Toxic element distribution analysis in tailing technozems of the lead-zinc deposits in Eastern Transbaikalia

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Abstract. An analysis of chemical element distribution in technozems of tailing dumps of the lead-zinc deposits of Eastern Transbaikalia is carried out. The potential toxicity of tailing mine technozems was calculated. A comparative analysis of the toxic element concentrations in the technozems of the lead-zinc deposit tailing dumps has revealed significant differences in the concentrations of toxic elements. It was found that the highest concentrations of toxic elements of the first class of hazard (As, Pb, Zn, and Cd) are characterized by the technozems of the Blagodatsky Deposit, while the lowest concentrations by those of the Khapcheranginsky Deposit. It has been established that the greatest ecological hazard is posed by the tailing dump of the Blagodatsky lead-zinc deposit, whereas a significantly smaller one by tailing dumps of the Khapcheranginsky and Novo-Shirokinsky deposits.

1. Introduction
The research object is the dump tailings of the mining and processing plants (MPC), formed during the exploitation of lead and zinc deposits of Eastern Transbaikalia (Fig. 1). The purpose of the study is ecological and geochemical assessment of potential hazard of anthropogenic formations appeared during the exploitation of the lead and zinc deposits in the Transbaikal region.

2. Research methods and material
The factual material was obtained during research on the basic projects of the Institute of Natural Resources, Ecology and Cryology of the Siberian Branch of the Russian Academy of Sciences from 2000 to 2019. In addition, published data and materials of territorial geological funds (Chita) were used. Analytical studies have been carried out at the Geological Institute of the Siberian Branch of the Russian Academy of Sciences (Ulan-Ude). Determination of elemental composition of rocks was carried out by the X-ray Fluorescence Analysis (XRFA) method on the EDPS-1 spectrometer (analyst is B. J. Zhalsaraev). The rare-earth element content was detected by the inductively coupled plasma–atomic emission spectrometry (ICP-AES) method. The measuring instrument is the OPTIMA 2000 DV atomic emission spectrometer manufactured by PerkinElmer company (analysts are L.A. Levantueva, T.I. Kazantseva, and A.A. Tsyrenova).
Figure 1. Location scheme of some polymetallic deposits in Eastern Transbaikalia. I – Locations of: a) tin-polymetallic deposits: 1 – Khapcheranginsky; 2 – Sherlovogorsky; b) polymetallic deposits: 3 – Klitschkinsky; 4 – Akatuevsky; 5 – Blagodatsky; 6 – Noyon-Tologoiskiy; 7 – Novo-Shirokinsky; II – administrative boundaries; III – state boundaries

2.1. Brief characteristic of natural-technogenic formations of the lead-zinc deposits

Tailings of the lead-zinc deposits are located in close proximity to mining settlements and occupy different areas and volumes (Table 1). Their proximity to the settlements produces a negative impact on the environment. The problem of environmental pollution is of vital importance. Toxic elements of sulfides are especially hazardous. The following stages of sulfide transformation in the oxidation zone are distinguished: sulfides – sulfates – oxide carbonates. Sulfate stage minerals have the highest solubility and are the most hazardous for the environment.

Table 1. Ore deposit tailings of Eastern Transbaikalia (data of the territorial geological fund in the Transbaikal region, Chita)

| Deposit                  | Area, ha | Object volume, ths m³/ths t | Average element concentration, % |
|-------------------------|----------|-----------------------------|---------------------------------|
| Akatuyevsky Pb-Zn       | 15       | 500/1374                    | Zn – 0.628%; Pb – 0.279%        |
| Blagodatsky Pb-Zn       | 37       | 747/2017                    | Zn – 1.188%; Pb – 0.595%        |
| Klitschkinsky Pb-Zn     | 56       | 1645/4392                   | Zn – 0.493%; Pb – 0.12%         |
| Khapcheranginsky Sn-Pb-Zn| 37       | 2340/6200                   | Sn – 0.09%; Zn – 0.2–1%; Pb – 0.1–0.2% |
| Sherlovogorsky Sn-Pb-Zn | 80       | 6648/17617                  | Sn – 0.068%, Zn – 0.52%, Pb – 0.26% |

Reduction of sulfide element concentrations in oxidation zones has a long time period: from 70 to 510 years for Zn, from 740 to 5900 for Pb, from 13 to 110 for Cd, and from 310 to 1500 years for Cu [1].
3. Environmental hazard assessment of tailing dumps

It has been established that among different types of deposits in Eastern Transbaikalia, the lead-zinc deposits produce the most negative impact on the ecological situation [2–4].

To estimate the "potential toxicity of ore deposits" in Russia (GEr), the formula offered in [5] was used:

\[ \text{GEr} = \sum_{i=1,n} Tl(i) \times B(i) \]

where \( Tl(i) \) is the coefficient of lithotoxicity of the element (Table 2); \( B(i) = X(i)/Q(i) \), \( X(i) \) shows the concentrations and \( Q(i) \) denotes crustal Clarke of element \( i \) according to Vinogradov [6], \( n \) is the number of considered elements.

Toxic element distribution analysis in the ores and tailing dumps has revealed the following pattern: the higher the toxic element concentration in the ores of the similar type of deposits, the greater the value of concentration ratios in the ore divided by their values in tailing dump technozems. Thus, the average As value in the ores of the Akatuevsky deposit is 30575, whereas in tailings it attains 8759. The average As value in the ores of the Blagodatsky deposit is 296825, while in tailings it amounts to 9079. The similar pattern is typical for other elements, namely, Pb, Zn, Cd, Cu, Sn, and Mo (Table 2). Herewith, the differences in the values of elements in the tailing dumps of deposits are approximately similar and seldom exceed by twofold. This can be explained by the higher rate of element removal in oxidation zones for the ores with higher element concentrations relatively to those with lower element concentrations.

One more factor plays an important role in the element concentrations in the tailing dumps which is improvement of the extraction processes of valuable components in the mining and processing plants. It has been revealed that technozems of lead-zinc tailing dumps are different in the content and distribution of rare-earth elements (REE). For some lead-zinc deposits, REE concentrations have been calculated. The highest average REE concentrations of the reviewed deposits are characterized by the technozems of the Sherlovogorsky Deposit (ΣTR = 222.6 g/t), while the lowest REE concentrations by the technozems of the Blagodatsky Deposit (ΣTR = 34.4 g/t) (Table 3, Figure 2).

The increase in the ratio of light (LREE/HREE) to heavy REE groups for the tailing technozems of the Akatuevsky Deposit is (LREE/HREE = 2.1), whereas for the Sherlovogorsky Deposit it is (LREE/HREE = 5.05). It indicates a decrease in the share of heavy REE. The features of REE distribution in tailings are determined by the composition of the containment rocks of the deposit. The major concentrators of heavy REEs are dark-coloured minerals and light REEs are feldspars. The ore minerals contain the minimum concentrations of REE. During the determination of REE in the lead-zinc ores, a significant number of samples were found to be outside the ICP-AES method of analysis.

4. Results and discussion

Research of the impact of technogenic formations of ore deposits on the environment is conducted in many countries. Thus, during the study of sphalerite mine in Northern China by a group of Chinese scientists it was found that Zn, Cu, Cd and Pb strongly affect the work of mines, especially their tailing dumps. Zn, Pb and Cd have been found in almost all soil samples, and Zn is responsible for about 80% of topsoil contamination with element concentrations decrease as it moves away from the mining area [7]. During the team studies carried out in Nigeria and Canada, the relationship between the occurrence and mining of the lead-zinc sulfide ores at the Ishiagu Deposit (Nigeria) and heavy metal and metalloid pollution was assessed. Spatial distribution analysis of Pb, As, Cd, Ni and Zn concentrations in surface waters, ground waters, river sediments and soil in the study area showed that Pb, As, Cd, Ni and, to a lesser extent, Cu concentrations were increased [8].

The highest concentrations of toxic elements among the tailing dumps of the lead-zinc deposits are characterized by the tailing dump of the Blagodatsky Deposit. An average Pb content here is 0.595 %, and that of Zn is 1.868 %. Calculation of "potential toxicity of ore deposits" (GEr) by Goleva et al. [5] showed the highest indices for this deposit, equal to 74441. Among the lead-zinc deposits, the lowest GEr = 4724 was revealed for the Khapcherginsky Deposit. These indicators reflect the composition peculiarities of the toxic element content in the ores of the reviewed deposits which are a consequence
of the concentration of toxic chemical elements in the ores. For some lead-zinc deposits, REE concentrations have been calculated. For some lead-zinc deposits, REE concentrations have been calculated. Among the reviewed deposits the highest average REE concentrations are characterized by the technozems of the Sherlovogorsky Deposit (ΣTR = 222.6 g/t), while the lowest ones by the technozems of the Blagodatsky Deposit (ΣTR = 34.4 g/t).

Table 2. An average element concentration in the ores and technozems of the lead and zinc deposits of Eastern Transbaikalia, g/t

| Element | As  | Pb  | Zn  | Cd  | Cu  | Sn  | Mo  | Sb |
|---------|-----|-----|-----|-----|-----|-----|-----|----|
| Clarke* | 1.7 | 16  | 83  | 0.13| 47  | 2.5 | 1.1 | 0.5|
| Tl      | 10  | 10  | 5   | 15  | 5   | 5   | 5   | 10 |
| X       | 30575| 62889| 122265| 1007| 798 | 10  | 6   | -  |
| S       | 46747| 72289| 136047| 829 | 558 | 14  | 3   | -  |
| x       | 8759 | 3491| 9311 | 56  | 241 | 6.9 | 3.3 | 51 |
| s       | 4770.4| 1881.0| 6552.3| 34.7| 143.7| 5.2 | 2.0 | 27.3|
| x       | 296825| 206403| 232968| 291 | 1223| 356 | 9.7 | 1226|
| s       | 911568| 271411| 350243| 404 | 1884| 612 | 8.1 | 1187.9|
| x       | 9078 | 7419| 17008| 76  | 174 | 85  | 1.1 | 322|
| s       | 5046 | 2739| 8706 | 37  | 66  | 37  | 0.4 | 108|
| X       | 1330 | 239720| 89941| 144 | 39661| 11  | 19  | 2159|
| S       | 1480 | 168213| 97489| 172 | 58882| 12  | 14  | 3297|
| x       | 398  | 1045| 1193 | 4.8 | 107/| 2.3/| 2.3 | 96 |
| s       | 376  | 500 | 583  | 1.5 | 41  | 1.6 | 0.5 | 8.5|
| X       | 11358| 5650| 54138| 319 | 1851| 499 | 6   | 5756|
| S       | 18126| 24  | 59684| 291 | 2471| 748 | 7   | 10190|
| x       | 676  | 578 | 3227 | 19  | -  | 40  | 4   | 21 |
| s       | 322  | 227 | 1313 | 8   | -  | 15  | 2   | 7  |
| X       | 33864| 28759| 81342| 1653| 15073| 3271| -   | 787|
| S       | 38986| 31241| 80988| 2271| 31896| 5686| -   | 659|
| x       | 498  | 1562| 1703 | 14  | 187 | 595 | -   | 55 |
| s       | 245  | 1513| 1206 | 14  | 77  | 459 | -   | 20 |
| X       | 6046 | 20869| 164303| 1541| 6167| 20454| 14  | 222|
| S       | 16607| 26659| 136994| 760 | 3630| 40165| 5   | 336|
| x       | 389  | 1215| 3211 | 5   | 145 | 418 | -   | 10 |
| s       | 235  | 1283| 3346 | 5   | 133 | 321 | -   | 5  |

*Clarke* – [7]; X – arithmetic mean; S – standard deviation; n – number of analyses; no data
Table 3. Rare earth element (REE) distribution in the technozems of the lead and zinc deposit tailings, g/t

|                | $\Sigma$TR | $X$ | $\Sigma$LREE | $X$ | $\Sigma$MREE | $X$ | $\Sigma$HREE | $X$ | $\Sigma$LREE/ HREE |
|----------------|------------|-----|--------------|-----|--------------|-----|--------------|-----|------------------|
| Akatuyevsky Deposit (n = 12) | 65.6 | 4.6 | 34.7 | 11.6 | 17.9 | 3.6 | 13.0 | 2.1 | 2.7 |
| Blagodatsky Deposit (n = 24) | 34.4 | 2.6 | 24.7 | 8.2  | 10.6 | 2.1 | 7.4  | 1.2 | 3.3 |
| Novo-Shirokinsky Deposit (n = 10) | 138.0 | 9.8 | 88.2 | 22.7 | 35.8 | 7.2 | 18.9 | 3.2 | 4.7 |
| Sherlovogorsky Deposit (n = 9) | 222.6 | 15.9 | 74.8 | 17.0 | 59.1 | 4.3 | 88.6 | 14.8 | 5.05 |

$^{a}\Sigma$TR – amount of REE.
$^{b}\Sigma$LREE – amount of light REE (La, Ce, and Pr).
$^{c}\Sigma$MREE – amount of middle REE (Nd, Sm, Eu, Gd, and Dy).
$^{d}\Sigma$HREE – amount of heavy REE (Ho, Er, Tm, Tb, Yb, and Lu).
$^{e}X$ – arithmetic mean

Figure 2. Diagram 100% $\Sigma$La–Nd – 100% $\Sigma$Sa–Tb – 100% $\Sigma$Dy–Lu+Y of the technozems of the lead and zinc deposit tailings. Deposits: 1 – Akatuyevsky. 2 – Blagodatsky. 3 – Novo-Shirokinsky. 4 – Sherlovogorsky.

To improve the ecological state of the environment, the methods of ecological restoration and, phytoremediation are applied [9]. These techniques are applicable to reduce concentrations of toxic elements in the tailings of the lead-zinc deposits of Eastern Transbaikalia. In order to improve environmental ecology, it is necessary to carry out the following measures: the introduction of biopreparations, structure-forming agents, and zeolites into contaminated soils.

5. Conclusions
Currently, the Novo-Shirokinsky Deposit is only being developed in Eastern Transbaikalia, while in the rest of the lead-zinc deposits mining has been stopped. Using the technique by Goleva et al. [5] the "potential toxicity" (GEr) of the tailing dumps of the lead-zinc deposits has been calculated. It has been revealed that the most ecologically hazardous is the tailing dump of the Blagodatsky lead-zinc deposit (GEr = 74441). The lower hazard is posed by the tailing dumps of the Khapcheranginsky (GEr = 4724).
and Novo-Shirokinsky (GER = 5607) deposits, which is explained by low contents of toxic elements in the ores. The highest concentrations of As, Pb, and Zn are observed in the technozems of tailings of the lead-zinc deposits, higher concentrations of Cu and Sb are also noted. In the technozems of the tin-polymetallic mine tailings, the highest Pb, Zn and Sn concentrations and increased As and Cu concentrations are observed. It has been established that the highest concentrations of REE are characterized by the technozems of the tailing dumps of the Sherlovogorsky Deposit (ΣTR = 222.6 g/t) and the lowest ones by those of the Blagodatsky Deposit (ΣTR = 34.4 g/t), which is explained by the composition peculiarities of the host rocks of the ore deposits.

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