GEOCHEMISTRY INTERNATIONAL, 2025, Vol. 70, No. 2, pp. 165–186

ASSESSMENT OF SOIL COVER GEOCHEMICAL COMPOSITION IN THE TECHNOGENICALLY ALTERED TERRITORY OF THE PIONEER GOLD DEPOSIT (UPPER AMUR REGION)

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Received July 11, 2024
Revised September 11, 2024
Accepted September 30, 2024

Abstract. The results of geochemical studies of soils and anthropogenic grounds within the territory of the large Pioneer gold ore deposit developed in the Amur Region are presented. Using the enrichment indices for the soil and ground cover of the Pioneer deposit territory, the following pollutant elements were determined: As, Sb, Mo, Bi, W, S, Cd, and Pb. Using the methods of mathematical statistics, the background contents of As, Sb, Bi, Mo, W, S, Cd, and Pb in the technogenically transformed territory at the sampling time accounted for 63, 8.84, 0.69, 3.54, 4.19, 529, 0.11, and 36.5 mg/kg, respectively. The exceedance of background values for As, Sb, Bi, Mo, W, and S is caused by the natural metallogenic features of the territory. It has been established that the sources of metal emissions into the environment are mining facilities and structures of the mining complex: quarries, waste dumps, heap leaching areas, gold extraction plant, and tailings dumps.

Keywords: *gold mining, soils, mine soils, pollution, elemental composition, geoaccumulation index, enrichment index, geochemical background*

DOI: 10.31857/S00167525250205e9

INTRODUCTION

The appearance of heavy metals (HM) in the soil cover is caused by two main factors: geogenic and anthropogenic. Geogenic HMs are elements inherited from parent rocks due to weathering and erosion of rocks and minerals, released as a result of decomposition of organic matter, various soil processes, or emissions from volcanoes and degassing processes on the earth's surface. Concentrations of HMs in the soil cover of deposits can significantly exceed average values for unpolluted soils due to anomalous concentrations of elements in the underlying rocks.

Anthropogenic HMs accumulate in the soil as a result of human industrial activities, including due to mining operations. The development of mineral deposits is accompanied by significant transformations not only of the natural landscape environment of the mining area (changes in terrain relief and surface runoff parameters, deterioration of permafrost conditions), but also by disturbances in the state and properties of soils and the soil layer, which leads to the penetration of chemical elements into vegetation cover, surface and underground watercourses (Radomskaya et al., 2016; Radomskaya et al., 2016a; Radomskaya et al., 2019; Pavlova, 2022; Okereafor et al., 2020; Radomskaya et al., 2021; Pavlova et al., 2022). According to current data (Kulikova, 2013), the volume of finished products in mining production does not exceed 10%, the remaining amount of mineral substance is stored as waste, which contains elements such as As, Sn, Cd, Cr, Cu, Hg, Pb, Ni and Zn, posing a danger not only to ecosystems but also to humans (Chopard et al., 2019; Okereafor et al., 2020) .

The development of gold deposits, among other things, leads to the formation of acidic sulfate solutions due to the weathering of sulfide minerals (pyrite, arsenopyrite) associated with gold in waste rock and their drainage by atmospheric precipitation. The resulting acidic water flows increase the migration capacity of released toxic elements, which, entering surface and underground watercourses, spread far beyond the source of their appearance (dumps, tailings). Toxic products of sulfide transformation, for example, during oxidation of pyrite (reaction 1) and arsenopyrite (reaction 2) – sulfates, arsenates, arsenites, immediately enter the components of terrestrial ecosystems (Plyusnin, Gunin, 2001), among which soil is the most vulnerable:

$$4FeS_2 + 15O_2 + 14H_2O = 4Fe(OH)_{3(s.)} + 16H^+ + 8SO_4^{2-} \qquad (1)$$

$$6FeAsS_{(s.)} + 21O_2 + 24H_2O = 6SO_4^{2-} + 2H_2AsO_4^- + 4HAsO_4^{2-} + 6Fe(OH)_{3(s.)} + 22H^+ \qquad (2)$$

At the same time, as the analysis of scientific literature shows, comprehensive soil geochemical surveys in the territories of deposits are carried out mainly at the pre-design stage and periodically – narrowly focused for monitoring the impact of mining operations on the environment (Abaturova et al., 2022; Chopard et al., 2019). The relevance of such works in mining landscapes of gold deposits is determined by the visualization of the distribution halos of chemical elements in the soil cover, which allows to assess the degree of mining impact, specify zones with high pollution levels, calculate potential risks for surrounding ecosystems, develop strategies to minimize the negative consequences of heavy metals spread and restore soil quality.

The Pioneer gold deposit, located in the Amur region, is one of the significant gold mining objects in Russia (Stepanov, 2019). Geochemistry of this deposit for the purpose of determining gold-bearing minerals, their sources, understanding mineral formation processes, searching for new gold deposits; structure of the deposit and ore processing technologies — for tasks of mining geology, have been studied quite thoroughly by many researchers (Konstantinov, 2010; Alekseev et al., 2013; Vlasov, Kurnik, 2013; Stepanov, Melnikov, 2016a; Stepanov, 2019a; Ostapenko, Neroda, 2023), while not many works are devoted to the environmental geochemistry of the deposit (Lyapunov, 2014; Zenkov et al., 2022). An important relative indicator that allows differentiating sources of heavy metals — whether they are of natural origin or caused by anthropogenic activities, is the determination of the geochemical background of the local mining area (Mazurek et al., 2019); and the calculation of various geochemical indices helps to assess the nature and degree of anthropogenic impact on the soil cover of a technogenically transformed territory.

The purpose of this study was to assess the chemical composition of the soil cover in the territory of the mining and processing enterprise JSC "Pokrovsky Mine" (Pioneer deposit, Amur region) — the largest gold mining enterprise in Russia, using a geochemical approach and statistical methods of analysis.

MATERIAL AND METHODS

Physical and geographical characteristics of the area. The Pioneer gold deposit is located in the Amur region, on the border of Magdagachinsky and Zeysky districts in the Ulungi River basin. The territory is located within the Amur-Zeya elevated plain, which has a hilly-ridge relief with leveled watersheds, wide and swampy valleys with weak surface water flow (Nature..., 1959). The study area is part of the southern area of permafrost distribution and is characterized by the development of insular permafrost, which is manifested in the floodplain of the Ulungi River and on the slopes of watersheds. The upper boundary of permafrost is fixed at a depth of 1–3 m, and in swampy areas at 0.7–1 m.

The climate of the territory is formed under the influence of both oceanic and continental factors. Continentality is manifested in large annual and daily air temperature amplitudes, while monsoon features – include almost exclusively northwestern winds in winter and a sharp predominance of summer precipitation. The characteristics of the air basin are provided according to the data from the nearest meteorological station, Tygda. The circulation of air masses is determined by the influence of the Asian continent and the Pacific Ocean and is characterized by well-defined periodicity. In the winter period, western and northwestern winds prevail; in summer, the wind is mainly from the eastern direction. Air temperature is characterized by sharply pronounced differences between winter and summer values; the average annual air temperature is – 2.0°C. The coldest month is January. In the period from 2015 to 2023, the average monthly air temperature in January was –23.5°C; the absolute minimum of –48.6°C was observed in 2023. The average monthly temperature in July – +20.5°C; the maximum is +35.6°C. Positive average daily air temperatures last for 180 days. The average annual air humidity is 65%. In spring months, air humidity drops, reaching 53–57%, and increases to 76% in July-August. The distribution of precipitation throughout the seasons is uneven, with the main amount falling during the warm period; the annual precipitation total is about 400 mm (Zimovets, 1967; Naprasnikov et al., 1983).

In the studied territory, under the larch-birch forest, zonal brown taiga soils or coarse humus brown soils according to the EGRPR classification (Unified..., 2019), Umbrisols – according to the WRB 2022 classification (IUSS..., 2022) are widespread, while bog soils (peat, peat-gley, peaty-gley), according to the EGRPR classification are peaty gley- and peat-bog soils, according to the WRB 2022 classification – Histic Gleysols, confined to river valleys, watershed plateaus, and depressions.

The underlying rocks for these soils are modern alluvial deposits, deluvial clays and loams. Brown-taiga soils are characterized by weak profile differentiation, low thickness of the humus horizon with significant humus content, acidic environment of the upper horizons, and medium loamy mechanical composition. Bog soils are characterized by the presence of a significant peaty horizon, signs of gleying in the illuvial horizon, have an acidic reaction throughout the profile, and low content of phosphorus and potassium (Terentyev, 1969; Ivanov, 1976).

The mining enterprise JSC Pokrovsky Rudnik began development of the Pioneer gold deposit in 2004. Before industrial development of the deposit, engineering and environmental surveys of the soil cover (horizons A and B) were conducted, which showed a high degree of contamination according to the total pollution index (Zc). The greatest contribution to Zc was made by As, Bi, P, K, Sb, W, Cd, Mo, P, which indicated a natural geochemical anomaly in the territory.

Initially, gold mining and processing was conducted by open-pit method, and from 2008 – according to the scheme: ore mining – crushing – disintegration – heap leaching – sorption cyanidation – regeneration of saturated resin – electrolysis. By now, a technogenic landscape has formed on the territory of the deposit, represented by objects and infrastructure of the mining complex: operating and mothballed quarries, non-recultivated and recultivated rock dumps, early placer mining by prospecting cooperatives, stockpiles of balance and off-balance ores, heap leaching site, gold extraction plant, technological tailings storage facilities, storage ponds, shift camp, solid municipal waste landfill, electrical substation, boiler house, and altered soil cover. The technogenically transformed soil cover is mainly represented by a mixture of gruss-gravelly soil with loamy filler, natural soils are present locally on the periphery of the developed deposit.

Geological characteristics. The Pioneer deposit is part of the North Bureya metallogenic zone of the Amur gold-bearing province of the Pacific ore belt (Stepanov, 2000; Konstantinov, 2006). Its geological structure and mineral composition of rocks have been described in detail earlier (Vlasov, Kurnik, 2013; Sokolov et al., 2016; Stepanov, Melnikov, 2016; Radomsky, Radomskaya, 2022), which allows us to limit ourselves to general information. The scheme of the geological structure of the Pioneer deposit is shown in Fig. 1. The deposit is localized at the contact of Early Cretaceous granitoids (Olginsky massif) and Late Jurassic sedimentary rocks of sandy-aleurolite composition (Ayak Formation).

Within the territory of the ore zones, Early Cretaceous dikes and small bodies of andesites and diorite-porphyrites of the Burinda complex are developed (Stepanov, Melnikov, 2016). The deposit is controlled by a system of faults with northeastern and northwestern strikes. The ore zones are represented mainly by stockworks of veinlet-reticulate silicification in all rock varieties with disseminated and veinlet gold-polysulfide mineralization. Nine ore zones have been explored and identified: Bakhmut, Promezhutochnaya, Yuzhnaya, Andreevskaya, Nikolaevskaya, Vostochnaya, Zapadnaya, Sosnovaya, and Zvezdochka. The host rocks are usually transformed into sericite-quartz and chlorite-sericite-quartz metasomatites.

Oxidized rocks are widely developed in the ore zones, their thickness averages 10 m on the western flank and reaches up to 220 m — on the eastern flank. Ores from the oxidation zone are clay formations with preserved quartz, on which iron oxides and hydroxides develop. In addition to quartz, limonite, hematite, and hydrogoethite, the oxidized varieties contain marcasite, pyrolusite, chalcocite, scorodite, jarosite, and lepidocrocite, which replace sulfides. The average gold content is 0.4-2.0 g/t, but among the poor ores there are also enriched areas with gold content of more than 4.0 g/t, and in some samples its value reaches 1500 g/t and up to 1030 g/t of silver

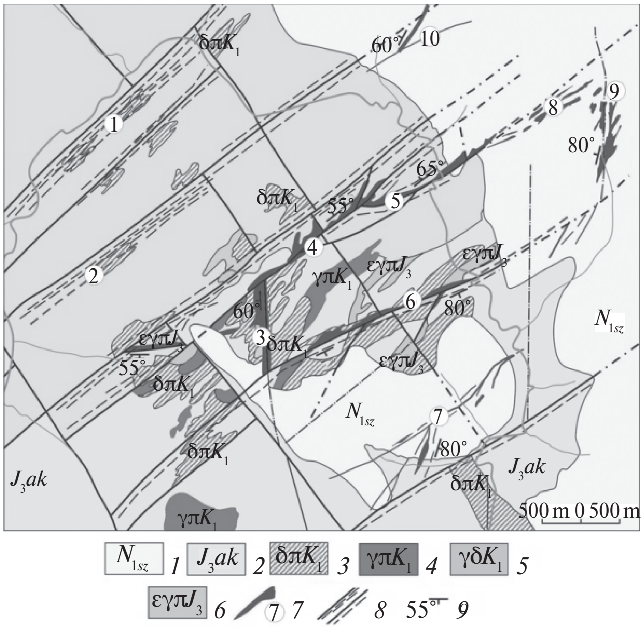

Fig. 1. Scheme of the geological structure of the Pioneer gold deposit (according to Vlasov, Kurnik, 2013). *Legend*: *1* – Neogene lacustrine-alluvial sands, clays; *2* – Upper Jurassic sandstones, siltstones; *3*–*5* – Early Cretaceous rocks: *3* – diorite-porphyrites, andesites, *4* – granite-porphyries, *5* – diorites, granodiorites; *6* – Late Jurassic coarse-porphyry granite-porphyries; *7* – ore stockwork zones (1 – Zvezdochka, *2* – Zapadnaya, *3* – Yuzhnaya, *4* – Promezhutochnaya, *5* – Bakhmut, *6* – Andreevskaya, *7* – Nikolaevskaya, *8* – Bakhmut – Severo-vostochnaya, *9* – Erozionnaya, *10* – Otvalnaya); *8* – faults and fracture zones; *9* – elements of the occurrence of ore zones

(Vlasov et al., 2012). The calculated gold reserves are estimated at more than 100 tons.

Methods of analysis. **Sampling.** Soil and ground sampling were conducted with geographic coordinates recorded GPS navigator (Fig. 2). Sampling was conducted to a depth of 10 cm in accordance with GOST 17.4.3.01-2017. A total of 32 soil and ground samples weighing up to 1 kg were collected. Soil and ground sampling sites were located in natural landscape areas (points 1, 4, 7g, 8, 14, 18, 22a, 23, 24, 25, 26, 28) and in zones influenced by potential sources of chemical element emissions: near waste rock dumps (1a, 2, 2a, 7a, 7b); quarries (5, 6, 6a, 9, 22b, 22c, 22d/1, 22d/2); heap leaching site (16, 17); tailings pond (12); reservoir (13); and near historic placer mining dumps (3, 11, 19) (Fig. 2).

In addition, 92 samples of sedimentary, igneous, and metasomatic rocks were collected from the Yuzhnaya, Promezhutochnaya, Bakhmut, Andreevskaya, and Nikolaevskaya ore zones of the Pioneer deposit. Laboratory processing of samples included drying at room temperature, sieving, removal of the coarse fraction (+1 mm), grinding of the –1 mm fraction for subsequent analyses.

Chemical and analytical studies. The elemental composition of the samples was determined by atomic emission (*iCAP*-6500, *Thermo Scientific*, USA) and mass spectral (*X-7*, *Thermo Elemental*, USA) methods at IPTM RAS (Chernogolovka).

Determination of physical and chemical characteristics of soils and ground soils, such as pH of water and salt extracts, inorganic carbon content, total and sulfate sulfur was carried out at the Core Facility "Amur Center for Mineralogical and Geochemical Research" of the IGiP FEB RAS. The content of sulfide sulfur was calculated from the difference between total sulfur and sulfate sulfur (Sulfur, 1986). The content of inorganic carbon was measured using a *TOC-VCPN* analyzer with *SSM*-5000A module (*Shimadzu*, Japan).

Determination of granulometric (grain) and microaggregate composition of soils was carried out according to GOST 12536-2014 (GOST 12536-2014, 2015).

Concentrate analysis of rock samples was performed at the IGiP FEB RAS. Crushed rocks were washed in water to separate the light fraction and obtain concentrate, which was divided into three fractions: magnetic, electromagnetic and non-magnetic. Minerals were identified using a stereomicroscope *MBS-10M* (*LZOS*, RF). Clay minerals were not determined by this method.

Determination of local background by statistical method. Determination of the local geochemical background for the selected elements was carried out using quantile-quantile (Q–Q) plots. These plots were used to check the data for conformity to normal distribution. Samples with normal distribution should group along a diagonal line. Often, the distribution of trace elements follows a lognormal distribution (Reimann, Garrett, 2005; Reimann et al., 2005; Yusupov et al., 2020), but if the original data did not conform to normal distribution, the concentration values were logarithmized to base 10. On Q–Q – plots for logarithmically transformed concentrations, outliers in the upper right (high values) and lower left (low values) corners were removed. Exclusion of outliers at the extreme points of the transformed data was carried out until the points of the distribution curve approached as close as possible to a straight line. The geochemical data obtained in this way, corresponding to lognormal distribution, were grouped into five classes to determine the background and anomalies, the thresholds of which were calculated based on the geometric mean (X_{geom})

and its deviation (d) (Miesch, 1967; Papastergios et al., 2011). Negative anomaly ($-C_A$), caused by rock weathering, corresponds to a value $< X_{geom}/d$. Background values are determined in the interval $X_{geom}/d–X_{geom}·d$. The background value equals X_{geom}. Positive low-contrast anomaly ($+C_{A1}$) is in the interval $X_{geomd}–X_{geom}·d^2$. Positive medium-contrast anomaly ($+C_{A2}$) is in the interval $X_{geom}·d^2–X_{geom}·d^3$. High-contrast anomaly ($+C_{A3}$) corresponds to an indicator $> X_{geo} · d^3$.

Geochemical indices. Geochemical indices, such as enrichment factors (EF), geoaccumulation indices (Igeo), concentration coefficient (K_c), soil pollution toxic hazard coefficient (K_o), and total pollution index (Zc) are used to determine concentrations of elements that pose environmental hazards.

The enrichment factor is an effective tool for identifying elements that have enriched soil and rock. The enrichment factor was calculated using the formula:

$$EF = (C_i/C_{Al})_{sample}/(C_i/C_{Al})_{crust}, \tag{3}$$

where $C_{i\ sample}$ is the content of element i in the soil cover; $C_{Al\ sample}$ is the content of Al in the soil cover; $C_{i\ crust}$ is the content of element i in the upper continental crust according to (Rudnick, Gao, 2014) (hereinafter in the text and tables “clarke”); $C_{Al\ crust}$ is the content of Al in the upper continental crust; element content in mg/kg.

The EF coefficients of elements are calculated in relation to the least mobile element that is naturally present in soils. These include Al, Sc, Zr, and Ti. Our choice of the most stable element in EF calculations was based on the coefficient of variation (V). We used Al as the element with the minimum V value. There is a gradation by the magnitude of the enrichment factor of a natural object: an EF value < 2 is considered minimal enrichment, a value from 2 to 5 — moderate enrichment; from 5 to 20 — significant enrichment, from 20 to 40 — very high enrichment, EF > 40 is considered extremely high enrichment.

The geoaccumulation index is used to assess soil contamination and is calculated using the equation:

$$Igeo = \log_2 \frac{C_i}{1.5C_b}, \tag{4}$$

where C_i is the element concentration, C_b is the geochemical background value, the constant 1.5 is a correction factor that compensates for natural fluctuations in the content of the element while minimizing anthropogenic impact (Müller, 1969). The geoaccumulation index scale consists of seven classes, defined as follows: 0 — practically no contamination (Igeo ⩽ 0); 1 — soils from uncontaminated to moderately contaminated (Igeo = 0—1); 2 — moderate contamination (Igeo = 1—2); 3 — contamination from moderate to severe (Igeo = 2—3); 4 — severe contamination (Igeo = 3—4); 5 — from severe to extreme contamination (Igeo = 4—5) and 6 — includes all Igeo values above class 5 values.

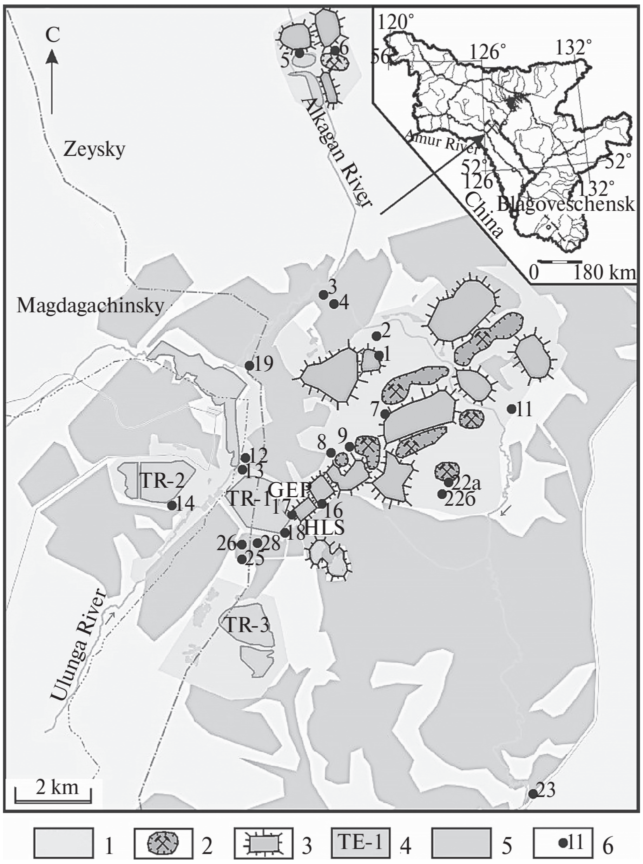

Fig. 2. Map-scheme of the study area of the Pioneer gold deposit development (1 — industrial sites; *2* — open pits; *3* — recultivated dumps, stockpiles of balance and off-balance ores; *4* — technological reservoirs of tailings ponds, storage ponds; *5* — mixed forest; *6* — soil and ground sampling points and their numbers; GEP — gold extraction plant; HLS — heap leaching site)

The coefficient of toxic hazard of soil contamination (K_o) was calculated according to the formula:

$$K_o = C_i/MPC_i \tag{5}$$

where C_i is the content of the polluting element, MPC_i is the maximum permissible concentration of the polluting element. The hazard of contamination is higher the more the actual content of soil contamination components exceeds the MPC, i.e., the hazard of contamination is higher the more K_o exceeds one (MU 2.1.7.730-99, 1999).

The concentration coefficient (SanPiN 1.2.3685-21) K_c was calculated as the ratio of the content of the determined element in the soil (C_i) in mg/kg to the background (C_{bi}). The values of the local background calculated in this work were used as background contents:

$$K_c = C_i / C_{bi}. \quad (6)$$

Assessment of the level of chemical contamination of soils as an indicator of adverse effects on public health is carried out using the total pollution index (Zc) (SanPiN 1.2.3685-21). The total pollution index equals the sum of concentration coefficients of chemical pollutants and is expressed by the formula:

$$Zc = \Sigma(K_{ci} + \ldots + K_{cn}) - (n-1) \quad (7),$$

where n is the number of determined summed substances; K_{ci} is the concentration coefficient of the i-th pollution component.

At values of Zc < 16, soil contamination is considered acceptable, while the content of elements of hazard classes 1, 2, and 3 should not exceed MPC; moderately hazardous contamination corresponds to the range of values 16–32; Z_C from 32 to 128 indicates a dangerous level of contamination. At the same time, the content of elements of hazard classes 1 and 2 in the soil should not exceed Kmax (the maximum value of the permissible level of element content according to one of the four hazard indicators). When Zc > 128, soil contamination is extremely hazardous, and the content of elements of hazard classes 1 and 2 in this case is greater than Kmax.

A cceptable levels of element content according to hazard indicators are provided in MU 2.1.7.730-99 (MU 2.1.7.730-99, 1999). The maximum level of hazard indicators for Sb was 50 mg/kg (general sanitary K4); for As — 15 mg/kg (migration-water K2); for Pb — 260 mg/kg (migration-water K2); for other elements, limiting hazard indicators have not been developed.

Assessment of the mobility of potentially toxic elements. For the predictive assessment of the mobility degree of toxic elements in soils under the influence of seasonal flows (rainwater and snowmelt) (Hageman et al., 2015; Dold, 2017; Radomskaya et al., 2021), acid-producing (AP) and acid-neutralizing (NP) potentials of soils were calculated (Edelev, 2009; Alekseev et al., 2011; Edelev, 2013; Paktunc, 1999). AP corresponds to the value equal to the maximum amount of acid resulting from the oxidation of sulfides, reactions 1–2 (Sobek et al., 1978). The AP value was determined by the content of sulfur in sulfides. The unit of measurement for AP is the amount of $CaCO_3$ (in kg/t) needed to neutralize the acid according to the formula (Edelev, 2013):

$$AP = 10 \times \eta(S_{\text{sulfide}}) \times \frac{M(CaCO_3)}{M(S)} \approx$$
$$\approx 10 \times \eta(S_{\text{sulfide}}) \times \frac{100}{32} = \eta(S_{\text{sulfide}}) \times 31.25, \quad (8)$$

where 10 is the conversion factor from kg/t to wt.%; $\eta(S_{\text{sulfide}})$ is the content of sulfide sulfur in the substance, wt.%; $M(CaCO_3)$ and M(S) are the molar masses of $CaCO_3$ (100 g/mol) and S (32 g/mol). The AP indicator is often used in experiments and research (Skousen et al., 2002; Gaskova, Bortnikova, 2007; Edelev, 2013).

NP is used as an assessment of the material's ability to neutralize acid drainages (Sobek et al., 1978; Skousen et al. , 2002) and is calculated according to equation (9):

$$H^+ + MeCO_{3(\text{solid})} = Me^{2+} + HCO_3; \text{ where}$$
$$Me = Ca^{2+}, Mg^{2+} \quad (9).$$

The main acid-neutralizing minerals are carbonates, among which calcite is the most effective in neutralizing acidic waters (Solomin, Krainov, 1994). The neutralization potential NP (kg $CaCO_3$/t) was calculated using total inorganic carbon: NP (kg $CaCO_3$/t) = 83.33 × C_{inorg}.% (Plante et al., 2012). The interpretation of the obtained data was carried out by the ratio of potentials (neutralization and acid-producing).

Statistical analysis. Data processing was carried out using the *Statistica* 10 software. The number of elements for statistical calculations was reduced to a smaller number, to 42, by removing elements for which 50% or more of the values were below the detection limit. Rare earth elements from La to Lu are presented as their sum (ΣREE). If the element content was below the detection limit, a value equal to half of the detection limit was applied (Golovin et al., 2002). Median, arithmetic mean and geometric mean contents, standard deviation, kurtosis coefficients, skewness and variation were calculated; cluster analysis was performed, box plots and quantile-quantile (Q–Q) plots were constructed. Graphical constructions of schematic maps were performed using *Surfer* and *CorelDRAW* software.

RESULTS AND DISCUSSION

Elemental and mineral composition of rocks of the Pioneer gold deposit. Data on the content of elements in rocks and ores of the deposit, as well as in the upper continental crust are presented in Table 1. Analysis of the obtained results shows that ore-bearing rocks are slightly enriched with Li, Cu, Zn, Mo, Cd, Cs, W, Tl, Pb, Rb, Bi, and the average bulk contents exceed the clarke values by 1.5–6 times. There is a significant enrichment of rocks with Sb, As and S (by median by 88, 16.5 and 16.1 times, respectively); the minimum-maximum contents of Sb in the deposit rocks vary from 3.20 mg/kg to 50461 mg/kg, As — from 7.30 mg/kg to 22436 mg/kg.

Antimony is part of lead sulfosalts, fahlores, antimonite, arsenic — part of arsenopyrite. Mineralogical analysis showed (Table 2) that the main vein minerals of ores are quartz, feldspars, and carbonates, while the ore minerals are native gold, antimonite, arsenopyrite, sphalerite, pyrite, magnetite, molybdenite, and minerals such as leucoxene, garnet, epidote, ilmenite, hematite, martite, limonite, Fe oxides and hydroxides, sphene, zircon, and apatite occur in single grains. The amount of sulfides is relatively small; pyrite is sometimes covered with films of iron hydroxides. Feldspar and quartz quite often occur with inclusions of magnetite, pyrite and are partially carbonatized. Rock fragments are represented by intergrowths of quartz, biotite, sericite, feldspar, amphibole, and calcite in different proportions.

Mining development causes changes in soil composition, both as a result of destructive processes and from the introduction of additional elements. This may be due to the weathering of rock minerals, as well as contamination from mining waste. As a result, based on data on the elemental composition of ore-bearing rocks of the Pioneer deposit, 14 elements (S, As, Sb, Mo, W, Cd, Pb, Bi, Li, Cu, Zn, Cs, Tl, Rb) were identified, the level of soil contamination with which needs to be monitored, as there is a probability of anthropogenic introduction of these elements into the soil cover as a result of production activities.

Elemental composition of soils and grounds of the deposit territory. The soil-ground cover of the deposit territory is represented predominantly by sandy loam-loamy mechanical composition. The content of physical sand (fraction > 0.01 mm) in technogenic grounds varies within 89–91%; in soil samples – 77–89%. The median pH value of the salt extract of soils and grounds was 4.33 (strongly acidic), varying from strongly acidic (2.54) to alkaline (8.42); while some samples of technogenic grounds (*5, 6a, 9, 13, 16*) had salt pH greater than 5.5.

The chemical composition of the studied soils and technogenic grounds is presented in Table 3. The average composition of the studied soil and ground samples compared to the upper continental crust is characterized by a relative deficit of many elements – Na, Mg, Al, P, Ca, Ti, Fe, Sc, V, Cr, Co, Ni, Zn, Ga, Sr, Y, Zr, Nb, lanthanides, Hf, Ta, Th, U; elevated concentration levels of K, Mn, Li, Cu, As, Mo, Sb, Cs, W, Pb, Bi, Cd, Rb, Ba, Tl were observed, for which the excess of the clarke value was from 1.1 to 60 times.

The chemical composition of soils and technogenic grounds does not have large variations in the content of most elements. Significant spatial heterogeneity of samples is characteristic for S (236%), Mn (194%), Co (118%), As (103%), Mo (118%), Cd (110%), Sb (123%), W (117%), Bi (123%). The ratios of maximum concentration to minimum for S, Mn, Co, As, Mo, Cd, Sb, W, Bi are 1424, 203, 84, 48, 80, 20, 92, 62, 94 respectively. For most elements, except Al, Ti, Fe, Sc, V, Ga, Th, U and ΣREE, a positive distribution asymmetry was revealed, which indicates that for these elements there are some elevated values either due to natural enrichment or due to human activity

Analysis of the distribution of elements (Fig. 3) showed a deviation of median values in pairs and triads of atomic numbers in the Mendeleev periodic table (3–4), (23–24), (40–41–42), (50–51–52) from the Oddo-Harkins rule, which states that “the abundance of chemical elements with even atomic numbers is always higher than the abundance of neighboring chemical elements with odd atomic numbers” (Nikanorov, 2009). The distribution of lithium, vanadium, molybdenum, and antimony does not comply with this rule. The discrepancy in the ratios of these chemical elements with the rule may be caused by two main reasons. First, by the special natural anomalous geochemical field of indicator elements for a type of mineralization; second, by the superimposed influence of the anthropogenic factor (mining complex), which enhances distortions of natural processes of formation of the chemical composition of soils and grounds within the boundaries of the Pioner gold deposit being developed.

Relationships between elements were analyzed using cluster analysis. The cluster tree was built according to the rule of association – Ward's method and the proximity measure – 1-r Pearson (Fig. 4).

The dendrogram with the geochemical spectrum of elements includes two large composite clusters. Cluster 1 {Ba–Sr; Bi–As–W–Cr; Te–Sb–Tl–Rb; Pb–Cd–Mo; Zn–Li}. It presents significant, positive strong correlations between elements-indicators of gold-sulfide-quartz mineralization.

Table 1. Elemental composition of ore-bearing rocks of the Pioneer deposit (from Na_2O to Fe_2O_3 – in %, other elements – in mg/kg, n = 92)

Component	m	X_{geom}	X_{med}	Min	Max	S	Clarke (Rudnick, Gao, 2014)	m/clarke	X_{med}/clarke
Na_2O	1.56	0.72	1.40	0.020	4.30	1.33	3.27	0.5	0.4
MgO	1.62	1.02	1.25	0.053	5.90	1.38	2.48	0.7	0.5
Al_2O_3	11.6	10.3	12.6	1.30	18.9	4.37	15.4	0.8	0.8
P_2O_5	0.11	0.08	0.11	0.0040	0.32	0.07	0.15	0.7	0.7
S	1.13	0.47	1.00	0.0015	7.20	1.05	0.062	18.3	16.1
K_2O	3.79	3.32	3.90	0.27	8.70	1.53	2.8	1.4	1.4
CaO	1.56	0.49	0.36	0.036	20.20	2.93	3.59	0.4	0.1
TiO_2	0.39	0.31	0.39	0.010	0.77	0.21	0.64	0.6	0.6
MnO	0.066	0.040	0.05	0.0010	0.28	0.062	0.1	0.7	0.5
Fe_2O_3	3.63	3.07	3.40	0.24	13.4	1.97	5.6	0.6	0.6
Li	63.7	54.1	54.8	11.4	177	37.5	21	3.0	2.6
Be	2.24	2.02	2.15	0.58	11.8	1.26	2.1	1.1	1
Sc	7.79	6.12	6.60	0.23	20.3	4.80	14	0.6	0.5
V	66.0	54.6	58.5	6.00	152	36.4	97	0.7	0.6
Cr	83.5	59.5	53.2	10.2	309	72.5	92	0.9	0.6
Co	13.6	7.75	9.15	0.40	331	34.1	17.3	0.8	0.5
Ni	26.4	20.4	23.0	2.80	151	22.4	47	0.6	0.5
Cu	86.1	33.5	31.4	3.20	2040	261	28	3.1	1.1
Zn	184.3	90.2	85.5	9.50	3481	446	87	2.1	1
Ga	15.0	13.3	16.3	1.50	28.3	5.96	17.5	0.9	0.9
As	469	89.4	79.1	7.30	22436	2396	4.8	97.6	16.5
Rb	164	141	165	12.7	330	75.2	84	2.0	2
Sr	183	127	164	6.50	497	132	320	0.6	0.5
Y	12.0	8.96	10.7	0.90	40.40	8.27	21	0.6	0.5
Zr	57.1	40.8	52.6	1.10	162	38.2	193	0.3	0.3
Nb	6.27	4.78	5.60	0.12	17.9	3.90	12	0.5	0.5
Mo	3.21	1.77	1.75	0.24	38.4	5.45	1.1	2.9	1.6
Cd	0.71	0.19	0.16	0.03	14.30	2.06	0.09	7.9	1.8
Sn	2.91	2.25	2.35	0.23	28.20	3.09	2.1	1.4	1.1
Sb	764	46.0	35.3	3.20	50461	5272	0.4	1911	88.3
Te	4.29	0.83	0.64	0.035	98.3	11.8	–	–	–

Table 1. (End)

Component	m	X_{geom}	X_{med}	Min	Max	S	Clarke (Rudnick, Gao, 2014)	m/clarke	X_{med}/clarke
Cs	9.06	7.39	7.20	2.10	28.20	5.85	4.9	1.8	1.5
Ba	464	389	488	22.7	883	208	624	0.7	0.8
ΣРЗЭ	104	83.4	97.9	11.4	361	64.3	148.14	0.7	0.7
Hf	1.80	1.35	1.70	0.045	4.30	1.09	5.3	0.3	0.3
Ta	0.49	0.36	0.45	0.0050	1.71	0.33	0.9	0.5	0.5
W	3.84	2.98	3.20	0.45	16.5	3.10	1.9	2.0	1.7
Tl	2.32	1.90	2.10	0.18	10.1	1.49	0.9	2.6	2.3
Pb	88.0	46.1	41.9	4.20	1115	155	17	5.2	2.5
Bi	0.68	0.41	0.46	0.027	5.80	0.80	0.16	4.3	2.8
Th	7.32	5.75	6.50	0.20	20.8	4.37	10.5	0.7	0.6
U	2.19	1.80	2.15	0.14	6.00	1.20	2.7	0.8	0.8

Notes. Dash "–" – no data; n – number of samples; m – mean; X_{geom} – geometric mean; X_{med} – median; Min – minimum; Max – maximum; S – standard

Table 2. Mineral composition of rocks and ores of the Pioneer deposit

Mineral	Sample, composition %								
	P-1	P-2	P-3	P-4	P-5	P-6	P-7	P-8	P-9
Amphibole	units	units	units	4.1	units	units	counts	–	–
Magnetite	–	–	units	0.1	units	–	units	–	–
Pyrite	1	4.1	–	counts	0.4	3	0.5	1.2	1.3
Arsenopyrite	–	–	13.2	–	–	–	–	–	–
Siderite	–	–	0.1	–	–	–	–	–	–
Antimonite	–	–	9.6	–	–	–	–	–	–
Sphalerite	–	–	1.6	–	–	–	–	–	–
Quartz	97.3	5	75.2	units	65.5	2	33.5	4	82.6
Feldspar	0.16	78.5	–	31.8	17	11.7	2.8	52.5	16.1
Calcite	1.5	9.7	–	counts	17	28.7	counts	42.2	–
Mica	–	2.6	–	0.8	units	units	counts	counts	–
Sericite	–	counts	–	1.2	counts	–	counts	counts	–
Rock fragments	–	–	–	63.2	–	54.5	63	–	–
Fe scrap	counts	counts	0.3	counts	counts	counts	–	units	–
Zircon	–	counts	units	units	units	–	counts	units	units
Native Au	–	1 grain	–	–	7 grains	1 grain	5 grains	–	–

Notes. Dash ("–") – not detected; "units" – mineral grain content (⩽10 grains per sample); "counts" – mineral grain content (11–100 grains per sample)

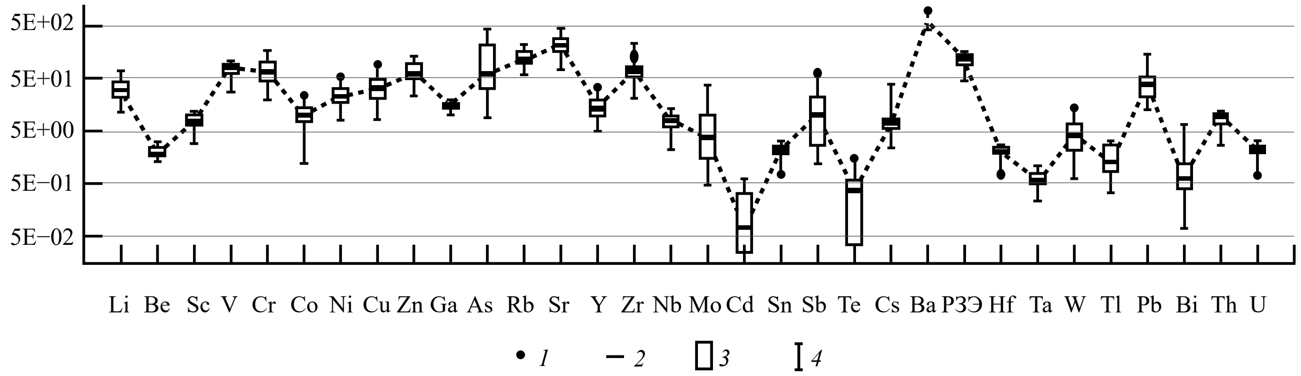

Fig. 3. Box plot diagram of total element content (mg/kg) in soils and grounds in the territory of the mining complex of the Pioner gold deposit (*1* – outliers, *2* – median, *3* – 25–75% percentiles, *4* – minimum-maximum)

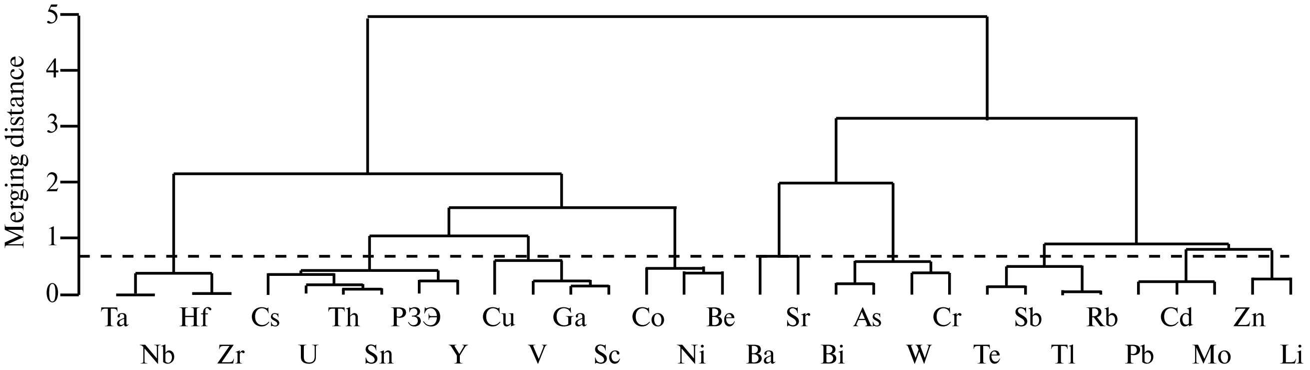

Fig. 4. Dendrogram of the correlation matrix of the geochemical spectrum of trace elements in soils and technogenic grounds on the territory of the mining complex of the exploited Pioneer deposit (dashed line of the critical level $1-r_{0.05} = 0.65$; n = 32)

Cluster 2 includes associations of elements {Ta–Nb–Hf–Zr; Cs–U–Th–Sn–REE–Y; Cu–V–Ga–Sc; Co–Ni–Be}. The significant strong correlation between them is apparently related to the influence of the geological factor “petrofund” and accessory mineralization of magmatic complexes within the deposit. Strong relationships between Th, U, Sn suggest their high content in clay minerals, between Zr and Hf — the presence of zircon mineral, which is confirmed by mineralogical analysis data; REE and Y are associated with clay minerals and zircon.

Determination of anthropogenically introduced elements. To identify elements of anthropogenic origin, their enrichment factors were calculated. According to the enrichment factors calculated by the median, the soil cover of the studied area is characterized by moderate enrichment of Mo, Bi, Pb, W, significant enrichment of As, very high enrichment of Sb, and background concentrations of other elements (Table 3).

Thus, in the territory of the Pioneer deposit, elements of interest from an ecological point of view are Mo, Bi, Sb, As, Pb, and W. S and Cd can also be included, which have EF values of 7.3 and 2.2 respectively, calculated by the mean. The high content of As and S is due to the presence of arsenopyrite (FeAsS) and pyrite (FeS_2) in the ore. Bi occurrences are spatially confined to outcrops of Upper Amur granitoids and may be genetically related to them. Mo and Sb are present both in low-temperature metasomatites and in metasomatites gravitating toward copper-porphyry type mineralization (Lyapunov, 2014). These elements have a wide range of concentrations at sampling points on the territory of the deposit. The contents of Mo, Bi, Sb, As, W and Pb varied from 0.47 to 37.5, from 0.07 to 6.6, from 1.2 to 111, from 12.9 to 149, from 0.62 to 38.3 and from 9.1 to 437 mg/kg respectively, with average concentrations of 7.44, 1.02, 24.9, 135, 6.7 and 47.4 mg/kg. The S content reached 4.7%

Table 3. Statistical characteristics and enrichment factor of the chemical composition of soil cover in the territory of the Pioner gold deposit (from Na_2O to Fe_2O_3 – in %, other elements – in mg/kg; n = 32)

Component	m	X_{geom}	X_{med}	Min	Max	S	V	A	E	Clarke*	EF by X_{med}	EF by m
Na_2O	1.61	1.28	1.60	0.16	3.10	0.87	54	0.08	–0.92	3.27	0.5	0.5
MgO	1.02	0.89	0.89	0.37	2.94	0.63	62	1.97	3.40	2.48	0.4	0.4
Al_2O_3	14.4	14.3	14.6	9.28	17.60	1.94	13	–0.45	–0.01	15.4	1.0	1.0
P_2O_5	0.13	0.10	0.10	0.02	0.29	0.07	57	0.59	–0.55	0.15	0.7	0.9
S	0.42	0.06	0.04	0.00	4.70	0.98	236	3.78	15.93	0.062	0.6	7.2
K_2O	3.29	3.10	3.15	1.30	5.80	1.11	34	0.29	–0.51	2.8	1.2	1.3
CaO	0.90	0.62	0.51	0.09	3.24	0.81	90	1.46	1.53	3.59	0.1	0.3
TiO_2	0.52	0.49	0.54	0.14	0.83	0.13	26	–0.80	1.98	0.64	0.9	0.9
MnO	0.20	0.08	0.06	0.01	2.03	0.38	194	3.95	17.92	0.1	0.7	2.1
Fe_2O_3	4.26	4.00	4.60	1.50	7.70	1.41	33	–0.13	0.04	5.6	0.8	0.7
Li	34.0	30.5	30.7	11.3	69.5	16.2	48	0.81	0.07	21	1.5	1.7
Be	2.05	1.99	1.90	1.30	3.10	0.51	25	0.52	–0.27	2.1	1.0	1.0
Sc	8.02	7.57	8.20	2.90	12.10	2.45	31	–0.49	–0.17	14	0.6	0.6
V	76.4	72.5	83.4	27.9	107	21.7	28	–0.89	0.04	97	0.9	0.8
Cr	85.0	71.4	70.6	19.7	233	51.2	60	1.08	0.80	92	0.8	1.0
Co	14.8	10.9	10.9	1.20	101	17.4	118	4.29	20.69	17.3	0.7	0.9
Ni	26.1	23.2	24.1	8.10	60.9	12.6	49	0.99	1.03	47	0.5	0.6
Cu	46.5	34.8	35.8	8.20	231	43.1	93	2.83	10.38	28	1.3	1.8
Zn	75.7	68.0	67.1	23.3	182	35.8	47	1.01	1.09	87	0.8	0.9
Ga	14.9	14.7	14.7	10.0	19.3	2.45	16	–0.16	–0.50	17.5	0.9	0.9
As	121	68.7	66.2	9.10	437	124	103	1.23	0.41	4.8	14.5	26.9
Rb	129	123	122	58.2	218	41.4	32	0.58	–0.36	84	1.5	1.6
Sr	229	208	218	72.8	456	103	45	0.81	–0.03	320	0.7	0.8
Y	15.9	14.3	15.4	4.90	36.1	7.47	47	1.04	1.34	21	0.8	0.8
Zr	89.6	75.0	72.0	21.2	244	59.2	66	1.63	2.13	193	0.4	0.5
Nb	8.31	7.74	8.10	2.20	16.5	3.07	37	0.69	0.95	12	0.7	0.7
Mo	7.20	3.85	4.10	0.47	37.5	8.46	118	2.21	6.05	1.1	3.9	7.0
Cd	0.18	0.10	0.08	0.03	0.61	0.20	110	1.12	–0.25	0.09	0.9	2.2
Sn	2.27	2.13	2.30	0.72	4.20	0.74	33	0.09	1.39	2.1	1.2	1.2
Sb	23.9	10.9	11.0	1.20	111	29.3	123	1.61	1.99	0.4	29.0	64.0

Table 3. (End)

Component	m	X_{geom}	X_{med}	Min	Max	S	V	A	E	Clarke*	EF by X_{med}	EF by m
Te	0.56	0.28	0.46	0.04	1.80	0.54	1.00	–0.08	96	–	–	–
Cs	8.15	6.74	7.30	1.40	39.6	7.00	86	4.02	18.55	4.9	1.6	1.8
Ba	743	709	675	424	1464	255	34	1.52	2.10	624	1.1	1.3
ΣРЗЭ	118	113	128	44.8	164	31.3	26	–0.60	–0.38	148.14	0.9	0.9
Hf	2.08	1.97	2.10	0.73	3.80	0.64	31	0.06	1.76	5.3	0.4	0.4
Ta	0.61	0.58	0.60	0.23	1.10	0.19	32	0.28	0.78	0.9	0.7	0.7
W	6.51	4.34	4.70	0.62	38.3	7.64	117	3.28	12.87	1.9	2.6	3.7
Tl	1.61	1.32	1.30	0.34	3.30	0.96	60	0.47	–1.33	0.9	1.5	1.9
Pb	43.7	37.0	39.8	12.9	149	28.2	64	1.93	5.22	17	2.5	2.7
Bi	0.99	0.65	0.66	0.07	6.60	1.26	127	3.91	17.45	0.16	4.3	6.6
Th	8.68	8.23	9.60	2.70	12.0	2.43	28	–0.97	0.47	10.5	1.0	0.9
U	2.20	2.07	2.30	0.68	3.30	0.66	30	–0.79	0.48	2.7	0.9	0.9

Notes. Dash “–” – no data; Min – minimum; Max – maximum; m – arithmetic mean; X_{geom} – geometric mean; X_{med} – median; S – standard deviation; A – asymmetry coefficient; E – excess coefficient; V – coefficient of variation; * – according to Rudnick, Gao, 2014

with an average of 0.43% (Table 3). The average values of the total content of the identified elements in the studied soils decrease in the following order: S > As > Pb > Sb > Mo > W > Bi > Cd. The median concentrations of these elements are less than their average values (Table 3), and the skewness values are greater than one.

Geochemical background of As, Sb, Mo, Bi, W, S, Pb, Cd in anthropogenically transformed territory. Elements can enter the soil both from underlying rocks and from anthropogenic sources. With open-pit ore mining, the natural background of elements in soils is overlaid with a technogenic component caused by atmospheric transfer of fine-dispersed rock from drilling and blasting operations, wind erosion from the surface of dumps, tailings storage facility and pit edges (Radomskaya et al., 2016a). The geochemical background indicator allows distinguishing between geogenic and anthropogenic enrichment with chemical elements of the studied soils and grounds and identifying the ratio of natural and anthropogenic pollution.

Determining the local geochemical background of a territory is one of the main tasks when studying the impact of mining enterprises on the environment and, in particular, on the parameters of soil cover. The geochemical background can be determined by direct measurement of indicators in a similar territory without anthropogenic contamination, or by statistical method. When determining the background contents of selected elements by statistical method, quantile-quantile plots were used. Figure 5 shows Q—Q plots for the concentrations of As, Sb, Mo, Bi.

The observed values were plotted on the x-axis, and values expected for a normal distribution were plotted on the y-axis. According to the obtained graphs (Fig. 5), the original data did not correspond to a normal distribution, which necessitated an appropriate transformation of the data for subsequent statistical analysis. The concentration values of 8 elements were logarithmically transformed using base 10. This transformation for Sb, W, S, Pb, and Cd led to a distribution with lower skewness values, which were 0.077, 0.21, 0.62, 0.25, and 0.28 respectively, and changed the skewness values for As, Bi, and Mo from positive to negative (–0.016, –0.87, and –0.057 respectively) (Table 4).

The distribution of logarithmically transformed values more closely approximates a straight line. Outliers at the extreme points of the transformed data were excluded until the distribution curve points approached the straight line as closely as possible (Fig. 6). The outliers identified in this way were classified as extreme values.

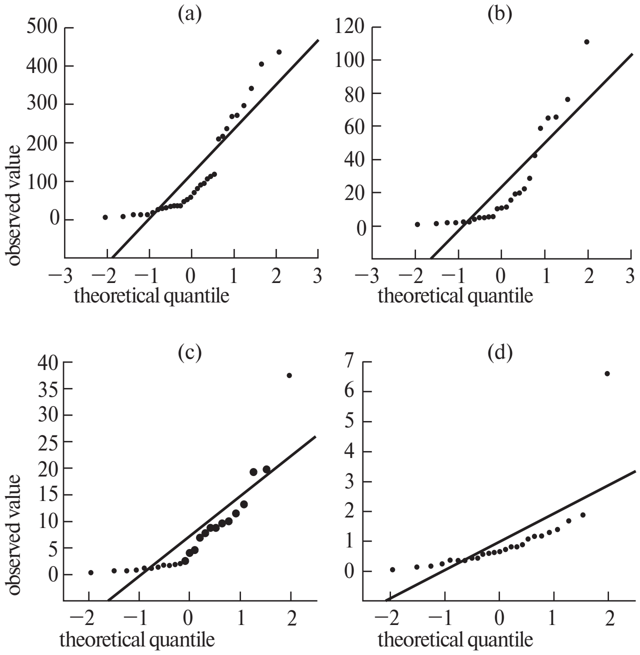

Fig. 5. Quantile-quantile plots for initial concentrations (mg/kg) of As (a), Sb (b), Mo (c), Bi (d) in soils and grounds on the territory of the Pioneer gold deposit being developed

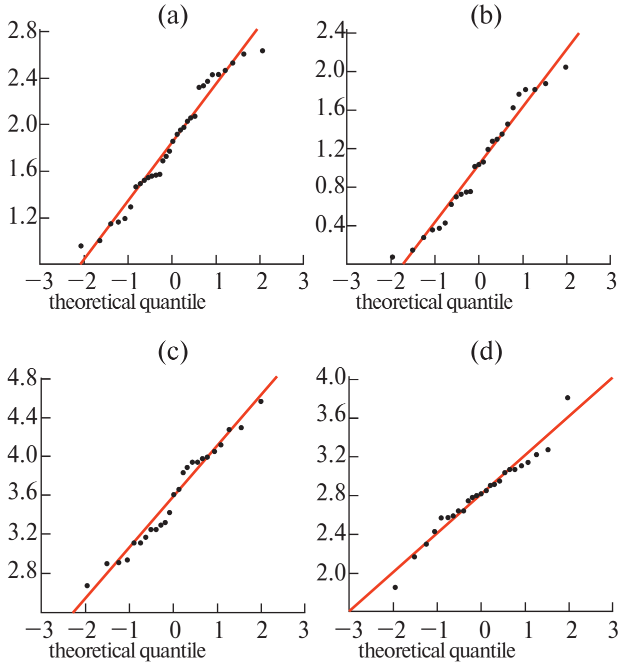

Fig. 6. Quantile-quantile plots for logarithmically transformed concentrations of As (a), Sb (b), Mo (c), Bi (d) after excluding extreme (high and low) values

Table 5 shows the calculated indicators of geochemical background and anomalous values for As, Sb, Bi, Mo, W, S, Pb and Cd for the soil cover of the mining complex territory of JSC Pokrovsky Rudnik at the Pioner deposit being developed.

It should be noted that the gold ore occurrence of the future Pioneer deposit was discovered in 1978 by the Umlekan party of the Zeya expedition. As a result of initial geochemical studies, halos of gold, silver, arsenic, antimony, and tungsten were identified in the soil cover, which made it possible to assess the prospects of the deposit (Stepanov, 2020). Before the start of mining operations in the territory of the Pioneer gold deposit, soil sampling was conducted within the mining allotment on an area of 52.7 km^2 using a 1 × 1 km grid (Lyapunov, 2014), which revealed elevated concentrations of the same elements that we identified. The average concentration of As, with its content fluctuating from 30 to 400 mg/kg, was 96 mg/kg; Bi – 0.55 mg/kg with fluctuations from 0.15 to 1.5 mg/kg; Sb – 31 mg/kg with fluctuations from 30 to 40 mg/kg; Mo – 1.7 mg/kg with a wide range of concentrations from 0.6 to 20 mg/kg, W – 4.0 mg/kg with variations from 3 to 6 mg/kg. The average concentration of Cd was 0.7 mg/kg with a range from 0.5 to 10 mg/kg. The data presented confirm the natural source of elevated concentrations of As, Sb, Bi, Mo, W, Cd, due to the metallogenic characteristics of the rocks. Thus, for the territory of the Pioneer deposit with the mining complex of JSC "Pokrovsky mine", background values for As, Sb, Bi, Mo, W, S, Pb, and Cd were determined based on the geometric mean and standard deviation, which at the time of sampling (2018) were 63; 8.84; 0.69; 3.54; 4.19; 529; 36.5 and 0.11 mg/kg respectively.

Analysis of the obtained geochemical background values showed a significant exceedance of the MPC for As — 63 and 10 mg/kg respectively, S — 529 and 160 mg/kg respectively, and Sb — 8.84 and 4.5 mg/kg respectively. The background content of Pb (36.5 mg/kg) also exceeds the MPC for sandy and sandy loam soils, which is 32. In addition to the high natural geogenic content of As in the studied soils and grounds, anomalous contents were identified at 6 sampling points with a maximum excess of the calculated background by up to 7 times, which indicates an additional input of the element during gold mining. Anomalous values of Sb, identified at 5 sampling points, indicate the contribution of the anthropogenic component to soil and ground contamination in the territory of the mining complex. Medium and high range of anomalous contents was also recorded for S, W, Bi, Pb.

Table 4. Statistical parameters of logarithmically transformed contents of Sb, As, Bi, Mo, W, S, Pb, and Cd for the studied soils and grounds of the Pioneer deposit area

Element	m	X_{geom}	X_{med}	A	E
As, mg/kg	1.84	1.77	1.82	–0.016	–1.05
Sb, mg/kg	0.96	0.75	1.02	0.077	–1.09
S, mg/kg	2.80	2.68	2.56	0.62	–0.62
Pb, mg/kg	1.57	1.55	1.60	0.25	–0.31
Bi, μg/kg	2.77	2.75	2.81	–0.87	0.81
Mo, μg/kg	3.54	3.51	3.52	–0.058	–1.28
Cd, μg/kg	1.98	1.92	1.89	0.28	–1.43
W, μg/kg	3.64	3.62	3.67	0.21	0.60

Notes. m – arithmetic mean; X_{geom} – geometric mean; X_{med} – median; A – skewness coefficient; E – kurtosis coefficient.

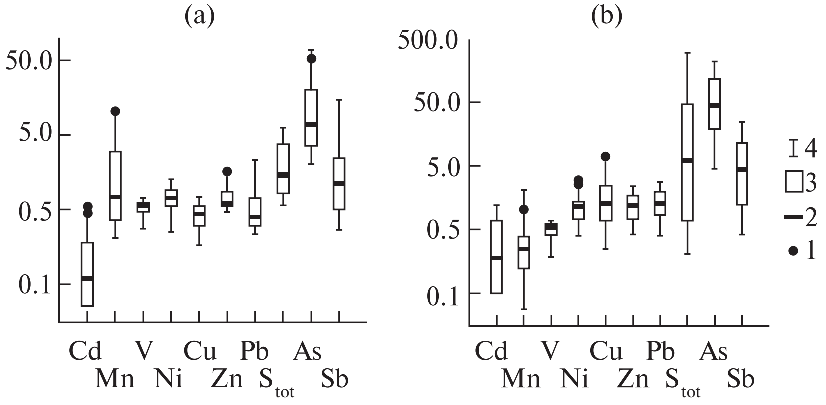

Fig. 7. Box plots of hazard coefficients for soil pollution (a) and technogenic grounds (b) for As, Cd, Pb, Zn, Cu, Ni, S, Ni, V, and Mn in the territory of the mining complex of JSC Pokrovsky Rudnik (legend in Fig. 3)

For Mo, W and Bi, MPCs in the Russian Federation are not established, but if guided by the standards of other countries (Fomin, Fomin, 2001), the geochemical background values for Mo (3.54 mg/kg) are significantly lower than the MPCs established, for example, for the Netherlands (40 mg/kg). Even the maximum content of Mo (37.5 mg/kg) in soils and grounds is lower than the standards we applied, which does not entail adverse environmental consequences.

Assessment of the degree of soil and ground contamination. Sanitary rules (SanPiN 1.2.3685-21) regulate the content of certain elements in environmental objects. According to GOST R 70281-2022, three classes of chemical elements are distinguished by their degree of hazard, among which As, Cd, Pb, Zn, Hg belong to the 1st hazard class and are the most highly toxic and carcinogenic for humans. Antimony has a similar but weaker general toxic effect than arsenic and belongs to the 2nd hazard class. Cu and Ni also belong to the 2nd hazard class. To the 3rd hazard class (low-hazard substances) belong V and Mn.

Figure 7 shows box plots of soil pollution hazard coefficients for As, Cd, Pb, Zn, Cu, Ni, S, Sb, V, and Mn. Since the studied soils and grounds have different pH values of salt extract and differ in clay fraction content, appropriate MPC values were applied according to SanPiN 1.2.3685-21. It was established that among the regulated elements, only V content did not exceed the MPC.

Islands of natural landscape, represented by loamy soils (points *1, 4, 7g, 8, 14, 18, 22a, 23, 24, 25, 26, 28*) are characterized by high contents of As, Sb and S, often exceeding hygienic standards. For As,

Table 5. Minimum-maximum, background, and anomalous concentrations of As, Sb, Bi, Mo, S, Pb, W, Cd in mg/kg for the soil cover of the mining complex territory of the Pioner gold deposit being developed (in brackets – sampling point numbers)

Element	Min	Max	Background	Background value range	Anomalies			
					$-C_A$	$+C_{A1}$	$+C_{A2}$	$+C_{A3}$
As	9.1	437	63	25–158 (1, 1a, 2, 2a, 4–6, 6a, 7b, 7g, 8, 9, 11, 13, 22b, 25, 28)	< 25 (3, 14, 19, 22a, 24, 26)	158–398 (7a, 16–18, 22v, 22g/2, 23)	398–999 (12, 22g/1)	> 999
Sb	1.2	111	8.84	3.44–23 (1, 2, 4–6, 6a, 7a, 7b, 7g, 8, 16, 18)	< 3.44 (9, 14, 19, 24)	23–58 (22g/ 1)	58–150 (12, 13, 22v, 22g/2, 23)	> 150
Bi	0.072	6.60	0.69	0.41–1.16 (1, 4, 5, 7a, 7b, 7g, 8, 12, 14, 16, 17)	< 0.41 (2, 9, 19, 22a, 22b, 23, 24)	1.16–1.94 (6, 6a, 13, 18, 22g/1, 22g/2)	1.94–3.25	> 3.25 (22v)
Mo	0.47	375	3.54	1.07–11.7 (1, 2, 4–6, 6a, 7g, 8, 9, 13, 14, 17, 18, 22v, 22g/1, 22g/2, 24)	< 1.07 (19, 22a, 22b, 23)	11.7–38.5 (7a, 7b, 12, 16)	38.5–127	> 127
S	33.0	47000	529	241–1165 (7b, 7g, 8, 9, 12, 18, 24)	< 241 (1, 2, 4, 17, 19, 22a, 22b, 22g/2, 23)	1165–2562 (6)	2562–5637 (7a, 13, 16)	> 5637 (5, 6a, 22v, 22g/1)
Cd	< 0.05	0.61	0.11	0.045–0.27 (1, 6, 7b, 8, 9, 13, 17, 18, 22g/2, 24)	< 0.045 (2, 4, 14, 19, 22a, 22b, 22v, 22g/1)	0.27–0.64 (5, 6a, 7a, 7g, 12, 16, 23)	0.64–1.57	> 1.57
W	0.62	38.3	4.19	2.26–7.75 (1, 2, 4, 5, 6, 6a, 7a, 7 g, 13, 17, 14)	< 2.26 (9, 18, 19, 22a, 22b, 23, 24)	7.75–14.3 (12, 16, |22g/2)	14.3–26.5 (22v)	> 26.5 (7b)
Pb	12.9	149	36.5	20.7–64.2 (1–6, 7g, 8, 9, 11, 13, 14, 17–19, 22a, 22v, 22g/1, 22g/2, 24)	< 20.7 (22b, 25, 26, 28)	64.2–113 (6a, 7a, 7b, 12, 16)	113–199 (23)	> 199

Notes. $-C_A$ – negative minimum-anomalous content level; $+C_{A1}$ – positive low range of anomalous contents; $+C_{A2}$ – positive medium range of anomalous contents; $+C_{A3}$ – positive high level of anomalous contents

the pollution hazard coefficient varied from 2 to 69, with a median of 7 units; for Sb – from 0.3 to 15, with a median value of 1.1; for S – from 0.6 to 6, with a median of 1.5. Probably, the geochemical features of the underlying rocks caused the MPC exceedance for As, Sb, and S; for Pb, Zn, Ni, MPC exceedance was noted at one point, for Mn – at 5 points.

In terms of As content, 100% of technogenic ground samples and 81% – in terms of Sb content were characterized by MPC exceedance; K_h of these elements reached 219 and 25 units respectively. More than half of the samples had MPC exceedance for S; K_h of sulfur varied in a wide range from 0.2 to 294 units. For Ni, Cu, Zn, Pb, K_h reached 3, 7, 2.4, 2.8 units respectively.

Thus, the soil and ground cover of the studied territory is characterized by polyelemental contamination. According to MU 2.1.7.730-99, for polyelemental contamination, the assessment of the degree of soil pollution hazard is calculated based on the most toxic element with the maximum

Table 6. Concentration coefficients for the soil cover of the mining complex territory of the operated Pioneer gold deposit

Element	m	X_{geom}	X_{med}	Min	Max
S	7.9	1.2	0.7	0.1	88.8
As	1.9	1.1	1.1	0.1	6.9
Mo	2.0	1.1	1.2	0.1	10.6
Cd	1.7	0.9	0.7	0.2	5.5
Sb	2.7	1.2	1.2	0.1	12.4
W	1.6	1.0	1.1	0.1	9.1
Pb	1.2	1.0	1.1	0.4	4.1
Bi	1.4	0.9	1.0	0.1	9.6

Notes. Min – minimum; Max – maximum; m – arithmetic mean; X_{geom} – geometric mean; X_{med} – median

content in the soil. Such an element is As – an element of the 1st hazard class. Coefficient of arsenic varied from 2 to 219 units, which corresponds to a very high degree of contamination in all soil and ground samples. The highest content of As was characterized by technologically processed rocks. These include samples taken in the vicinity of the Nikolaevsky and Alexander quarries, leaching piles, tailings dumps, reservoirs, and dump soils.

To assess the multi-element toxication of soils, the total pollution index (Zc) is currently used. The concentration coefficients (Table 6) used in calculating Zc were calculated based on the local background concentrations of As, Sb, Mo, Bi, W, S, Pb, Cd obtained during the study, which allows taking into account local lithological and geochemical conditions.

According to the gradation of the concentration coefficient, the value of $K_c < 1$ means no contamination, $1 < K_c < 2$ – low contamination, $2 < K_c < 3$ – moderate, $3 < K_c < 5$ – strong, $K_c > 5$ very strong (Kowalska et al., 2018). High and very high pollution ($K_c > 3$) was detected at 13 sampling points: near the exhausted Aleksandra quarry (point *5*) for S; near the active Aleksandra quarry (6*a*) for S and As; in the area of the mothballed Nikolaevsky quarry (points *22c, 22d/1, 22d/2*) for S, As, Mo, Cd, Sb, W; in the vicinity of the leaching heap (points *16, 17*) for S, As, Mo, Cd, Sb; near the tailings pond (point *12*) for As, Mo, Cd, Sb, W; near the reservoir (*13*) for S, Sb; in the territory of waste dumps (*7a, 7b*) for As, Mo, Cd, W; in natural soils (*7d, 18, 23*) in different variations for As, Cd, Sb, Pb.

Based on the calculated values of the total pollution index Zc, it was established that technogenic soils (points *5, 7a, 7b, 12, 13, 16, 22d/2*) and a sample of natural soil (point *23*) are characterized by a moderately hazardous pollution category; 3 samples of technogenic soils (6*a, 22c, 22d/1*) – the Aleksandra and Nikolaevsky quarries have a hazardous level of pollution. Thus, the total pollution index allows for identifying local areas of contamination. Zc exceeds the permissible level (16) under the influence of the rock from the Aleksandra and Nikolaevsky quarries, waste rock dumps, tailings pond, soils near the reservoir and leaching heap. Soils from the remaining sampling points, according to the gradation, were classified as clean or had a permissible level of pollution. The maximum Zc values were formed in samples closest to the quarries, and as the distance from them increased, there was a gradual decrease in these values.

However, such a breakdown by pollution level contradicts the regulated content of elements of hazard classes 1–3. For soils with Zc < 16, the content of elements of hazard classes 1–3 should be less than MPC. This requirement is not met for any of the sampling points in terms of arsenic content, partially in terms of sulfur and antimony content, and in technogenic soils also in terms of lead. For technogenic soils with a hazardous level of pollution according to Zc, the content of As exceeds Kmax, and in sample *22c* Sb is also added, although according to the requirements of SanPiN 1.2.3685-21, the content should not exceed Kmax, which gives reason to classify the local territories of these 3 points as having extremely hazardous pollution. On the other hand, since the Zc indicator was developed for soils of populated areas and agricultural lands, it is not entirely correct to apply it to soil-grounds of technogenic territories. Therefore, in our opinion, this indicator in such territories can only be used as reference information, and the gradation by pollution level in this case is rather conditional.

In addition to the above, according to the assessment of the degree of soil contamination by inorganic substances based on their content provided in SanPiN 1.2.3685-21, all collected samples of natural soils and technogenic grounds are characterized by very strong contamination. But this situation arises as a result of the natural geochemical anomaly of the deposit.

Assessment of the degree of soil-ground cover pollution using the geoaccumulation index. The geoaccumulation index characterizes the level of element input into environmental objects as a result of natural geological processes and anthropogenic activities. This index was first proposed by G. Müller for assessing the level of contamination in bottom sediments. For calculating the geoaccumulation index, the local background values determined in this study were used as the geochemical background.

The geoaccumulation indices for the elements under consideration in soil and ground samples in most cases belong to class 0 or class 1 (Fig. 8). The Igeo value above class 3, indicating severe soil and ground contamination, was observed for S at points *5, 6a* (Alexander quarries – inactive and active), at points *22c, 22d/1* (mothballed Nikolaevsky quarry): for Sb at point *22d/2* (mothballed Nikolaevsky quarry); for As – near the tailings storage facility (*12*); for Mo, W – in the area of overburden dumps (*7b*); for Bi – in the area of the mothballed Nikolaevsky quarry (*22c*). Thus, the Igeo values indicate that for some sampling points no anthropogenic input was noted, while in areas near quarries, tailings storage facility, overburden dumps, i.e., in the production zone, human activity contributed to local contamination of soils and grounds.

Acid-producing and acid-neutralizing potentials of the soil-ground cover. To determine the possible consequences of drainage effluents impact on natural components, methods of predictive assessments of the degree of mobility of toxic components during the interaction of atmospheric precipitation with the material of dumps, soils, and technogenic grounds are used. The prediction of the acidity of possible effluents is based on the calculation of acid-producing and acid-neutralizing potentials of the dump ground material.

Analysis of the obtained results shows that most samples are characterized by acid-forming properties, as the indicators of acid-producing potential varied from 0.05 to 121 kg $CaCO_3$/t, while the values of acid-neutralizing potential were low, at the level of zero. Only for points (*7d*) and (*12*) the values of acid-neutralizing potential were 0.89 and 7.97 kg $CaCO_3$ /t. This is also confirmed by the pH values of the water extract of soils and grounds, which ranged from acidic (2.54) to alkaline (8.42). Two samples had an alkaline reaction, 37% of samples – neutral, and the rest – acidic. Low pH values of solutions are characteristic of dumps with the presence of sulfide minerals in the form of pyrite or arsenopyrite and in the absence of organic carbon (the content of inorganic carbon in the samples was below the detection limit). Thus, the mobility of toxic elements will be minimal only locally (at points *7d* and *12*), and the dispersion of elements by surface runoff during heavy rains will be insignificant, which cannot be said about the rest of the territory, where due to prolonged oxidation, erosion and leaching, heavy metals will have increased mobility and will contaminate the adjacent territory, ground and surface waters of the basin.

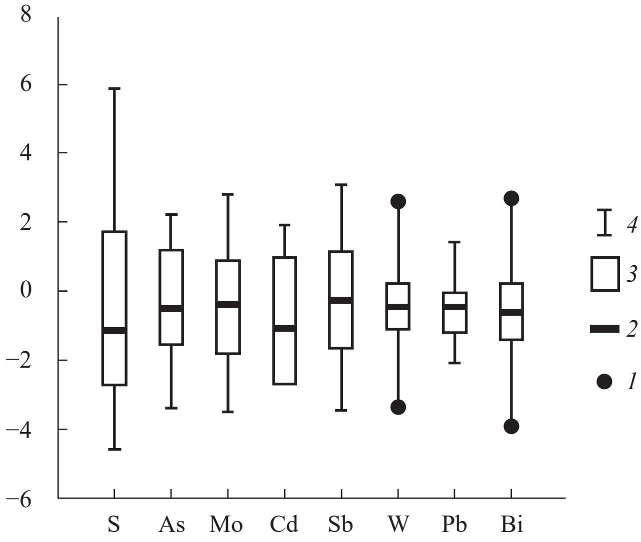

Fig. 8. Box plots of Igeo for some elements in soils and grounds in the territory of the mining complex of JSC Pokrovsky Rudnik (legend in Fig. 3)

To identify anomalous areas in the study area, map schemes of the distribution of As, Mo, Bi, Sb in soils and grounds were constructed, presented in Fig. 9.

The isolines of As distribution on these map schemes were similar to the distribution of Sb. The highest values of As and Sb, significantly exceeding the established background values, were characteristic of the same points: near the gold extraction plant and tailings pond (technological capacity 1) – (*12*),

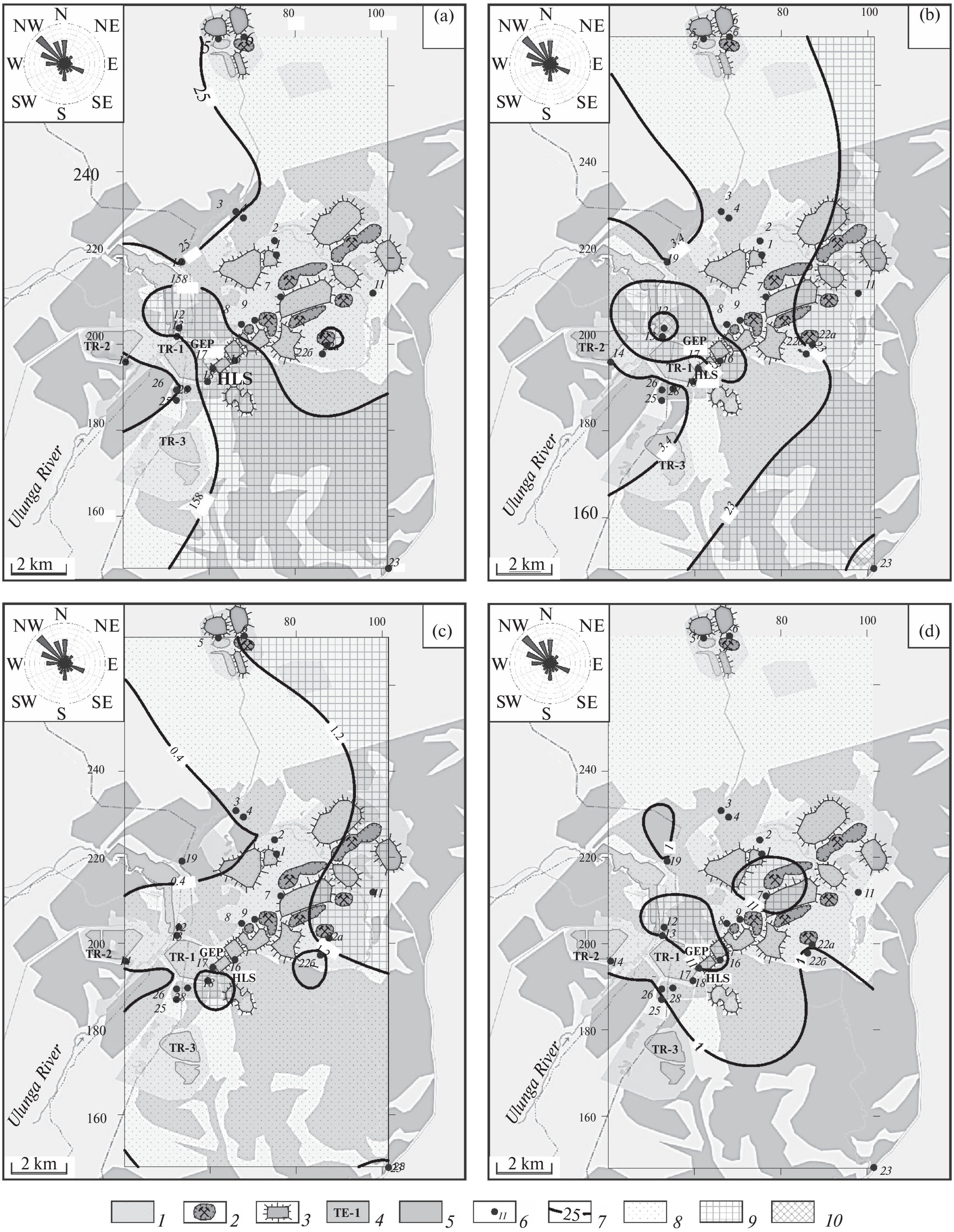

Fig. 9. Distribution of As (a), Sb (b), Bi (c), Mo (d) in the soil cover of the Pioneer gold deposit mining area. Legend *1–6* is shown in Figure 2; *7* – isolines of chemical element concentrations (mg/kg); *8* – halos of above-background minimally anomalous contents ($X_{geom}/d–X_{geom}\cdot d$); *9* – halos of medium range of anomalous contents ($X_{geom}\cdot d–X_{geom}\cdot d^2$); *10* – halos of high anomalous contents ($X_{geom}\cdot d^2 – X_{geom}\cdot d^3$); isolines and halos are depicted in relative coordinates; inset – annual wind rose

near the quarry of the Nikolaevskaya ore zone (point *22a*) and at point (*23*).

Lithochemical anomalies of As and Sb near the southeastern quarry are associated with the fact that the ores of the Nikolaevskaya zone belong to the gold-sulfosalt-antimonite association. The primary ores of the Nikolaevskaya zone have the highest content of arsenic and antimony among all ore associations at the Pioneer deposit. Exceedances of background concentration ranges for As and Sb were also observed near the heap leaching site at sampling point (*16*).

According to the configuration of halos, higher concentrations of As and Sb appear on the leeward side of tailings dumps, indicating an important role of mechanical transfer and element migration under wind action (deflation) (Dorokhova et al., 2020). Elevated concentrations of Bi and Mo have a local distribution: Bi – around quarries and dumps of the Bakhmut, North-Eastern and Nikolaevskaya ore zones (points *11* and *22a*) and the heap leaching site (point *18*); Mo – in the area of dumps (point 7) and tailings storage (point *12*); likely because Mo and Bi are characterized as low-mobility and moderately mobile elements that are difficult to release from minerals.

CONCLUSION

The assessment of the chemical composition of soil and ground cover on the territory of the mining complex of Pokrovsky Rudnik JSC in the area of the Pioneer gold deposit in the Amur region, using a geochemical approach and statistical analysis methods, revealed significant enrichment (enrichment coefficient by median in parentheses) of As (14.5), Sb (29), Bi (4.3), Mo (3.9), W (2.6), Pb (2.5). The presence of high concentrations of toxic elements in the soil and ground cover of the study area is due not only to anthropogenic input but also to the natural metallogenic features of the territory. The study area is located in a region of natural geochemical anomaly. Significant enrichment of ore-bearing rocks with Sb and As compared to the clarke of the upper continental crust was found to be 88 and 16 times higher by median, respectively.

Background values of As, Sb, Bi, Mo, S, W, Pb, and Cd for the soil and ground cover of the technogenically altered territory of the Pioneer gold deposit, calculated using mathematical statistics methods, were 63; 8.84; 0.69; 3.54; 529; 4.19; 36.5 and 0.11 mg/kg, respectively.

A moderately hazardous and hazardous category of the total pollution index of soil and ground cover by heavy metals was identified in the territory of the mining and processing enterprise of Pokrovsky Rudnik JSC (Pioneer deposit) near quarries, both conserved and operating, apparently as a result of blasting operations, in the area of overburden dumps, tailings storage facility, heap leaching pad.

Analysis of the acid-producing and acid-neutralizing potentials of the soil material confirmed that the areas of greatest potential pollution risk are the Nikolaevskaya ore zone quarry, the heap leaching site, and the tailings storage facility.

ACKNOWLEDGEMENTS

The authors express their gratitude to the scientific editor of the article and the reviewers for their useful comments that helped improve the quality of the publication.

FUNDING

The work was carried out under the state assignment of the IGiP FEB RAS (theme No. 122041800128-5).

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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