Polarforschung 88 (2), 125 – 133, 2018 (erschienen 2019)

Content of trace elements in selected permafrost-affected soils of Yamal region with different functional load

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Abstract: Soils are an important component of polar ecosystems and play a key role in their functioning. They have a significant role in processes of accumulation, mobilization, redistribution of chemical, and especially, trace elements in landscapes and ecosystems. Both anthropogenic factors and climate change may affect biogeochemistry of soils in permafrost-affected landscapes, which are considered as highly sensitive to climate change and anthropogenic forcing. Involvement of additional portions of trace elements into the soils due to permafrost degradation and thawing is considered as one the main risk factors for natural environments in polar regions. Therefore, trace elements contents in soils of urban areas (Kharsaim, Aksarka, Salekhard, Harp and Labytnangi) and natural environments of the Yamal region (Ust'Uribey and Beliy island) were investigated. Soil samples from Kharp settlement show the highest content for Cu, Pb, Zn, Ni, connected with existing galvanizing plant "Kongor-chrome". The highest values for Pb occur in soil samples from Aksarka and Labytnangi key plots. Soil samples from Kharsaim and Kharp key plots are characterized by the highest median values for Zn. Analysis of trace elements content show poorly manifested eluvial-illuvial differentiation of soil profiles of natural soils. The highest content for most of the studied trace elements has been revealed in topsoil horizons. Trace elements content in soil samples collected from urban environments ranged significantly high due to differences in the functional zones of the sites and a predominant anthropogenic source of trace elements additions. The results of statistical analysis show that statistically significant differences in Ni and Cu content in soils appear only between Kharp settlement and each of natural sites Ust'-Uribey and Beliy Island. Almost all studied urban soils reveal significant differences in Pb, Zn, As, and Fe contents between natural sites.

Highlights: Trace-element contents in soils of the Yamal region were studied. The highest contents were recognized in Histic topsoil horizons (natural soils). High sensitivity of ecotoxicological state of studied soils to anthropogenic forcing was found.

Zusammenfassung: Böden stellen eine wichtige Komponente polarer Ökosysteme dar und spielen eine Schlüsselrolle. Deren Funktionsweise ist von großer Bedeutung für Prozesse der Akkumulation, Mobilisierung und Neuverteilung von chemischen und Spurenelementen in Landschaften und Ökosystemen.
Sowohl anthropogene Faktoren als auch Klimaveränderungen können die Biogeochemie von Böden in Permafrost-Gebieten beeinflussen, welche als hochempfindlich gegenüber Klimaveränderungen und anthropogenen Faktoren gelten. Der Einschluss zusätzlicher Anteile von Spurenelementen in den Böden durch Permafrost-Degradation und Auftauprozesse stellen die Hauptrisikofaktoren für die natürliche Umwelt in Polargebieten dar. Aus diesem Grund wurden Spurenelemente in Böden urbaner Gebiete (Kharsaim, Aksarka, Salekhard, Kharp und Labytnangi) und aus natürlicher Umwelt in der Yamal-Region (Ust'Uribey und Beliy Island) untersucht. Bodenproben der Kharp-Siedlung zeigen den höchsten Gehalt an Cu, Pb, Zn, Ni. Dies steht im Zusammenhang mit der bestehenden Galvanisierungsanlage „Kongor-chrome". Die Siedlungen Kharsaim und Kharp sind durch die erhöhte Werte für Pb charakterisiert. Die höchsten Werte für Pb wurden in Bodenproben von den Aksarka- and Labytnangi-Standorten gefunden. Böden der Kharsaim- und Kharp-Standorte sind durch die höchsten Median-Werte für Zn gekennzeichnet. Analysen des Spurenelementgehalts zeigen eine kaum manifestierte eluvial-illuviale Differenzierung der Bodenprofile in natürlichen Böden. Der höchste Gehalt der Mehrzahl der untersuchten Spurenelemente wurde in Mutterboden-/Oberboden-Horizonten nachgewiesen. Der Spurenelementgehalt in Bodenproben aus urbaner Umwelt war deutlich höher auf Grund der Unterschiede der funktionalen Zonen der Standorte und des vorherrschenden anthropogenen Eintrags von Spurenelementen. Die Ergebnisse statistischer Analysen belegen statistisch signifikante Unterschiede hinsichtlich des Ni- und Cu-Gehalts in Böden zwischen der Kharp-Siedlung und jeder der natürlichen Standorte Ust'-Uribey und Beliy Island. Fast alle untersuchten urbanen Böden weisen signifikante Unterschiede im Pb-, Zn-, As- und Fe-Gehalt im Vergleich zu natürlichen Standorten auf.

Hauptbefunde: Der Gehalt an Spurenelementen in Böden der Yamal-Region wurde untersucht. Die höchsten Gehalte wurden in Histosolen in den Mutterboden- und Oberboden-Horizonten (natürliche Böden) gefunden. Daneben wurde ein hohe Sensibilität des ökotoxikologischen Zustands der untersuchten Böden gegenüber anthropogenen Einflüssen nachgewiesen.

Keywords: trace elements; polar environments; soils; permafrost.
Schlüsselwörter: Spurenelemente; polare Umwelt; Böden; Permafrost.

doi:10.2312/polarforschung.88.2.125

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Manuscript received 23. November 2017; accepted 15. October 2018

INTRODUCTION

Soil is a crucial component of geochemical flows and implements the functions of accumulation, redistribution, and transformation of chemical elements (ANTCIBOR et al. 2014; GORYACHKIN et al. 2010; SCHUUR et al. 2015; TARNOCAI et al. 2009; TOMASHUNAS & ABAKUMOV 2014). Permafrost plays a significant role in soil-forming processes in the Arctic region. Pedogenesis, which includes cryogenic mass transfer and supra-permafrost accumulation, determines complicated vertical profile of trace elements (TOMASHUNAS & ABAKUMOV 2014).

Trace elements on the one hand are naturally present in parent materials and soils occurring in the form of sulfides, oxides, silicates, and carbonates. On the other hand, trace elements are considered as a main group of anthropogenic contaminants in soils (ANTCIBOR et al. 2013; MOSKOVCHENKO 2010). Studies conducted earlier, showed that trace elements can reach the Arctic at different paths and are both of anthropogenic and natural origin (AKEREDOLU et al. 1994; BARRIE 1985, 1992; RAHN et al. 1997; ROVINSKY et al. 1995; THOMAS et al. 1992).

Permafrost-affected soils serve as a huge reservoir of carbon and store a great amount of organic matter (TARNOCAI et al. 2009; SCHUUR et al. 2015). Organic matter is capable of forming organo-mineral associations (HÖFLE et al. 2013), and therefore, soil organic matter hence can retain various trace elements by different mechanisms: the ion-exchange, proton displacement, and inner or outer-sphere complex formation (SCHNITZER 1986).

Urban areas can be considered as areas with increased risk in the context of trace elements and will continue to be so for a long time, according to predictions (LINDE 2005). Studying of pollutant behavior in both urban and natural soils seems to be one of the most important issues for investigations in further decades. Such investigations could be used for making accurate risk assessments, concerning such aspects as human health and long-term ecological effects. Approaches to the establishment of limit values and identifying priorities concerning the remediation of contaminated sites could be also developed (LINDE 2005).

The problem for studying the anthropogenic impact on Arctic environments is the presence of quite significant differences in approaches of soil sampling. In this study, we superposed two approaches: The first approach includes collecting the samples only from the depth of 0-20 cm, as established in Russia. The second approach is connected with collecting the samples from all parts of the soil profile. The latter approach seems to be more applicable and relevant (especially to the Arctic region where permafrost factor significantly complicates soil profile distribution of elements).

The objectives of this study are: (1) to investigate trace elements content in soils of both urban and natural environments of Yamal region; (2) to deduce profile trends of distribution trace elements in permafrost-affected soils of Yamal region natural environments in relation to pedogenesis.

MATERIALS AND METHODS

Study sites

This study was conducted in the territory of the Yamal autonomous region within the settlements of Aksarka, Kharsaim, Kharp, Labytnangi, Salekhard as well as within key plots in natural environments on the western and astern parts of Yamal peninsula and the eastern shore of Beliy Island) (Fig. 1). The area of study belongs to the arctic-subarctic climatic zone.

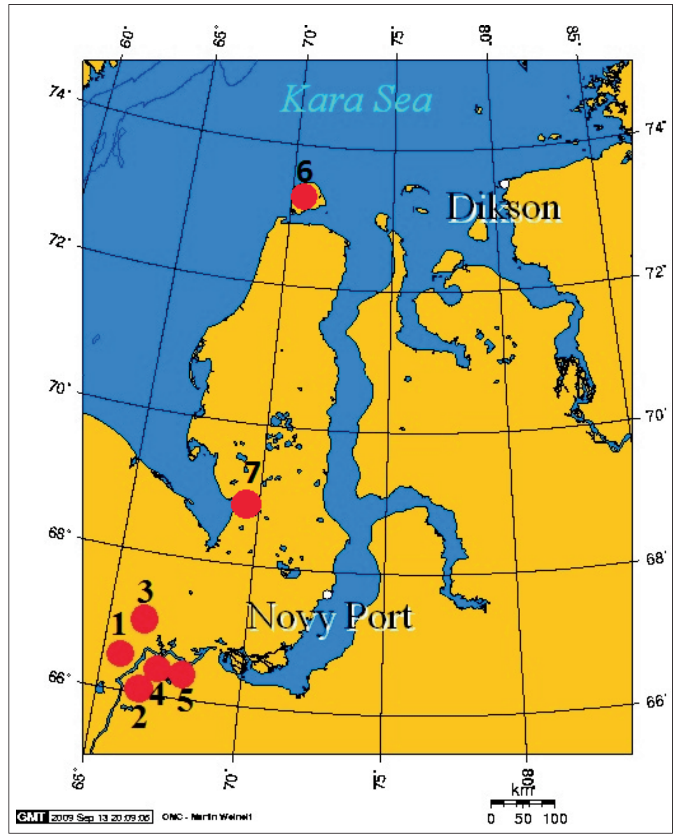

Fig. 1: Map of the study sites. Urban environments: 1 – Kharp, 2 – Salekhard, 3 – Labytnangi, 4 – Aksarka, 5 – Kharsaim. Natural environments: 6 – Beliy island, 7 – Ust'-Uribey.

Abb. 1: Karte der Untersuchungsstandorte. Urbane Umwelt: 1 – Kharp, 2 – Salekhard, 3 – Labytnangi, 4 – Aksarka, 5 – Kharsaim. Natürliche Umwelt: 6 – Beliy island, 7 – Ust'-Uribey.

The climate of southern Yamal is severe and continental. Relative humidity in the entire peninsula is high (70-90 %) throughout the year. It is caused by low air temperatures and proximity to the cold waters of the Kara Sea. Average precipitation varies from 230-270 mm in the northern part of peninsula to about 350-400 mm in the southern part. Small amount of precipitation in the northern part of the peninsula is caused mainly by slight moisture content of arctic air masses (DOBRYNSKY 1995). The annual amount of evaporation is 250 mm. The number of days with snow cover is 233 per year. Winter lasts 7 to 7.5 months, the average temperature of January is -23 to 25 °C. Spring is usually short (35 days) and cold, with a sharp change in weather, with frequent returns of cold and frost. The vegetation season is 70 days. Average temperature of the warmest month is +5°C. The average annual temperature is -5.8 °C. Autumn is short, with a maximal volatility of the pressure gradient, an abrupt change in temperature and frequent early frosts. The site is in a zone of excessive moisture (SHIYATOV & MAZEPA 1995).

The characteristic feature of Beliy Island climate is the predominance of cyclonic type of weather throughout the year, especially during transitional seasons and early winter. The average annual air temperature is -10.6 °C. Winter is cold, lasts about eight months. The average annual temperature is -10.4 °C. The average temperature of February, the coldest month, is -24.2 °C, the average temperature of August, the warmest month, is +5.3 °C. Annual precipitation is 258 mm (SHIYATOV & MAZEPA 1995).

Soil samples have been collected in industrial (Labytnangi, Kharp), residential (Salekhard) and recreational functional zones (Aksarka, Kharsaim) (Table 1). Soil samples in natural environments have been collected from Beliy island and second terrace of Ust'-Uribey River. These environments are not close to the sources of contamination (ports, factories, oil and gas exploration facilities) and weakly affected by functioning of surrounding settlements. So trace elements content in soils from these sites could be assumed as background content.

Methods

Trace elements content has been detected with X-ray fluorescence analyzer "Spectroscan-MAX" according to the methodics (INTERNATIONAL ORGANIZATION FOR STANDARDIZATION 2014). A total of 30 soil samples from selected key plots have been collected. Soil samples were collected from the depth of 0-5 cm and 5-20 cm (in urban conditions) and from all the soil profile (in natural environments). Trace elements content (Cu, Pb, Co, Zn, Ni, As, Cr) has been investigated in selected soil

Key plot	Geographical coordinates	Functional zone/ Landscape description	Name of the soil in WRB (2014) / Russian soil classification system (2008)
Aksarka	N 66°33'54,3" E 67°48r04,8"	Recreational functional zone	Urbic Technosol/ Urbanozem
Kharsaim	N 66°35'54,7" E 67°18'34,2"	Recreational functional zone	Urbic Technosol/ Urbanozem
Salekhard	N 66°33'31,9" E 66°34'07,2"	Residential functional zone	Urbic Technosol/ Urbanozem
Labytnangi	N 66°40'01,1" E 66°20'59,6"	Industrial functional zone	Urbic Technosol/ Technozem
Kharp	N 66°48'34,0" E 65°47'08,0"	Industrial functional zone	Urbic Technosol/ Technozem
Beliy island	N 73°16'15,2" E 71°32'87,2"	Bedrock coast, sedge-moss-lichen tundra	Arenosol/ Stratificated Psammozem
Ustr-Uribey	N 68°53'59,0" E 69°29'15,3"	Second terrace of Ust'-Uribey river, shrub-lichen-moss tundra	Spodic Cryosol/ Podzolised Cryozem

Tab. 1: General field information on studied key plots.

Tab. 1: Allgemeine Informationen über die untersuchten Standorte.

samples. Soil classification and diagnostics was conducted according to "Classification and diagnostics of Russian soils" (Shishov et al. 2004) and IUSS Working Group WRB (2015). Background concentrations of trace elements have been taken from the data obtained for natural soils of Beliy island (Moskovchenko 2010; Tomashunas & Abakumov 2014). For background content of lead it has been taken its clarke content in Earth's crust.

To better clarify the vertical profile distribution of trace elements its volumetric content in topsoil horizons and lower horizons have been calculated and plotted both for urban and natural soils. Volumetric trace elements (Cu, Pb, Co, Zn, Ni, As, Cr) content TMvol (gm^{-2} cm^{-1}) for each soil horizon has been calculated according to the formula:

$$TMvol = C \times BD / d$$

where C is trace element content in soil genetic horizon (mg kg^{-1}), BD is the bulk density and d is the soil genetic horizon depth. Chemical elements content was analyzed at least in triplicate (n=3-6). Calculated mean contents were provided with standard deviations (a ± b). One-way analysis of variance (ANOVA) was carried out in order to identify relationships between obtained data. This method is based on estimation of the significance of averages differences between three or more independent groups of data combined by one feature (factor). The null hypothesis of the averages equality is tested during the analysis suggesting the provisions on the equality or inequality of variances. In case of rejection of the variances, equality hypothesis basic analysis is not applicable. If the variances are equal, F-test Fisher criterion is used for evaluation of intergroup and intragroup variability. If F-statistics exceeds the critical value, the null hypothesis is rejected considering inequality of averages. Post-hoc-test (Fisher LSD) was used for detailed evaluation of significance of averages differences between analyzed groups of data. A feature of post-hoc-test is application of intra-group mean squares for the assessment of any pair averages. Differences were considered to be significant if $p < 0.05$. All calculations were carried out via STATISTICA 10.0 software. Also one-factor dispersive analysis on the base of average arithmetic values of studied sample units has been used for getting estimation of reliability of differences between them.

RESULTS

General soil properties

Urban environments

Data on soil chemical properties determined for fine earth (Table 2) indicates that soils are characterized by following features. Soils were characterized principally by strongly acidic (pH 5.1-5.5) conditions in Kharsaim, slightly acidic and almost neutral (pH 6.1-6.9) conditions in Aksarka and Labytnangi settlements (Table 2). For Salekhard and Kharp key plots the pH values were characterized mostly as strongly acidic (pH 4.7-5.1). Particle size distribution analysis showed predominance of silt fraction in soils of key plots located on the river terraces of Ob River (Aksarka, Kharsaim) and predominace of sand fraction in soils of other studied key plots (Salekhard, Labytnangi, Kharp) (Table 2). The total organic carbon content in studied soil samples showed relatively high variability (values ranged between 0.19 % and 14.58 %). It might be connected with high heterogeneity of soil material in studied Technosols due to mixing caused by human activity.

Natural environments

Data on soil chemical properties (Table 2) shows that fine earth of soil samples collected from natural environments are characterized by following features. Soils were characterized principally by strongly acidic (pH 5.1-5.8) conditions in Ust'-Uribey, slightly acidic and almost neutral (pH 6.1-6.9) conditions in soil samples collected from Beliy island. Particle size distribution analysis showed predominance of sand in all of studied soil samples from both natural sites (Table 2). The organic carbon content in studied soil samples ranged between 0.1 % and 11.3 % with median value 0.5 %. Highest values of organic carbon content are not connected with topsoil horizons. It confirms hypothesis about essential role of cryogenic processes in formation of chemical elements peaks and heterogeneity of soil profile.

Trace elements in soils

Urban environments

Results on trace elements content for investigated key plots in urban environments of Yamal region are summarized in Table 3. The highest content for Cu, Zn, Ni was found in Kharp key plot. The highest median values for Pb were found in soil

Soil ID	Depth, cm	TOC, %	pH_{H2O}	Texture fractions, %		
				Clay	Silt	Sand
Kharsaim						
Km1	0-5	9.47	5.70	20	65	15
Km1	5-20	2.13	5.20	17	70	13
Km2	0-5	0.41	5.20	31	53	16
Km2	5-20	0.19	5.25	25	62	13
Aksarka						
Aks1	0-5	0.23	5.87	20	73	7
Aks1	5-20	3.23	6.93	17	61	12
Aks2	0-5	3.49	6.42	25	63	12
Aks2	5-20	5.69	6.33	35	48	17
Salekhard						
Sal1	0-5	3.24	4.92	23	30	47
Sal1	5-20	0.93	4.78	12	25	63
Sal2	0-5	1.56	5.67	17	31	52
Sal2	5-20	3.26	6.39	6	19	75
Kh1	0-5	0.84	4.71	16	20	64
Kh1	5-20	14.58	5.43	14	34	52
Kh2	0-5	6.34	5.06	15	29	56
Kh2	5-20.	3.75	6.09	14	25	61
Labytnangi						
Lab1	0-5	3.89	6.39	17	28	65
Lab1	5-20	4.38	6.32	12	18	70
Lab2	0-5	4.54	6.42	9	19	72
Lab2	5-20.	5.23	4.90	9	27	64
Lab3	0-5	5.23	6.42	11	35	54
Lab3	5-20	4.53	6.32	12	17	71
Ustr-Uribey						
Y2	6–10	3.40	5.70	23	15	62
Y2	10–29	11.30	5.22	27	19	54
Y2	29–50	1.10	5.70	29	19	52
Y2	50–64	0.40	6.46	37	23	40
Y2	64–77	0.30	5.38	38	23	39
Y2	77–85	0.50	5.54	39	23	38
Y2	85-150	0.10	5.75	54	32	24
Beliy island						
BEL	0–5	1.00	6.12	12	21	67
BEL	5–10	0.50	6.48	15	12	73
BEL	15–20	0.80	6.00	13	15	72
BEL	20–45	0.10	6.87	25	16	59
BEL	45–54	5.40	6.45	27	12	61
BEL	54–110	0.10	6.70	29	12	59
BEL	110–290	0.10	6.73	32	13	55

Tab. 2: Standard soil characteristics of studied soils.

Tab. 2: Standard-Bodencharakteristik der untersuchten Böden.

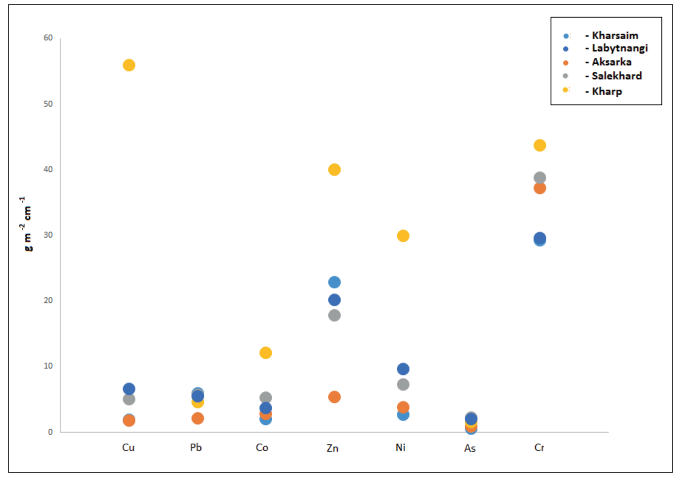

Fig. 2. Volumetric content of trace elements in topsoil horizons (0-5 cm) of urban soils of Yamal region.

Abb. 2: Volumetrischer Gehalt an Spurenelementen in Oberboden-/Mutterboden-Horizonten (0-5 cm) in urbanen Böden der Yamal-Region.

samples from Aksarka and Labytnangi key plots. Soil samples from Kharsaim and Kharp key plots were characterized by the highest median values for Zn.

It has been found that most of the soil samples collected in urban environments contain higher volumetric amounts of measured trace elements in the 0-5 cm depth layer compared to the 5-20 cm layer (Figs. 2, 3). Soil samples collected in Kharp contains the highest volumetric content of Cu, Co, Zn, Ni, Cr in 0-5 cm layer. Kharp and Aksarka soil samples are described as samples with the highest volumetric content of measured elements in 5-20 cm layer.

Natural environments

Results on trace elements content in selected soils of Yamal region natural environments are summarized in Table 3. The highest content for most of the studied trace elements is connected with topsoil horizons (Figs. 2-5) and with Histic material in particular (Table 3). This is shown most prominently in the Beliy island key plot. Another type of peaks for trace elements content is connected with predominance of clay in texture class. But it does not play so significant role in sorption of trace elements in studied soils due to low amount of clay. For the Ust'-Uribey key plot it has not been noticed clearly pronounced correlation between trace elements content and organic matter content and quality (Tables 2, 3). Morphological descriptions for all studied soils have been also used for determination of the possible reasons for trace elements profile distribution features. Trace elements content (excluding Pb) are essentially increased at the depth of 64-77 cm in the Ust'-Uribey soil.

Soil samples collected from natural environments are characterized by significantly lower volumetric elements content (up to 10 times) in contrast to the soil samples collected from urban environments (Figs. 4, 5). Soil samples both from Beliy island and Ust'-Uribey key plots are characterized by the highest volumetric element content in Cr (7-7.5 gm^{-2} cm^{-1} in upper layers and 1.5-1.7 in bottom layers). It should be noticed

Soil ID/ horizon depth, cm	Cu	Pb	Co	Zn	Ni	As	Cr	Fe_2O_3, %	MnO, %
Km1/0-5	10.50	36.00	6.00	143.00	13.00	2.60	80.10	2.53	0.06
Km1/5-20	8.00	7.00	2.20	27.00	16.00	3.70	127.20	3.57	0.05
Km2/0-5	1.60	2.30	6.30	5.70	4.00	0.80	93.10	1.44	0.03
Km2/5-20	1.60	2.30	10.20	5.40	4.40	0.70	49.10	0.65	0.01
Aksarka									
Aks1/0-5	3.80	4.00	7.10	11.60	8.30	2.10	102.20	1.86	0.03
Aks1/5-20	9.10	7.60	8.40	25.00	15.00	2.90	104.10	3.21	0.04
Aks2/0-5	5.50	10.00	9.20	17.00	12.00	2.40	107.10	2.27	0.04
Aks2/5-20	6.00	150.00	11.20	17.00	14.00	2.40	91.40	3.29	0.04
Salekhard									
Sal1/0-5	7.10	8.90	18.00	27.00	9.00	2.90	103.30	3.55	0.05
Sal1/5-20	7.50	8.90	10.30	25.00	9.00	3.00	106.20	2.76	0.05
Sal2/0-5	6.30	6.20	10.10	20.00	10.00	3.00	101.20	2.92	0.06
Sal2/5-20	7.00	6.70	5.20	24.00	11.00	3.40	152.20	7.70	0.15
Kharp									
Kh1/0-5	73.00	7.90	25.10	56.00	50.00	2.70	121.10	3.43	0.17
Kh1/5-20	80.00	3.00	27.30	46.00	19.00	1.00	475.20	3.71	0.19
Kh2/0-5	74.00	4.20	39.10	49.00	28.00	1.40	108.20	6.80	0.18
Kh2/5-20	86.00	3.90	20.40	49.00	30.00	1.10	95.30	6.20	0.06
Labytnangi									
Lab1/0-5	9.00	9.10	9.10	31.00	13.00	2.80	108.30	8.44	0.04
Lab1/5-20	6.00	6.10	5.10	19.00	10.00	3.10	119.20	8.15	0.04
Lab2/0-5	6.20	6.60	13.20	19.00	9.00	2.40	77.10	8.07	0.16
Lab2/5-20	7.40	7.00	6.40	21.00	12.00	2.70	55.20	3.90	0.14
Lab3/0-5	9.50	7.30	10.30	27.00	17.00	3.10	65.30	6.75	0.05
Lab3/5-20	11.20	7.70	7.20	28.00	17.00	4.00	63.10	6.50	0.05
Ust'-Uribey									
Y2/6-10	22.00	n.d.	5.00	21.00	17.00	n.d.	79.00	1.30	0.02
Y2/10-29	13.00	n.d.	n.d.	22.00	15.00	5.00	82.00	2.00	0.02
Y2/29-50	17.00	8.00	4.00	20.00	13.00	4.00	97.00	1.50	0.03
Y2/50-64	15.00	1.00	5.00	21.00	13.00	3.00	73.00	1.20	0.02
Y2/64-77	26.00	n.d.	10.00	45.00	24.00	3.00	91.00	3.00	0.05
Y2/77-85	24.00	2.00	5.00	30.00	20.00	4.00	84.00	2.40	0.04
Y2/85-150	17.00	n.d.	5.00	16.00	10.00	2.00	63.00	0.70	0.02
Beliy island									
BEL/0-5	20.00	n.d.	8.00	29.00	16.00	4.00	75.00	0.90	0.02
BEL/5-15	11.00	n.d.	5.00	12.00	8.00	2.00	57.00	0.60	0.01
BEL/15-20	12.00	1.00	5.00	12.00	10.00	4.00	64.00	0.70	0.01
BEL/20-45	15.00	n.d.	6.00	14.00	12.00	2.00	67.00	0.90	0.02
BEL/45-54	33.00	n.d.	n.d.	32.00	38.00	3.00	109.00	0.20	0.02
BEL/54-110	21.00	14.00	6.00	18.00	15.00	5.00	66.00	0.90	0.02
BEL/110-290	19.00	n.d.	11.00	16.00	14.00	2.00	65.00	0.90	0.02

Tab. 3: Trace elements content (mg kg^{-1}) in soils of study sites.

Tab. 3: Spurenelementgehalte content (mg kg^{-1}) in Böden der Untersuchungs-Standorte.

that this trend has been observed for both upper and bottom layers of studied soils. Volumetric element content of the rest of measured trace elements vary in relatively low range and coincide with the content described earlier for Yamal region (Moskovchenko 2010).

Statistical processing of the data has been produced in the STATISTICA 10 software. Obtained probabilities for One-way ANOVA revealed statistically significant differences between content of most chemical elements analyzed in soils of urban and natural sites (Table 4). Calculated p values for Cu, Pb, Zn, Ni, As and Fe2O3 were multiple times lower than 0.05 significance level (<<0.01). However, MnO content showed no significant differences. Significance of differences for each analyzed chemical element was additionally checked using Post Hoc Fisher LSD test. The results show statistically significant differences in Ni and Cu content in soils were found only between Kharp settlement and each of natural sites – Ust'-Uribey and Beliy Island. Almost all studied urban soils showed significant differences in Pb, Zn, As and Fe content between natural sites (Fig. 3). Cr content is significant only between pares of Salekhard compared with both Ust'-Uribey and Beliy Island natural sites ($p < 0.02$; $p < 0.03$), and Kharp settlement with Beliy Island ($p < 0.03$). Although group One-way ANOVA did not revealed any significant differences in MnO content ($p < 0.05$), nevertheless Post Hoc test found one to be significant between Kharp settlement and both natural sites ($p < 0.01$). Differences in Co content between urban and natural site were found only between pares of Kharp with both Ust'-Uribey and Beliy Island natural sites ($p < 0.02$; $p < 0.02$) and Salekhard/Ust'-Uribey ($p = 0.002$) as well as Salekhard/Beliy Island ($p < 0.003$).

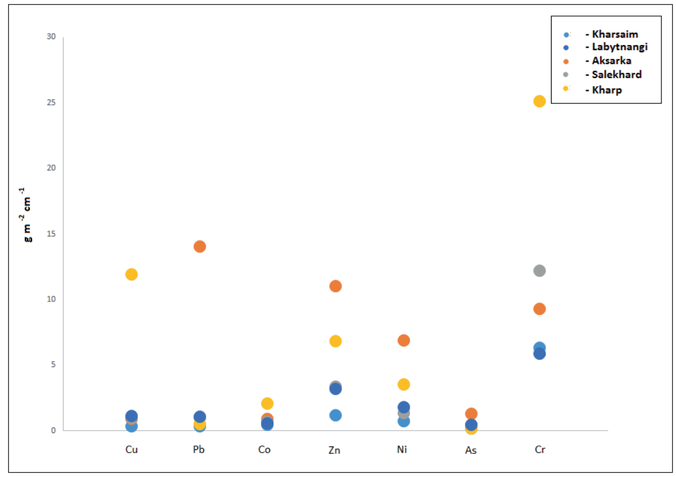

Fig. 3: Volumetric content of trace elements in 5-20 cm layer in urban soils of Yamal region.

Abb. 3: Volumetrischer Gehalt an Spurenelementen in 5-20 cm-Schicht urbaner Böden der Yamal-Region.

Chemical element	Urban sites					Natural sites		*p* One-way ANOVA
	Kharsaim (n = 4) Mean ± SD	Aksarka (n = 4) Mean ± SD	Salekhard (n = 4) Mean ± SD	Kharp (n = 5) Mean ± SD	Labytnangi (n = 6) Mean ± SD	Ust'-Uribey (n = 3) Mean ± SD	Beliy Island (n = 3) Mean ± SD	
Cu	5.42 ± 4.53	6.10 ± 2.21	6.97 ± 0.50	68.00 ±23.5	8.22 ± 2.04	20.66 ± 1.53	20.00 ± 1.00	<0.01
Pb	4.65 ± 2.71	7.90 ± 2.83e	7.67 ± 1.43	5.78 ± 2.97	7.30 ± 1.04	0.00	0.00	<0.01
Zn	16.27 ± 12.38e	17.65 ± 5.52	24.00 ± 2.94	49.00 ± 4.30	24.16 ± 5.15	22.00 ± 1.00	29.00	<0.01
Ni	9.35 ± 6.07	12.32 ± 2.95	9.75 ± 0.96	31.40 ± 11.35e	13.00 ± 3.41	17.66 ± 1.15	1666.00 ± 1.15	<0.01
As	1.95 ± 1.46	2.45 ± 0.33	3.07 ± 0.22	2.38 ± 1.97	3.02 ± 0.55	0.00	4.00 ± 1.00	<0.01
Cr	87.37 ±32.33	101.20 ± 6.84	115.73 ± 24.40	109.34 ± 11.87	81.37 ± 26.27	80.33 ± 1.53	75.33 ± 1.53	<0.04
Co	6.17 ± 3.26	8.97 ± 1.71	12.80 ± 4.50	27,98 ± 7,96	8,55 ± 2,94	4,86 ± 2,91	5,86 ± 3,33	<0.02
Fe_2O_3	14318.00 ± 8912.53	18584.00 ± 4930.87	29598.00 ± 16340.25	28188.00 ± 18818.11	48729.83 ± 11891.12	9091.00	6291.67 ± 2.08	<0.01
MnO	302.75 ± 89.54	290.25 ± 59.19	613.25 ± 380.52	948.60 ± 634.76	626.17 ± 437.98	160.67 ± 0.58	153.33 ± 0.58	<0.05

e – mean values have been obtained for data with an exception of highly deviated values

Tab. 4: Average content of trace elements in topsoil horizons of studied objects (mg kg^{-1}) and probabilities for One-way ANOVA.

Tab. 4: Mittlerer Gehalt an Spurenelementen in Oberboden/Mutterboden-Horizonten der Standorte (mg kg^{-1}) und Wahrscheinlichkeit für One-way ANOVA.

DISCUSSION

The highest content for Cu, Zn, Ni which was found in Kharp key plot seems to be caused by existing galvanizing plant "Kongor-chrome". Almost all soil samples collected from urban environments of Yamal region were characterized by exceedance of Maximum Allowable concentrations (threshold concentrations) in As (Ministry of Health of USSR, 1987). It should be connected with high values of regional background content. This coincides with data obtained previously (Moskovchenko 2010; Tomashunas & Abakumov 2014).

Analysis of trace elements content in natural soils showed poorly manifested eluvial-illuvial differentiation of soil profiles. It coincides with previous data (Vasilevskaya et al. 1986; Moskovchenko 2010). Illuviation of iron and aluminium compounds are predominant processes among those responsible for accumulation of matter in studied soils. Histic material accumulation and formation of buried Histic (or humus) horizons also serve as significant factors for redistribution of elements in the soil profile. Histic material, which are widespread in topsoil horizons of Yamal soils is a powerful sorbent of microelements. Another reason for increased levels of trace elements content in soil profile of studied soil in natural environments This is caused by the formation geochemical barrier (as it is seen in Ust'-Uribey soil at the depth of 64-77 cm). It is forming due to seasonal stagnation of water and sharp change of reductive-oxidative conditions in this layer. Absence of trace elements differentiation is connected with cryogenic mass transfer and homogenization of soil mass.

Since numerous investigated plots are faced to urbanization process, we have emphasized the special aim to determine anthropogenic influence on the chemical composition of urban soils. It has been previously discussed how to detect presumable anthropogenic element additions to soil ecosystems (Reimann et al. 2008; Sucharova et al. 2012; Walker et al. 2003; Zhulidov et al. 1997). Usually the ratio of trace elements in the top and bottom soil horizons is used. Analysis of soil samples from Kharp in both 0-5 cm and 5-20 cm layers showed that volumetric content of Cu and especially Cr are significantly high and caused by higher rates of anthropogenic influence (due to the functioning of galvanizing plant "Kongor-chrome").

A comparison of data obtained in this investigation for soils in natural environments with the similar data from other regions of the Russian Arctic (Antcibor et al. 2014; Moskovchenko 2013; Moskovchenko et al. 2017; Rovinsky et al. 1995; Zhulidov et al. 1997) and Canada (Walker 2012) showed that mean values of trace metals content both for Ust'-Uribey and Beliy island soils are commonly higher (except of Pb, Fe and Mn) (Table 5). The data reported in this work and reported previously for Beliy island (Moskovchenko et al. 2017) showed that trace elements content is generally comparable. Higher average Cr content reported in our work can be related to the soil contamination in particular part of the island due to aerosol particles fallout from the atmosphere since the predominant southwestern winds which can transfer metal aerosols from industrial regions of continental part of Yamal region (Moskovchenko et al. 2017). We should also note that we have not found such an abnormal Pb concentrations as it was found previously (Moskovchenko et al. 2017). High average content of trace elements (Pb, Co, Zn, Ni) reported for soils of Lena River Delta are connected with their concentration in organic matter (since organic matter is capable of forming organo-minerals associations), whose average value in the soils is also higher comparing to studied soils of Ust'Uribey and Beliy island. Soil organic matter can retain a number of trace elements by the mechanisms of ion-exchange, proton displacement, and inner or outer-sphere complex formation (Schnitzer 1986).

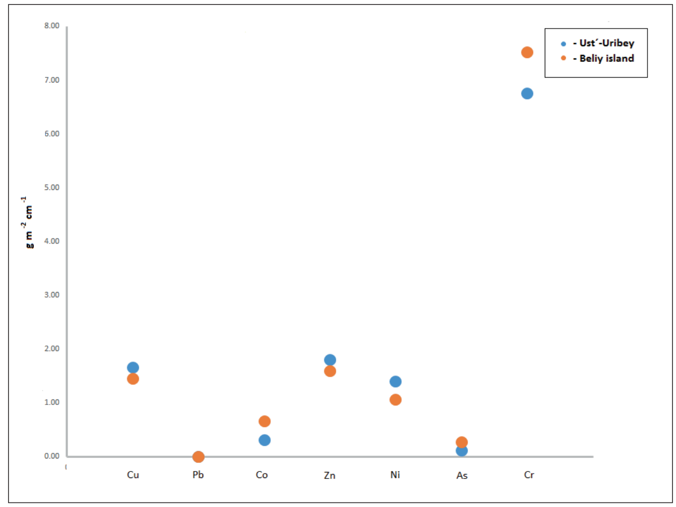

Fig. 4: Volumetric content of trace elements in topsoil horizons of natural soils of Yamal region.

Abb. 4: Volumetrischer Gehalt an Spurenelementen Oberboden/Mutterboden-Horizonten natürlicher Böden der Yamal-Region.

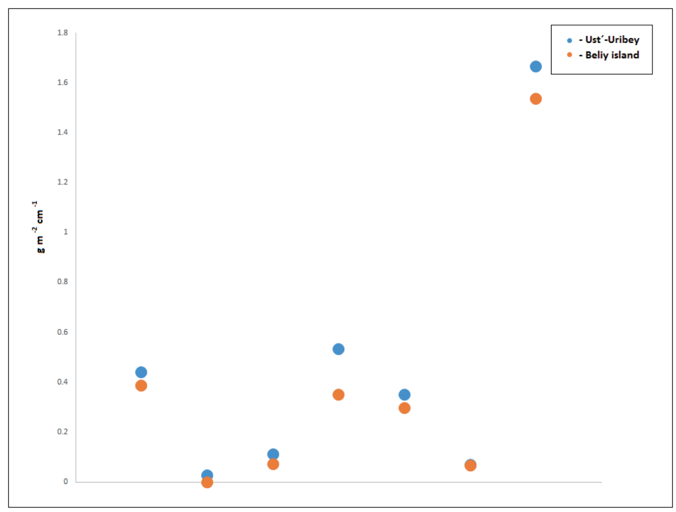

Fig. 5: Volumetric content of trace elements in bottom layer horizons of natural soils of Yamal region.

Abb. 5: Volumetrischer Gehalt an Spurenelementen in Bodenschicht objects (mg kg^{-1}) natürlicher Böden der Yamal-Region.

Analysis performed showed significant differences in trace elements profile distribution between urban and natural soils. However, human activities complicates significantly soil cover of the urban areas and profile distribution of different soil parameters especially (Linde 2005).

Investigation	Cu	Pb	Co	Zn	Ni	As	Cr	Fe	Mn
Ust'-Uribey (This study)	19.14 (13.00-26.00)	1.57 (<0.50-8.00)	4.86 (<0.50-10.00)	25.00 (16.00-45.00)	16.00 (10.00-24.00)	3.00 (<0.50-5.00)	81.29 (63.00-97.00)	6046.07 (2448.41-10493.18)	207.59 (121.61-356.31)
Beliy island (This study)	18.71 (11.00-33.00)	2.14 (<0.50-14.00)	5.86 (<0.50-11.00)	19.00 (12.00-32.00)	16.14 (8.00-38.00)	3.14 (2.00-5.00)	71.86 (57.00-109.00)	2548.34 (699.55-3147.95)	135.45 (79.78-189.78)
Beliy island (Moskovchenko et al. 2017)	2.90 (<0.50-19.20)	(<0.50-132.00)	(<0.50-10.30)	20.90 (9.50-126.00)	-	-	23.50 (7.60-108.00)	8998.00 (3943.00-37899.00)	250.00 (119.00-561.00)
Kharasavey, Yamal peninsula (Moskovchenko 2013)	10.20	5.10	7.50	17.90	-	-	12.90	-	258.00
East Siberian Arctic (Rovinsky et al. 1995)	2.50 (0.72-5.00)	-	-	13.00 (6.80-18.90)	-	-	-	-	-
Western Siberia, Wetland soils (Zhulidov et al. 1997)	(2.00-8.00)	(1.70-44.00)	-	(2.20-154.00)	-	-	-	-	-
Lena River Delta (Antcibor et al. 2014)	7.76	7.32	29.18	53.58	21.3	4.97	-	25980.80	346.83
Labrador, Churchill river valley (Walker 2012)	8.00 (2.00-15.00)	4.81 (1.10-24.00)	-	25.82 (7.00-48.00)	-	-	13.81 (2.00-34.00)	6760.00 (500.00-17000.00)	220.97 (12.00-1100.00)

Tab. 5: Trace elements content (mg kg^{-1}) in soils of different regions of the Arctic, mean values (min-max).

Tab. 5: Spurenelementgehalte (mg kg^{-1}) in Böden verschiedener Regionen der Arktis, mittlere Werte (min-max).

Data concerning the trace elements content in soil of the Arctic is limited and should be state as insufficient. Moreover evaluation of anthropogenic impacts on Arctic ecosystems requires not only background levels of trace elements, but also landscape distribution of elements in permafrost-affected soils in relation to soil properties (Antcibor et al. 2014).

Trace elements content maximums for natural soils reported in this work soils have been connected with Histic topsoil horizons and geochemical barriers on the superficial layer. It coincides fairly well with the data reported previously for the Arctic region (Antcibor et al. 2014; Moskovchenko 2010; Nikitina et al. 2015; Plichta et al. 1991). Therefore we can suppose that predicted global warming and high sensitivity of Arctic ecosystem to effects of human activity will lead to significant changes in permafrost-affected landscapes and increasing of biogeochemical cycling rates in this key region in context of climate change (since it is a big reservoir of carbon). Degradation of permafrost could alter the behavior of trace elements in soils. It will affect the rates of accumulation, transformation, translocation, leaching and transportation of trace elements and other pollutants within the permafrost-affected landscapes. The depth of geochemical barriers connected with superficial layer will increase. Impact of permafrost on soil formation will be decreased due to less pronounced cryoturbation, cryogenic mass transfer and other permafrost-related soil-forming processes. Degradation of permafrost seems to be a prerequisite for release of additional portion of CO_2 and CH_4 to the soil. It will significantly change the behavior of trace elements in soils since the majority of them are bound by organo-mineral associations (Höfle et al. 2013). Rates of biological accumulation of trace elements hence will be increased.

CONCLUSIONS

Investigation of both urban and natural soils trace element content revealed the significance of studying the role of every single factor in formation of the trends in chemical composition of the soil. Trace elements content in soil samples collected from urban environments ranged significantly high due to difference in functional zones of the sites and predominant anthropogenic source of trace elements additions.

The highest values for Pb were found in soil samples from Aksarka and Labytnangi key plots. Soil samples from Kharsaim and Kharp key plots were characterized by the highest median values for Zn. Analysis of trace elements content showed poorly manifested eluvial-illuvial differentiation of soil profiles of natural soils. The highest content for most of the studied trace elements has been revealed in topsoil horizons since Histic material serves as a strong sorbent of microelements. Another reason for increased trace elements content in natural soils is connected with the formation of geochemical barrier on the superficial layer compared to the topsoil horizons. It explains the mechanism according to which permafrost table serves as a geochemical barrier accumulating trace elements. So this geochemical barrier slacks the process of migration of trace elements into deeper soil horizons. However, texture class, organic matter content and accumulation of iron and aluminium also significantly affects profile distribution of trace elements.

Analysis of volumetric element content revealed correlations between the soil depth, soil properties and element content. Soil samples collected from Kharp key plot were characterized by the highest volumetric content of Cu, Co, Zn, Ni, Cr in 0-5 cm layer. Most of the measured elements have their maximums in volumetric content at the depth 5-20 cm in soils samples collected from Kharp and Aksarka. Natural soils were characterized by significantly lower volumetric elements content (up to 10 times) in contrast to the soil samples collected from urban environments. The highest content was measured for chrome (Cr).

Our investigation showed that data obtained fairly coincide with those reported in previous works (dedicated to the northern Siberia and other parts of the Arctic). Studied natural can be considered as reference region for the further investigations of trace elements in Yamal region. Trace elements content described for the natural sites could be used as background content at least for the northern part of Yamal region. Permafrost-affected soils are those with significant complication of their vertical element profiles due to cryogenic processes. It seems to be very prominent to study the behavior of trace elements and their accumulation, transformation and transport within the soil profiles in more details. In its turn the uniform approach for studying urban soils in polar region environment should be developed.

ACKNOWLEDGEMENTS

This study was supported by Russian Foundation for Basic Research, project No. 16-34-60010 and a grant of Saint-Petersburg State University "Urbanized ecosystems of the Russian Arctic: dynamics, state and sustainable development" please add this reference.

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