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Ecological Risk Assessment of PTEs in Topsoils Impacted by Diamond Mining (Yakutia, Russia)

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Abstract. The concentrations of potentially toxic elements (PTEs) in the topsoils of Udachny mining area were determined. The soil samples were taken from the 42 topsoil samples at a depth of 0-20 cm. The concentrations of PTEs (Pb, Cd, Cr, Zn) were analyzed by the atomic absorption method on MGA-1000. In addition, the pH and soil organic matter (humus) were measured for each sample. The potential ecological risk was quantitatively estimated for each site. The most severe PTEs soil contamination in the study area was Cd, followed by As, Pb, Cr, and Zn. Local areas with a significant potential environmental risk ($300 \leq RI < 600$) have been established near the kimberlite pipe and overburden dump.

1 Introduction

The influence of anthropogenic factors can lead to the disruption of natural flows and the redistribution of chemical elements in the components of the environment [1–4]. Mining is the main source of PTEs in the environment [5–7]. And anthropogenic processes leading to environmental pollution proceed faster than natural ones [8].

Soil is the most important component of the environment because it is not only a geochemical absorber of pollutants, but also acts as a natural buffer by controlling the transfer of chemical elements and substances to the atmosphere, hydrosphere and biosphere [9].

Yakutia is the largest region of the Russian Federation, a unique territory in terms of diversity, quantity and quality of minerals. Accordingly, Yakutia is characterized by a potentially high level of soil pollution and the destruction of the fertile layer of the earth due to the accumulation of toxic substances, including PTEs [10]. Therefore, conducting such studies becomes extremely important.

2 Materials and methods

The studies were carried out in the central part of the Daldyn-Alakit mining region of North-Western Yakutia (North-East of Russia) on the territory of the Daldynsky kimberlite

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field (N 66°25′47″ E 112°24′07″). The Udachny Mining and Processing Division (Udachny MPD), which is one of the largest industrial enterprises in Yakutia, is located on the territory of the Daldynsky kimberlite field (Fig. 1). Mining is carried out by the open-pit method. Emissions into the atmosphere from the Udachny MPD had increased from 1.36 thousand tons in 2005 to 3.85 thousand tons in 2020 [11].

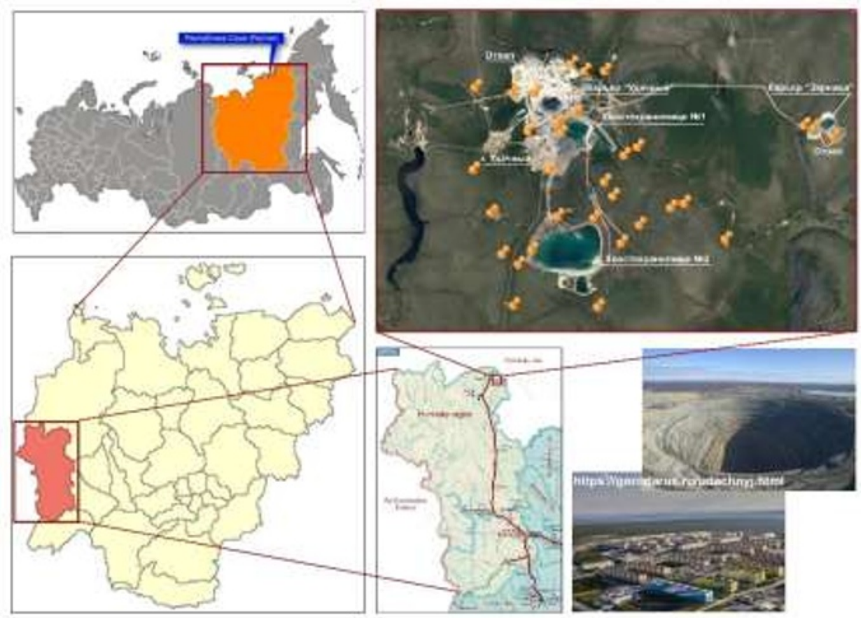

Fig. 1. Map of the location of the study area with plotting soil sampling points on the territory of the Udachny Mining and Processing Division (MPD)

Cryozems (according to the WRB Cryosols) occupy 40.7% of the total area of the soil cover of the Daldino-Alakit district. Permafrost alluvial soils (according to WRB Fluvisols) belong to the intrazonal type and are located within this area in 19.4% of the area. Permafrost soddy calcareous incompletely developed (according to WRB Rendzic Leptosols) and permafrost soddy gley (according to WRB Umbric Gleysols) soils are subordinate types soils [12].

In the course of field work, the key areas on the territory of the industrial site of Udachny Mining and Processing Division (near the kimberlite pipe pit, dumps, tailings ponds, factories, and other technogenic objects) were selected during fieldwork, where soil samples were taken. Soil sampling in the study area was carried out from the topsoils to a depth of 0–20 cm, where the main changes in physicochemical properties associated with anthropogenic load occur. A total of 42 samples of soil material were taken.

The mobile forms of Pb, Cd, Cr, Zn, and As were determined in soil samples by atomic absorption spectrometry on an MGA-1000 GK Lumex in 1 N HNO_3 extractant, which, unlike H_2O and 1 N HCl extracts acid-soluble elements that are more firmly bound to the soil. Physical and chemical indicators were determined by the potentiometric method (pH), by colorimetry - the organic matter content according to I.V. Tyurin. The quantitative data were processed using Statistica 13.0, SPSS Statistics, OriginPro 2021, and Surfer.

The quantitative approach developed by Hakanson was applied to a broader assessment of the environmental risk associated with contamination of the topsoil of the study area with potentially toxic elements [13]. The potential environmental risk factor of a given contaminant (E(i)) is defined as:

$$E(i) = Ti \times (Ci/C_0), \tag{1}$$

where Ti is the toxic-response factor for a given substance (i.e., Cd=30, As=10, Pb=Ni=5; Cr=2; Zn=1), Ci is the PTEs content in the topsoil, and C_0 is the regional background value of heavy metal in the topsoil.

Regional background values for the content of mobile forms of trace elements are based on the average geometric values of soil samples (n=179) of natural/undisturbed landscapes outside the zone of influence of the mining and processing division. Statistically reliable sampling, and calculated parameters (variability, standard deviation) allow us to accept the calculated geometric mean values as background parameters of the content of mobile forms Pb, Cd, Cr, Zn and As. And apply them in the formation of geoecological load or calculation of the ecological risk assessment.

The sum of the individual potential risks factors (*E(i)*), that is the potential ecological risk index (RI), is the potential risk index for a region. *RI* can be expressed as:

$$RI = \sum_{i=1}^{n} E(i) \tag{2}$$

The following terminology was used to describe the potential ecological risk factor:

a) $E(i) < 40$; $RI < 150$ → low potential ecological risk;
b) $40 \leq E(i) < 80$; $150 \leq RI < 300$ → moderate potential ecological risk;
c) $80 \leq E(i) < 160$; $300 \leq RI < 600$ → significant potential environmental risk;
d) $160 \leq E(i) < 320$ → high potential ecological risk;
e) $E(i) \geq 320$; $RI \geq 600$ → very high potential ecological risk.

In this study, the Hakanson method was used to assess the ecological risk from studied PTEs in the topsoil of the study area.

3 Results and discussion

The content of organic matter (humus) in the topsoils of the study area is quite high and is characterized by high spatial variability (from 0,4 to 34%), the maximum value exceeds the minimum by 30 times. Areas with the maximum values of the indicator were noted on the territory of the tailing, quarry and dump, which indicates the anthropogenic introduction of carbon-containing components (various oils, gasoline, fuel) into the studied soils. Soil pH ranges from 6.3 to 7.4. Most of the soil samples were neutral, and their proportion was 40%, 35% of the soil samples were slightly alkaline and only 25% had a slightly acidic reaction. There is a concept of pH precipitation, where certain trace elements can precipitate at certain pH intervals. Thus, the elements Pb and Zn at a given pH range of the studied area, fall within the pH limit of hydroxide precipitation and, accumulating in the soil, represent only a potential hazard so far. When the pH of the environment changes toward acidification, these elements will change from an inert form to an acid-soluble form, i.e., the most mobile, which poses an ecological hazard to adjacent environments.

The descriptive statistics of PTEs concentration are summarized in Table 1. Mobile forms of PTEs are the most active pollutants, capable of transferring from solid phases to soil solutions and being absorbed by plants [14]. The geochemical series of mean values of PTEs distribution in descending order for the topsoils (0–20 cm) is as follows: Zn > Cr > Pb > As > Cd.

Table 1. Statistical characteristics of PTEs (mg/kg) in soils of study area, n=42

Index	Pb	Cd	Cr	Zn	As
Mean	2.30	0.12	4.53	20.74	0.20
Geometric mean	1.48	0.06	2.49	12.36	0.14

Min	0.12	0.00	0.14	1.29	0.02
Max	5.23	0.88	8.52	101.3	0.70
Standard deviation	1.58	0.16	3.30	22.3	0.025
Variation coefficient	2.51	0.03	10.86	499.3	0.16

It is supposed that elements of natural origin usually have low CVs, while elements associated with anthropogenic sources have high CVs and reflect a heterogeneous distribution of concentrations [15]. However, in the environmental conditions, the soils of ore fields often acquire their characteristic content of trace elements as a result of the transformation of the original rocks by the soil-forming process [16]. Based on this, it is quite logical that associations of elements in significant concentrations reflecting the geochemical specific nature of the territories of deposits will also be found in environmental conditions and, accordingly, they will differ in high variability, which forms a natural anomaly, which is reflected in the soil cover. And technogenic anomalies are characterized by the chaotic nature of their occurrence, the absence of any regularities and their confinedness to a certain source of influence. The variation coefficients of PTEs in the topsoil of the Udachny Mining and Processing Division decrease in the order Zn > Cr > Pb > As > Cd. These results indicate that the distribution of Cd, Pb, As, and Cr in the study area is more homogeneous than that of Zn. Thus, Zn is more likely to be of technogenic origin.

In this study, the Hakanson method was used to assess the potential environmental risk from the investigated PTEs in the topsoil. The Hakanson method considers different potential toxic response factors for different PTEs concentrations. And other methods, such as contamination factor method (CF), pollution load index method (PLI), geoaccumulation index method (Igeo), and enrichment factor method (EF), are based on the content of the contaminants, without taking into account the different toxicity of the contamination to human and various types of biota [17, 18]. Therefore, the method of Hakanson is more comprehensive.

Fig. 2 shows the potential ecological risk factors (E(i)) of different PTEs in the topsoil in this study. The order of the mean E(i) for the PTEs in the topsoil was as follows: Cd > As > Pb > Cr > Zn. The mean values of E(i) of Pb, Cr, Zn and As, are all less than 40, indicating that these heavy metals posed a low ecological risk in the topsoil of the study area. Cd has a higher average E(i) value (60.69), indicating that Cd represents a moderate potential environmental risk at some sampling sites. Some study sites showed an increased potential environmental risk for one or more types of PTEs, namely those located in close proximity to a kimberlite pipe, tailings and overburden dump. In general, Cd poses a higher individual environmental risk than other studied PTEs. Studies show that almost all enterprises emit dust into the environment, which differs in the content of Cd, which significantly exceed its levels in the upper horizon of soils [14, 19]. Therefore, the frequently observed surface layer enrichment in Cd is related to pollution [20]. Also, the greatest influence can be exerted by a high content of organic matter, which acts as a biogenic barrier due to the slightly decomposed organic matter characteristic of this area, which accumulates high concentrations of Cd. As evidenced by the positive correlation of humus content with cadmium concentrations (r=0,45).

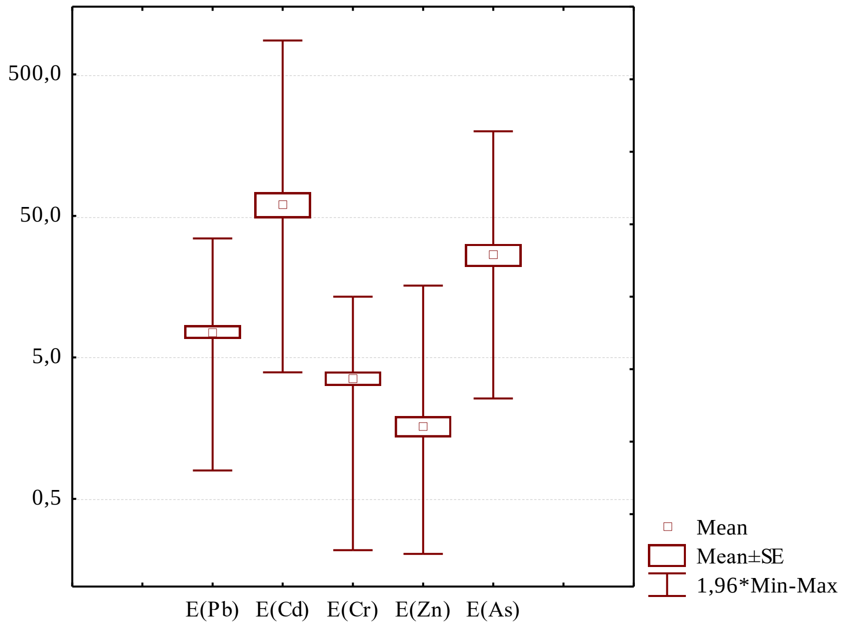

Fig. 2. Potential environmental risk factors (E(i), the maximum, mean, and minimum values) in the topsoil of the study area

Potential environmental risk indices (RI) were calculated to assess the contamination of several PTEs in the topsoil. RI values were less than 300 for most of the sampling sites, identifying these sites as low to moderate environmental risk. RI values ranged from 300 to 600 for the topsoil located near the kimberlite pipe and overburden dump, confirming that these sites were subject to very high potential environmental risk associated with PTEs. Local areas with a significant potential environmental risk ($300 \leq RI < 600$) have been established near the kimberlite pipe and overburden dump.

Thus, industrial discharges are considered to be responsible for the highest environmental risk of pollution by several PTEs.

4 Conclusions

The geochemical series of distribution of mean values of PTEs for the topsoil of the territory of the industrial site of the Udachny MPD in descending order is as follows: Zn > Cr > Pb > As > Cd.

Some sampling sites concentrated in mining areas showed a higher potential environmental risk for one or more PTEs species. The most serious soil pollution by PTEs in study area was Cd, followed by As, Pb, Cr and Zn.

Thus, all these PTEs in the topsoil cause serious concern in terms of the environmental hazard they pose for the topsoil of the territory of the industrial site of the Udachny MPD.

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