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2 Geochemical risks of diamond mining in Siberia

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13 Abstract: Geochemical risk is caused by the release of hazardous chemicals to the earth surface. 14 Primary diamond deposits are located in difficult mining and geological conditions. They represent 15 natural geochemical anomalies associated with the mineral composition of rocks and groundwater, 16 which contain a number of impurity elements with high toxic properties (Tl, Di, As, Cd, Hg), 17 increased concentrations of heavy metals (Cu, Zn, Pb, Ti, V and others). The paper presents the 18 physical-geographical and mining-geological conditions of the diamondiferous region, where three 19 large mining and processing divisions operate: Udachninsky, Aikhalsky and Nyurbinsky. pH, 20 organic matter (humus), total nitrogen, physical clay were identified in the study samples, by using 21 potentiometric, photoelectric colorimetric, spectrophotometric methods and pipette method for 22 particle size analysis. Gross and mobile forms of trace elements were determined by atomic 23 absorption and emission spectrometry. The groups of elements were identified, that determined the 24 natural and man-made anomalies. The accumulation of Cr, Ni and Co determines the influence of 25 kimberlite magmatism in general. Cu, Sr and Li are accumulated in the soils of the Daldyn-Alakit 26 diamond-bearing region. Increased concentrations of Mn and Cu are typical in the soils of the 27 Sredne-Markhinsky diamond-bearing region. An assessment of the ecological and geochemical state 28 of the study areas was carried out according to the indicator of total pollution (Zc), which is the sum 29 of the excess of the concentration coefficients of chemical elements accumulating in anomalies. Areas 30 of pollution and zones of the greatest risk are localized, which occupy up to 75% of the total area of 31 industrial sites. They confined to quarry-dump complexes and to areas of impact of tailing dumps of 32 processing plants.

Keywords: physical and geographical conditions, industrial waste, Yakutia, kimberlite pipe,
 permafrost

35 1. Introduction

Mining activities significantly impact the environment and often determine anxiety in the local population. Diamond mining in Siberia is the most ambitious and impressive, since the primary diamond deposits are associated with vertical pipe-like kimberlite geological bodies that go to a depth of many kilometers. Therefore, their development leads to the formation of deep cone-shaped open pits. For example, at the Udachny quarry, open-pit mining was completed at a depth of 640 m, and the size of the quarry on the surface is 2000x1600 m. To date, mining is carried out using the mine method, and diamond reserves have been explored to a depth of 1400 meters [1, 2]. The development of diamond-bearing areas involves geological prospecting of various level of

The development of diamond-bearing areas involves geological prospecting of various level of details, where drilling, geophysical, mining operations are used, and a network of openings (in a

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45 forest) is cut. In addition, the operation of the largest diamond-bearing pipes is complicated by the 46 arrival of brines from subpermafrost high-pressure water-bearing horizons, their safe disposal in 47 underground storage is a cornerstone of ensuring a favorable environmental situation [3]. Rock 48 elevated from the depths, accumulate in the overburden rock dumps with a height of approximately 49 100 meters, and enrichment products are stored in extensive tailing dumps. Thus, significant 50 amounts of chemical elements and their compounds rise from the earth's interior to the day surface, 51 which forms technogenic geochemical anomalies in soils, bottom sediments, and surface waters. 52 Composition and contrast of technogenic geochemical anomalies represent technogenic geochemical 53 risks for the state of landscape components and its biotic component.

54 The number of papers devoted to various aspects of ecological and geochemical studies or 55 ecological and geochemical assessment of the consequences of mining activities is extremely large 56 [4-13]. Various relevant methodological recommendations and suggestions for improving the 57 methodology and technology of ecological and geochemical study of industrial and urban areas 58 have been developed. This paper examines the geochemical risks on the territories of the 59 Udachninsky, Aikhalsky and Nyurbinsky mining and processing plants (MPP), which are located in 60 the basin of the Markha river-the left tributary of the Vilyui river, which flows into the great Siberian 61 Lena river. About 60% of ALROSA's diamonds are extracted here.

62 **2.** Overview of the study area

63 The studied area is located in Western Yakutia (Eastern Siberia of Russia). The Udachninsky64 and Aikhalsky (MPP) are located within the Daldyn-Alakit diamond-bearing area, Nyurbinsky

65 (MPP) - in the Sredne-Markhinsky diamond – bearing area- (Figure 1).



66 67

Figure 1. The layout of the territory, Scale 1:100 000

In regional tectonic terms, the territories are located in the junction zone of anticline and syncline of the Siberian platform complicated by a fault system, kimberlite and trap magmatism. The kimberlite fields are localized at the intersections of fracture zones with the aulacogens, which

- 71 represent an ancient rift. In the geological structure, the Archean crystalline basement is covered
- 72 with a sedimentary cover from 2.4 km to 4 km in the area of the middle Markha. The sedimentary
- 73 cover is made up of the Vend - lower Paleozoic, middle Paleozoic and Mesozoic layers of geology,
- 74 represented by limestones, dolomites and their clay and marly differences (Figure 2).





Figure 2. Geological map of Daldyn-Alakit (a) and Sredne-Markhinsky (b) diamond-bearing areas 77 Q - Quaternary system, undivided sediments – lluvial sands, pebbles, lacustrine-bog silts, peat; J -78 Jurassic system, undivided sediments - sandstones, siltstones, mudstones, conglomerates, coal 79 lenses; T - Triassic system, undivided sediments - sandstones, siltstones, mudstones, conglomerates, 80 limestones; P - Permian system, undivided sediments - sandstones, mudstones, shales, 81 conglomerates, coals; O1 - Ordovician system, lower section - dolomites, limestones, calcareous 82 sandstones; \mathfrak{E}_3 – Cambrian system, upper section - dolomites, limestones, calcareous conglomerates, 83 gypsum-bearing mudstones;

84 The climate of the territory is sharply continental and belongs to the subarctic zone of the 85 Siberian region in the north. Winter is severe and long with minimum temperatures below -50°C and 86 a short summer, the average annual air temperature in the area of Udachny Is -11.8°C. The entire 87 basin of the Markha river is located in the zone of permafrost rock mass, the depth of its bottom 88 varies in the study areas from 350 m (in the south) to 1050 m (in the north). The seasonal thawing 89 layer varies from 0.2 to 3 m. The following occurrences of cryogenic processes and phenomena are 90 observed on the territory: solifluction, thermokarst, frost heaving, frost cracking, thermal erosion 91 and frost weathering [14]. In the areas of deposits, there are all types of underground water typical 92 for the cryolithozone: supra -, intra-and subpermafrost water. The supra permafrost water is 93 represented by the fresh waters of the seasonally thawed layer, waters of the underflow and 94 sub-lacustrine taliks (ice-free zones within permafrost region). The Upper Cambrian, Middle 95 Cambrian, and Lower Cambrian aquifer systems are distinguished in the sedimentary cover. 96 Underground waters are brines with mineralization from 350 to 410 g/l. The most difficult 97 hydrogeological conditions are typical for the Udachnaya kimberlite pipe. The brines contain high 98 concentrations of trace components: Br, Li, Rb, Cs, Sr. The leading position is occupied by Sr, which 99 content varies from 438.1 to 894.2 mg / dm³. The Li content varies from 67.4 to 165.9 mg/dm³, and Rb, 100 respectively, from 4.89 to 18.9 mg / dm³. Cs concentrations in brines are not more than 0.01 mg / dm³. 101 Brines belong to mineral bromine water type. Brines are highly aggressive, due to their high 102 mineralization, ion composition, and low pH values. According to the aggressive effect on metals, 103 calcium chloride is at the first place. The miming of deep horizons of the diamond deposit is related 104 to the arrival of a large number of aggressive and environmentally dangerous calcium chloride

- brines thousands and the first millions of cubic meters that require their subsequent disposal back
- 106 into the subsurface [15].
- 107 The landscapes of the territories are represented by north taiga open subshrub-moss-lichen
- larch forests in the zone of continuous distribution of permafrost rocks. The soil cover is dominated
 by different subtypes of cryozems (O-CR-Cg), lithozems (AO-C), carbolitozems (H-(C)–MCA) and
- 110 gleezems (AO–GC).

111 3. Experiments

112 3.1. Material Survey and Sampling

113 The original exclusive materials of the field geo-ecological surveys performed earlier at the 114 previous stages of research (1994-2019) were used as sources of initial information. The project 115 materials of the state environmental expertise of large engineering projects on the territory of the 116 West Yakutian diamond-bearing province were also involved. A large amount of information 117 provides a sufficient degree of representativeness and updating of the obtained results.

Sampling was carried out at the sites of mining and processing plants, where a network of observations was established with a sampling step of 2x2 km on a scale of 1:100,000 km. Sampling frequency in summer every 3-4 years from the near-surface layer to a depth of 0-20 cm. In parallel, soil sections were made in different biotopes with the horizon-oriented sampling for the entire depth of defrosting, to characterize the soil cover. In total, in 2004-2019, 63 soil sections were made on the

123 territory of two diamond-bearing regions and 3120 soil and subsoil samples were taken.

124 3.2. Data analysis and processing

125 The pH, Organic Matter (Humus), Total Nitrogen (TN), Physical Clay (PC) were determined 126 using pH meter method (Mettler Toledo, SevenCompact Advanced), photoelectric colorimetric 127 method (KFK-2 UHL 4.2), spectrophotometric method (PE-5300VI), pipette method for particle size 128 analysis (Kachinsky method), respectively.

Heavy metal contents was determined in mobile forms by atomic absorption spectrometry on multichannel gas analyzer (MGA-915 GC Lumex). 1 N HNO₃ was used for complex characterization of forms of heavy metals, which, in contrast to H2O and 1 N HCl extracts acid-soluble elements that are more firmly bound with the soil. Total gross trace elements were determined using emission spectrum analysis at diffraction spectrograph DFS-8.

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:

139 $K_c =$

$$=\frac{c_i}{c_f},\tag{1}$$

- where C_i is the actual content of the pollutant in the soil, mg/kg; C_f is the background content of thepollutant in the soil, mg/kg;
- 142 $Z_c = \sum_{i=1}^n K_c (n-1)$ (2)

143 where K_c is the concentration factor of the i-th component of pollution with values K_c>1.5; n is the 144 number of anomalous elements. Items with very low background content are not included in the 145 count.

- The gradations of the degree of soil cover contamination are: Z<16 permissible; 16 to 32 –
 moderately hazardous; 32 to 128 hazardous; ≥128 extremely hazardous [16].
- The obtained quantitative data were processed using software Microsoft Excel 2016, OriginPro
 8.5.1, ArcGIS 9.0. Correlation analysis was performed using Statistica 6.0.

150 **4. Results**

151 Significant excesses over the background concentrations of gross and mobile forms of trace-and 152 macroelements in soils are observed throughout the territory in the zone of impact of quarry-dump 153 complexes of the studied diamond-bearing areas. Their sources are local impact effects that differ in 154 level and geochemical spectrum from regional inhomogeneities. In this sense, physical and chemical 155 properties of soils are criteria for assessing the environmental and sanitary-toxicological state of 156 soils. And variations of integral indicators for assessing the state of the soil cover (Kc and Zc) - are 157 criteria that characterize the degree of evolution of geochemical risks at a particular site. Analysis of 158 geochemical risks allows you to determine the level of accumulated geoecological damage and 159 assess the level of pollution. In turn, to develop recommendations for reducing environmental risks 160 and plan activities aimed at eliminating the negative consequences of productive activities.

161 Table 1 shows an integrated assessment of the geochemical conditions of the Daldyn-Alakit and162 Sredne-Markhinsky diamond-bearing areas.

163

Table 1. Geochemical characteristics of soils of the diamond-bearing regions of Siberia

Land -based ecosystem component		Zc-forming elements	Total ZC pollution index	Other integral indicators
Daldyn-Alakit diamond-bearing area				
Udachny MPP	out of impact zone	Co, Cr, Cu	6,7-30,3	STI – 0, 037 pH – 5,8 – 6,9 Degree of salinity – not saline
	in the impact zone	Ni, Cr, Co, Mn, Cu, As, Ti, Y, Nb, Li, Be, Sr	18,7 – 144,3	STI – 1,2 – 1,5 pH – 7,8 – 8,4 Degree of salinity-highly saline Type of salinity-chloride /sulfate-chloride
Aikhalsky MPP	out of impact zone	Mn, Cr, Ni, Cu	32,5 – 55,9	STI – 0, 01 - 0, 4 pH – 5,2 – 7,3 Degree of salinity – not saline
	in the impact zone	Mn, V, Cr, Ni, Cu, Zn, Pb	20,7- 184,9	STI – 0,3- 0,5 pH – 6,8 – 7,2 Degree of salinity-slightly and moderately saline Type of salinity-chloride
Sredne-Markhinsky diamond-bearing region				
Nyurbinsky MPP	out of impact zone	Mn, Cu, Ni, Cr, Co	8,7 – 25,9	*STI –0,04 pH – 4,5 – 6,12 Degree of salinity – not saline
	in the impact zone	Mn, Cu, Ni, Zn,Pb	30,1 -840,0	$\begin{array}{llllllllllllllllllllllllllllllllllll$

164 Note: * STI - sum of toxic ions

165 5. Discussion

166 The impact of geochemical factors on the near-surface parts of the lithosphere creates 167 prerequisites for the formation of environmental risks within certain areas and territories [17]. On 168 the territory of the studied diamond-bearing areas, quarry-dump complexes have been formed,

- which include ground-based technogenic storage of mining products (waste rock dumps) and enrichment products (tailing dumps). The impact of quarry-dump complexes is manifested by the formation of areal technogenic geochemical anomalies in the soil cover. Therefore, directly on the territory of the industrial site, along with natural types of soils – cryosemes, soils that are in the immediate zone of impact of man-made objects are formed, with identified surface contamination, as well as man-made surface formations (MMSO) in the form of soil dumps and tailing dumps.
- Geochemical risks for the Daldyn-Alakit diamond-bearing region appear as an accumulation of a wide range of trace elements, such as Cr, Co, Ni, Mn, Li, Be, Sn on the day surface during mining operations. Biogenic accumulation of Ni, Mn, and Cd in the upper layer of the soil and Cr, Ni, Co, Mn, Cu in the suprapermafrost soil horizon are typical for the soils of the studied area – cryozems.
- Geochemical risks for the Daldyn-Alakit diamond-bearing region are the spatial variation of the trace element composition of soils, bottom sediments and water. That appears in increased concentrations of Cr, Ni, Co, Ti, Si, Y, Nb, Li, Be, Sr. At the same time, Sr and Li are markers of the impact of highly mineralized groundwater.
- Most of the trace elements are in an inert bound state, due to aerotechnogenic dispersion and accumulate in the upper organic-mineral horizons of soils. If the integrity of the soil profile is preserved, the accumulation only of trace elements occurs, which is a potential threat in the environmental aspect. Changes in soil and geochemical conditions (chemical pollution, water flood, water logging, development of salinization processes), mechanical violation of the integrity of the soil profile, etc. will lead to a gradual, and possibly mass transition of trace elements into mobile forms.
- 190 The ecological and geochemical situation of the territory of Udachninsky MPP is characterized 191 mainly by an acceptable and moderately dangerous category of pollution, Aikhalsky MPP and



192 Nyurbinsky MPP - by moderately dangerous one (Figure 3).

193

Figure 3. Ecological and geochemical characteristics of research objects based on the total pollution
indicator (Zc) of soil cover: (a) Udachninsky MPP, (b) Aikhalsky MPP, (c) Nuyrbinsky MPP.
At the same time, local areas with a dangerous category of pollution are observed at industrial
sites of the Daldyn-Alakit diamond-bearing region. The territory of the Sredne-Markhinsky

- 198 diamond-bearing region is characterized by a higher level of pollution with the category extremely
- 199 dangerous. Thus, these studies allowed us to identify and localize areas of technogenic anomalies
- 200 that characterize the active accumulation of gross and mobile forms of trace elements.

201 5. Conclusions

202 The combination of mining-geological and physical-geographical conditions with various 203 aspects of the development of diamond resources determines the spectrum and nature of the 204 distribution of chemicals in the natural environment and their danger to ecosystems. When the soil 205 and vegetation layer is disturbed, gravitational movement of soil and subsoil material along the 206 slopes occurs with cryogenic solifluctional spreading of clay masses, mixing of their composition, 207 and activation of geochemical processes. Rocks on the surface are subject to cryogenic weathering. In 208 addition, violation of the soil cover or its destruction are a catalyst for geochemical processes of 209 migration of matter, and within the boundaries of anthropogenic landscapes they cause the 210 formation of technogenic geochemical anomalies. Within the latter, the processes of water migration 211 are most intensively expressed, leading to the accumulation or dispersion of the most mobile trace 212 elements, removal of biogenic elements, salinization, leaching of soils and a sharp violation of the 213 natural balance. The presence of geochemical risk objects on the territory of the studied diamond 214 mining areas led to an average threefold increase in the area of the sites characterized by an 215 extremely dangerous category of soil contamination compared to the state of 2014.

On the territory of the Sredne-Markhinsky diamond-bearing region, the area of highly dangerous pollution increased by 120 km², three areal and two point high-contrast anomalies were recorded with an extremely dangerous level of soil contamination, which total conditional area is about 51.6 km². The increasing trend has a north-west and south-east direction. On the territory of the Daldyn –Alakit diamond-bearing region, a dangerous ecological situation is recorded on 75% of the entire area.

Changes in the chemical composition of soils and waters, in turn, are reflected in the biogeochemical parameters of the ecosystems of the region as a whole, increasing the concentration of chemical elements, primarily in edificator plants.

Studies of ecological-geochemical state of Daldyno-Alakit and Sredne- Markhinsky diamond-bearing areas allowed us to localize the area of soil pollution of the Udachninskiy, Aihalsky and Nyurbinsky mining and processing plants that represent a potential threat to the ecosystem as a whole.

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 and agreed to the published version of the manuscript.
- 238 **Conflicts of Interest:** The authors declare no conflict of interest.

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