



Long-term geochemical monitoring of the soil cover in the impact zone of diamond mining enterprises: a case study in the Nakyn kimberlite field, Russia

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Abstract The most severe disturbance of the earth's surface occurs when the open-cut method of mineral deposits mining is used. The geoecological situation was assessed based on the nature of the soil cover based on the example of an industrial site of a diamond mining and processing plant located in the permafrost zone. During the period from 2007 to 2018, the soil cover of the industrial site is characterized by polyelement contamination. In the surface, soil horizons were an increase in the concentrations of mobile forms of Mn, Zn, Cd, Cr, Co, and Ni. It is identified that AO, ABcr, and CR are the accumulation horizons if the soil profile is preserved. Mobile forms Mn, Zn, Ni, Cr, Co, and As can migrate along with the soil profile to a depth of 40–50 cm depending on the amount of soil organic matter, the degree of its decomposition, and the scale of the cryoturbation. Research in 2018 allowed us to localize and confirm the increase in the area of contamination of the industrial site. Areas with an extremely dangerous category of soil cover contamination increased by

3 times compared to 2014. The results obtained are the basis for a more detailed study of the horizons of geochemical accumulation and the creation of artificial geochemical barriers with the development of technologies for the subsequent extraction of useful components.

Keywords Heavy metals · Soil contamination · Trace metals · Western Yakutia · Diamond mining quarries · Kimberlite pipes

Introduction

On the territory of Yakutia, five commercial diamond-bearing kimberlite fields are grouped within the central part of the Siberian craton: Malobotuobinsky, Nakynsky, Daldynsky, Alakit-Markhinsky, and Verkhnemunsky. Intensive development of open fields using high-power machinery and mining equipment inevitably leads to a violation of the natural landscape, the water regime of rivers, and, as a result, the formation of vast areas with technogenically transformed relief. As a rule, during mining operations, the territories adjacent to the deposit are polluted; there are centers of erosion; and the soil layer is subjected to physical, mechanical, and chemical effects. Migration geochemical flows that are characterized by high concentrations, including heavy metals, extend beyond the limits of the mining area (Sorokina & Kiselev, 2005; Liakopoulos et al.,

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2010; Basova et al., 2010, 2012; Ismailov, 2011; Belosheikina et al., 2020; Sun et al., 2018). The situation is complicated by the weak resistance of northern ecosystems to various forms of anthropogenic activity (Volpert & Martynov, 2011). In the northern regions, the soil, which is considered a “self-cleaning filter” of nature, largely lose their disinfecting properties due to the not large thickness of the profile; poor drainage annual freezing, which contributes to the concentration of pollutants in the soil water; and a short period of biological life, as well as the presence of a water-resistant rock (confining layer) in the form of a suprapermafrost horizon. These features cause low stability of cryogenic soils and acceleration of their pollution processes in zones of technogenic pressure (Makarov, 2010; Tentyukov, 2013; Gololobova & Legostaeva, 2017). Therefore, there is a need to assess soil contamination in the cryolithozone that is an integral part of complex geoecological research that creates a basis for planning measures to reduce the consequences of mining ore and placer deposits of diamonds in the conditions of cryogenesis.

Overview of the study area

The study area is located in the Republic of Sakha (Yakutia), Russia, on the territory of the Nakyn kimberlite field, where the Nyurbinsky mining and processing plant is situated (Fig. 1).

The analysis of the geoecological situation on the territory of the development of primary diamond deposits in the Western Yakutia is carried out on the example of the industrial site of the Nyurbinsky mining and processing plant based on the generalization and interpretation of archived data and the results of our own observations in the period 1994–2018.

Nakyn field is on the left bank of the Markha river in the interfluvium of the Nakyn and Khannya; it includes highly diamondiferous kimberlite of the Botuobinsky pipe (discovered 1994, mining started in 2015), Nyurbinsky (discovered 1996, worked since 2001), Markhinsky (discovered 1999, mining not started), and Maysky (discovered 2006, mining not started), followed by buried diamond placers, and refers to a site with complex search conditions

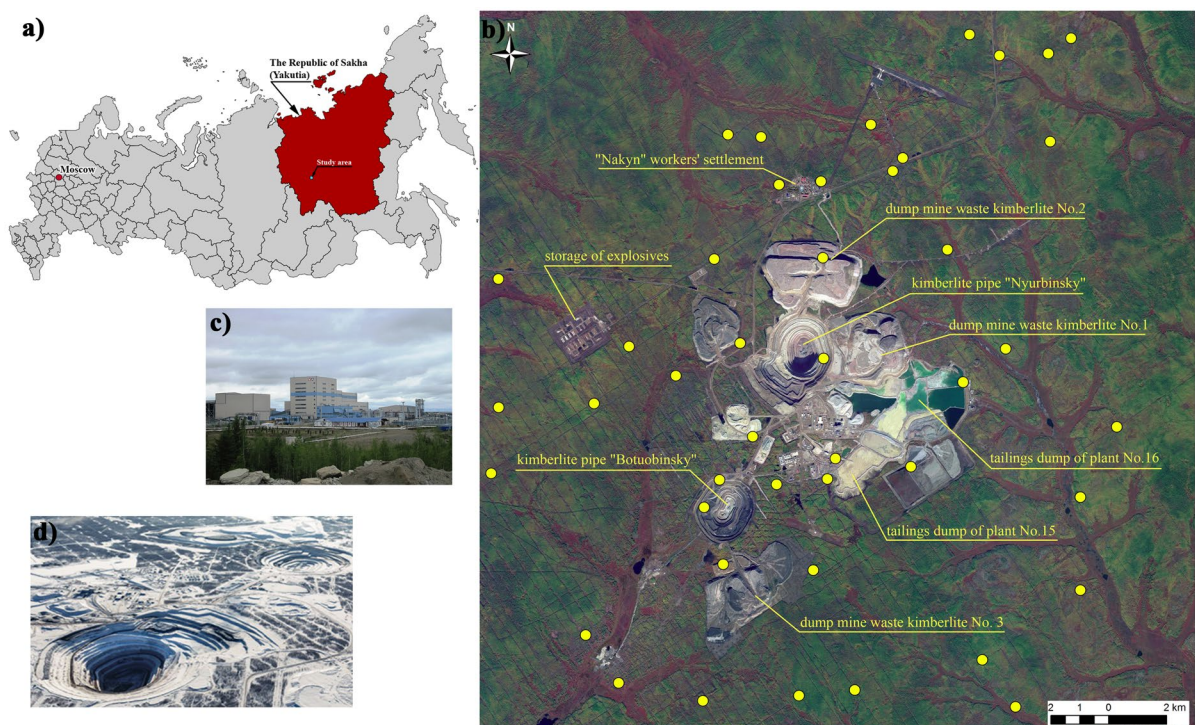


Fig. 1 Location of the study area. (a) Location of the study area on the map of Russia, (b) photo of the Nyurbinsky mining and processing plant territory, (c) photo of plant no. 16, (d) Nurbinsky and Botuobinsky open-pits

(Kilizhekov, 2016, 2017; Tolstov et al., 2009). All formations and magmatic occurrences that host kimberlites are processed by the ancient Mesozoic weathering crust, karst processes and overlain by a thick (from 40 to 100 m or more) cover of the Jurassic marine sediments, and accordingly characterized by low magnetization intensity (Ignatov et al., 2012; Korobkov et al., 2013). In contrast to the deposits of Mirninsky and Daldino-Alakitsky districts of the western Yakutia, where kimberlites are located close to the surface, for example, as at the “Zarnitsa”, “Mir”, or “Udachny” pipes. Therefore, to get to the ore body, it is necessary to make a removal in the amount of about 8 million m³ (Geography, 2008).

As a result of such large-scale works, huge areas of dumps of removed rocks are formed on the territory of the industrial site, which is an additional source of dust and various gases emissions. And at the stage of ore concentration, storages of liquid fraction of pulp containing slags are organized by blocking the upper reaches of nearby streams and small rivers. During the development of the fields of the Nakyn kimberlite field, a natural and technogenic system was created, which included two quarries for the extraction of kimberlite ore “Nyurbinsky” and “Botuobinsky”: processing plant № 15, operating since 1999; geological factory № 17, a small factory built on the site in 2007; processing plant № 16, put into operation since 2003; a rotation camp for 1000 people; runways; a warehouse of explosives materials; and other sources related to mining and concentration processes – tailing storage facility, waste dumps, and pulp lines.

The Nakyn kimberlite field is located at the junction of the Anabar-Olenek anteklise and Viluy synclise and is confined to the Viluy-Markha kimberlite-controlling tectonic zone of deep faults (Gorev et al., 2011). The territory is a flat ground with a height difference of no more than 50 m. Relief—mid-divided plateau.

The sharp continental climate is characterized by a long severe winter with minimum temperatures in January of – 61,5 °C and a short relatively warm summer with maximum temperatures of + 23,8 °C in July. The difference in average temperatures between the cold and warm seasons is very large and is 50 to 60⁰. In summer, light south-east winds of 1 to 3 m/s prevail. The main amount of precipitation falls during the summer period, which is up to

70% of the annual mass. The duration of the frost-free period increases from 47 to 103 days in the north–south direction.

The main feature is the location of the site in the permafrost zone, where a sharply continental climate, due to thermal shock and the duration of the winter period, creates a favorable condition for the preservation and development of the permafrost. In conditions of low relative humidity, high summer temperatures, and insufficient precipitation, summer thawing of permafrost contributes to constant soil moisture, creating a kind of zone of development of cryogenic processes. According to geobotanical zoning, the territory under study is included in the middle-taiga and north-taiga subzones of the boreal region. They are characterized by the development of a tree layer; the dominant species are larch Gmelin (*Larix gmelinii*) and Kayandera (*L. cajanderi*).

Complex geological history of the development of the territory of the Nakyn kimberlite field, specific physical and geographical conditions, continuous distribution of the permafrost predetermined the formation of geochemical types of landscapes, which stability is an urgent issue today with increasing technogenic impact. Monitoring of the state of the soil cover of an industrial site allows to track changes in the geocological situation in the impact zone of one of the most power diamond mining enterprises operating in the cryolithozone.

Materials and methods

Material survey and sampling

The specificity of any geosystems, including mining regions, is shown in the fact that the soil is its basic component. Soil cover as the main deposit environment, to the greatest extent, reflects the scope and nature of environmental changes in the anthropogenic period (Basova et al., 2010; Naeth & Wilkinson, 2014; Sena et al., 2015).

In soil cover of the Khannya-Nakyn interfluvial, coarse-humus cryogenic soils, peaty cryogenic soils, taiga gley cryogenic soils, cryoarid typical, cryo-humus typical, humic gley cryogenic, and grey-humus soils are common. The structure of the soil cover of the industrial site of the Nyurbinsky mining and

processing plant is dominated by Crysolts – 84% of the total area, which are characterized by a thin soil profile with distinct cryoturbation processes, that lead to a violation of the integrity of genetic horizons and mixing of soil material (Gololobova & Legostaeva, 2019).

On the territory of impact, comprehensive environmental monitoring has been carried out since the 2000s – the initial stage of development of the field and ecological and geochemical observations of the Khannya-Nakyn interfluvial started during the exploration of the Nakyn kimberlite field (1994 to 1998) (Yagnyshev et al., 2005).

In 2007, a network of observations was laid evenly throughout the site with a sampling step of 2×2 km on a scale of 1:100,000 km. Sampling was performed at intervals of 3 to 4 years from the surface layer at a depth of 0 to 20 cm. In parallel, to characterize the soil cover, soil sections were laid in different biotopes with horizon sampling for the entire depth of defrosting. In total, 436 soil samples were selected and analyzed for the period 2007 to 2018. The classification of soil types is based on the World Reference Base for Soil Resources (2015).

Data determination

All these samples were air-dried at room temperature and sieved through a < 1.0-mm sieve to remove coarse debris. The soil samples were then ground with a pestle and mortar until all particles passed a 0.25-mm sieve. Then, 10 g (± 0.1 g) of soil was taken, ground in a mortar to a powder state (ISO 11,464–2015).

The content of mobile forms of elements (Pb, Ni, Mn, Cd, Co, Cr, Zn, Cu, and As) in air-dry soil samples was determined with an atomic absorption spectrophotometer (MGA-915 GC Lumex) by opening the sample 1 N HNO₃ (soil to extractant ratio 1:10) (by the method M 03–07-2014). The studied soils are characterized by a low content of organic matter ($C < 20$ g/kg), and according to French (NFX 31–147 (1996); NF ISO 14,870 (X31-427) 1998; NF X 31–151 (1993)) and international (Pr ISO CD 14,869 (1998); ISO 14,869–1:2001 (2001)) standards of nitric acid treatment, as a rule, it is sufficient for soils formed in cold regions (Pansu et al., 2001). In addition, in contrast to H₂O and 1 N HCl, the extractant – 1 N HNO₃ defines the most mobile acid-soluble

forms of elements that are more strongly bound to the soil (Ilyin, 1991; Ladonin, 2002; Syso, 2007).

The ranges of the measured mass fractions of the analyzed elements are presented in the Table 1.

To control the accuracy of measuring the concentration of elements in soils, state standard samples of soil composition (state standard reference sample) of the following series were used: Albic Podzols (SDPC-1,-2,-3) and Haplic Calcisols (SSC-1,-2,-3). Certified values of the mass fraction of chemical elements in standard samples are given in the corresponding publications (Shafrinsky, 1998).

In addition, the pH, organic matter (humus), TN (total nitrogen), and PC (physical clay) were determined using pH meter method (Mettler Toledo, SevenCompact Advanced), photoelectric colorimetric method (KFK-2 UHL 4.2), spectrophotometric method (PE-5300VI), and pipette method for particle size analysis (Kachinsky method), respectively.

Data processing and analysis

The ecological and geochemical characterization of soil pollution was carried out according to geochemical indicators, which take into account the distribution of both individual metals involved in the pollution and their associations due to the polyelement nature of the chemical composition of technogenic flows that form the pollution. The concentration factor (K_c) of chemical elements and the total pollution indicator (Z_c) are these indicators. The calculation formulas are:

Table 1 Ranges of measured mass fractions according to the Method M 03–07-2014

Element	Measuring range, mg/kg	
	Whole-rock composition	Mobile forms
Cd	0,1–400	0,05–400
Co	1–4000	0,5–4000
Mn	20–40,000	20–40,000
Cu	2,5–4000	0,5–4000
As		0,25–4000
Ni	2,5–4000	2,5–4000
Pb	2,5–4000	1–4000
Cr	1–2000	1–2000
Zn	25–40,000	5–40,000

Table 2 Basic variational-statistical characteristics of the state of soils on the territory of the industrial site of the Nyurbinsky mining and processing plant

Index	M ± m	Lim	Confidence interval at P=0.05	V, %
pH _{water}	5.38 ± 0.12	4.5–7.1	5.2–5.6	13
Humus, %	5.6 ± 1.1	0.9–22.8	2.7–8.5	94
TN, %	13.1 ± 3.1	2.8–40.6	7.0–19.2	82
Physical clay (<0.01 mm), %	22.1 ± 1.7	3.3–31.6	18.7–25.5	39

$$K_c = \frac{C_i}{C_f}, \tag{1}$$

where C_i is the actual content of the pollutant in the soil, mg/kg, and C_f is the background content of the pollutant in the soil, mg/kg:

$$Z_c = \sum_{i=1}^n K_c - (n - 1) \tag{2}$$

where K_c is the concentration factor of the i -th component of pollution with values $K_c > 1.5$ and n is the

number of anomalous elements. Items with very low background content are not included in the count.

The gradations of the degree of soil cover contamination are: $Z_c < 16$, permissible; 16 to 32, moderately hazardous; 32 to 128, hazardous; and ≥ 128 , extremely hazardous (Methodical ... 1982).

The obtained quantitative data were processed using software Microsoft Excel 2016, OriginPro 8.5.1. Correlation analysis was performed using Statistica 6.0. Maps of total pollution of the soil cover were created using the program ArcGIS 9.0.

Results and discussion

The assessment of the degree of transformation of the main physical and chemical characteristics of soils for the territory of the Khannya-Nakyn interfluvium is based on the calculated background parameters; the total sample is $n = 175$. The average geometric values $n = 212$ of soil samples of natural undisturbed landscapes outside the impact zone of mining and processing operations are taken as the values of the regional background for the content of mobile forms of trace

Table 3 The content of trace elements in the soils of natural landscapes of the Khannya-Nakyn interfluvium outside the impact zone

Index of horizons and depth, cm	Mobile forms of trace elements, mg/kg								
	Pb	Ni	Mn	Cd	Co	Cr	Zn	Cu	As
Background, $n = 212$	2.9	1.8	13.2	0.03	2.2	4.7	6.3	11.5	0.22
Turbic Gleyic Crysol (Thixotropic), P-3–08-H									
AO 0–5(10)	4.2 ± 1.0	4.2 ± 1.1	56 ± 13	0.022 ± 0.005	2.3 ± 0.6	2.3 ± 0.5	3.7 ± 0.9	7.7 ± 1.9	0.22 ± 0.05
CR 5(10)–35(45)	2.8 ± 0.7	4.2 ± 1.0	39 ± 9	0.008 ± 0.002	2.0 ± 0.5	2.2 ± 0.5	6.4 ± 1.5	8.0 ± 1.9	< 0.05*
Cg 35(45)–∞	3.0 ± 0.7	5.1 ± 1.2	39 ± 9	0.015 ± 0.004	2.3 ± 0.5	2.1 ± 0.5	6.9 ± 1.6	10.4 ± 2.5	< 0.05
Turbic Gleyic Crysol (Reductaquic), P-28–08-H									
AO 0–6(14)	3.8 ± 0.9	2.6 ± 0.6	23 ± 6	0.023 ± 0.006	1.5 ± 0.4	2.2 ± 0.5	4.5 ± 1.1	4.8 ± 0.02	0.25 ± 0.06
Acr 6(14)–43(50)	2.1 ± 0.5	5.3 ± 1.3	42 ± 10	0.011 ± 0.003	2.4 ± 0.6	2.6 ± 0.6	6.8 ± 1.6	6.7 ± 1.6	< 0.05
CR g 43(50)–80(83)	2.3 ± 0.5	5.0 ± 1.2	47 ± 11	0.014 ± 0.003	2.5 ± 0.6	2.5 ± 0.6	7.5 ± 1.8	8.1 ± 2.0	0.07 ± 0.02
Cg 80(83)–∞	1.4 ± 0.3	3.8 ± 0.9	44 ± 11	0.016 ± 0.004	2.2 ± 0.5	3.3 ± 0.8	6.2 ± 1.5	3.9 ± 0.9	< 0.05
Turbic Crysol (Reductaquic), P-33–08-H									
AO 0–19(26)	2.1 ± 0.5	1.7 ± 0.4	56 ± 13	0.012 ± 0.003	2.6 ± 0.6	1.1 ± 0.3	3.3 ± 0.8	3.3 ± 0.8	< 0.05
CR 19(26)–40(45)	1.7 ± 0.4	3.8 ± 0.9	33 ± 8	0.014 ± 0.003	2.3 ± 0.5	1.5 ± 0.4	3.4 ± 0.8	5.7 ± 1.4	< 0.05
C 40(45)–∞	1.6 ± 0.4	7.4 ± 1.8	40 ± 10	0.04 ± 0.01	2.5 ± 0.6	1.7 ± 0.4	5.1 ± 1.2	9.5 ± 2.0	0.1 ± 0.02
Turbic Gleyic Natric Crysol (Reductaquic), P-34–08-H									
A 0–40(42)	2.6 ± 0.6	1.5 ± 0.4	15.2 ± 3.4	0.006 ± 0.001	1.5 ± 0.4	1.7 ± 0.4	4.6 ± 1.1	2.1 ± 0.5	< 0.05
ELB 40(42)–61(72)	2.2 ± 0.5	3.4 ± 0.8	27 ± 7	0.008 ± 0.002	2.2 ± 0.5	2.1 ± 0.5	5.1 ± 1.2	2.9 ± 0.7	< 0.05
C g 61(72)–∞	2.2 ± 0.5	4.7 ± 1.1	40 ± 10	0.019 ± 0.005	2.5 ± 0.6	1.8 ± 0.4	7.1 ± 1.7	4.7 ± 1.1	< 0.05

*Below the limit of sensitivity

elements (Legostaeva et al., 2014; Gololobova & Legostaeva, 2019).

The soil cover of the territory is characterized mainly by an acidic reaction of the soil environment, and significant changes in the years of research due to an increase in the man-caused load are not observed (Table 2).

The humus content is characterized by a very high variation ($V=94\%$). High values of humus cause the presence of medium and slightly decomposed organic residues in the soil that is typical for the soils of the northern regions. The calculation of the ratio of carbon to nitrogen ($C/N=13$) indicates a slight decomposition of plant residues. The highest content was observed at points located directly in the zone of influence of industrial facilities (near the “Nyurbinsky” pipe quarry, dump №2, tailing storage facility №16, helicopter pad), which shows not so much the content of organic matter as the presence of a technogenic component in the soil. In conditions of soil

contamination, they lose their natural features due to man-made suppression of soil formation processes. Therefore, the existing methods for determining humus reflect not so much the actual high humus content of soils as the total carbon content in them, which contains a significant technogenic component (fuel hydrocarbons, lubricating oils, etc.) (Prokhorova, 2005). At the same time, no significant variations in the humus content were identified over the years of research.

The amount of physical clay is typical for a light loamy granulometric composition, with a predominance of fractions of fine sand (0.25 to 0.05 mm) and silt (<0.001 mm). The concentration of many elements in the composition of fine-dispersed fractions of soils in both natural and man-made landscapes is usually 2 to 4 times higher than in the soil as a whole. This is mainly due to the absorption capacity of clay minerals (Motuzova, 2000).

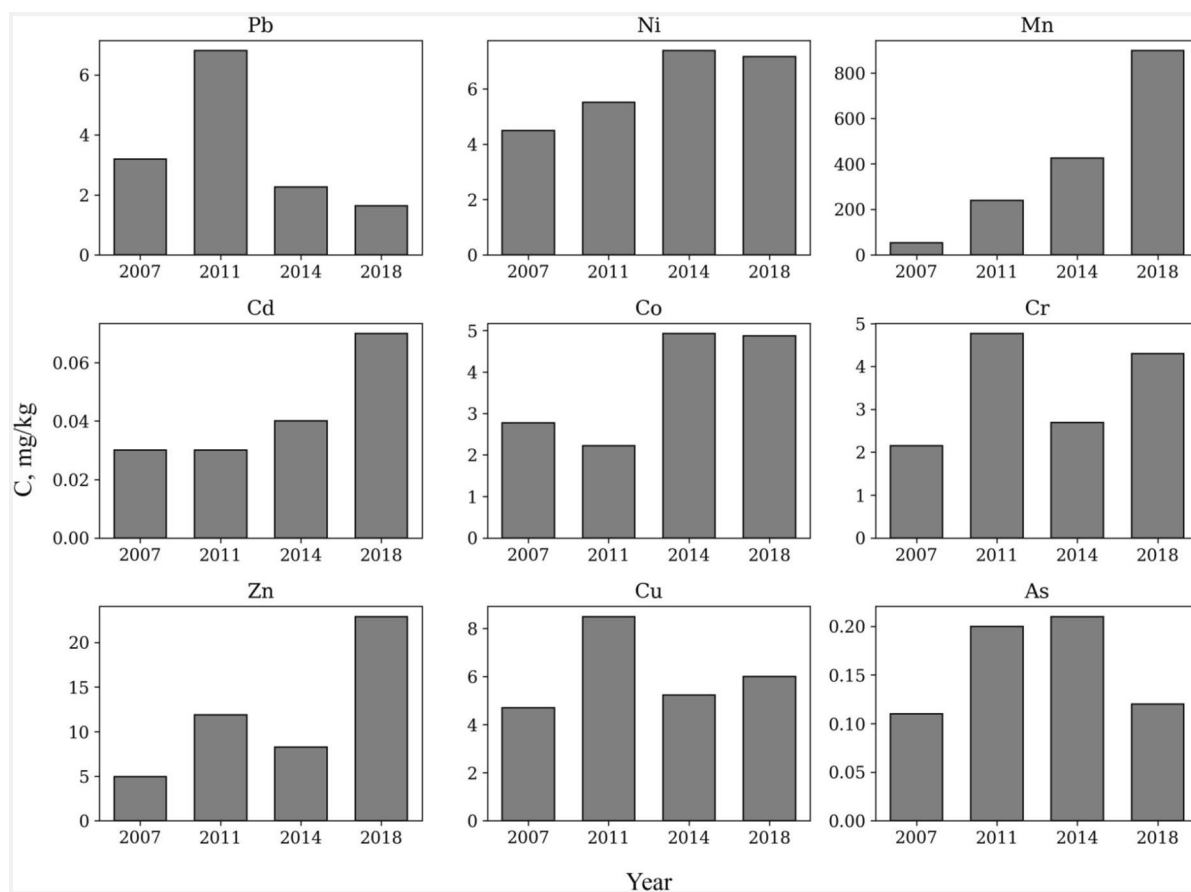


Fig. 2 The dynamics of the content of the mean values of trace elements from 2007 to 2018

The most active agents of contamination are mobile forms of trace elements that can pass from solid phases to soil solutions and be absorbed by plants (Mikhailchuk, 2017). The content of mobile forms of heavy metals in permafrost soil is not significantly different by type (Table 3).

The genetic dependence of the composition of trace elements of soils on the composition of the underlying rocks is well known (Geochemical... 1975). The natural background content of trace elements in soils, their distribution in the soil profile, the processes of accumulation and removal of chemical elements, and the ecological and geochemical state of the soil cover directly depend on the composition and properties of the underlying rocks. This mechanism is particularly clear in soils with a homogeneous thin profile, where there is no noticeable redistribution of soil matter (Basova et al., 2010). The intraprofile distribution of mobile forms of trace elements is characterized by the presence of two maxima: biogenic accumulation in the upper layer of the soil with a subsequent decrease down the profile and a second peak in the suprapermafrost horizon. As a rule, mobile forms of elements Mn, Zn, Co, Ni, Cd, As, and partially Cu differ by biogenic accumulation in cryosols.

Biogenic accumulation of Ni, Mn, and Cd is typical for the cryosols of the Khannya-Nakyn interfluve.

A different degree of correlation of mobile forms of heavy metals with humus content, pH values, and granulometric composition was identified, which characterizes the selectivity of the element (or group of elements) in combination with the main components of the soil. A positive correlation of Co, As, and Mn with the content of humus, Cu and Cr, physical clay, and pH and a negative correlation between Pb and humus were determined. Fractions of fine-dispersed dust and silt bind the largest number of elements – Zn, Ni, Cr, Cu, Pb, and As (Gololobova & Legostaeva, 2019).

The geochemical distribution series of chemical elements for the upper 0–20 cm soil layer in descending order of their average values is as follows:

$$\text{Mn} > \text{Zn} > \text{Ni} > \text{Cu} > \text{Co} > \text{Cr} > \text{Pb} > \text{As} > \text{Cd}.$$

During the period of active development of the fields of the Nakyn kimberlite field from 2007 to 2018, there was a significant change in the composition of trace elements of soils with an increase in the concentrations of mobile forms Mn (17 times), Zn (5 times), Cd (2.6 times), Cr (2 times), Co (1.8 times), and Ni (1.6 times). At the same time, there is a slight

Table 4 The content of trace elements in the soils and grounds of an industrial site in the zone of impact of diamond mining facilities

Index of horizons and depth, cm	Mobile forms of trace elements, mg/kg								
	Pb	Ni	Mn	Cd	Co	Cr	Zn	Cu	As
Background, n=212	2.9	1.8	13.2	0.03	2.2	4.7	6.3	11.5	0.22
Grounds of the quarry of the “Nyurbinsky” pipe, T-34 H									
0–10	2.5 ± 0.8	14 ± 5	370 ± 130	0.031 ± 0.011	8.9 ± 3.0	32 ± 11	51 ± 17	11.4 ± 3.9	0.44 ± 0.15
10–20	2.4 ± 0.8	14 ± 5	300 ± 100	0.063 ± 0.021	9.7 ± 3.3	49 ± 17	64 ± 22	11.5 ± 3.9	0.49 ± 0.17
Turbic Cryosols 10 m from the “Botuobinsky” pipe quarry, T-61-1H									
AO 0–12	1.7 ± 0.6	8.5 ± 2.9	1600 ± 500	0.095 ± 0.032	5.3 ± 1.8	6.1 ± 2.1	31 ± 11	7.5 ± 2.5	0.21 ± 0.07
CR 12–17	2.4 ± 0.8	9.3 ± 3.2	130 ± 40	0.057 ± 0.019	4.7 ± 1.6	4.9 ± 1.7	16 ± 6	4.3 ± 1.5	0.27 ± 0.09
C _⊥ 17–37	1.6 ± 0.5	3.2 ± 1.1	43 ± 15	0.017 ± 0.006	1.8 ± 0.6	4.9 ± 1.1	9.6 ± 3.2	4.0 ± 1.4	< 0.05*
Turbic Cryosols 5 m from the dump №1, T-35-1H									
AO 0–2(5)	1.1 ± 0.4	30 ± 10	8830 ± 3002	0.13 ± 0.04	7.4 ± 2.5	3.7 ± 1.3	46 ± 16	5.3 ± 1.8	0.11 ± 0.04
CR 2(5)–40	1.1 ± 0.4	3.2 ± 1.1	39 ± 13	0.011 ± 0.004	1.2 ± 0.4	3.8 ± 1.3	7.8 ± 2.7	1.8 ± 0.6	< 0.05
C _⊥ 40–71	1.1 ± 0.4	3.9 ± 1.3	87 ± 30	0.012 ± 0.004	2.3 ± 0.8	5.9 ± 2.0	10.9 ± 3.7	1.6 ± 0.5	< 0.05
Turbic Cryosols 1 m from the dump №2, T-19-1H									
AO 0–7	1.4 ± 0.5	8.0 ± 2.7	920 ± 310	0.103 ± 0.035	4.0 ± 1.4	5.6 ± 1.9	26 ± 9	8.7 ± 3.0	0.29 ± 0.10
CR 7–12	2.1 ± 0.7	21 ± 7	105 ± 36	0.058 ± 0.020	3.2 ± 1.1	4.9 ± 1.7	10.4 ± 3.6	11.7 ± 4.0	0.25 ± 0.09
CR 12–32	2.1 ± 0.7	9.1 ± 3.1	170 ± 60	0.036 ± 0.012	2.4 ± 0.8	4.1 ± 1.4	21 ± 7	8.9 ± 3.0	0.13 ± 0.04

*Below the limit of sensitivity

Table 5 The content of trace elements in the soils and grounds of the industrial site in the zone of impact of ore concentration facilities

Index of horizons and depth, cm	Mobile forms of trace elements, mg/kg								
	Pb	Ni	Mn	Cd	Co	Cr	Zn	Cu	As
Background, $n=212$	2.9	1.8	13.2	0.03	2.2	4.7	6.3	11.5	0.22
Grounds of tailings storage facilities processing plant No.16, T-31-1H									
0–3	2.6±0.9	12.7±4.3	1680±570	0.12±0.04	9.8±3.3	47±16	38±13	11.1±3.8	<0.05*
3–20	1.0±0.3	4.7±1.6	58±20	0.019±0.006	3.9±1.3	7.3±2.5	8.9±3.0	8.1±2.8	<0.05
30–40	0.49±0.17	6.9±2.3	130±40	0.015±0.005	3.5±1.2	11.3±3.8	10.9±3.7	8.8±3.0	<0.05
50–52	0.66±0.22	6.2±2.1	69±24	0.039±0.013	4.0±1.4	9.3±3.2	9.7±3.3	7.6±2.6	<0.05
Turbic Gleyic Crysol (Reductaquic) 30 m from processing plant No.15, T-33 H									
AO 0–3	1.2±0.4	22.7±7.7	2400±820	0.102±0.035	7.6±2.6	6.5±2.2	59±20	6.6±2.2	0.22±0.07
ABcr 3–10(16)	1.1±0.4	4.5±1.5	796±270	0.043±0.015	19.9±6.8	2.4±0.8	9.2±3.1	2.1±0.7	0.07±0.02
CRg 10(16)–47(58)	1.1±0.4	2.6±0.9	78±26	0.035±0.012	5.4±1.8	2.4±0.8	5.2±1.8	2.4±0.8	<0.05
Cg 47(58)–62	0.9±0.3	2.7±0.9	13±4	0.011±0.004	0.8±0.3	2.2±0.7	3.6±1.2	3.4±1.1	0.07±0.02

*Below the limit of sensitivity

decrease in the amount of Pb, and the content of Cu and As in the soils remains almost the same (Fig. 2).

Today, the soil cover of the industrial site is characterized by polyelement contamination. As many researchers note, the specificity of the elemental composition of the soil cover is related, on the one hand, to the metallogenic features of the deposit. On the other hand, it is likely that heavy metals will enter as part of dust particles formed during drilling and blasting operations in the quarry, loading operations, ore transportation, wind erosion of the surface of dumps, tailing storage facilities, and open-pit sides of the quarry (Belosheikina et al., 2020).

According to the results of the research 2007 to 2014, it was found that the most active mobile forms

are Pb, Mn, Cu, Ni, Cr, Zn, Cd, Co, and As. At the same time, Cr, Ni, and Co are elements that are typomorphic to kimberlites, and the accumulation of Mn and Cu reflects in general the geochemical specific nature for the soils of the entire territory of the western Yakutia (Vorobiev, 2001, 2004; Legostaeva et al., 2014). Geochemical spectra based on the concentration coefficient (Cs) revealed the degree of transformation of the soil elemental composition during the observation period. Soils of technogenic landscapes (quarries, dumps, tailings storage facilities, and embankments for various purposes) are characterized by the following trace element spectrum: $Mn_{28,0} \rightarrow Zn_{8,0} \rightarrow Ni_{7,7} \rightarrow Cr_{6,8} \rightarrow Co_{4,2} \rightarrow As_{2,0}$. At the same time, the variability of concentration coefficients

Table 6 Correlation analysis between heavy metals and soil properties

	pH	Humus	Pb	Ni	Mn	Cd	Co	Cr	Zn	Cu	As
pH	1	-0,51	0,02	0,35	-0,13	-0,10	0,37	0,76*	0,28	0,46	0,30
Humus		1	0,10	-0,03	0,54*	0,57*	-0,14	-0,38	0,27	-0,17	-0,30
Pb			1	-0,11	0,50*	-0,04	-0,12	0,11	0,08	0,24	0,07
Ni				1	0,35	0,31	0,31	0,21	0,47*	0,22	0,34
Mn					1	0,47*	-0,06	-0,19	0,46*	0,03	-0,17
Cd						1	0,18	-0,15	0,47*	0,04	-0,10
Co							1	0,24	0,18	0,07	0,13
Cr								1	0,38	0,50*	0,42
Zn									1	0,21	0,27
Cu										1	0,30
As											1

*The correlation is significant for a confidence level of 0.01

Table 7 Characteristics of the trace element composition of soils in key areas of the Nyurbinsky mining and processing plant industrial site according to research data from

No. of observation point	Trace element spectrum by year of observation			
	2007	2011	2014	2018
In the impact zone of dead rock dumps				
19	Mn _{4,3} → Ni _{2,9} → Co _{2,4}	Mn _{13,3} → Ni _{4,8} → Pb _{2,7}	Mn _{137,2} → Ni _{26,8} → Co _{12,9} → Cd _{3,4} → As _{2,3} → Zn _{1,9}	Mn _{69,7} → Ni _{4,5} → Zn _{4,1} → Cd _{3,4} → Co _{1,9}
35	Mn _{2,6} → Ni _{1,9}	Mn _{57,3} → Ni _{5,4} → Co _{3,8} → Pb _{3,6} → Zn _{3,2}	Mn _{85,1} → Co _{3,2} → Ni _{2,5}	Mn _{669,4} → Ni _{16,11} → Zn _{7,3} → Cd _{4,2} → Co _{3,4}
In the impact zone of tailings storage facility of processing plant				
11	Mn _{8,7}	Mn _{24,2} → Zn _{10,7} → Cd _{9,1} → Co _{5,2} → Ni _{2,0} → Pb _{1,7}	Mn _{20,0} → Ni _{3,5} → Co _{3,0} → Cd _{2,2} → Zn _{1,5} (As _{1,5})	Mn _{290,4} → Zn _{5,4} → Ni _{3,8} → Co _{3,5} → Cd _{3,0}
16	Mn _{6,8} → Ni _{2,3}	Mn _{20,6} → As _{1,5}	Mn _{116,2} → Ni _{6,1} → Zn _{3,3} → Co _{3,1} → Cd _{3,0}	Mn _{186,8} → Zn _{4,7} → Ni _{2,0}
14	Mn _{10,6} → Co _{5,3} → Ni _{4,8} → Cd _{2,0}	Mn _{44,7} → Ni _{4,1}	Mn _{19,6} → Ni _{7,0} → Co _{3,7} → Zn _{2,2} → Cr _{2,0} → Cd _{1,5}	Mn _{141,4} → Zn _{2,5}
31	Mn _{3,5} → Co _{1,8} → Ni _{1,7}	Mn _{6,6} → Ni _{3,9} → Co _{2,5} → Cr _{1,6}	Mn _{5,0} → Ni _{3,5} → As _{2,1} → Co _{1,8}	Mn _{127,0} → Cr _{10,0} → Ni _{7,2} → Zn _{6,0} → Co _{4,6} → Cd _{4,1}
In the impact zone of quarries				
34	-*	Mn _{8,0} → Pb _{3,3} (Co _{3,3}) → Ni _{2,9} → Zn _{2,3}	Mn _{7,1} → Ni _{1,6}	Mn _{27,9} → Zn _{8,0} → Ni _{7,7} → Cr _{6,8} → Co _{4,2} → As _{2,0}
61	-	-	Mn _{22,2} → Ni _{2,7} → Co _{1,6}	Mn _{119,1} → Zn _{4,9} → Ni _{4,8} → Cd _{3,2} → Co _{2,5}

*No background parameters exceeded, K_k ≤ 1.5

is very wide. Soils that fall into the zone of direct impact of man-made objects are characterized by surface accumulation of trace elements of the same spectrum (Tables 4 and 5).

If the soil profile is preserved, the accumulation horizons are AO, ABcr, and CR. Depending on the amount of soil organic matter, the degree of decomposition and the scale of cryoturbation occurrence in the form of, for example, frost cracking, mobile forms Mn, Zn, Ni, Cr, Co, and As can migrate along the soil profile to a depth of 40 to 50 cm.

As reference points of technogenic load, the sites characterized by a significant level of soil contamination are selected (Table 6). Analysis of trace element spectra over the years of research showed a significant increase in the concentrations of mobile forms and expansion of the trace element range. By 2018, active accumulation

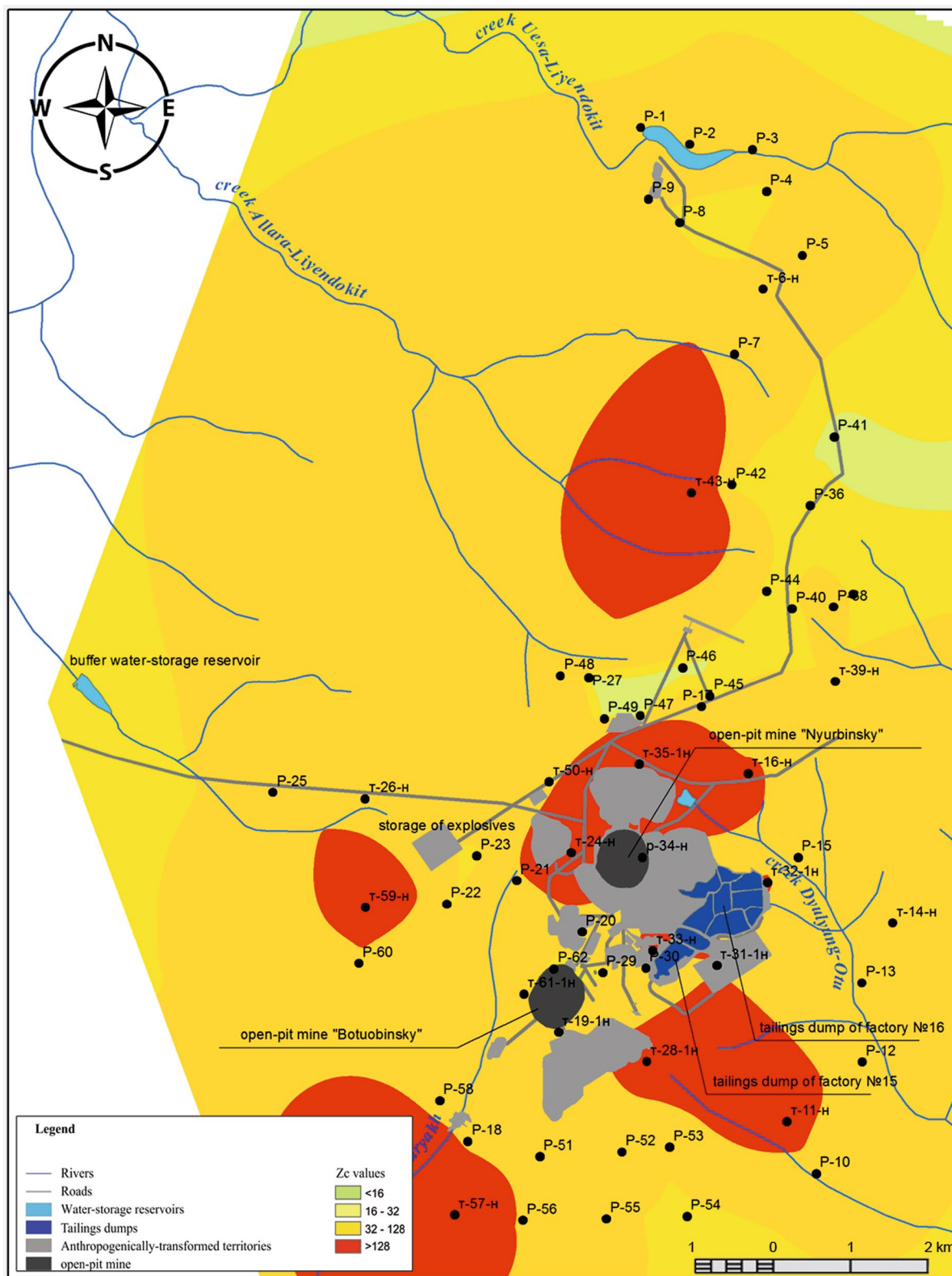
of mobile forms of Mn, Zn, and Ni with abnormally high concentration coefficients is observed in the composition trace elements of the soil cover of the industrial site of the Nyurbinsky mining and processing plant.

There are noticeable positive correlations ($P < 0.01$) between the pairs, which indicate a synergism between the above groups; i.e., an increase in the content of one trace element leads to an increase in the concentration of the other (Table 7).

Manganese and zinc have the largest number of pairs, which explain their presence in the first rows of all trace element spectra that characterize both the soils of the entire Khannya-Nakyn interfluvium and technogenic-transformed soils of the industrial site, as well as soils of technogenic landscapes. In addition, it was found that the amount of organic matter affects the content of mobile forms

Table 8 Area and pollution level of soil cover on the territory of the industrial site of Nyurbinsky mining and processing plant

Pollution category	Level of indicator of Z _c total pollution	Area by research years, km ²			
		2007	2011	2014	2018
Permissible	less 16				61.0
Moderately hazardous	16–32	210.0	305.0	-	104.9
Highly hazardous	32–128	45.0	1.44	122.0	260.9
Extremely hazardous	over 128	-	-	18.2	51.6



◀ **Fig. 3** Map scheme of the total pollution of the soil cover of the territory of the Nyurbinsky mining and processing plant, by 2018 years of research

of manganese ($r=0.54$). A fairly close relationship is identified between the pH and the concentration of mobile forms of chromium ($r=0.76$) and copper ($r=0.46$). At the existing pH values, chromium and copper are inert; i.e., they almost completely precipitate (Sokolova, 2006), what can be associated with the absence of these elements in the trace element spectra that characterize soils, despite the fact that the eluvium-deluvium of the Nakyn kimberlite field contains Cr and Cu at very high levels, forming a large area of anomalies particularly in the zones of tectonic faults (Makarov, 2010; Gorev et al., 2011; Legostaeva et al., 2014; Gololobova & Legostaeva, 2019).

Using the Saeta formula, it is possible to estimate the degree of total soil contamination (Z_c) by several trace elements and heavy metals. According to research data from 2007, the territory of the industrial site is characterized mainly by a moderately dangerous situation in terms of the content of mobile forms of trace elements, which was approximately 210 km² (Table 8). At the same time, about 10% of the territory belongs to the highly dangerous category of pollution and covers 45 km².

In 2011 there was an increase in the conditional boundaries of the areas of soil contamination. The ecological and geochemical situation still corresponds mainly to the category of moderate hazard (~ 305 km²) if there are areas with a highly hazardous degree of contamination (~ 1.44 km²).

According to research in 2014, the ecological and geochemical situation on the territory of the Nyurbinsky mining and processing plant industrial site is characterized mainly by a highly dangerous level of pollution in terms of Z_c . There was an increase in the area of highly dangerous pollution in comparison with the data of 2011 by 120 km². In addition, three areal and two point high-contrast anomalies were recorded with an extremely dangerous level of soil contamination, the total conditional area of which is about 18.2 km².

Research in 2018 allowed us to localize and confirm the increase in the area of soil contamination on the territory of the Nyurbinsky mining and processing plant industrial site. The ecological and geochemical

situation has changed significantly with the predominance of a highly dangerous category of pollution, which occupies 260.9 km² (Fig. 3). There is a spatial increase in the contrast of the identified anomalies that characterize the active accumulation of mobile forms of trace elements in the surface organogenic horizons of soils. The increase trend has a north-west and south-east direction. It should be emphasized that along with the overall increase in the area of pollution, the absolute values of the concentration coefficients and, accordingly, the total indicator of pollution have increased. Mn, Zn, and Ni are Zc-forming elements.

Conclusion

The legacy of industrial development has left many polluted soils (Krumins et al., 2015). And in this aspect, the Nakyn kimberlite field is a kind of model polygon, allowing to assess the level of technogenic transformation of the ecosystem over more than 11-year period of intensive development of diamond deposits in the cryolithozone.

The data obtained from the analysis of the geochemical situation contribute to the development of general ideas that not all contaminated or anthropogenic soils function equally. If the morphological integrity of the soil profile is preserved, there are no significant changes in the main geochemical indicators in the soil cover. Exceptions are areas that have been directly affected as a result of land acquisition and the formation of new technogenic-transformed landscapes (Pouyat et al., 2006).

Research in 2018 allowed us to localize and confirm the increase in the area of contamination of the industrial site. The pollution is especially contrasted by the characteristics of the soil cover. The area of geographic ranges characterized by an extremely dangerous category of soil contamination increased by 3 times compared to 2014.

Analysis of the concentration coefficients showed that the soil cover is intensively accumulating manganese, zinc, and nickel, in areas that cover the main objects of pollution. The geochemical series of distribution of chemical elements in descending order of their average values is compiled: Mn > Zn > Ni > Cu > Co > Cr > Pb > As > Cd. The synergistic interaction of manganese with zinc, cadmium, lead,

as well as zinc with nickel and cadmium, caused by stress due to excessive concentrations of heavy metals, was revealed.

In grounds and soils that have been subjected to man-made impact, there is a redistribution in the composition of mobile forms of trace elements. The elements typomorphic to kimberlites are in the first place. And also in general, the percentage of mobile forms of almost all certain trace elements increases. Therefore, if the soil is disturbed, the integrity of the soil profile is failed, the upper organic horizon is removed, mineral part of the soil profile is “exposed”, and there is a change in geochemical conditions; as a result, most of the trace elements transform into a mobile state – water-soluble forms and acid-soluble forms. That is, it becomes more accessible to plants, including wild plants, which are directly consumed, soluble in water, what creates tension in the overall environmental situation on the territory of the impact of the mining and processing plant. Similar processes occur in the case of surface filling, the exposure of soil-forming rock material to the surface, which are mainly characterized by the predominance of finely dispersed clay fraction and an increased content of CR-Ni-Co and Cu-Mn associations; this is manifested in high concentrations of mobile forms of these elements.

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Data availability For further information, please contact the corresponding author (ylego@mail.ru).

Declarations

Conflict of interest The authors declare no competing interests.

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