The Novotroitsk tailing dump influence on the arsenic and heavy metals accumulation in living organisms

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Abstract. To determine the Novotroitsk gold-arsenic deposit dumps influence on the ecological situation, soil samples were taken from 4 wells drilled in the tailing dump territory. The Southern Urals species plant material typical Samples were collected within a 2 m radius from the wells. Wool, muscle tissue, liver, and kidney samples were taken from the European moles caught on the dump. The comparison objects were plants and animal tissues samples from background areas at a distance of > 15 km from the tailing dump. In the samples, the elements' contents were determined, incl. arsenic and heavy metals by inductively coupled plasma mass spectrometry. Heavy metals increased content in the soil was found, and the average content of arsenic exceeded the maximum permissible concentration in soils by 1256 times. As and Hg large amounts were also found in plant samples. In the mole wool and tissues, the As accumulation was noted 181.3 - 273.9 times higher than the background values, Hg - 9.9 - 70.8 times and somewhat less pronounced - copper, lead and zinc. The research results are recommended to be taken into account when organizing reclamation and reclamation measures, as well as mining waste storage and disposal.

1. Introduction

In our time, environmental pollution is becoming a serious problem. Urbanization and industrialization high rates lead to a toxic waste ever-increasing volume, such as heavy metals, radionuclides, organic and inorganic nature various toxic substances. Heavy metals (HM) are among the most commonly observed pollutants in the environment. HMs and arsenic similar to them in their properties can lead soils and entire ecosystems to irreversible degradation since it is impossible to reduce their gross content in a polluted environment [1, 2].

Heavy metals are known to be highly toxic to living organisms at relatively low concentrations and bioaccumulate, although many are not essential elements; moreover, they do not undergo physicochemical or biological degradation. These elements group includes more than 40 metals, which atomic mass is above 50 atomic units. HMs can enter the soil in various ways: with wastewater, as part of gas and dust emissions, with atmospheric precipitation. HMs spread by air with industrial emissions can be dispersed over vast areas around mining and metallurgical industries and generating energy by burning coal and oil products [3-6]. As a result of toxic elements entering the soil and water, technogenic biogeochemical provinces are formed.
Flora representatives HM contamination assessment remains a difficult task due to regulation and a factors variety poor elaboration that determine the HM accumulation degree by plants [7]. The arsenic and heavy metals accumulation by plants is influenced by heredity, in other words, taxonomic affiliation, elemental chemical composition and the soil properties, and penetration ways. Herbaceous and shrub plants tend to more intensively capture and involve arsenic in biochemical processes than arsenic and shrub plants, and species with a rough leaf surface accumulate toxic elements from the air to a greater extent than species with smooth leaves [8].

Toxic elements enter the animal's body with contaminated water and plant food and are transmitted further along the trophic chain. Intoxication with arsenic and heavy metals can last asymptomatically for a long time, further leading to organs and their systems functions disorder, impaired young animals' growth, and the tumour diseases development.

There are no methods to completely extract toxic elements from biogeocenoses. Existing techniques are aimed at their inactive compounds formation and reducing the availability for plants. In the fight against anthropogenic pollution of ecosystems with heavy metals, sorbents of natural origin are often used: diatomite, sludge, clay, peat, zeolite, etc. [9]. Another approach involves planting toxicant storage plants that take toxic elements from the soil. To reduce dust emissions, the tailing dumps surfaces and worked-out mines are flooded [10].

One of the toxic elements sources in the Southern Urals is the Novotroitsk gold-arsenic deposit discovered at the 18th-century end. Since the 19th century middle, its development has been underway, as a result of which a technogenic massif was formed from the processing plant dumps - the Novotroitsk tailing dump, located within the Plast city. Due to the arsenic present in the extracted rocks, such formation can pose a threat to the local ecology.

The study purpose is to reveal the Novotroitsk tailing dump technogenic massif influence on the arsenic and heavy metals accumulation by living organisms.

2. Materials and methods
The Novotroitsk tailing dump and background areas study near the Plast city, the Chelyabinsk region took place in 2019-2020. To obtain soil samples, the tailing dump surface was opened by 4 wells, reaching a 10-18 m depth. The material was removed from the well with a drill auger at 1-2 m intervals and averaged. The plant material was taken from the Umbelliferae representatives, feather grass, and sedge, typical for the region, within a 2 m radius from each well. Samples of similar species were also collected in the background territories, to which the territories near the village Demarino and the river Kabanka at a distance of more than 15 km from the tailing dump.

The European mole (Talpa Europaea) inhabiting the South Urals region was also selected as an indicator species. Liver, kidney, muscle, heart and hair samples were collected from animals from the dump (n=4) and background areas (n=5) in compliance with the conditions of humane treatment set out in the European Community Directive (86/609/EEC) and the Helsinki Declaration.

All obtained samples were investigated for the 25 mineral elements content on Nexion 300D equipment (manufactured by Perkin Elmer, USA) by inductively coupled plasma mass spectrometry. For the determination, 3 parallel weighed samples were taken; the measurement error did not exceed 10%. Further data processing was carried out using mathematical methods accepted in scientific research using the Statistica 13.5 software (Statsoft Inc.). The differences’ significance in indicators was determined using the Student's t-test. The ecological situation in the region was assessed by the concentration in the arsenic (As) samples, copper (Cu), mercury (Hg), lead (Pb), nickel (Ni), zinc (Zn).

3. Results and discussion
During the soil samples elemental analysis results consideration from the Novotroitsk tailing dump, a heavy metals most content excess taken into account over the standard values (maximum permissible concentrations, MPC [11]) and an As extremely strong excess were found (table 1).

In the technogenic massif upper layers samples, the heavy metals content exceeded the LOC by 1.4 - 12.4 times, the most excess was typical for nickel and copper - by 11.1 and 12.4 times, respectively.
The arsenic exceeded the LOC amount by 981 times. On average, for all samples, the HM content is 2.0 - 20.4 times higher than the norms, among them nickel - 9.1 times, copper - 20.4 times, and arsenic - 1286. The mercury concentration in the studied samples was below the threshold definitions.

Table 1. Heavy metals and arsenic As content in gold-arsenic ores stale tailings samples from the Novotroitsk deposit, mg/kg.

| Element         | Occupational exposure limits | Content on the surface (0 - 2m) | Average grade (0 - 18m) |
|-----------------|------------------------------|---------------------------------|------------------------|
| Arsenic (As)    | 2.0                          | 1962.9 ± 628.2                  | 2.572.00 ± 1 259.36    |
| Copper (Cu)     | 3.0                          | 37.14 ± 11.72                   | 61.33 ± 33.40          |
| Mercury (Hg)    | 2.1                          | Below the detection threshold   | Below the detection threshold |
| Lead (Pb)       | 32.0                         | 45.71 ± 7.01                    | 64.00 ± 32.33          |
| Nickel (Ni)     | 4.0                          | 44.29 ± 18.24                   | 36.33 ± 22.51          |
| Zinc (Zn)       | 23.0                         | 92.86 ± 14.47                   | 127.33 ± 39.99         |

The high As content in the tailing dump soil confirms its negative impact possible on the Plast city ecology and adjacent objects. For some plant species, the As toxic concentration is already 25 mg/l, for example, in cereals, seed germination decreases and growth is inhibited. The HM toxic effects and arsenic are manifested to varying degrees in different species, some of them exhibit a tolerance high degree to specific toxicants. There is evidence that As low doses can stimulate plant growth [12]. But still, for technoids, scanty, uneven vegetation with a poor species composition is typical.

Under the Novotroitsk tailing dump conditions, the HM penetration main way into the plant organism is their entry in dissolved forms through the root system. We analysed the HM and As content in plant samples from the technogenic massif and background areas. As we can see from table 2, the arsenic accumulation in both plants aboveground and underground parts was quite active. The highest concentrations are observed in feather grass shoots - 50.4 times more than the norm given in the literature, and in sedge roots - 50.9 Umbelliferae - 80.7 times [13]. The excess in comparison with the plant samples results from the background territories is 5.0 - 62.5. Also, in comparison with the background territories, the mercury content in plants of technogenic formation increased by 3.2 - 30.3 times.

Table 2. Heavy metals and As content in roots and plants aboveground parts collected within the Novotroitsk tailing dump and in background areas, mg/kg.

| Element         | Feather grass | Sedge | Umbelliferae |
|-----------------|---------------|-------|--------------|
|                 | Shoots | Roots | Shoots | Roots | Shoots | Roots |
| Arsenic (As)    | 75.58 | 11.53 | 12.49 | 76.36 | 24.64 | 121   |
| Copper (Cu)     | 4.01 | 23.78 | 3.35 | 10.63 | 6.17 | 8.22  |
| Mercury (Hg)    | 3.50 | 10.87 | 4.62 | 6.77 | 7.08 | -     |
| Lead (Pb)       | 0.0018 | 0.1300 | 0.0136 | 0.0359 | 0.0545 | 0.0079 |
| Nickel (Ni)     | 0.0056 | 0.0093 | 0.0141 | 0.0076 | 0.0014 | -     |
| Zinc (Zn)       | 0.301 | 4.23 | 0.284 | 4.24 | 0.805 | 9     |
|                 | 0.687 | 4.39 | 0.583 | 3.76 | 1.2 | 1.4   |
|                 | 0.351 | 8.52 | 0.9 | 5.49 | 1.94 | -     |
|                 | 14.59 | 18.25 | 17.52 | 93.38 | 31.98 | 48.32 |
|                 | 12.68 | 22.43 | 36.33 | 21.4 | 34.17 | -     |

Note: The Novotroitskoye tailing dump, below - background areas.

Normally, mercury is absent in living organisms, even its small amounts can disrupt physiological functions. Plants most actively absorb their mobile methylated form; in animals, methylated mercury leads to neurotoxic lesions, and in the inorganic form causes tremors, the gums' inflammation,
spontaneous abortions and fetal malformations [15]. Other heavy metals in plants were unevenly distributed, in some samples from the dump they exceeded the background values, in others, on the contrary, they were lower than the background values.

We also analysed the European mole tissue samples, in which organs and wool it was possible to establish the toxic elements' accumulation (table 3). The animal is a biocoenosis state good indicator, due to its close connection with the soil, in our case, which is the toxic elements accumulator and their supplier to living organisms.

Table 3. The heavy metals and As content in the common mole organs and wool tissues (T. Europaea) from the Novotroitsk tailing dump and background areas' mg/kg.

| Element     | Liver    | Kidneys  | Muscle   | Wool    |
|-------------|----------|----------|----------|---------|
| Arsenic (As)| 6.57 ± 0.32* | 4.71 ± 0.43* | 4.97 ± 0.68* | 212.75 ± 24.11* |
| Copper (Cu) | 6.46 ± 0.53* | 5.86 ± 0.57* | 3.03 ± 0.25 | 12.72 ± 2.27* |
| Mercury (Hg)| 0.178 ± 0.0137* | 0.291 ± 0.0232* | 0.1275 ± 0.0115* | 0.3675 ± 0.0856* |
| Lead (Pb)   | 0.23 ± 0.02* | 0.15 ± 0.03* | 0.16 ± 0.5 | 4.26 ± 0.83* |
| Nickel (Ni) | 0.12 ± 0.02 | 0.14 ± 0.04 | 0.26 ± 0.04 | 1.01 ± 0.17 |
| Zinc (Zn)   | 28.45 ± 1.04* | 27.87 ± 1.88 | 29.07 ± 2.81* | 174.5 ± 10.31* |

Note: The Novotroitsk tailing dump, below - background areas; * - the difference is significant (P <0.05).

Just as in plant samples, arsenic high concentrations were found in mole tissues samples from the Novotroitsk deposit dumps, which are many times higher than the samples indicators from animals taken from background areas. The element amount in the liver exceeds the average for the sections of the river Kabanka and the village Demarino - 273.9 times, in the kidneys - 181.3 times, in the muscles - 198.9 times, in the wool - 238.8 times. The HM accumulation was established in tissues and wool samples: Zn - 1.1 - 1.5 times higher than background values, Cu - 1.4 - 2.1 times, Pb - 1.8 - 5.8 times. It was also found that moles from the tailing dump are characterized by a Hg pronounced accumulation: 9.9 - 70.8 times higher than the tissues background parameters and 34.7 times higher than wool.

To a greater extent, arsenic accumulates in the mammals' hairline, which is also confirmed in our case. Among the internal organs, the liver acts as an arsenic depot, which also accumulates copper and lead. The mercury highest concentration was found in muscle tissue and wool.

The arsenic, mercury and other HMs significant concentrations' detection in plant cover and animal tissues samples from the Novotroitsk gold-arsenic deposit dump, which exceed those in samples from background areas, indicate the technogenic massif dangerous impact on the local ecology.

4. Conclusion

In the soil samples taken from the Novotroitsk tailing dump, we found arsenic high concentrations, which, on average, are 1286 times higher than the established LOC. The heavy metals content' an excess was also revealed: copper, lead, nickel, zinc.

Toxic elements were actively accumulated by plant community representatives: when comparing the obtained indicators with the literature sources and LOC data, the arsenic and mercury content strong excess was found in the plants aboveground and underground parts.

In the European mole tissues and wool, an arsenic noticeable accumulation was also revealed - 181.3 - 273.9 times higher than the background values, mercury - 9.9 - 70.8 times and somewhat less pronounced - copper, lead and zinc.

The collected information should be taken into account when planning land reclamation and reclamation works. Based on this study results, measures more thorough study is recommended to
ensure the mining and processing industries environmental safety and their waste disposal. The dump storage facilities organization should not the least take into account the mineral elements’ ability to migrate in soil layers and be transmitted along with the living organisms’ trophic chain.

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