A Baseline Survey of The Geochemical Characteristics of the Arctic Soils of Alexandra Land Within the Franz Josef Land Archipelago (Russia)

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Abstract

The composition of soils and their parent materials were studied within one of the most northern land areas of the world – the island of Alexandra Land of the Franz Josef Land archipelago. Contents of 65 trace and major elements were determined using atomic emission spectrometry (ICP-AES) и inductively coupled plasma spectrometry (ICP-MS). Other analyzed characteristics included soil pH, particle-size distribution and contents of carbon and nitrogen. The mineralogical composition of rocks was determined in thin sections. The studied soils were formed on basalts with high contents of MgO, Fe_2O_3, TiO_2, Cu, Co, V, Ni, Cr, Zn, and low contents of Pb and Hg. The composition of soils was generally similar to that of the bedrock. The median concentrations (mg kg^{-1}) of trace elements in the soils were as follows: Cu - 160, Zn - 101, Ni - 74, Pb - 2.9, Cd - 0.14, and Hg - 0.031. The bedrock had an alkaline pH, whereas the soil pH ranged from weakly acid to alkaline. The textural class of the soils predominantly corresponded to sandy loam. The contents of clay and silt increased with depth due to the migration of these fractions with groundwater. The concentrations of ecologically hazardous Hg and Pb were slightly increased in the upper layer of soils and correlated with carbon contents, which was indicative of bioconcentration processes.

Introduction

Research on the chemical composition of soils of the Arctic has recently become increasingly important, primarily, due to the risks of pollution from both local and distant sources. The long-range transport of air pollutants from the industrial regions of Europe, Asia and North America has been described in many studies (Barrie et al. 1992; Akeredolu et al. 1994; Headley 1996; AMAP 1998; 2005). The composition of arctic soils is also affected by local sources of pollution (Gulińska et al. 2003; Wojtun et al. 2019). The majority of the studies on arctic soils have been conducted on the island of Spitsbergen, for example, the analyses of baseline concentrations of heavy metals in soils (Plichta and Kuczyńska 1991; Hao et al. 2013; Kryauchyunas et al. 2014; Szymański et al. 2019; Aslam et al 2019), the assessment of impacts of different pollution sources on soils (Gulińska et al. 2003) and the estimations of deposition rates of airborne heavy metals (Wojtun et al. 2013; Kozak et al. 2013, 2016). It has been found that the soils of Spitsbergen are locally contaminated by Cd, Co, Cu, Ni, Pb, and Zn (Wojtun et al. 2019). Several studies on heavy metal concentrations in soils have also been conducted within the Russian sector of the Arctic, e.g., the Novaya Zemlya archipelago (Laverov et al. 2016; Usacheva et al. 2016) and the Bely Island (Abakumov et al. 2017; Moskovchenko et al. 2017). In addition, the accumulation of polycyclic aromatic hydrocarbons has been detected in arctic soils (Abakumov et al. 2015).

The Arctic vector is currently one of the most important in the domestic policy of Russia (Serova and Serova 2021). Russia is one of the most important players in the Arctic zone energy shelf with significant economic, security, and political interests in the region (Carayannis et al. 2017). The industrial development of the Russian Arctic sector increases the risks of ecosystem degradation. Increasing anthropogenic pressures, which result from either intentional or unintentional changes of terrestrial, freshwater or marine ecosystems as well as the forecasted climate change will probably lead to a significant and mostly irreversible loss of biodiversity in the Arctic (Hudson et al. 2017).

The importance of research on soil composition within polar regions is also associated with the current problems of global warming, which has the strongest impact on the Arctic (IPCC 2014). The thawing and degradation of permafrost triggered by global warming are regarded as one of the most important drivers of soil evolution processes within the polar regions of Russia (Kaverin et al. 2014). The consequences of global warming include an increased rate of seasonal ground thawing, which induces significant changes in the biochemical processes within soils (Vonk et al. 2019; Pokrovsky et al. 2020). Thawing permafrost could result in the release of organic and inorganic forms of biologically active elements and heavy metals (Pogojeva et al. 2021). Therefore, data on the contents and migration processes of chemical elements within such high-latitude soils are needed for making forecasts of changes in the arctic ecosystems, which are the most vulnerable under the conditions of a changing climate (Usacheva et al. 2016).

The present study on the composition of soils and their parent materials (bedrock) was conducted within Alexandra Land, which is one of the largest islands of the Franz Josef Land (FJL) archipelago. It is one of the most northern land areas, being located at a distance of approximately 1000 km from the North Pole. Although the number of studies in the Arctic has generally increased over the last decade, the soils of the FJL are still new materials for specialist research in almost any aspect of soil science and ecology (Nikitin et al. 2020).

The aims of this study were (1) to analyze the chemical composition of the soils and parent materials within Alexandra Land in order to determine the baseline concentrations of elements and 2) to identify the effects of soil particle-size composition, acidity/alkalinity levels and organic matter contents on the concentrations of trace and major elements.

Materials And Methods

Study area

The island of Alexandra Land is found in the Barents Sea, in the western part of the FJL archipelago, between 80°28' - 80°46' N and 45°17' - 47°27' E (Fig.1).

Alexandra Land has a total area of about 1300 km^2. The island's highest altitude of about 390 m a.s.l. is found on an ice cap in the southern part of the island, whereas the land free from ice has a maximal height of only 70 m a.s.l. The FJL archipelago is located within the zone of arctic climate, where soils are formed under conditions of extremely low temperatures (the mean annual T from -6° to -10°C and the mean T of July from +0.2 to + 1.1 °C). Over a half of the island's total area is covered with ice. The ice-free areas have a continuous permafrost with the active layer depth between 15 and 50 cm and a ground temperature between -7 and -13 °C (Kondrat'eva 1980). According to the data from the local weather station, which is located on Hayes Island (80^{o}37' N, 58^{o}02' E), the current warming of the Arctic severely affects the FJL archipelago due to the increase in the mean annual temperature by more than 5°C over the period of 1958-2018 (Fig. 2). The mean annual precipitation is about 300 mm. The vegetation cover is sparce due to the low temperatures and mainly consists of moss-lichen-grass communities of the High Arctic tundra, where mosses and lichens predominate over vascular plants (Safronova et al. 2020).

The soil cover is represented by alternating areas of permafrost-affected soils i.e. Skeletic Oxyaquic Cryosols (Loamic, Humic), permafrost-affected gray-humus soils i.e.Oxyaquic Cryosols (Loamic, Humic), mucky raw-humified gray-humus soils i.e. Oxyaquic Cryosols (Loamic, Humic), and mucky cryoturbated pelozems (Oxyaquic Turbic Cryosols (Loamic, Humic)) (Nikitin et al. 2020).

The topography of the FJL archipelago is dominated by residual landforms of the basalt plateau. There are only very small areas of erosional-denudational and depositional coastal landforms composed of loose sediments that occur in eastern and some central islands (Sukhodrovskii 1970). Basalts of FJL were formed between 197–121 Ma, i.e., from the Early Jurassic to the Early Cretaceous (Simonov et al. 2019). Despite its remote location, FJL is affected by the long-range transport of air pollutants. The most significant sources of such airborne pollutants are located on the Kola Peninsula, in Northern Europe and the Norilsk region (Vinogradova and Ponomareva 2012).

Soil sampling and analyses

The soils and bedrock of Alexandra Land were sampled during the UMKA-2021 complex Arctic expedition, which was organized by the Russian Geographic Society. Soil samples were taken from three layers (0-10, 10-20 and 20-30 cm depths) from 12 locations (Fig. 1). The composition of bedrock was investigated by coring to the depth of 5 m in a single location, with a total of seven core samples taken from the following depths: 0.4, 0.8, 1.4, 2.0, 3.2, 4.0 and 5.0 m. The studied soils were identified as follows: lithozems (Sites 1, 2, 4, 5, 6, 9), cryoturbated raw-humus lithozem (Turbic Cryosol, S3), Arenic Cryosol (S10), permafrost-affected gray-humus soil (S7), humified pelozem (S8) and soils of non-sorted circles within periglacial zones (S11 and S12).

In the laboratory, plant root fragments were removed and soil samples were air-dried at 25°C to constant weight. The pH values were measured potentiometrically in continuously mixed 1:2.5 soil:water and soil:KCl suspensions using a Starter 3100 conductivity meter (OHAUS, Germany). Total carbon (TC) and total bound nitrogen (TNb) measurements were taken using a vario TOC (Elementar) device. The particle-size composition of the 0-2 mm fraction was determined by a Mastersizer 3000 (Malvern) laser diffraction particle size analyzer using water and ultrasonic sample dispersion.

The chemical composition of soil and bedrock samples was investigated by the methods of inductive coupled plasma mass spectrometry (ICP-MS) and inductive coupled plasma atom emission spectrometry (ICP-AES). The contents of B, Li, Be, Al, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Ga, Ge, As, Se, Br, Rb, Sr, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Cd, In, Sn, Sb, Te, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Th, and U in the samples were determined using a Thermo Scientific X-7 ICP-MS (USA). The contents of Li, B, Na, Mg, Al, Si, P, S, K, Ca, Ti, V, Mn, Fe, Cu, Zn, Sr, and Ba were determined using a Thermo Scientific iCAP-6500 Duo ICP-AES (USA). Digestion of samples was performed in open beaker system using a certified procedure (with a combination of three acids $HClO_4$, HF, and HNO_3), which has been described in detail earlier (Fedotov et al. 2016; Ermolin et al. 2018). Along with the analyzed samples, the decomposition of standard samples was carried out. To check the accuracy of measurements, we used multi-element standard samples Trapp ST-2a (Russian State Standard GSO 8671-2005) and Basalt BHVO-2 (US Geological Survey). The comparison with the standard samples showed a sufficient repeatability (85-115%) for the analyzed elements.

Thin sections prepared from six bedrock samples were investigated under a polarizing microscope.

Statistical data processing was performed using Statistica 10.0 software. Median values were used due to the absence of normal distribution in the concentrations of many elements (K_2O, S, As, Rb, Mo, Cd, Cs, Ba, Tl, Bi, U as well as TC). The median absolute deviation (MAD) was used as a measure of variability. Spearman rank coefficients were calculated (with the probability value $P<0.05$) in order to analyze relationships between the element contents, pH values, particle-size distribution and the contents of TC and TN.

Results And Discussion

Bedrock composition

The geology of the FJL archipelago has been well studied (Ntaflos and Richter 2003; Karyakin et al. 2009, 2011). The archipelago is mostly composed of sedimentary and volcanic rocks. The upper geological strata of the Alexandra Land consist of basalts and dolerites (Karyakin and Shepilov 2009). The FJL basalts are geologically classified as continental tholeiites (Ntaflos and Richter 2003).

In this study, the mineralogical analysis of thin sections of bedrock showed that it was formed of basalt with porphyritic texture, consisting mainly of plagioclase crystals and small grains of augite, which were immersed into a yellowish brown altered obsidian (palagonite). Inclusions of carbonates and ore minerals were observed at the 4.0 m depth. According to the previous petrographic study (Simonov et al. 2019), the archipelago's volcanic rocks are generally homogeneous in composition and usually consist of basalts with 5-20% obsidian and small inclusions of predominantly plagioclase and clinopyroxene (augite) and occasionally olivine. Therefore, the studied samples of bedrock were typical for the FJL in terms of mineralogy.

The element composition of bedrock was characterized by relatively high contents of Fe_2O_3 and Al_2O_3, i.e., 15 and 14%, respectively (Table 1). Other elements were less abundant, with their contents decreasing in the following order: CaO, MgO, NaO, TiO_2, K_2O, P_2O_5 and MnO. The studied basalts, especially in the upper part of the core, were very poor in K_2O, the content of which ranged between 0.33-0.38%, which is 7-8 times as low as the value of its world crust average (WCA). It should be noted that the high Fe_2O_3

content in the studied core was 3 times higher than the WCA. The observed TiO2 content of 2% on average is also above the WCA value.

It is known that basalts of FJL had formed in two stages. According to (Karyakin et al. 2009), the basalts that formed during the first stage of volcanic activity in the Early Jurassic, 191±3 Ma, have medium concentrations of TiO_2 (1.38-2.25%) and consistently low concentrations of Y (24-37 $mg \cdot kg^{-1}$), Zr (98-156 $mg \cdot kg^{-1}$) and Nb (5.5-10 $mg \cdot kg^{-1}$), whereas the basalts of the second stage of the Late Mesozoic have relatively higher contents of TiO_2 (2.56-3.94.%), Y (32-49 $mg \cdot kg^{-1}$), Zr (170-320 $mg \cdot kg^{-1}$) and Nb (12-33 $mg \cdot kg^{-1}$). Therefore, the data obtained on the analyzed bedrock core (Table 1) show that it consists of basalts of the first, most ancient stage.

Table 1. Statistical parameters of the chemical composition of the studied core sample of bedrock (Alexandra Land, FJL)

Element	Me	MAD	min	max	World Crust Average (Rudnik and Gao 2003)	Me/WCA
Na_2O	2.25	0.27	2.07	2.97	3.27	0.69
MgO	4.69	0.73	2.67	5.20	2.48	1.9
Al_2O_3	13.2	1.0	11.8	17.2	15.4	0.86
P_2O_5	0.18	0.02	0.08	0.19	0.15	1.2
S_{total}	0.031	0.04	0.01	0.16	0.0621	0.50
K_2O	0.38	0.30	0.33	1.63	2.8	0.13
CaO	9.0	2.5	1.1	10.9	3.59	2.5
TiO_2	2.0	0.19	1.38	2.11	0.64	3.2
MnO	0.17	0.04	0.04	0.23	0.1	1.7
Fe_2O_3	14.8	0.5	14.3	16.6	5.04	2.9
Li	6.8	4.1	5.8	23.5	24	0.28
Be	0.86	0.07	0.75	1.10	2.1	0.41
Sc	39.1	1.8	34.4	42.1	14	2.8
V	376	25	313	413	97	3.9
Cr	132	16	113	178	92	1.4
Co	48.7	10.7	37.1	78.8	17.3	2.8
Ni	94.9	10.3	75.2	112.0	47	2.0
Cu	220	58	206	533	28	7.0
Zn	101	5	85	112	67	1.5
Ga	18.5	0.7	17.5	20.0	17.5	1.1
As	1.8	1.1	0.4	4.6	4.8	0.38
Rb	9.1	4.0	5.7	22.0	84	0.11
Sr	159	21	128	197	320	0.50
Y	30.9	2.9	20.9	31.5	21	1.5
Zr	116	5	106	129	193	0.60
Nb	8.5	0.6	6.5	8.7	12	0.71
Mo	0.56	0.12	0.16	0.65	1.1	0.51

Cd	0.15	0.05	0.08	0.27	0.09	1.7
Sb	0.11	0.01	0.09	0.14	0.4	0.28
Cs	0.53	0.24	0.19	1.03	4.9	0.11
Ba	70.9	118.1	62.3	674.8	624	0.11
La	8.6	0.4	7.3	9.3	31	0.28
Ce	22.7	1.7	17.1	24.0	63	0.36
Pr	3.2	0.2	2.5	3.3	7.1	0.44
Nd	15.2	1.2	12.1	16.3	27	0.56
Sm	4.4	0.4	3.4	4.6	4.7	0.94
Eu	1.6	0.1	1.2	1.6	1	1.57
Gd	5.1	0.5	4.0	5.5	4	1.29
Tb	0.9	0.1	0.7	0.9	0.7	1.24
Dy	5.6	0.4	4.3	5.7	3.9	1.43
Ho	1.2	0.1	0.9	1.2	0.83	1.41
Er	3.3	0.2	2.7	3.5	2.3	1.45
Tm	0.46	0.03	0.38	0.49	0.3	1.52
Yb	3.1	0.2	2.6	3.2	2	1.53
Lu	0.5	0.0	0.4	0.5	0.31	1.47
Hf	3.2	0.1	2.7	3.4	5.3	0.60
Ta	0.52	0.03	0.39	0.52	0.88	0.59
Tl	0.19	0.11	0.04	0.40	0.9	0.21
Pb	1.5	0.3	1.4	2.5	17	0.09
Bi	0.03	0.04	0.02	0.15	0.16	0.16
Th	1.13	0.10	1.05	1.43	10.5	0.11
U	0.57	0.07	0.53	0.79	2.7	0.21

Note: Contents of Se, Rh, Pd, Te, Re, Ir, Pt, Au and Hg in the studied samples were below their detection limits.

The studied basalts were characterized by an abnormally high concentration of Cu, which was by an order of magnitude higher than the WCA for this element. The highest Cu concentration of 533 $mg \cdot kg^{-1}$

was observed at the depth of 5 m, whereas the other samples contained generally lower concentrations, within a narrow range of 206-266 mg·kg^{-1}. Concentrations of Co, V, Ni, Cr and Zn were also higher than their WCA values (see Table 1). The generalized data on the composition of different rocks of the world (Voitkevich et al.1990) show that mafic rocks such as basalts and gabbro tend to have increased concentrations of Fe, Ti, Cr, Ni, Co, Mn, Cu and Zn. Therefore, the composition of the studied rocks generally reflects the common geochemical features of basalts, except for the Cu concentrations being significantly above its average content of 100 mg·kg^{-1} in the Earth's mafic rocks. It is known that Cu concentrations in basalts are mainly predetermined by sulfide concentrations (Krivolutskaya and Kedrovskaya 2020), which gives us the basis to suggest that the studied samples have high sulfide contents. This suggestion was confirmed by the presence of high concentrations of S_{total} in the studied samples as compared to the composition of the precursor of volcanic rocks, i.e., primitive mantle, which has a mean sulfur content of 0.025 % (McDonough and Sun 1995).

The studied rocks had low contents of Pb, Th, U, La, Bi, Sb and Sn. The lanthanides (Ln) were subdivided into two groups – one with concentrations below WCA (La, Ce, Pr, Nd, Sm) and the other with concentrations above WCA values (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). The Ln/WCA ratio increased with increasing atomic numbers of the lanthanides (see Table 1). It is known that the increase in the lanthanide atomic numbers in the periodic table is accompanied by a decrease in their ionic radii, which predetermine their distribution within the Earth's crust (Perelman and Kasimov 1999). Therefore, the observed growth of lanthanoid concentrations proportional to their atomic numbers can be explained by changes in their ionic radii.

We have shown that the studied rocks belong to the continental tholeiitic series (platobasalts) by analyzing the distribution and indicator ratios of accessory elements. For example, the studied basalts had a Rb concentration of 9 mg·kg^{-1}, which is a triple of that found in oceanic basalts according to (Gale et al. 2013). Moreover, there was a highly significant difference in terms of the Rb/Cs ratio, which had values of 17.2 and 77.6 in the studied basalts and their oceanic counterparts, respectively. According to (Krivolutskaya and Kedrovskaya 2020), the continental basalts of the Siberian Platform have a Gd /Yb ratio of 1.3-2.0, with a mean of 1.56, which is very close to the data obtained in the present study on the Alexandra Land basalts (the Gd /Yb ratio of 1.4-1.7, with a mean of 1.6). Likewise, there are comparable values of the TiO_2/Y ratios, with a mean of 644 in the Siberian Platform basalts and a mean of 661 (range of 562-711) in the FJL basalts. Therefore, the present study confirms that the FJL basalts are similar to the Siberian Platform basalts in composition and belong to the continental basalt series.

Soil composition

The total carbon content of the arctic soils of FJL is known to be very sensitive to the climate change impacts (Nikitin et al. 2020). For that reason, it was important to determine the current TC concentrations in the studied samples of soils and bedrock. The data obtained on the TC and TN contents as well as pH values are presented in Table 2.

Table 2. The total carbon and nitrogen contents and the pH of soils and parent materials of the Alexandra Land (median± MAD)

Depth	TC, %	TNb, %	TC : TNb	pH $_{H2O}$	pH $_{KCl}$
0-10 cm	3.0±2.7	0.16±0.10	18.7±8.8	7.15±0.48	5.98±0.68
10-20 cm	0.97±0.85	0.09±0.03	10.8±6.36	7.22±0.44	5.74±0.52
20-30 cm	0.80±1.25	0.07±0.03	11.9±14.5	6.89±0.57	5.68±0.58
Bedrock	0.48±0.20	0.03±0.02	13.7±24.5	8.36±0.43	7.38±0.11

As expected, the TC and TN values decreased with depth (see Table 2). The TC had a median value of 3.0% within the 0-10 cm layer, which decreased to less than 1% in the deeper layers of soils and bedrock. The TC contents broadly varied within each studied layer, e.g., from 0.7% in Arenic Cryosol (S10) to 17.6% in Humic Cryosol (S6) at the 0-10 cm depth. Such wide variability is known to be caused by the heterogeneity of vegetation cover. According to (Nikitin et al. 2020), the lowest TC values are associated with the sites where vegetation consisted of algae and lichen communities, and the highest TC values (up to 30.7%) are found at the sites with moss and grass communities. It should be noted that one of our sites (S3) had an inverse vertical distribution of TC and TN in the soil, with the maximum at the 20-30 cm depth and the minimum at the 0-10 cm depth. As it has been mentioned by (Nikitin et al. 2020), such a phenomenon is frequently observed in soils of FJL and can be explained by cryogenic processes (ground heaving and cryoturbation).

The TNb contents in the studied samples ranged from 0.01 to 0.59%. The highest TN contents with a median value of 0.16% were found in the upper 0-10 cm layer and decreased with depth to 0.07% within the 20-30 cm layer. The parent materials had even lower TN contents, i.e., a median of 0.03% and a range between 0.01-0.08%. There was a strong positive correlation (R=0.86) between the TNb and TC contents. The TC:TN ratio had a mean value of 18.7 at the 0-10 cm depth and decreased to 10.8 at the 10-20 cm depth and further to 11.7 at the 20-30 cm depth. There were spatial variations in TC:TNb ratio. Its lowest values ranging between 4.8-11.4 were observed in lithozems in the northern part of the island (S4 and S5), pelozem (S8) and soils of non-sorted circles within periglacial zones (S11 and S12), which was explained by their very weakly developed humus layer with low carbon contents. The highest TC:TN ratios of 34-36 were found in lithozems in the southern part of the island (S3 and S6).

The pH_{H2O} of the studied soils was predominantly neutral, with a median value of 7.21, and a range of variations from weakly acid to alkaline, i.e., from 6.45 to 8.87. The pH_{KCl} had a median of 5.74, with a variation range from 4.71 to 7.47. Soils with relatively higher organic matter contents had the lowest pH, i.e., there was a significant negative correlation (R=-0.72) between the pH and TC values. However, the increase in pH with depth did not correlate with the decrease in TC, which could be explained by cryoturbation processes resulting in soil mixing. The Alexandra Land's soils with mostly neutral pH values can be contrasted to the soils of the Novaya Zemlya archipelago with the pH between strongly acid and acid (Usacheva et al. 2016). Apparently, rates of organic acid production are very low in the soils of the Alexandra Land due to the sparce vegetation cover. Despite the very slow development of soil acidification processes within the study area, the Mann-Whitney test showed that the observed values of soil pH significantly ($p<0.05$) differed from the bedrock pH, with the latter being more alkaline (see Table 2).

The textural class of the studied soils predominantly corresponded to sandy loam, with the average proportions of sand, silt and clay being 58%, 37% and 3%, respectively. The contents of fine fractions (PM2, PM10, PM50) regularly increased with depth, e.g., the clay (<0.002 mm) content increased from 2.4 to 2.7% and the silt (0.002-0.05 mm) content – from 35.8 to 42.6% (Table 3). The total content of sand fractions reached the maximum of 68.3% in the Arenic Cryosol of S10 (Fig. 3). The highest proportion of PM2 was observed in the soils of periglacial zones (S11 and S12), with the clay content of 5.9% and the silt content of 59.7% on average (see Fig. 3). The soils of periglacial zones are probably affected by deposition of fine particles from glacier's meltwaters. A similar process of formation of clay deposits within glacial valleys has been described in Spitsbergen (Dobrovol'skii 1990).

Table 3. The particle-size distribution at different depths in the studied soils.

Depth	Fractions, %						
	<0.002 mm	0.002-0.01 mm	0.01-0.05 mm	0.05-0.1 mm	0.1-0.25 mm	0.25-0.5 mm	0.5-1.0 mm
0-10 cm	2.4	7.7	28.0	23.4	25.1	6.7	1.6
10-20 cm	2.6	9.1	31.2	28.4	24.4	4.3	0.2
20-30 cm	2.7	8.7	33.8	27.9	23.2	4.0	0.2
Mean	2.6	8.6	30.6	27.2	24.0	4.9	0.6

The statistical parameters of major and trace element concentrations in the studied soils of Alexandra Land, the reference data on soil world average (SWA) contents of the same elements according to (Kabata-Pendias 2010), and the ratios of the median values of element contents in the studied soils and parent materials are presented in Table 4.

Table 4. Summary statistics of major and trace element concentrations ($mg \cdot kg^{-1}$) in the soil samples from the Alexandra Land.

Elements	Median	MAD	min	max	SWA (Kabata-Pendias 2010)	Median /SWA	Median soil/Median rock
Na_2O	2.0	0.3	0.6	2.9	3.27	0.61	0.9
MgO	5.0	0.8	1.3	7.3	2.48	2.0	1.1
Al_2O_3	15.2	1.3	12.7	25.6	15.4	0.99	1.2
P_2O_5	0.14	0.03	0.0	0.2	0.150	0.93	0.8
S_{total}	0.029	0.020	0.0	0.2	0.0621	0.47	0.9
K_2O	0.48	0.27	0.2	2.9	2.8	0.17	1.3
CaO	9.3	1.7	0.4	10.9	3.59	2.6	1.0
TiO_2	1.7	0.3	1.0	2.9	0.64	2.7	0.9
MnO	0.16	0.02	0.1	0.2	0.10	1.6	0.9
Fe_2O_3	13.3	1.4	6.4	22.3	5.04	2.6	0.9
Li	9.1	5.1	5.2	62.3	21.0	0.43	**1.3**
Be	0.79	0.12	0.6	1.8	1.34	0.59	0.9
Sc	39.2	3.0	25.4	60.6	11.7	3.4	1.0
V	357	36.9	263.1	498.3	129	2.8	0.9
Cr	130	21.2	86.8	249.1	59.5	2.2	1.0
Co	42.2	4.9	30.7	76.1	11.3	3.7	0.9
Ni	72.3	9.3	47.4	117.3	29	2.5	0.8
Cu	142	37.0	78.2	381.3	38.9	3.6	0.6
Zn	99.7	9.1	73.2	130.7	70	1.4	1.0
Ga	18.8	1.8	16.5	31.9	15.2	1.2	1.0
As	2.2	2.3	0.1	13.3	6.83	0.32	1.2
Rb	12.7	7.2	3.7	72.6	68	0.19	**1.4**
Sr	187	16.2	50.1	217.4	175	1.1	1.2
Y	25.0	2.8	9.1	32.9	23	1.1	0.8
Zr	107	15.4	83.1	220.7	267	0.40	0.9
Nb	7.5	1.7	4.8	21.5	12.0	0.63	0.9

Mo	0.62	0.41	0.1	2.0	1.1	0.56	1.1
Cd	0.10	0.05	0.05	0.47	0.41	0.24	0.7
Sb	0.16	0.06	0.1	0.7	0.67	0.24	**1.4**
Cs	0.46	0.30	0.1	4.4	5.06	0.09	0.9
Ba	80.4	54.9	35.4	629.1	460	0.17	1.1
La	8.5	1.6	3.7	20.8	27	0.31	1.0
Ce	20.8	4.0	9.3	47.0	56.7	0.37	0.9
Pr	2.9	0.4	1.1	5.4	-	n.d.	0.9
Nd	13.9	1.9	4.7	22.3	26	0.53	0.9
Sm	3.9	0.5	1.4	5.1	4.6	0.85	0.9
Eu	1.4	0.1	0.7	1.7	1.4	1.00	0.9
Gd	4.4	0.5	1.5	5.7	3.9	1.1	0.9
Tb	0.74	0.07	0.3	0.9	0.63	1.2	0.8
Dy	4.7	0.5	2.1	6.0	3.6	1.3	0.8
Ho	0.98	0.09	0.5	1.3	0.72	1.4	0.8
Er	2.7	0.3	1.5	3.7	2.2	1.2	0.8
Tm	0.4	0.0	0.2	0.5	0.37	1.1	0.8
Yb	2.6	0.2	1.8	3.6	2.6	1.0	0.8
Lu	0.4	0.0	0.3	0.5	0.37	1.1	0.8
Hf	2.8	0.4	2.3	5.8	6.4	0.44	0.9
Ta	0.45	0.10	0.3	1.3	1.39	0.32	0.9
Hg	0.031	0.023	<0.007	0.086	0.07	0.44	N.D.
Tl	0.047	0.062	0.0	0.7	0.5	0.09	0.3
Pb	2.4	0.8	1.2	12.6	27	0.09	**1.6**
Th	1.2	0.4	0.8	5.7	9.2	0.13	0.8
U	0.45	0.32	0.2	2.2	3.0	0.15	1.1

Note: The SWA is the soil world average (Kabata-Pendias 2010). The concentrations of Se, Rh, Pd, Re, Te, Ir, Pt, Au and Bi are below their detection limits. The highest Median soil/Median rock ratios are shown in bold. n.d.- not determined

The ratios of the median contents of elements in the studied soils to the soil world average contents of those elements show that the studied soils are enriched in MgO, CaO, TiO_2, Fe_2O_3, Sc, V, Cr, Co, Ni, Cu and Zn, with the bedrock being enriched in the same elements (Table 1). In the Arctic, the bedrock composition is well reflected in that of soils due to the predominance of physical alteration of rocks with only insignificant contributions of chemical processes, as compared to the regions to the south of the Arctic (Dobrovol'skii 1990).

According to the conclusions of the Arctic Monitoring and Assessment Program (AMAP 2005), assessments of heavy metals should focus on Hg, Pb and Cd, because these elements are potentially highly hazardous to the cells of living organisms in the Arctic. The present study showed that the content of Pb in the soils of the Alexandra Land was extremely low, with its median value being by an order of magnitude lower than its SWA. Even the highest Pb content (12.6 $mg \cdot kg^{-1}$) detected by us in the periglacial soil was below the SWA value. The Cd content was also low, with its median being by 4 times lower than its SWA. The Hg content varied significantly, with the higher concentrations being found in the cryoturbated raw-humus lithozem (S3).

A majority of the analyzed elements had slightly lower concentrations in the soils as compared to the bedrock, with the Median soil/Median rock ratios being around 0.8-0.9 (Table 4). Such differences between the soils and the bedrock within Alexandra Land were generally less significant than soil-bedrock differences on the more southern islands of the Novaya Zemlya archipelago, where soils are relatively impoverished in Ti and Fe and enriched (by multiples of 2-5) in P, S, Cl, Cu, Pb and Zn (Laverov et al. 2016).

Most of the analyzed elements had similar contents in the 0-10, 10-20 and 20-30 cm soil layers and parent rocks, with the Mann-Whitney test showing only insignificant differences ($p<0.05$). Likewise, upper and lower soil horizons in Spitsbergen insignificantly differ by the contents of elements, except for Cr (Krajcarova et al. 2003). The absence of statistically significant differences can be explained by (1) slow rates of soil-forming processes and low contents of organic substances in soils and (2) impacts of cryogenic processes, which cause mixing of soil materials.

However, the concentrations of some of the analyzed elements differed by 1.4-1.5 times between the upper, middle and the lower soil layers. As is shown in Figure 4, the contents of K_2O, Fe_2O_3, Co, Ni, Zn, Li, Cu and As in the 0-10 and 10-20 cm layers are significantly lower than those in the 20-30 cm layer. The contents of CaO, P_2O_5, Hg and Pb are only slightly (by 1.1-1.2 times) decreased in the upper layer as compared with their contents in the lower layer.

The distribution of chemical elements in the arctic soils and sediments depends on the contents of clay and silt fractions, organic matter contents, pH, moisture content and the presence of anthropogenic pollutants. For example, the contents of Zn, Cu, Hg and Cr in soils of the Bely Island (Kara Sea) have a significant positive correlation with the clay contents (Moskovchenko et al. 2017). The contents of Pb and Cu in the soils of Spitsbergen negatively correlate with the percentage of the 1-0.1 mm sand fraction

(Melke 2006). The organic matter content has positive correlations with concentrations of Hg (Halbach et al. 2017), Pb and Zn (Melke 2006). An intensive leaching of Mn from acid arctic soils results in the low concentrations of this element (Moskovchenko et al. 2017). Soil moisture distribution also affects the element contents, e.g., heavy metals tend to accumulate within waterlogged areas (Wojtun et al. 2013).

Factors that control the distribution of elements in the soils of the Alexandra Land were assessed on the basis of correlation analysis. The obtained values of correlation coefficients between the element contents and their distribution factors (clay content, soil pH and organic matter content) indicated that none of those factors was absolutely dominant. As a rule, values of $R<0.7$ prevailed, i.e., strong correlations were absent (Table 5). The TC content positively correlated with concentrations Hg, Pb and most lanthanoids and negatively correlated with Ni, Cr and Na concentrations in the studied soils. The observed relationship between Hg, Pb and TC confirms the dependence of those element concentrations on the organic matter content, which has been previously identified in the soils of Spitsbergen (Melke 2006; Halbach et al. 2017), and accounts for the accumulation of those elements within the upper layer of soils of the Alexandra Land (see Fig. 3).

Table 5. The physicochemical parameters and their correlations with the element contents.

Parameters	Positive correlation	Negative correlation
TC	Hg (0.64), Pb (0.55), La (0.54), Th (0.54), Pr (0.6), Ce (0.62), Nd (0.63), Gd (0.56), Dy (0.43), Tb (0.42)	Na (-0.68), Ni (-0.48), Cr (-0.44)
TN	P_2O_5 (0.53), Sn (0.53), Hg (0.38)	Na (-0.54), Ce (0.47), Nd (0.54), La (0.39)
pH_{H2O}	Ni (0.59), Cr (0.39)	Mo(-0.60), V(-0.45), La(-0.45), Ce(-0.45), Pr(-0.49), Nd(-0.54), Sm(-0.52), Eu(-0.50),Gd(-0.50), Tb(-0.50), Dy(-0.41), Hg(-0.64), Th(-0.44), U(-0.50), TiO_2(-0.45)
Clay content	Al_2O_3 (0.49), K_2O (0.41), Co (0.77), Cu (0.71), Sc (0.47), Tl (0.62), Ba (0.43)	P_2O_5 (-0.59), CaO (-0.46), As (-0.50)

Note: Values in brackets are Spearman correlation coefficients.

The soil pH positively correlated with Ni and Cr concentrations and negatively correlated with TiO_2, V, Mo, Hg and most lanthanoid concentrations (Table 5). It is known that Ni and Cr are most mobile in acid medium and least mobile in alkaline medium (Perelman and Kasimov 1999). An alkaline pH may decrease metal mobility by the formation of precipitates, by increasing the number of available adsorption sites and by decreasing the competition of H^+ for adsorption (Petruzzelli 1989). The increased concentrations of Ni and Cr in soils with high pH were probably due to their weak leaching from alkaline and neutral soils.

The concentration of lanthanoids were positively correlated with the TC content and negatively correlated with the pH. Lanthanoids have a low biological activity (Perelman and Kasimov, 1999). Therefore, the observed positive correlation with TC is unrelated to the organic matter accumulation directly. However, the organic enrichment causes a decrease in the soil pH, and lanthanoids are not very mobile in a weakly acidic medium. Perelman and Kasimov (1999) mention that alkaline groundwaters of the Kola Peninsula are enriched in rare-earth elements. It is highly probable that lanthanoids are actively leached from neutral and alkaline layers of the studied soils and rocks of Alexandra Land. This suggestion is confirmed by the fact that light lanthanoids with low atomic numbers, from La to Gd, are relatively more mobile than heavy lanthanoids, from Tb to Lu (Kabata-Pendias 2010). Lanthanoids of the light group correlate with the pH, whereas many elements of the heavy group (Ho, Er, Tm, Yb and Lu) don't show any statistically significant correlation. The soils that were relatively enriched in organic matter (primarily, the raw-humus lithozems) have relatively higher concentrations of Ln, Pb and Hg, but lower concentrations of Ni and Cr. It is known that Ni and Cr are very weakly concentrated by plants (Kabata-Pendias 2010) and they are mobile in acid medium (Perelman and Kasimov 1999). The latter results in their leaching from soils.

Correlations between the metal concentrations and the clay content in the studied soils were, contrary to our expectations, only weak in most elements (Al_2O_3, K_2O, Tl, Sc, Ba), although significant and always positive. Only Co and Cu had a strong correlation (R>0.7) with the clay content (Table 5). Therefore, the above-mentioned increase in Co concentrations in the lower layers can be explained by the migration of elements in colloidal forms with groundwater, which is typical for soils of northern regions (Pokrovsky et al., 2006).

Comparison with other islands of the Arctic

The islands of the FJL archipelago are mainly composed of basalts, which accounts for their differences from the other archipelagos of the Arctic. For that reason, it is interesting to compare our data with results of other studies on islands of the Arctic Ocean, which are summarized in Table 6.

In Alexandra Land, the soils have a relatively low concentration of Hg due to its even lower concentration (below detection limit) in the parent materials. The low concentration of Hg in the studied soils is also due to the fact that the FJL archipelago is very far from the main industrial sources of Hg emissions. The Pb concentration within the study area has the lowest value ever reported for arctic soils, which is explained by the composition of basalts.

The Cd concentration in the soils of Alexandra Land was similar to that in some soils of Spitsbergen (Plichta and Kuczynska 1991; Wojtun et al. 2019), but significantly lower than that in the soils of Novaya Zemlya (Usacheva et al 2016). Even the highest Cd concentrations (0.33 - 0.47 mg kg^{-1}) detected at site S3 are below its maximal permissible concentration of 1.1 mg kg^{-1}, i.e., below the level that indicates the Cd pollution of soils (Kabata-Pendias 2011).

The Cu concentration within the study area is very high as compared to the other arctic islands. However, even higher Cu concentrations were found in some parts of Spitsbergen, e.g., the Cu concentration of

658.6 mg kg^{-1} in soil has been reported from the Pyramiden settlement area (Krajcarova et al. 2016). The soils of Alexandra Land also have relatively high concentrations of Fe, Mn and Co. The concentrations of Zn, Ni and Cr in the studied soils are at an intermediate level between the enriched soils of Novaya Zemlya and soils of the other islands of the Arctic Ocean.

Table 6. A comparison of concentrations (mg kg^{-1}) of potentially toxic elements in soils of the Alexandra Land and other Arctic Islands

Data source	Mn	Cu	Zn	Cd	Co	Fe	Cr	Pb	Hg	Ni
1	1215[1]	160	101	0.14	43.6	9.2[1]	139	2.9	0.031	74
2	250	2.9	20.9	0.8	(<DL-10.3)	9.0	23.5	(<DL – 32)	0.022	-
3[2]	1200	59	135	-	24	8.3	216	52	-	157
4	392	23.4	75	0.14	7.4	2.9	-	12.5	-	24.1
5	365	111	79	0.2	35	2.54	42	19	0.05	27
6	217	9.8	64	0.38	-	1.08	19	10.7	0.111	11.9

Data sources: 1 – our data on Alexandra Land, median values; 2 – Bely Island, Kara Sea, median values (Moskovchenko et al 2017); 3 – Novaya Zemlya, mean values (Usacheva et al 2016) 4 – maritime lowland of western Spitsbergen, mean values (Plichta and Kuczyn´ska, 1991); 5 – Longyearbyen, Spitsbergen, median values (Wojtun et al. 2019); 6 – Svalbard, median values (Halbach et al. 2017). <DL – below the detection limit

[1]Oxide contents have been recalculated into pure element contents.

[2]In the surface layer

Conclusions

A baseline survey of the mineralogical composition, particle-size distribution, major and trace element composition and the chemical properties (pH, TC and TN) of soils and bedrock within arctic ecosystems of Alexandra Land, belonging to the Franz Josef Land archipelago, was performed. It was found that the parent materials were basalts composed of plagioclase, augite and obsidian, with a very high concentration of Cu, which was by an order of magnitude higher that the world crust average content of this element. The concentrations of Mg, Fe, Ti, Co, V, Ni, Cr and Zn were relatively high and the concentrations of Pb, Th, U, La, Bi, Sb and Sn were low. Based on the values of Gd/Yb and TiO_2/Y ratios, the studied rocks were similar to the continental trapp rocks of the Siberian Platform.

The studied bedrock had an alkaline pH. The soil pH ranged from weakly acid to alkaline, with the lowest pH values being associated with the highest carbon (TC) contents in the soils. The proportions of clay and silt fractions increased with depth. The highest proportions of fine fractions were found in the soils of periglacial zones.

The carbon (TC) contents had median values of 3% within the upper (0-10 cm) layers and less than 1% in the deeper layers of the studied soils. The nitrogen (TN) contents ranged from 0.01 to 0.59%, with the highest median value (0.16%) within the upper layers. However, soil mixing due to cryogenic processes occasionally resulted in an inverse vertical distribution of both TC and TN.

As compared to the soil world average values, the studied soils were enriched in MgO, CaO, TiO_2, Fe_2O_3, Sc, Co, V, Cr, Ni, Cu and Zn. The composition of soils was generally similar to the bedrock composition and differences between the analyzed soil layers were statistically insignificant. In particular, there was an insignificant increase (by multiples of 1.1-1.2) in the concentrations of ecologically hazardous Hg and Pb within the upper layer, which can be explained by bioconcentration processes, based on the positive correlation between the Hg and Pb concentrations and the TC contents. The concentrations of Ni, Cr and lanthanoids depended on the soil pH, with Ni and Cr being more mobile in acid medium and the light lanthanoids – in alkaline medium. For that reason, Ni and Cr were leached from the acid layers and lanthanoids – from alkaline layers. As a result, the acid soils that were relatively enriched in organic matter (raw-humus lithozems) were distinguished by the high concentrations of lanthanoids, Pb and Hg and the low concentrations of Ni and Cr.

As compared to the other islands of the Arctic, the soils of Alexandra Land had high concentrations of Cu, Mn and Fe and low concentrations of Hg, Pb and Cd. Such properties of the studied soils were predetermined by the composition of their parent materials, which were identified as continental tholeiitic basalts.

The data obtained on the soil composition within Alexandra Land can be used as the baseline criteria for the monitoring of any heavy metal pollution arising from any potential future industrial development of the island.

Declarations

Conflict of interest The authors declare that they have no competing interests.

Ethics approval The author declare that all principles of ethical and professional conduct have been followed.

Consent to participate All authors agreed to participate.

Consent for publication All authors consent for publication.

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Figures

Figure 1

Location of the study area, the soil sampling sites (S1-S12) and the bedrock core (B1).

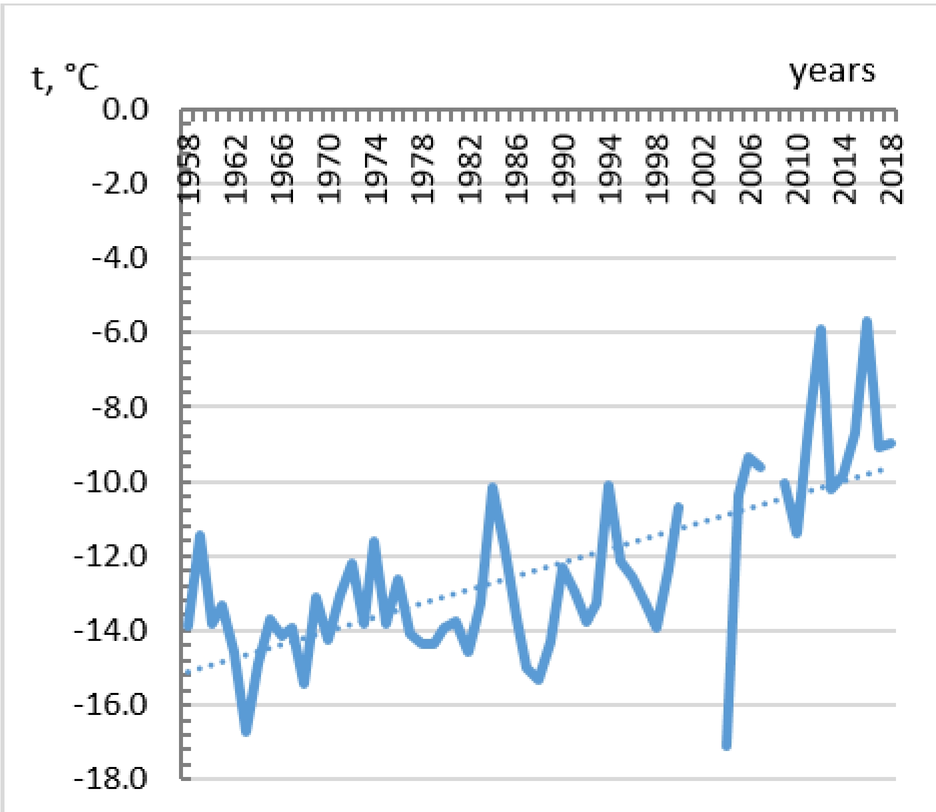

Figure 2

Mean annual temperatures of the air at the Hayes Island weather station, FJL (Bulygina et al. 2021)

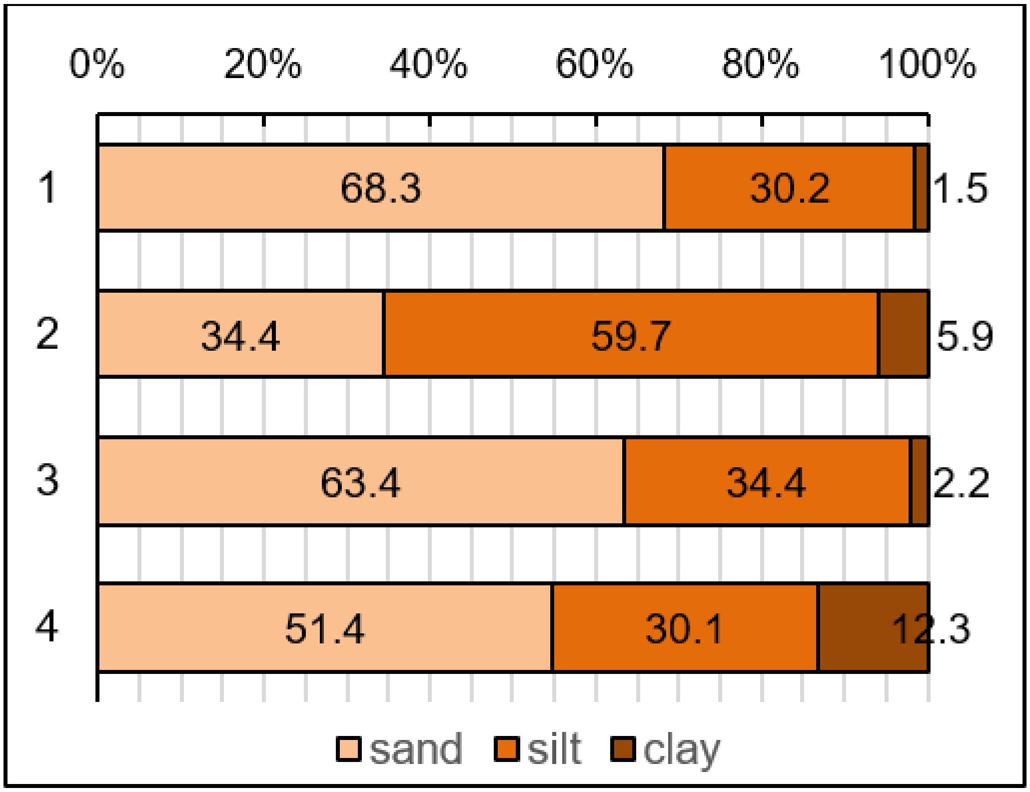

Figure 3

The distribution of particle-size fractions in different soil types: 1 – Arenic Cryosol (S10), 2 – soils of non-sorted circles within periglacial zones (S11 and S12), 3 – lithozems (S1, S2, S3, S4, S6), and 4 – pelozem (S8).

Figure 4

Chemical element contents in the soil layers: 1 – upper (0-10 cm), 2 – middle (10-20 cm), and 3 – lower (20-30 cm). The contents are expressed in % for Fe_2O_3, K_2O, CaO, P_2O_5 and in mg kg^{-1} for all other elements.