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Landscape–Geochemical Assessment of Content of Potentially Toxic Trace Elements in Arctic Soils

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Abstract: The importance of research to assess the impact of potentially toxic trace elements (PTEs) on the environment and the importance of environmental monitoring, taking into account the natural variability of soil properties, shaped the aim of our study: to determine the background concentrations of PTEs in different soil profiles in the European Northeast, specifically in the Republic of Komi in Russia, taking into account the landscape and geochemical characteristics of the area. We analysed 173 soil samples from five main soil subtypes. The acid soluble forms of PTEs (Cu, Pb, Zn, Ni, Cd and Mn) were measured using an atomic emission spectrometer. We developed a database of PTE contents and created distribution maps for the Komi Republic using GIS technologies. The study found that PTE levels in soils from accumulative landscapes (such as depressions and floodplains) were generally higher than those in soils from eluvial landscapes (interfluves). We identified correlations between the levels of different PTEs and certain soil properties, providing insights into the biogeochemical migration patterns of these elements. The differentiation of PTEs in soil profiles was more pronounced in loamy automorphic soils and less so in sandy semi-hydromorphic and hydromorphic soils. Most soils, except floodplain soils, showed a clear eluvial–illuvial pattern of PTE distribution within the mineral soil profile, whereas floodplain soils showed a more uniform PTE distribution. The results of this study are useful for assessing the contamination levels of these soil types in high-latitude regions.

Keywords: heavy metal; background concentration; soil; tundra; Cambisol; Gleysol; Cryosol; Retisol

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1. Introduction

The global nature of current problems requires modern approaches to assessing the ecological situation in specific natural biogeocenoses. Human economic activities lead to changes in the structure and functions of natural complexes: the directions and rates of migration of chemical elements change and the zones of their removal and accumulation shift [1].

Potentially toxic trace elements (PTEs), as an important component of the global economy, play a prominent role in the development of modern heavy industry and serve as an important resource on which society depends [2,3]. However, due to intensive demand and use, PTE compounds inevitably enter into soil and groundwater [4,5]. Therefore, for various reasons, natural environments are overloaded with PTEs compounds [6]. Due to their chemical interactions with soil biology, once in the soil, they are more or less included in the biological cycle. PTEs are among the most widespread and persistent pollutants in contaminated areas [7].

PTE-based contaminants entering soil can cause various manifestations of soil contamination and thus pose a threat to soil [8,9]. PTE contamination can cause phytotoxicity, affecting plant biomass by altering the shape and colour of leaves and roots [10]. In addition, PTE contamination has devastating effects on ecosystems and human health. The carcinogenic and mutagenic properties of PTEs can lead to various diseases in humans and other organisms [11,12]. Consumption of food contaminated with PTE compounds is associated with cell malformation and tumour development, making them an aetiological agent of cancer [13]. According to numerous studies, animals exposed to PTEs show symptoms such as loss of balance, slowed movements and reduced stability [14]. Pollution causes changes in the populations of wild species, often leading to death. These organisms may play a critical role in nutrient transport, further emphasising the detrimental effects of PTE pollution on ecosystem functioning [15].

In the European North-East of Russia, on the territory of the Komi Republic, there are large deposits of polymetallic ores, which are actively exploited, leading to a significant increase in PTE extraction and deterioration of the environmental situation in the region (which includes taiga and tundra zones) [16]. Anthropogenically disturbed landscapes are becoming increasingly common in the areas of PTE deposits. This degradation is caused by both mechanical disturbance of the soil cover and the direct release of toxic compounds of PTEs [17].

One of the many programmes aimed at improving the ecological situation in the Russian Federation is the environmental monitoring programme, which is designed to monitor changes in the content of PTEs in soils [18]. Their background concentration should serve as a reference point. Such information has local and regional significance, so the specificity of the chemical composition of the investigated soils must necessarily be taken into account [19,20]. However, such data are usually not available in environmental monitoring, which forces users to use global indicators, such as clusters of chemical elements in soils of the world, continents, etc. In case of a significant difference between the regional background and the global background, it is possible to overlook the local anthropogenic pollution of the land cover or, on the contrary, to consider the natural regional background as a result of anthropogenic impacts. To exclude such assessments, information on the PTE concentration in the land cover and the main soil types of each region is required [21]. Therefore, obtaining reliable information on the natural content of PTEs in Arctic soils and the processes of their accumulation and redistribution becomes crucial.

According to Russian legislation in the field of environmental regulation and standardisation [22], in order to assess the level of chemical pollution of soils as one of the indicators of negative impact on human health, it is necessary to use the characteristics developed during complex ecological and geochemical studies of the environment of territories with active sources of pollution. One of these characteristics is the chemical concentration factor, which is calculated as the ratio of the actual concentration of a given pollutant in the soil to the regional background. Existing regulatory requirements in Russia for the content of PTE in soils do not take into account differences in natural and climatic zones, which makes it difficult to apply them to assess the impact on soil cover in the regions [23,24].

Information on the background concentration of PTEs in different soil types in the Arctic regions is practically non-existent, and the little data available do not take into account the variability of their content depending on the soil genesis [25,26]. Therefore, an important task is to assess the natural level of PTE concentration in soils, which will allow an objective assessment of soil contamination and impose the necessary restrictions on industrial processes during the extraction and processing of PTEs. In addition, soils in the harsh climatic conditions of northern regions have a low self-purification capacity, which requires continuous monitoring of the levels of PTEs in them [27].

The aim of our work was to assess the background concentrations of PTEs in the profiles of different soil types in the European Northeast (Republic of Komi, Russia), taking into account the landscape and geochemical peculiarities of this territory (relief, orographic elements, soil-forming rocks, etc.).

2. Materials and Methods

2.1. Study Area

The subjects of the study were background soils of the European Northeast (Vorkuta district, Komi Republic, Russia) (Figure 1). The soils studied are mainly located in the Bolshezemelskaya tundra. The tundra zone is divided into northern and southern subzones and occupies about 10% of the total area of the Komi Republic [28]. The territory is characterised by the distribution of permafrost. In the northern subzone, the permafrost is continuous; in the southern subzone, it is discontinuous and island-like. The upper limit of permafrost varies from 0.3 to 2 m, and its thickness ranges from 40 to 100 m. Its temperature is −2–−5 °C in the zone of continuous distribution, and −2–0 °C in the zone of discontinuous and island-like distribution. The southern tundra subzone belongs to the Atlantic–Arctic climatic region, where southerly winds blow in winter and cold northerly winds blow in summer. The climate of this area is characterised by considerable severity and continentality [29].

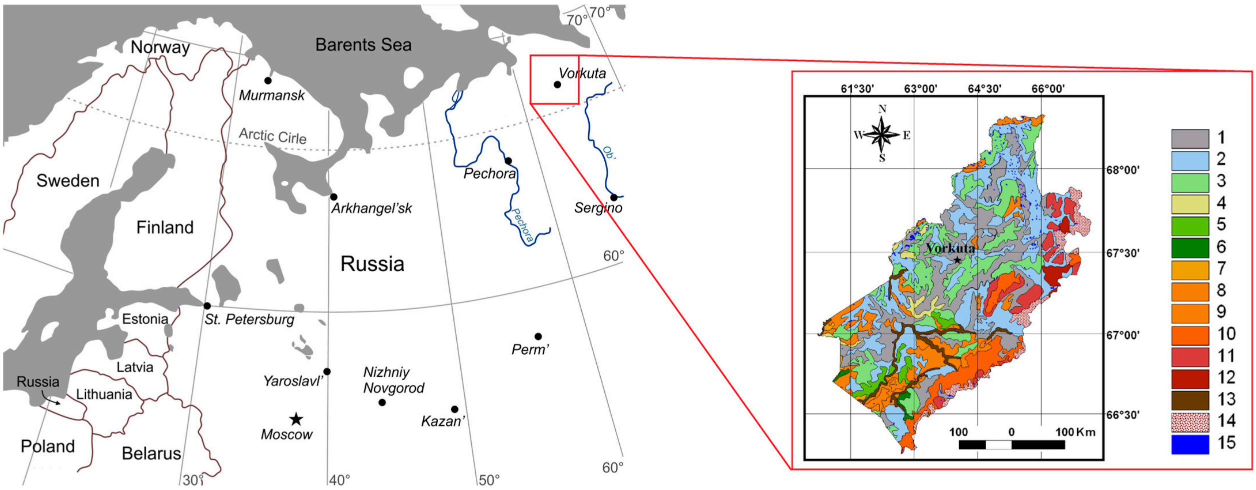


Figure 1. Soil map of Vorkuta district (Komi Republic, Russia): (1) Stagnic Cambisols; (2) Histic Gleysols; (3) Histic Cryosols; (4) Haplic Cambisols; (5) Folic Stagnic Retisols; (6) Histic Stagnic Retisols; (7) Albic Podzols; (8) Stagnic Podzols; (9) Histosols; (10) Cambisols (Skeletic); (11) Haplic Leptosols (Skeletic, Humic); (12) Haplic Cryosols; (13) Fluvisols; (14) golets (rock placers and outcrops); (15) bodies of water.

The tundra area is characterised by an average annual temperature of −6 °C (at the latitude of Vorkuta). This area is covered with snow for 7–8 months. The thickness of the snow cover is very heterogeneous and varies from 0.1 to 1.5 m and more, depending on the relief and vegetation cover. Frequent and strong winds, with a maximum speed of 30 m/s, contribute to the uneven accumulation of snow. The period of the year with negative temperatures lasts from October to May; the coldest month is January with a long-term average monthly temperature of −20 °C and the warmest month is July with a temperature of +12 °C. The period with a temperature of 0 °C lasts about 125 days, above +5 °C—90 days. The frost-free period lasts 52 days. The biologically active temperature above +10 °C is observed for 43 days. The annual rainfall is 550 mm, most of which falls between June and September. In the warm period, the atmospheric humidity is characterised by a low evaporation rate [30].

Yernik tundra is the most widespread formation in Vorkuta district, where it occupies about 60% of the territory [28]. Large massifs of yernik tundra are located on various relief elements, especially on gentle slopes. The height of the yernik varies from 15 to 20 cm to 1 m and more, depending mainly on the height of the snow cover; in the lower parts of the leeward slopes, the highest yernik thickets are observed; as one moves up the slope, the yernik becomes more stunted and sparser. Small shrubby mossy fine tundra is most common on the upper and middle parts of slopes with a shrub layer height of 30–60 cm. The composition of the latter is dominated by dwarf birch (*Betula nana*), with willows (*Salix lanata*, *S. glauca* and *S. phylicifolia*) and ledums (*Ledum palustre* and *L. decumbens*) in a subordinate position. Cowberry (*Vaccinium vitis-idaea*) and bog blueberry (*V. uliginosum*) are found in the shrub layer. The herbaceous plants are represented by reed grass (*Calamagrostis neglecta* and *C. purpurea*), tall fescue (*Festuca arundinacea*) and sedges (*Carex cinerea*, *C. limosa*, *C. rotundata* and *C. aquatilis*). The moss cover is continuous and consists of gypsum moss (*Warnstorfia exannulata*, *W. fluitans* and *Straminergon stramineum*), common haircap moss (*Polytrichum commune*) and, rarely, sphagnum mosses (*Sphagnum fuscum*, *S. riparium*, *S. flexuosum* and *S. cuspidatum*). Lichens are mainly found in inter-hill depressions [31].

The vegetation cover in the watershed and on the river overflow terraces is dominated by willow–fern moss tundra. The tundra is characterised by mosaic vegetation cover and micro-complex soil cover due to micro-relief.

The prevailing climatic conditions in the Vorkuta district exert a significant influence on soil formation. The onset of soil freezing occurs in late September, with the establishment of snow cover in October. The soil freezes deeply, and on topographical features where permafrost is present, the seasonally freezing layer merges with it. The process of soil thawing commences after the snow cover melts in early June. In some years, the complete thawing of the seasonally frozen layer is not completed during the warm period [32].

2.2. Sampling Sites

All the soils studied are located in the plain part of the Vorkuta district and are formed on claystone. All soil sampling sites were located away from potential sources of anthropogenic impact—more than 20 km from Vorkuta city, coal mines and thermal power plants, more than 10 km from other settlements and more than 5 km from railways and motorways. Organic horizon (O) samples were collected as composite samples from 5 subsamples collected by the envelope method from an area of 100 m^2. To collect the mineral horizon samples, a soil profile was dug at some of the O horizon subsample sites. The envelope method was used for sampling because it allows us to identify patterns of soil formation in different landscapes, from watersheds (automorphic soils) to geochemically subordinate landscapes in depressed areas (semi-hydromorphic and hydromorphic soils). We sampled 101 mixed samples from organic horizons and 72 from mineral horizons of five soil subtypes (Figure 2). The soil names were determined according to the World Reference Base of Soil Resources [33]. Some chemical and physical properties of the soils are given in Table 1. A more detailed description of the profiles and properties of these soils has been published previously [28].

Table 1. Soil characteristics.

Soils	Horizon	Sampling Depth, cm	pH (H_2O)	C, %	Silt, %	Clay, %
Stagnic Cambisols	O	0–7	6.0	37.5	– *	–
	G	20–50	5.2	0.50	71.3	14.4
	Bg	50–90	5.9	0.49	62.1	26.8
Histic Gleysols	O	0–21	3.7	41.8	–	–
	G	21–40	4.5	0.92	69.4	9.2
	Bg	60–95	4.7	0.51	57.1	21.0
Histic Cryosols	O	0–41	3.8	39.6	–	–
	G	41–55	3.9	3.14	68.3	9.7
	Gf	55–70	4.3	1.27	62.5	11.2
Folic Stagnic Retisols	O	0–12	4.8	39.4	–	–
	Eg	15–40	5.1	0.85	54.3	13.7
	Bg	50–140	5.6	0.17	46.6	26.2
	Cg	140–160	6.1	0.05	52.9	18.9
Histic Stagnic Retisols	O	0–30	4.5	35.6	–	–
	Ehg	30–40	4.8	10.6	53.1	12.1
	Bg	55–90	6.0	0.36	49.2	22.5
	Cg	110–120	6.7	0.08	44.2	28.0

* Not analysed.

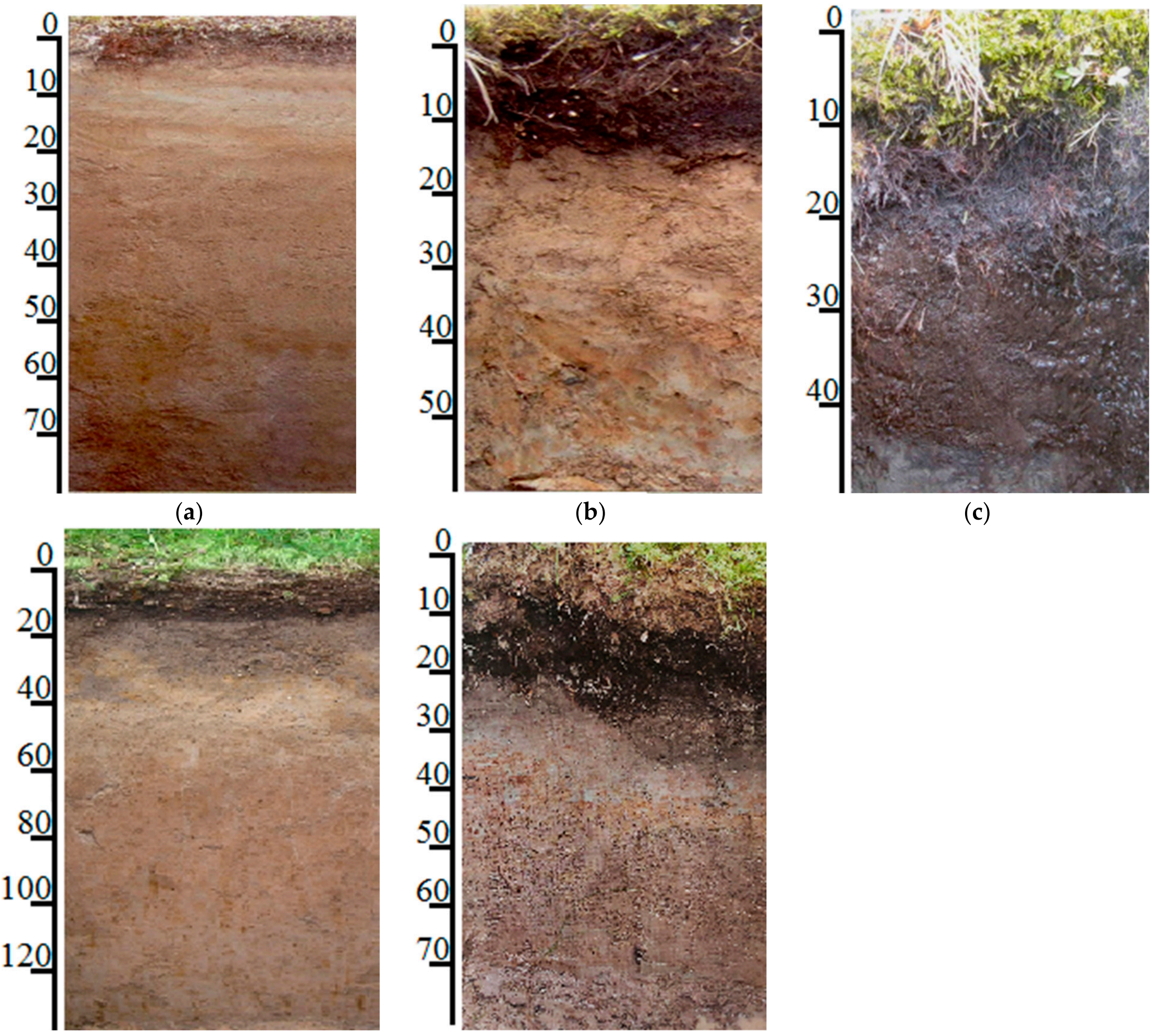


Figure 2. Soil profiles: (**a**) Stagnic Cambisols; (**b**) Histic Gleysols; (**c**) Histic Cryosols; (**d**) Folic Stagnic Retisols and (**e**) Histic Stagnic Retisols.

Stagnic Cambisols are widespread under automorphic conditions. They are confined to convex surfaces of river and watershed uplands, slope edges and are developed under sierra-lichen moss vegetation. The peculiarity of the tundra soil formation is that, despite good drainage, the over-watered gley thixotropic horizon G develops under low moisture bedding (O horizon) (Table 1).

The thixotropic horizon is underlain by a drier illuvial horizon Bg with weak evidence of gleying. The moisture-saturated gley thixotropic layer determines the development of tundra microrelief and soil tubercle stained microcomplexes [34]. The water regime of Stagnic Cambisols is stagnant-leaching. The stagnant regime is characteristic of the thixotropic gley and the upper part of the transitional horizons—they cause difficult drainage in soils. However, deep but slow infiltration of soil layers is possible throughout the warm season. In terms of temperature regime, Stagnic Cambisols belong to cold soils—to the long-frozen type of moderately cold to very cold subtypes. The noted peculiarities of tundra soil formation on loamy soil-forming rocks are formed outside the influence of permafrost, mainly determined by heavy mechanical composition of rocks and modern climate—significant excess of precipitation over evaporation [28].

Histic Gleysols are formed under bryophyte vegetation in automorphic conditions and in subordinate landscapes. They are characterised by poorly decomposed peaty litter (O) up to 20 cm or slightly more, below which lies the thixotropic G horizon (Table 1). The illuvial layer shows signs of gleying and is differentiated at depth. Soil-forming rocks may show signs of seasonal permafrost. The soils are acidic and poor in exchangeable bases. Iron dissolved under the conditions of the G horizon accumulates in the form of non-silicate forms in the upper parts of illuvial and cryogenic strata, which can act as geochemical barriers [35].

Histic Cryosols have a wide distribution and are restricted to flat, level watershed slopes, depressions, foothills and the periphery of large swamp massifs. The microrelief is tubercular. The vegetation consists of ruff, leddum, polytrichum and sphagnum mosses. The water regime is permafrost–stagnant–wet; seasonal permafrost may not be interlocked with long-term permafrost soils. Soils are gleyed throughout the profile [32].

Ritisols occupy an insignificant area of Vorkuta district (2.5%) and are distributed in the forest–tundra subzone [28]. Folic Stagnic Ritisols develop on poorly drained surfaces of watershed escarpments and on gentle slopes of river banks under coniferous and mixed forests with hypnic–polytrich, polytrich and polytrich–sphagnum ground cover. In the soil profile, the litter is a peaty horizon (O) up to 15 cm thick, under which are developed flow-humus Ehg and podzolic gleyed Eg horizons with a mass of small orthosteins. Illuvial horizon B is the least gleyed and contains orthosteins, bluish and rusty bracts. The reaction is acidic throughout the profile, with high base unsaturation in the upper part of the profile [36]. The upper horizons are significantly depleted in silt and ferrous oxides. Overwetting of these soils is associated with stagnation of atmospheric precipitation [18].

Histic Stagnic Retisols are formed in flat watersheds, in inter-valley depressions, on the edges of oligotrophic bogs, where there is almost no run-off of atmospheric precipitation and a high level of low-mineralised soil water. They form under the cover of birch and spruce forests. The thickness of the peaty litter is up to 30 cm. A podzolic gley horizon Ehg of grey or brownish colour, specific for these soils, is formed underneath, into which dark-coloured colloidal humic acids, almost devoid of bases, are released from the litter. The mineral horizons are poorly differentiated and gleyed throughout the profile [37].

2.3. Methods

The chemical analysis of the soil samples was carried out in the laboratory "Ecoanalit" of the Institute of Biology (Komi Science Center, Syktyvkar, Russia), accredited in the system of accreditation of analytical laboratories of Rosstandart. The determination of the content of acid soluble forms of PTEs (Cu, Pb, Zn, Ni, Cd and Mn) in soils was carried out according to the metrologically certified method, based on the determination of metal ions on an atomic emission spectrometer with inductively coupled argon plasma (Spectro Ciros, Kleve, Germany). The method involves the treatment of soil samples with a mixture of 70% HNO_3 and 33% H_2O_2 in the MARS 5 Microwave Accelerated Reaction System (CEM, Matthews, NC, USA) [38].

In order to visualise the background PTE concentrations, a soil map (scale 1:1 M) of the study area was digitised with already existing contours of different soil subtypes [39]. Each contour (soil subtype) was assigned a colour depending on the concentration of particular PTEs. Based on the results of the analyses, a database of PTE content in soil horizons was created using GIS technologies (ArcView GIS 3.2a). PTE concentrations in organic horizons, which are characterised by a high accumulation capacity and serve as an integral indicator of the aerotechnogenic load on the soil cover, were used to map PTE concentrations in soils (https://ib.komisc.ru/db/heavymetal, accessed on 5 November 2024).

A one-way ANOVA test was performed using Statistics 10.0 to determine differences in PTE content in organic soil horizons ($p < 0.05$).

3. Results and Discussion

Data on the background content of PTEs in the organic and mineral horizons of the studied soils are given in Table 2. They were included in the database created with the help of a GIS programme (ArcView GIS 3.2a), which is the basis for mapping the spatial distribution of natural PTEs in the soils of the Komi Republic.

Table 2. Background concentrations of PTEs in soils, mg/kg.

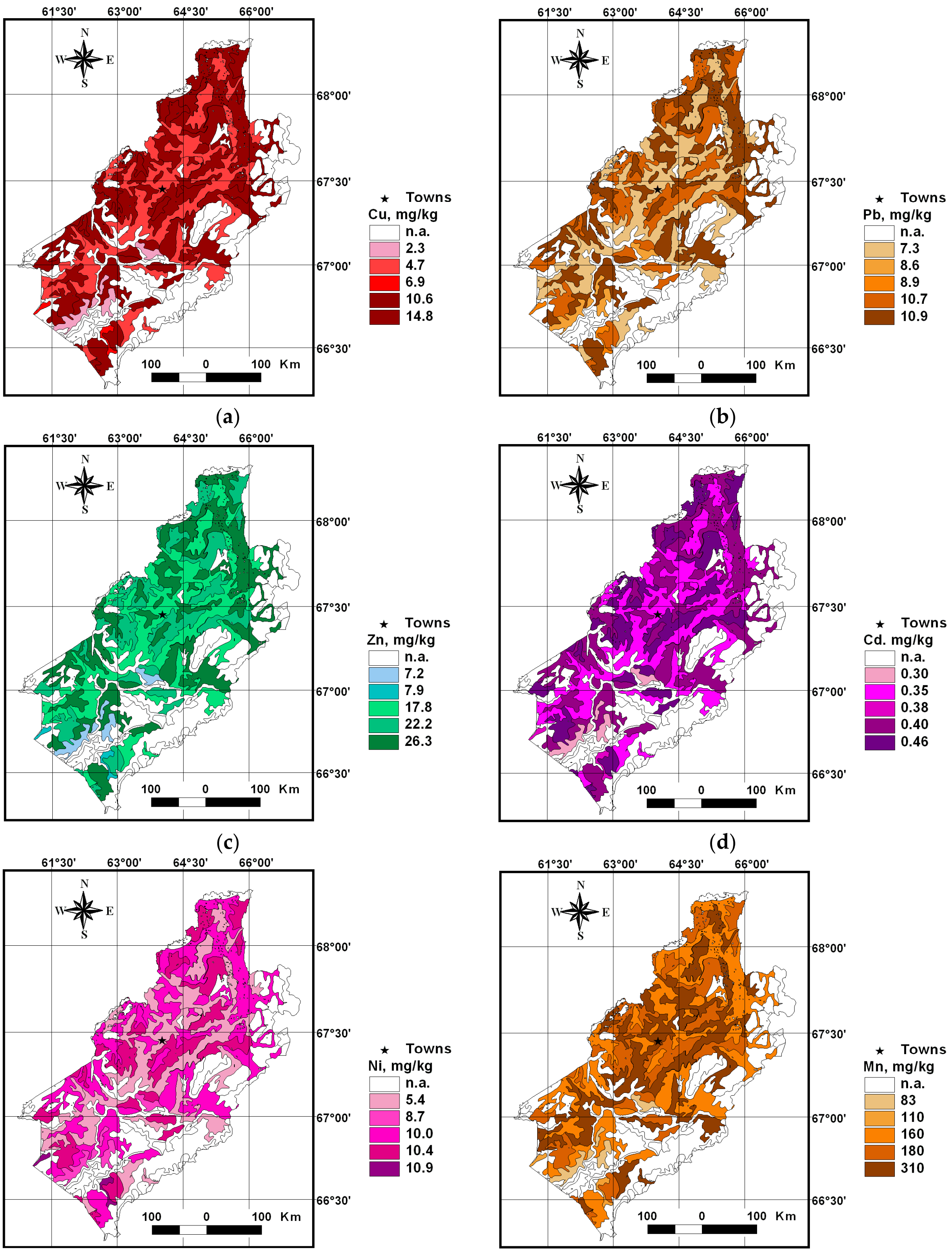
Horizons	***n***	**Cu**			**Pb**			**Zn**			**Cd**			**Ni**			**Mn**		
		$\overline{X}$	$\pm S$	V, %	$\overline{X}$	$\pm S$	V, %	$\overline{X}$	$\pm S$	V, %	$\overline{X}$	$\pm S$	V, %	$\overline{X}$	$\pm S$	V, %	$\overline{X}$	$\pm S$	V, %
Stagnic Cambisols																			
O	30	4.7 ^{a}	1.8	37.5	7.3 ^{a}	2.2	29.4	17.8 ^{a}	4.3	24.2	0.35 ^{ab}	0.23	64.2	5.4 ^{a}	1.7	30.6	310 ^{a}	110	35.9
G	6	3.8	1.2	38.6	6.2	1.9	19.7	14.2	3.8	26.6	0.22	0.12	32.4	5.3	1.9	21.4	180	40	31.5
Bg	6	9.6	2.2	36.8	6.4	1.9	25.0	16.6	4.2	36.4	0.27	0.16	28.4	7.6	2.2	29.4	210	50	42.7
Histic Gleysols																			
O	18	14.8 ^{b}	1.9	12.6	10.9 ^{b}	3.1	28.2	26.3 ^{b}	5.9	22.5	0.40 ^{a}	0.15	37.3	10.0 ^{bc}	3.6	35.7	160 ^{b}	60	35.2
G	6	15.6	1.7	24.6	9.8	2.4	27.4	26.9	6.4	29.0	0.24	0.11	35.0	12.1	3.8	27.4	140	50	40.4
Bg	6	16.2	2.1	20.1	10.5	2.6	19.4	28.0	6.0	32.4	0.31	0.17	33.4	12.8	3.9	34.8	120	40	34.2
Histic Cryosols																			
O	18	10.6 ^{c}	1.6	15.4	10.7 ^{bd}	3.3	31.1	22.2 ^{b}	7.1	32.2	0.46 ^{a}	0.20	43.8	10.4 ^{bc}	3.1	29.6	180 ^{b}	120	63.9
G	6	13.4	1.8	29.1	10.2	3.0	22.0	23.8	6.8	34.5	0.32	0.14	37.6	11.6	3.0	36.1	100	40	41.6
Gf	6	16.9	2.0	18.7	10.4	2.8	26.9	22.9	8.0	41.2	0.41	0.21	30.8	13.7	3.2	31.8	140	40	29.8
Folic Stagnic Retisols																			
O	20	2.3 ^{d}	0.7	29.7	8.6 ^{ac}	2.5	28.5	7.2 ^{c}	3.0	40.9	0.30 ^{b}	0.13	44.5	8.7 ^{b}	2.7	30.7	83 ^{c}	32	38.1
Eg	6	1.7	0.5	43.6	2.5	0.8	16.7	2.7	0.5	39.3	0.23	0.07	31.5	1.8	0.4	26.1	18	4	18.4
Bg	6	4.7	1.4	33.6	8.3	1.5	29.4	6.4	1.7	24.4	0.26	0.09	36.4	8.9	1.6	29.8	73	26	26.5
Cg	6	5.9	1.0	27.5	9.5	2.5	36.1	6.8	1.9	27.8	0.23	0.12	42.1	10.2	2.4	32.4	64	19	25.0
Histic Stagnic Retisols																			
O	15	6.9 ^{e}	1.5	22.0	8.9 ^{cd}	2.0	22.1	7.9 ^{c}	1.8	22.9	0.38 ^{ab}	0.14	38.4	10.9 ^{c}	3.1	28.7	110 ^{d}	35	32.2
Ehg	6	2.7	0.9	16.2	1.7	0.4	22.7	4.1	1.9	26.1	0.08	0.02	40.7	0.8	0.2	30.7	17	8	16.8
Bg	6	4.4	1.8	28.7	6.3	1.1	30.7	6.2	2.7	16.2	0.26	0.08	32.4	6.8	1.8	38.4	61	17	31.0
Cg	6	5.9	1.9	22.5	8.4	2.8	26.2	8.0	1.5	17.1	0.35	0.14	34.9	14	3.8	31.5	70	20	27.4

$\overline{X}$—arithmetic mean; S—standard deviation; V—variation coefficient; n—number of mixed soil samples. Different lowercase letters (i.e., a, b, c, d, and e) show significant differences among PTE contents in organic horizons ($p < 0.05$).

The accumulation and distribution of PTEs in the soil surface depends on a number of factors: the qualitative and quantitative composition of soil organic matter [40]; the granulometric and chemical composition of soil-forming rocks [41]; the relief of the territory, which determines the direction of geochemical runoff [42]; the type of soil formation, which determines the current movement of elements in the zone of hypergenesis; and for anthropogenic soils, also the type of use of the territory, the amount of dust load, vehicle emissions, the structure of the building, the degree of greening and the sealing of soils [1].

In mapping the content of different PTEs in soils, the mass fractions of these components in organic horizons were used, which have an accumulation capacity and are an integral indicator of the aerotechnogenic load on the soil cover (Figure 3).

The results of the studies show that in the soils of the tundra zone of the Komi Republic formed on loamy sediments, the content of PTEs in organic horizons follows or is close to the normal distribution law. The data of Table 2 show that the range of background fluctuations of the content of most PTEs in organic horizons with the significance level of 0.5 is close for two Retisols (Pb, Zn and Cd), as well as for Gleysols and Cryosols (Pb, Zn, Cd, Ni and Mn). This is due to the uniformity of the soil-forming rocks, the close granulometric composition of the soils on loams, and the common patterns of material migration across the landscape. Similar patterns of PTE contents were observed in soils formed on ancient alluvial and water–glacial sandy sediments (Albic Podzols) and on poorly drained plain watersheds of sloping hill, fluvioglacial terraces covered with sandy sediments (Histic Podzols), but the absolute PTE content in these soils is lower than in soils formed on loamy soil-forming rocks [43].



(**a**) (**b**)

(**c**) (**d**)

(**e**) (**f**)

Figure 3. Maps of PTE content in soils of the Vorkuta district (Komi Republic, Russia): Cu—copper (**a**), Pb—lead (**b**), Zn—zinc (**c**), Cd—cadmium (**d**), Ni—nickel (**e**), Mn—manganese (**f**), n.a.—not analysed.

The results of the determination of the PTE content in the studied soils allowed us to establish that during their distribution along the profile, there is a noticeable accumulation of elements in organic O and mineral C horizons. These horizons act as a geochemical barrier to the migration of PTEs within the profile.

Copper. The most abundant form in the environment is Cu^{2+}. Toxicity is low to moderate [22]. Excessive copper ions in food lead to liver disease and Wilson's disease. Sources to the environment include metal coatings, copper pipes and the pre-mining industry [44]. The background copper content in organic horizons of soils formed on loams has a wide range from 2.3 to 14.8 mg/kg soil (Figure 3). The maximum copper content was found in Histic Gleysols. The accumulation of copper in soil profiles is generally poorly expressed. The correlation coefficients are $r_{\mathrm{Cu–Pb}} = 0.75$, $r_{\mathrm{Cu–Zn}} = 0.73$ and $r_{\mathrm{Cu–Cd}} = 0.67$, reflecting the similar orientation of biochemical processes during soil formation: accumulation in organic horizons, intra-soil migration and migration in landscapes.

Lead. The most common form in the environment is Pb^{2+}. The level of toxicity is very high [22]. Toxic effects include anaemia, kidney failure, brain damage and its replacement of calcium in bones. Sources to the environment include lead pipes, paints, antioxidant additives in petrol and metallurgy [45]. The lead content in the organic horizons of the soils studied varies within the range of 7.3–10.9 mg/kg (Figure 3). Significant correlation coefficients were found between lead and copper ($r_{\mathrm{Cu–Pb}} = 0.75$), nickel ($r_{\mathrm{Pb–Ni}} = 0.66$) and cadmium ($r_{\mathrm{Pb–Cd}} = 0.62$) concentrations.

Lead ions are able to form strong complexes with organic matter and soil minerals and therefore have better sorption properties than other metals, which limits the ability of lead ions to migrate. As a result, the distribution of lead in the profiles is relatively uniform. The exception is the podzolic horizons (E) of the Retisols, which have much lower organic matter and silt fractions and cannot retain lead ions. For the same reason, soils formed on sandy sediments are depleted in lead compared to soils formed on loams [43].

Zinc. The most common form in the environment is Zn^{2+}. The degree of toxicity is low [22]. Toxic effects include vomiting on ingestion of large doses. Sources to the environment include alloys, metal plating, metallurgy and ore waters [46]. The zinc content in the upper horizon of the soils investigated varies between 7.2 and 7.9 mg/kg. The degree of zinc enrichment in tundra soils (Cambisols, Gleysols and Cryosols) is significantly higher than in Retisols formed in forest tundra (Figure 3). The increase in the degree of hydromorphism and the thickness of the peat layer favours an increase in zinc content. Statistical processing of the analytical material allowed us to identify correlations between zinc and copper ($r_{\mathrm{Cu–Zn}} = 0.73$), zinc and cadmium content ($r_{\mathrm{Zn–Cd}} = 0.57$).

Hernandez-Soriano and Jimenez-Lopez [47] reported that increased Zn release in wet soils is significantly correlated with organic matter solubilisation, which is similar to our results. This may also be due to the strong complexation of Zn with some organic ligands in the aqueous phase (logK = 11) [48] and the increase in Zn solubilisation with increasing humic and fulvic acid content in soil solution [49]. However, Zn^{2+} binding in the soil solid phase can be complex, either by adsorption and salt formation or by the formation of chelate and complex bonds. Zn sorption processes associated with organic matter as well as with other substances in the solid phase, such as clay minerals and oxides, require further investigation.

Cadmium. The most common oxidation level in the environment is Cd^{2+}. The level of toxicity is very high [22]. Toxic effects include the appearance of protein in urine, kidney stone disease, hypertension, reduction in haemoglobin in blood, accumulation of poison and destruction of the nervous system. Sources of input into the environment include metal coatings, mining, silver-cadmium batteries and cigarette smoke [50]. Under the influence of biological factors, surface soil horizons are enriched with cadmium in the process of development, and its content in the organic part of the soil profile in the investigated areas reaches 0.30–0.46 mg/kg (Figure 3). Cadmium content in soils correlates with copper ($r_{\mathrm{Cu–Cd}} = 0.67$), with lead ($r_{\mathrm{Pb–Cd}} = 0.62$) and with zinc ($r_{\mathrm{Zn–Cd}} = 0.57$).

Accumulated landscapes are the most enriched with cadmium, and eluvial landscapes are the least enriched. The highest Cd concentrations were observed in soils further down the slope (Histic Cryosols, Histic Gleysols and Histic Stagnic Retisols) (Table 2), which may be related to the good solubility of Cd compounds and lateral transport capacity. In slowly and shallowly thawing loamy soils, summer moisture movement is difficult. It accumulates above the permafrost water table. Lateral discharge above the permafrost moisture is activated during intensive thawing of the frozen layer and during the period of incipient soil freezing, when the moisture of the permafrost horizons is squeezed between the upper and lower freezing fronts and receives additional pressure [51].

The soils with the highest Cd contents also contained high amounts of organic matter, with the exception of the Histic Stagnic Retisols. This result is consistent with previous findings for Cd in riparian soils of reservoirs [52]. Illuvial horizons usually represent a geochemical barrier to cadmium migration in the soil profile [43,53].

Nickel. The most abundant form in the environment is Ni^{2+}. Its toxicity is low [22]. Toxic effects include its being suspected to be carcinogenic. Sources to the environment include alloys, metal coatings and waste gases from nickel production by carbonyl decomposition of $Ni(CO)_4$ and fuel combustion [54]. Nickel distribution is heterogeneous not only in space but also in the vertical profile of soils [43]. The highest absolute nickel contents are characteristic of the most hydromorphic soils—Histic Stagnic Retisols (10.9 mg/kg) and Histic Cryosols (10.4 mg/kg) (Figure 3). The soils investigated are not characterised by accumulation in illuvial horizons. A correlation dependence was found between nickel and lead ($r_{Pb-Ni} = 0.66$).

Manganese is one of the most abundant elements in the Earth's crust. The most common oxidation states in the environment are Mn^{2+} and Mn^{4+}. Its toxicity is low [22]. Chronic manganese poisoning can occur in both nervous and pulmonary forms. Symptoms include indifference and apathy, drowsiness, anorexia, headache, dizziness and asthenia. There may be attacks of excitability, difficulty in walking and coordination, cramps and back pain [55]. In the soils studied, the maximum manganese content is characteristic of the organic horizons (zone of active accumulation) and ranges from 83 mg/kg in Folic Stagnic Retisols to 310 mg/kg in Stagnic Cambisols (Figure 3). The accumulation of manganese in the upper soil horizons is due to its high content in autumn. In hydromorphic soils, manganese migration is associated with high moisture and reducing conditions. Periodic reducing conditions increase the solubility of manganese compounds and lead to its removal outside the soil profile. When reducing conditions are replaced by oxidising conditions (summer period), segregation of iron and manganese hydroxides and formation of various types of ferrous-manganese neoplasms (nodules, admixtures) takes place. At the boundary between reductive and oxidative processes, manganese is deposited at the oxygen barrier in the form of hydroxides, which can act as a sorption geochemical barrier for other PTEs.

That some PTEs are strongly enriched in organic horizons compared to mineral horizons, regardless of soil type, is supported by data from the Barents Ecogeochemical Project [56,57] and forest soils from central Norway [58].

The organic horizons of natural soils are important geochemical barriers where fractionation, especially of PTEs, occurs during soil formation according to their physicochemical properties. Many elements tend to be enriched in the O horizon by uptake by plants and sediments. The extent of enrichment at the Earth's surface depends on the binding properties and kinetics of organic layer formation and decay, and on bioproductivity [59]. This fact is often ignored in modern environmental science, and the accumulation of these elements in the O horizon or topsoil is usually referred to as anthropogenic pollution [60]. The fact that plants can absorb and accumulate many trace elements has been successfully exploited by exploration geochemists in the search for mineral deposits [61].

Human impact on the environment at continental and global scales has been a widely discussed topic in recent years. Long-range transport, especially of heavy metals through the atmosphere, has been demonstrated using various samples such as snow and ice cores [62,63] and terrestrial mosses [64]. However, there is still no consensus on the relative influence of anthropogenic and natural sources of PTEs in soils of remote areas. When comparing the geochemistry of organic horizon samples with that of soil mineral horizons, the analytical results differ significantly (Table 2). However, the question of whether such differences, especially for PTEs, are due to the composition of the geological substrate, biogenic processes or anthropogenic influence remains unresolved.

Several pieces of environmental legislation mention background concentrations or "normal" levels of contaminants in soils [22,65]. Our results showed that PTE concentrations can vary widely even within the same soil type. Therefore, for ecological purposes, it is more appropriate to use the upper threshold of the PTE concentration for each soil type rather than the arithmetic mean or median. This threshold can be expressed as the background PTE concentration, defined as the upper 95 percent confidence limit of the 95th percentile for the results associated with a particular soil type [66]. In this case, PTE concentrations up to (and including) the calculated threshold concentration can be considered typical and widespread for a particular soil type. The choice of the 95th percentile is somewhat arbitrary, but it covers a significant part of the normal background variation, excluding extreme values. It is also common practice to use the mean ($\overline{X}$) plus $2S$ (S = standard deviation), which represents 95% of the data for a normalised distribution, when determining the geochemical background, which is of great economic importance in the search for ore bodies.

The calculation of PTE threshold concentration values for the studied soils (Table 3) shows that their maximum values occur in tundra soils—Histic Gleysols (for Cu, Zn and Ni), Histic Cryosols (for Pb and Cd) and Stagnic Cambisols (for Mn). These three soil types are dominant in the Vorkuta district and cover more than 60% of the area.

Table 3. Threshold concentrations of PTEs in organic soil horizons, mg/kg.

Soils	Cu	Pb	Zn	Cd	Ni	Mn
Stagnic Cambisols	8.3	11.7	26.4	0.81	8.8	530
Histic Gleysols	18.6	17.1	38.1	0.70	17.2	280
Histic Cryosols	13.8	17.3	36.4	0.86	16.6	420
Folic Stagnic Retisols	3.7	13.6	13.2	0.56	14.1	147
Histic Stagnic Retisols	9.9	12.9	11.5	0.66	17.1	180

4. Conclusions

The results of the landscape–geochemical assessment of the ecological status of soils allowed us to establish norms of the regional background PTEs for the Arctic soils of the European Northeast of Russia. Based on the obtained data set, an up-to-date database was created and is freely available (http://ib.komisc.ru/db/heavymetal, accessed on 5 November 2024). It allowed us to automate the input, storage and analysis of materials and served as a basis for the creation of cartograms of spatial distribution of PTEs in background soils.

The thresholds of PTE concentrations were found to be in a wide range. Their maximum values fall on tundra soils—Histic Gleysols (for Cu, Zn and Ni), Histic Cryosols (for Pb and Cd) and Stagnic Cambisols (for Mn). These three soil types are dominant in Vorkuta district, occupying more than 60% of the territory. The results will be in demand for systematic monitoring studies and comprehensive assessment of the ecological situation of the European Arctic territory. The obtained standards can be used in the preparation of projects on engineering and environmental expertise of territories proposed for the construction of new facilities and development of mineral deposits.

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