

In Gydan Peninsula, soil groups were qualified as Cryosols. The soil profile (Yavai) located in Yavai Peninsula (northern Gydan Peninsula) was describe as Turbic Cryosols. Turbic Cryosols are typical for relatively drained landscapes of Yavai watersheds. It consisted of an upper histic horizon (raw humus with some cryogenic cracks) and a homogeneous mineral soil layer. The depth of active layer (thawing depth) is approximately 80 m. Gleying condition was observed at the bottom of the soil profile along the mineral layer, which was close to the permafrost table. Soil profile of Gydan Bay (Gyda) was described as Oxyaquic Cryosols with an upper gleyic horizon and a ground ice horizon. The surrounding landscapes were predominantly flat and moist. The permafrost table was approximately 90-cm deep. The soil profile of the Enysei Gulf (Enysei) was classified as Histic Cryosols with two gleyic horizons. The landscapes were flat without differentiations in relief and highly moist. The depth of permafrost table reached 45 cm.

All investigated soils showed heterogeneous vertical profiles, which can result in variable concentrations of trace metals. Turbic or gleyic properties can affect vertical distribution of soil chemical properties.

Soil Physicochemical Characteristics

In Northern Trans-Ural area, PU1 showed a silty loam texture. PU2 showed a heterogenous texture within depth, which is due to cryogenic processes. PU3 showed a sandy texture of the suprapermafrost layer. The soil textures of Gydan Peninsula varied from sandy loam to clay loam. This is due to the presence of relatively homogenous loamy sediments in the northern part of this peninsula. All top organic layers and deeper gleyic-histic layers of the investigated soil profiles were acidic in reaction. The middle horizons of soil profiles showed alkaline in reaction. Soils from the Polar Ural plot showed the sharply decreasing content of organic matter within depth. The highest contents were fixed for superficial organic horizons (O_i, O_e, and O_a) in line with the previous data for Yamal region (Alekseev et al. 2016).

Soils in Yamal region were characterized by relatively high content of nitrogen (0.05–1.86%) for western Siberian soils (0.12–0.38%) (Antcibor et al. 2014), which is in accordance with the published data in this region (Abakumov et al. 2017; Ejarque and Abakumov 2016; Moskovchenko et al. 2017). The highest C/N ratios were observed in histic horizon and the lowest ones were for mineral and organo-mineral horizons. The highest variability of C/N ratios within the soil profiles was fond in Turbic Cryosols due to not the homogenous profile. The values of basal respiration were medium for all soils except for the organic layer (3–12 cm) of PU3 soil pit with a very high CO_2 emission (362.0 mg CO_2 100 g^{-1} 24 h^{-1}) can be related to the increasing content of organic matter (Abakumov and Mukhametova 2014). Generally, the data of basal respiration suggested normal biological activity of soils for undisturbed soils (Ejarque and Abakumov 2016).

Distribution and Levels of Trace Metals in Investigated Soils

Results for mean concentrations of trace metals at all investigated sites are summarized in Table 4. All investigated sites showed the similar order of metals' concentrations: Fe > Mn > Zn > Co (Co > Zn for Gaya and Enysei) > Pb > As (As > Pb for PU1) > Cd. The high variation of metals was showed in Gydan Peninsula with exceptional values in some soil layers (Fig. 2). In soil profile of Yavai, the significant higher concentrations of Fe, Zn, Pb, and As were observed in O horizon. This may be due to organic matter appears to have a significant influence on the formation of Fe oxides, and Zn can be easily adsorbed by organic components (Meharg 2011). Besides, despite As minerals and compounds are readily soluble, migration of As is very limited due to the strong sorption by organic matters. In Gyda, the higher concentrations of Fe and Zn were found in C horizon with condition of stagnant water, and lower concentrations of Zn and As were found in O horizon. While Pb and As were found to be lower in O horizon in Enysei. This can be explained by the upper materials, which were transported to the freezing front through convective water and accumulated in subsurface horizon.

In depth of soil profiles, the surface was enriched by Cd and Co in PU1, PU2, and Gyda (Fig. 3). Soil profiles in Gydan Peninsula revealed the slightly higher concentrations of majority of trace metals in gleyic layer above the permafrost table. The similar trends of trace metals' distribution were reported for permafrost-affected soils in Russian tundra in Lena River Delta (Antcibor et al. 2014) and Yenisei River delta (Fiedler et al. 2004; Korobova et al. 2003). The mean concentrations of Cd and Pb in Trans-Ural area were slightly higher than those in Gydan Peninsula (Fig. 4). One of reason may be wind influences blown from anthropogenic activities in urban region.

In comparison of our results with references reported for other Siberian areas (Table 4) showed the levels of Mn, Fe, and Co were significantly higher those in other Siberian areas. The levels of Pb and Cd in Gydan Peninsula were comparable to those in Lena River Delta. Both sites were far from the human activities, which reflects the air long-range transport or geology background. Pb and Cd concentrations in Urals area were slightly higher than those in Lena River Delta and other natural sites of Yamal regions. Notably higher concentrations of Pb, Cd, and Zn in Western Siberian than our results were due to sampling sites close to the industrial areas (Zhulidov et al. 1997a, b, 2011). The levels of As in Gydan Peninsula were comparable to our results in Gydan Peninsula, while slightly higher concentrations of As in Urals area. However, these values are still in the range of background As concentrations (0.07–0.35 mg kg^{-1}) in permafrost regions of former Soviet Union (Rovinskiy et al. 1979).

The concentrations of metals revealed different accumulation in organic and mineral layer from Urals area and Gydan Peninsula (Fig. 5). In Northern Trans-Urals area, there is no much differences of Zn in organic and mineral layers. However, obvious pattern can be seen that more Pb and Cd accumulated in organic layers, whereas Mn, Fe, As, and Co showed more accumulations in mineral layers. In Gydan Peninsula, only site Yavai appeared to be more contents of Pb in organic layer than that in mineral layer. However, all other sites showed more Pb, Mn, Fe, and Co in mineral layer. The levels of Zn and Cd were relatively equal in organic and mineral layer. While more contents of As in organic layer were only found in Yavai (Table 5).

In case of significant changes occurred in investigated soils, the significance of metal concentrations in Northern Trans-Urals area and Gydan Peninsula was separately analyzed (Table 6). The results showed most metals did not show a difference in the same region, except that Pb and Zn

Table 4 Mean concentrations of the trace metals (mg kg^{-1}) in each soil horizon in all investigated soil profiles

	Soil horizon	Depth (cm)	Cd	Pb	Zn	Mn	Fe	As	Co
Northern Trans-Urals area									
PU1	O_i	3–7	0.12	3.79	57.37	364.29	23266.64	4.62	19.28
	O_e	7–41	0.05	3.53	45.87	670.93	31059.30	7.38	24.87
	CR_s	41–56	0.06	5.82	50.70	647.18	29385.38	6.79	27.24
PU2	O_i	4–12	0.68	13.94	87.46	684.26	14272.91	2.30	33.86
	CR_s	12–29	0.36	8.39	77.75	1002.18	36725.18	5.86	61.99
	C_g	29–46	0.07	27.58	46.54	876.30	53747.01	4.90	81.38
	C	46–63	0.06	7.20	59.44	1286.05	52956.81	8.24	67.11
PU3	O_i	0–3	0.18	8.70	56.42	578.22	6862.38	1.75	22.77
	O_e	3–12	0.43	33.83	65.39	170.14	9017.21	3.80	26.02
	O_a	12–23	0.13	18.95	24.09	62.24	10551.27	3.89	80.02
	C_g	23–27	0.07	14.85	92.45	550.15	65173.78	18.20	51.64
Gydan Peninsula									
Yavai	O_i	0–10	0.07	14.85	92.45	550.15	65173.78	18.20	51.64
	CR	10–20	0.08	7.53	45.09	327.67	18820.56	2.82	54.83
	CR	20–30	0.09	7.55	46.82	329.17	20643.86	3.33	48.88
	CR	30–55	0.10	7.30	43.93	473.14	18988.57	2.60	30.52
	CR_s	55–70	0.11	7.88	49.65	393.62	20277.71	3.08	58.71
	C_g	70–83	0.12	7.40	47.10	541.73	20628.86	4.46	43.47
	C	> 83	0.09	6.81	43.45	236.83	16836.66	2.36	41.19
Gyda	O_i	0–7	0.12	5.96	31.06	1810.36	18100.12	3.18	74.01
	C_g	7–25	0.08	7.90	38.11	583.44	21212.44	5.35	42.10
	CR_g	20–40	0.09	13.31	40.42	337.50	18675.91	4.53	37.43
	C_g	40–60	0.10	7.97	45.61	382.92	17544.45	5.01	57.94
	C_f	60–65	0.09	16.93	40.78	394.54	16279.77	5.03	62.86
Enysei	O_i	0–6	0.10	4.14	36.43	1038.96	21075.09	0.74	80.42
	C_s	6–9	0.06	6.60	35.73	231.39	29789.52	3.02	40.13
	C_g	9–18	0.09	6.69	38.36	627.88	27315.65	2.65	49.09
	C_s	18–35	0.09	6.61	39.31	497.00	26847.40	2.34	45.70
	C_{gh}	35–40	0.12	6.60	42.72	388.03	23145.54	2.28	57.04
	C_f	> 40	0.11	6.26	40.37	441.00	21545.01	1.82	58.13

show the significant differences ($p < 0.05$) for Urals areas and Gydan Peninsula, respectively. This differences for Pb in Urals areas can result from the heterogeneous profiles of the soils where PU2 has an obvious influence of parent materials by cryoturbation and followed by a gleying horizon that is capable of retention of metals, which was observed by Antcibor et al. (2014). Besides, PU3 has relatively thicker organic horizon where the highest concentration in middle layer of organic horizons, which may be due to the mean residence time in the organic horizon (Klaminder et al. 2006), e.g., deposited Pb decreased to the $1/e$ (ca. 37%) of its initial magnitude through biochemical and physical process (50–150 years in forest areas) (Kaste et al. 2003). However, boreal areas of cold climate and coniferous tree species favors O-horizon development with acid humus having low biological activities and slow mineralization rate (Klaminder et al. 2006). Therefore, we speculated Pb in organic layer could be mostly affected by eluviation, which caused this difference in Urals sampling sites. In Gydan Peninsula, only Zn showed the great difference, which may result from different condition CR horizons with limited organic layer. A factor analysis was conducted to reveal similarities among the metals that would indicate common sources. In Urals area (Fig. 6a), F1 (Mn, Fe, As) accounted for 45% of variance explained, which most likely reflect the mineral soil and bedrock. F2 (Cd, Zn, and Mn) is dominated by Zn and Mn and may reflect a deposition of long-distance atmospheric transport (Halbach et al. 2017), which is same to F3 (Cd, Pb, and Co). Compared with Gydan Peninsula without direct anthropogenic influences (Fig. 6b), Fe, Zn, As and Pb more reflects on natural geology background while Cd and Co may be transported by air and deposited in Mn-rich soil. These results may suggest Pb, Cd, and Co were likely to be originated from air long-distance transport from human-induced areas and accumulated in surficial organic layers of soils. Besides, Site Yavai may be more influenced by

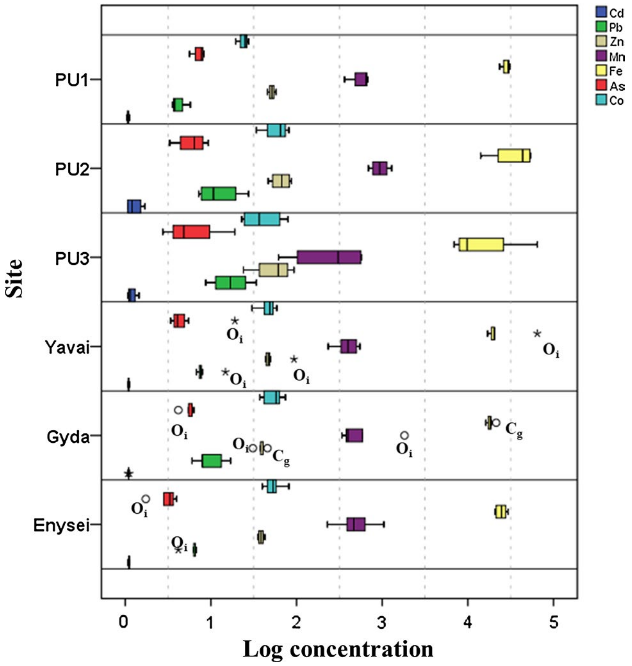

Fig. 2 Log-boxplot comparison of concentrations and variations of 7 trace metals in the soil profiles of investigated sites. Note that the soil horizons are added for exceptional values

atmospheric deposition than Gada and Enysei sites, because Yavai is closer to industrial areas in Yamal region.

Pollution Status of Trace Metals in Investigated Soils

The comparison of our results with threshold limit values (TLV) defined by Russian Siberian legislation for topsoil horizons (0–10 cm), Fe was only the metal which was three magnitude higher than values of the TLV in all sites (Fig. 7). However, Fe can be immobilized from the fine earth due to redoximorphic, gleying, and stagnic processes. Therefore, the majority of tundra and peatland soils usually showed pronouncedly exceeding Fe concentrations of value of MLV (Abakumov et al. 2017; Antcibor et al. 2014; Moskovchenko et al. 2017; Rovinsky et al. 1995; Salminen et al. 2004, 2011). The contents of Cd were lower than TLV (0.5 mg kg^{-1}) in all investigated sites expect for PU2 where the accumulation of Cd was observed in superficial soil layers. The concentrations of Hg were below the TLV (32 mg kg^{-1}) in all sites. However, the strikingly higher concentration of Hg (33.83 mg kg^{-1}) in the Histic layer below the superficial organic layer was found in PU3. This result for tundra

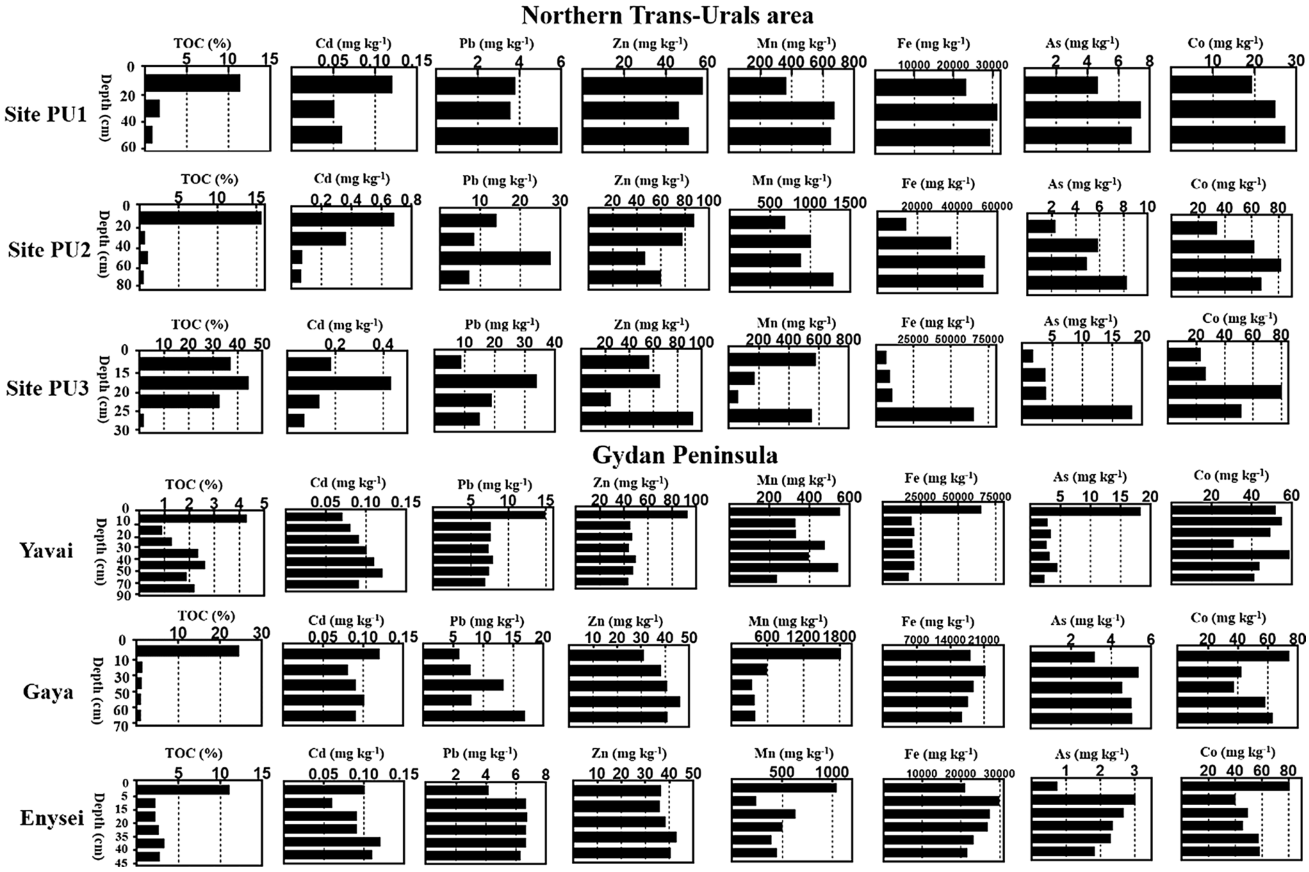

Fig. 3 Vertical distribution of concentrations (mg kg^{-1}) of 7 trace metals in the soil profiles of investigated sites

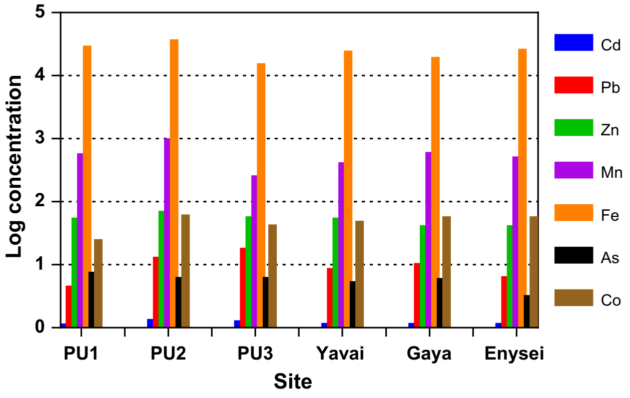

Fig. 4 Bar plot comparison of log-transformed mean concentrations (mg kg^{-1}) for 7 trace meals in each investigated sites

Histosols was also reported in the Siberian region (Alekseev et al. 2016; Moskovchenko 2013). The contents of Zn were higher than that of the TLV (55 mg kg^{-1}) in superficial soils in all Polar Urals, whereas the value Zn in Yavai also exceeded the TLV. Moskovchenko (2013) reported that the mean concentrations of soils in northern and central part of Yamal region varied from 25 to 47 mg kg^{-1}, and the increasing concentrations of Zn were only found in Novy Urengoy and were influenced by anthropogenic activities. However, Polar Urals are also close to anthropogenic activities of urban areas, which may be the source of Zn contents in Gydan Peninsula. The contents of As were more than that of the TLV in the majority of sites, which was same trend for Co.

According to I_{geo} values, Pb was considered as unpolluted in all sites (Table 7). In Polar Ural area, Cd was found to be slightly polluted in PU2, and Zn was slightly to moderately polluted (1.50 for PU1, 2.11 for PU2, and 1.48 for PU3). Fe was only considered to be slightly polluted in PU1. In the Gydan Peninsula, Zn and As were considered as moderately polluted while Fe was considered as moderately to highly polluted. Fe and Mn were slightly polluted in Gyda and Enysei. Mn was shown as moderately polluted in Gyda. This indicates these detected metals in both urban and natural areas were not varied significantly. However, data for background concentrations are highly depended on soil characteristics. Therefore, I_{geo} values support data comparing trace metals' contents of the relatively close area for reference.

Correlations of Trace Metal Levels and Soil Properties

The data were not identical to normal distribution by confirmation of Shapiro–Wilk test. Thus, the Spearman correlations between the concentrations of trace metals and some soil properties for mineral horizons were performed (Table 8). The results showed quite different correlations between the Trans-Urals area and Gydan Peninsula. This result did not show the obvious differences caused by anthropogenic activities, instead of different origin of soils and parent materials. However, strong correlations between Pb and Cd (0.63) in Urals area may reflect the deposition from long-distance atmospheric transport. Cd is strongly associated with Zn in its geochemistry in natural soils (Meharg 2011). Correspondingly, Cd has the strong correlation with Zn in

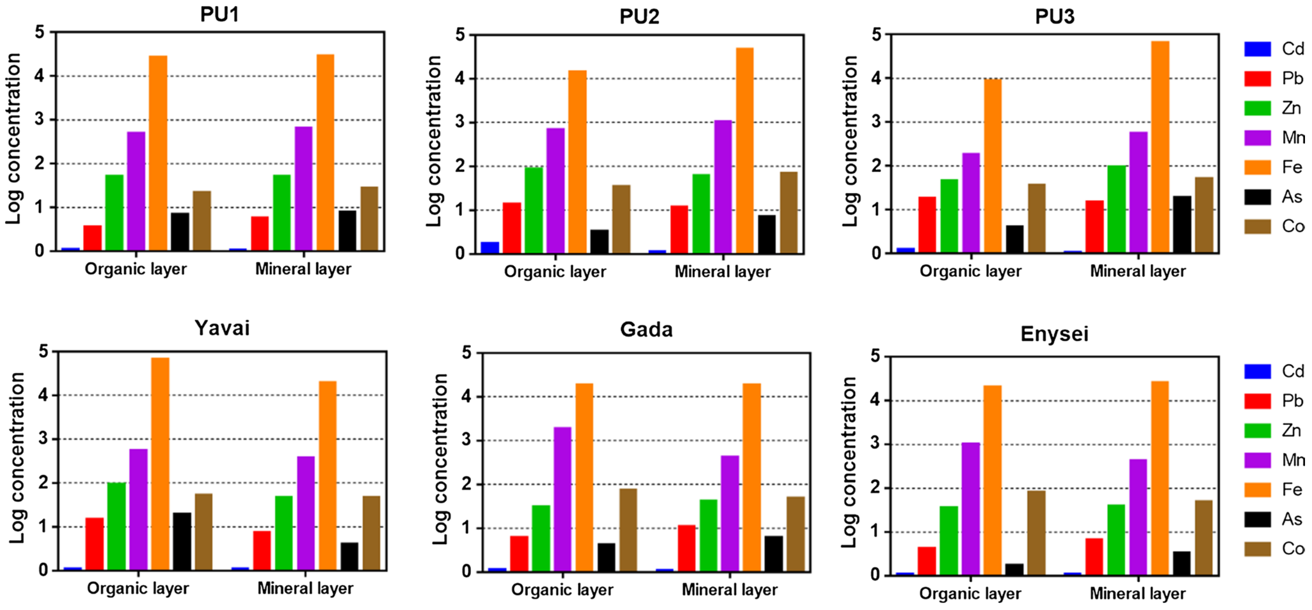

Fig. 5 The distribution of log-transferred concentrations of 7 trace metals in organic and mineral of investigated sites

Table 5 Range (min–max) and median values (denominator) of trace metals concentrations for investigated areas and other reported Siberian areas

Site	Metal (mg kg^{-1})						
	Cd	Pb	Zn	Mn	Fe	As	Co
Present study							
Northern Trans-Urals area	3.53–5.82	3.53–33.83	24.09–92.45	62.24–1286.05	6862.38–65173.78	1.75–18.2	19.28–81.38
	4.38	13.33	60.32	30274.35	30274.35	6.16	45.11
Gydan Peninsula	0.06–0.12	4.14–16.93	31.06–92.45	231.39–1810.36	16279.77–65173.78	0.74–18.2	30.52–80.42
	0.10	9.24	44.30	532.52	23494.49	4.04	51.89
Other reports							
Lena River Delta[a]	0.01–2.40	2.14–31.20	14.40–84.00	23–606	6300–44850	1.29–11.3	10.6–146
	0.046	6.71	52.20	283.66	24043.75	4.42	23.5
Belyi Island[b]	0.08–0.80	0.5–132	9.5–126	119–561	3943–37899	–	0.5–10.3
	2.50		20.9	250	8998		
Yamal Peninsula[c]	–	5.1	17.9	258	–	–	7.5
The lower Lena River Delta area[d]	0.03–0.40	–	6.80–18.9	–	–	0.02–0.78	–
	0.12		13.0			0.22	
North-eastern Siberia[e]	0.05–0.81	1.80–44.0	4.40–137	–	–	–	–
Western Siberia[f]	0.05–64.0	1.50–274	12.0–878	–	–	–	–

The values underlined mean the range of the concentrations, and the values without underline are the average concentration

[a] Antcibor et al. (2014)

[b] Abakumov et al. (2017)

[c] Moskovchenko (2013)

[d] Rovinsky et al. (1995)

[e] Zhulidov et al. (1997a)

[f] Zhulidov et al. (1997b)

background soils of Gydan Peninsula. Pb correlated with Fe and Co in soils of Urals area while Pb correlated with As and pH in soils of Gydan Peninsula, indicating arsenates and arsenites where As is combined with some metals, such as Pb and Fe, and Co and Pb are highly absorbed by Fe oxides (Meharg 2011). Other positive correlations were observed between Zn-C/N, Zn-As, and Co-pH in Urals area; Zn-pH, Fe-TOC, and Fe-TN in Gydan Peninsula. This is interpreted by the solution of these metals in different soil textures.

Table 6 The significance of each metal concentration in Northern Trans-Urals area ($p < 0.05$, p one-way ANOVA)

	Northern Trans-Urals area	Gydan Peninsula
Cd	0.432	0.929
Pb	**0.023**	0.635
Zn	0.679	**0.029**
Mn	0.066	0.868
Fe	0.273	0.344
As	0.898	0.161
Co	0.076	0.507

p value < 0.05 is shown in bold

Conclusions

The concentrations of seven selected trace metals were evaluated for different horizons within depth of permafrost-affected soils from Yamal region, Russian Arctic. Two groups of environments were set for comparison: southern tundra surrounding by cities, Labytnangi and Salekhard (PU1-PU3); and natural river and lacustrine terraces of tundra in northern part of Gaydan Peninsula (Yavai, Gyda, Enysei). The results showed that organic (Histic) horizon appeared to accumulated by majority of metals. Cd and Pb were transported by air transport to surficial organic layers in urban areas while other metals trended to dwell in mineral horizons except that similar levels of Zn in both organic and mineral horizons. In mineral layers, gleying processes and cryogenic mass exchange played an important role to transport metals. However, gleying horizon played a role as geochemical barrier for metals transporting to permafrost.

According to threshold limit values (TLV) of Russian Siberia, the levels of As, Mn, Fe apparently exceeded TLV values. However, this TLV was not decided for natural metals levels of accumulation in semi-hydromorphic soils in polar environment. Comparison with I_{geo} values, polluted values for metals in Gydan Peninsula were different with

Fig. 6 Rotated component matrix for soils in the northern Trans-Urals (**a**) and Gydan Peninsula (**b**)

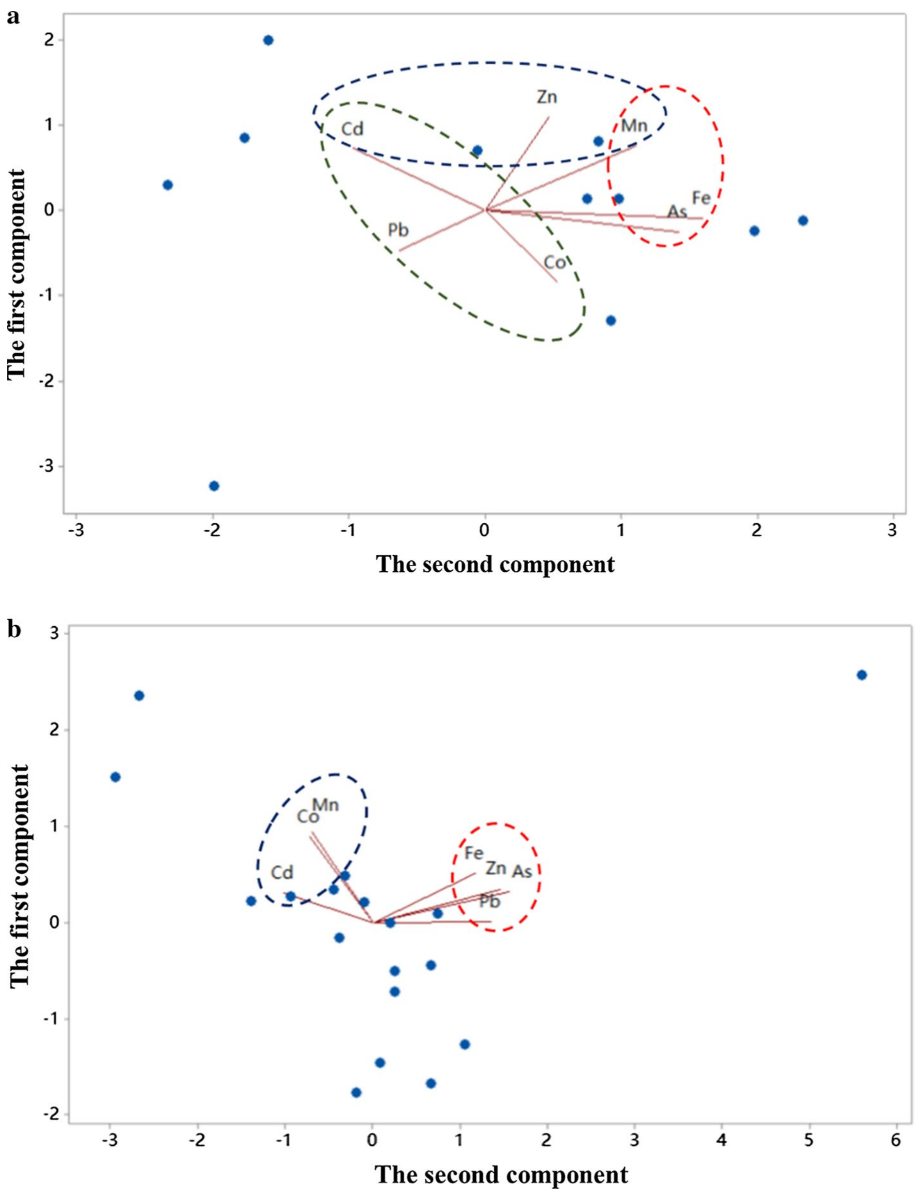

Fig. 7 Comparison between the average concentration of 7 trace metals in topsoil of investigated sites and threshold limit values (TLV) of Siberia Russia for topsoil (0–10 cm)

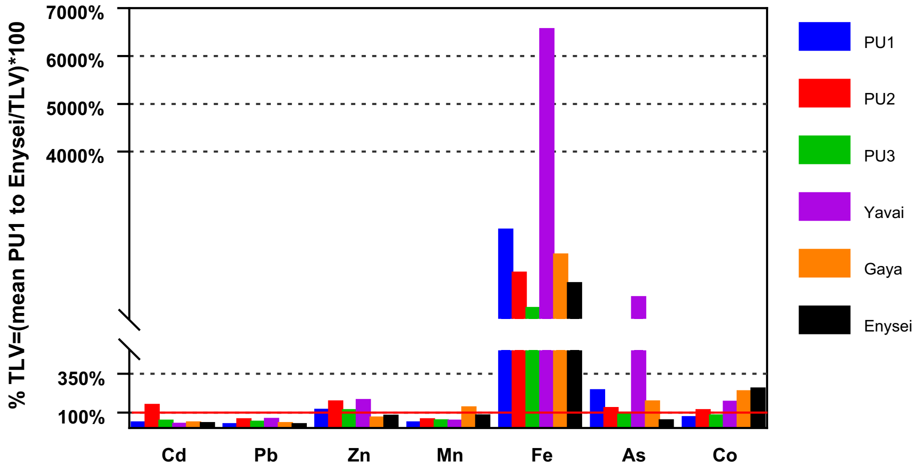

Table 7 Geoaccumulation index (I_{geo}) of 7 trace metals in surface soil samples (0–10 cm) collected from investigated sites

	Cd	Pb	Zn	Mn	Fe	As	Co
Northern Trans-Urals area							
PU1	−0.70	−0.92	*1.50*	−0.31	*1.63*	0.30	−0.96
PU2	*1.80*	0.89	*2.11*	0.60	0.93	−0.71	−0.15
PU3	−0.12	0.21	*1.48*	0.36	−0.13	−1.10	−0.72
Gydan Peninsula							
Yavai	−1.48	0.99	*2.19*	0.29	*3.12*	*2.28*	0.46
Gyda	−0.70	−0.33	0.62	*2.01*	*1.27*	−0.24	0.98
Enysei	−0.96	−0.86	0.85	*1.20*	0.69	−2.34	*1.10*

The values above 1 are given in italic

Table 8 Spearman correlation coefficients between concentrations of 7 trace metals and soil properties in mineral soil horizons of studied soils in the Northern Trans-Urals area and Gydan Peninsula

	Cd	Pb	Zn	Mn	Fe	As	Co	pH	TOC	TN	C/N
Northern Trans-Urals area											
Cd	1	**0.63**	0.36	−0.53	0.26	−0.36	0.21	0	−0.15	−0.31	**0.58**
Pb		1	0	−0.20	**0.80**	−0.30	**0.60**	0.30	−0.10	0.30	0.20
Zn			1	−0.20	0.30	**0.70**	−0.40	−0.70	−0.10	−0.70	**0.70**
Mn				1	−0.30	−0.30	**0.60**	**0.70**	−0.90	−0.50	−0.70
Fe					1	0.30	0.40	0	−0.10	0.20	0.20
As						1	−0.50	−0.70	0.10	−0.30	0.30
Co							1	**0.90**	−0.70	0.10	−0.60
pH								1	−0.60	0.20	−0.80
TOC									1	**0.60**	**0.50**
TN										1	−0.20
C/N											1
Gydan Peninsula											
Cd	1	−0.15	**0.54**	0.31	−0.68	−0.28	0.34	−0.17	**0.50**	0.38	0.31
Pb		1	0.35	−0.02	−0.71	**0.87**	0.12	**0.52**	−0.75	−0.83	−0.47
Zn			1	−0.18	−0.52	0.13	0.27	**0.56**	−0.14	0.25	0.01
Mn				1	0.29	−0.30	0.09	−0.24	0.23	0.26	0.19
Fe					1	−0.41	−0.11	−0.65	**0.57**	**0.73**	0.28
As						1	0.01	0.24	−0.76	−0.75	−0.43
Co							1	0.004	0.02	0.16	−0.41
pH								1	−0.47	−0.58	−0.22
TOC									1	**0.92**	**0.66**
TN										1	**0.50**
C/N											1

The significant correlation $p \geq 0.05$ is given in bold

TOC total organic carbon, *TN* total nitrogen

those in Polar Urals. This suggests different sources of pollution. We suggest the pollution of Gydan Peninsula is prone to local geology while Northern Trans-Urals area is due to the air transport.

Furthermore, the depth of geochemical barriers linked with the permafrost active layer boundary layer will increase due to the climate changing. Degradation of permafrost will release more portions of carbon gases (CO_2 and CH_4), which can sharply change the fate and behavior of trace metals in soils since most metals are bound by organo-mineral associations. Therefore, more plots in different soil types and soil groups in permafrost region need to be investigated for behavior of trace metals and baseline values for different landscapes.

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