Geochemical characteristics of soils in natural and disturbed landscapes of the Tunka basin

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Abstract. The paper evaluates the distribution of chemical elements in the soil of the Tunka basin (the Republic of Buryatia, Tunka National Park). In this regard, we studied their gross concentration in natural and agrogenically transformed soils: arable land, fallow lands, hayfields, and pastures. The distribution of chemical elements in the soils of the Tunka basin is extremely uneven, except for Fe, Al, Mg, P, Sr, Zn, and Co. The concentrations of chemical elements, as a rule, do not exceed standard values, except for Cr, Ni and Pb. Opposite patterns characterize the nature of the interaction of mercury with chemical elements of groups of different geochemical classifications, depending on the degree of anthropogenic load. In natural soils, the concentration of mercury increases with an increase in the concentration of silicon and phosphorus and a decrease in other heavy metals: Fe, Pb, Cu, Co, Ti, Ni, V, Cr, as well as aluminum and magnesium. In disturbed soils, Hg is directly proportional to all of the above elements other than manganese. The change in the content of most of the studied chemical elements with depth in natural soils decreases with depth. In disturbed soils, there is no such tendency due to mixing of the soil layer in the upper 50 cm layer due to the use of land for arable land.

1. Introduction
The development of civilization is based on the development of mineral resources by man. The human activity resulted in a new type of migration of chemical elements, anthropogenic migration, the scale of which, according to V.I. Vernadsky, is comparable to the scale of geological processes. The intensity of artificial concentration, redistribution and penetration of chemical elements from the lithosphere into the biosphere is incomparable with the rate of migration of matter characteristic of evolutionary geological processes. The natural mechanisms of self-purification in the biosphere cannot cope with the ever-increasing load, which leads to environmental degradation manifested in the irreversible disruption of chemical equilibrium in ecosystems at the regional and global levels. [1].

Investigation of the concentrations and the distribution characteristics of chemical elements both throughout the area and along the profile is an important task of geoecology. Particular attention should be paid to the character of the interaction of elements with each other, both in native landscape ecosystems and experiencing various anthropogenic impacts [2].

The main soil properties that determine fertility depend on its chemical composition, which, in turn, is directly related to the mineralogical composition of parent rocks. The soil is the upper part of the weathering crust in the lithosphere and, therefore, mainly reflects its chemical composition. At the same time, the soil is a product of the impact on the lithosphere of living organisms, which also affects its chemical composition [3].
2. Objects, data and methods

This study aims to assess the distribution of the concentrations of chemical elements, including mercury, in the soil of the Tunka basin (the Republic of Buryatia, Tunka National Park). In this regard, the total concentrations of chemical elements, individual forms of chemical elements (Hg) in natural and agrogenically transformed soil samples was investigated [4]. Groups of geochemical classifications of elements, their distribution with depth as well as the influence on the geochemistry of elements of the main physical and chemical properties of soils (native and anthropogenically disturbed) were determined. These samples were taken from arable land, sediments, hayfields, and pastures. Soil samples were taken in the summers of 2015 and 2016 by two methods: the envelope method according to [4] and the method of studying genetic horizons, including soil material. A total of 26 sites were selected and 77 soil samples were taken. Under laboratory conditions, the samples were brought to an air-dried state at room temperature and sieved (sieve size 1 mm).

The Tunka basin is a continuation to the west of the Baikal Rift Zone. Its length from east to west is 190 km. From the south, it is bounded by the Khamar-Daban mountains and the spurs of the Khangarul ridge; from the north – by the Tunka bald peaks; from the west – by the southeastern ridge of the Big Sayan. The basin includes six separate basins separated by narrowing of the Irkut-Bystraya, Tory, Tunka, Turan, Khoytogol and Mondy channels (figure 1).

![Figure 1. Location of the Tunka basin within the Baikal Rift Zone [5].](image)

The physical and technological characteristics of soil samples, the concentration of Corg and the group composition of humus, chemical elements, including mercury, were determined. Analytical studies of mercury were carried out in the laboratory of the International Innovation Academic Center "Geology of Uranium", Tomsk Polytechnic University, on an RA-915 + atomic absorption spectrometer.
with a PYRO-915 (pyrolysis method). The accuracy was 5 ng/g. The mercury concentration was calculated per gram of dry matter. The forms of mercury in soil samples were determined by the method of thermal desorption using a modification of the RA-915+ add-on to the mercury analyzer. The method of processing the results included the calculation of ecological and geochemical indicators: concentration factor relative to the background, MPC, percentage relative to the Earth's crust and soil, determination of relationships with the physical and technological characteristics of the soil as well as the concentration of Corg, CO₂ carbonates, fulvic acids and humic acids.

3. Results and discussion
The concentration of chemical elements in the soils of the Tunka basin varies over a wide range but is a background and does not exceed the maximum permissible concentrations. The group of elements, the concentrations of which in soils exceed the standards, is lead, nickel and chromium. It should be noted that the excess is observed both in the first genetic horizon and with depth. This tendency was revealed both for native soils and those experiencing this or that anthropogenic impact. The excess is up to 1.1 for nickel, 1.25 for lead and 1.21 for chromium, which indicates the accumulation of these elements in the soils of the study area. It should also be noted that heavy metals are in the group of elevated elements in the soils of the Tunka basin. These metals belong to the first (lead) and second hazard classes (nickel and chromium), which is especially alarming because the research area does not belong to the area with an increased industrial load.

Average mercury concentration in the soil of the Tunka basin is equal to 23 ng/g, assuming spread from 1 to 124 ng/g. All depth profiles of mercury concentration in studied soil cross-sections are similar: the maximum values appear in the upper part of the profile with subsequent decrease. Acquired data corresponds to principles of mercury allocation in the soil of many other countries [5]. Moreover, it is worth mentioning that the highest mercury concentrations are detected in upper horizons, in the interval from 0 to 0.2 meters.

The concentrations of elements that comprise the main exchangeable cations of soils do not exceed the standard values and typical concentrations of these soils and vary in the following ranges: Ca – 2560-17656 mg/kg, Mg – 2412-13398 mg/kg, Na – 157-909 mg/kg, K – 1077-5683 mg/kg, Al – 9188-32653 mg/kg, Fe – 8255-27386 mg/kg, and Mn – 120-1104 mg/kg.

The typical Ca to Mg ratio is 5 to 1, which is considered normal. In the studied soils, the Ca to Mg ratio averages 1.3. When the ratio is shifted towards magnesium, an ecological disharmony of the soil environment occurs. This may indicate the leaching of soils when the Ca to Mg ratio changes towards magnesium. In this case, magnesium itself causes an increase in alkalinity due to the presence of magnesium carbonates and bicarbonates in the soil. The presence of magnesium maintains the properties of solonetzic soils and even leads in some cases to the formation of special soils, magnesium solonetzes. With a high concentration of exchangeable magnesium, the solubility of humic substances increases, and the structure of the soil deteriorates; water permeability decreases, which negatively affects the water regime. With an increased concentration of exchangeable magnesium, the negative effect of exchangeable sodium increases, with a low concentration of the latter in the soil [6].

The elements that comprise the main exchangeable anions are defined as silicon and phosphorus. The concentration of Si, as the most abundant element on the Earth, averages 851 mg/kg, with a range of values from 307 to 1582 mg/kg. It should be noted that the silicon concentration in the samples practically does not differ from the type of soil and tends to decrease with depth. The phosphorus concentration ranges from 318 to 1278 mg/kg.

The most widely represented group of metals with varying degrees of toxicity are as follows: Fe, Al, Ti, Mn, Zn, Cu, Ni, Pb, Co, Cr, and Hg. Aluminum and iron have a wide range of interactions with other metals in the studied soil samples. And this fact is not particularly influenced by the type of soil, or the genetic horizon, or the degree of anthropogenic disturbance of the soil. With an increase in the aluminum concentration in disturbed soils, the concentration of other metals also increases, except for titanium (no connection) and manganese (its concentration decreases). In natural soils, the trend is the same, except for manganese (no connection) and mercury (its concentration decreases).
Titanium is the least dependent on the degree of accumulation of other metals in disturbed soils. Its concentration increases in these soils with decreasing lead concentration. In native soils, the Ti concentration directly depends on other metals, except for manganese (no connection) and mercury (feedback).

An interesting process is the accumulation of lead in soils experiencing anthropogenic impact: with an increase in the concentration of iron, the concentration of lead also increases; with an increase in the concentration of titanium, the Pb concentration decreases. In undisturbed soils, we revealed a stable direct connection of lead with other metals, except for manganese. Cobalt, copper and titanium showed the same accumulation character.

The concentration of manganese in the studied samples of native soils increases only with an increase in zinc, nickel and chromium. The concentration of mercury in native soils decreases, as the concentration of other metals increases, except for manganese and zinc (no connection). At the same time, in disturbed soils, mercury, on the contrary, increases with an increase in the concentrations of other metals, except for titanium (no connection) and manganese (reverse connection).

The obtained concentrations of chemical elements have varying degrees of distribution over the study area. So, Fe, Al, Mg, P, Sr, Zn, and Co are more evenly distributed in the soils of the Tunka basin. According to the Goldschmidt classification [7], siderophile elements (Ni, Co), lithophilic elements (Si, Ti, Ca, K, Na, Mn, Ba, Cr), as well as chalcophilic ones (Cu, Pb, Hg), differ in extremely uneven concentrations, depending on type of landscape and the type of soil. All obtained concentrations of trace and macro elements are background and do not exceed the maximum permissible concentrations.

Based on the data on correlation analysis, the mercury concentration in soils is associated with the concentration of other metals and trace and macro elements. In the natural soils of the Tunka basin, mercury concentrations in natural soils increase with increasing concentrations of silicon and phosphorus and with a decrease in other heavy metals: Fe, Pb, Cu, Co, Ti, Ni, V, and Cr as well as aluminum and magnesium. In disturbed soils, Hg is directly proportional to all of the listed elements, except for manganese.

Hg, Pb, Zn, and Cu, which are also heavy metals (HM), represent the group of chalcophilic elements. With an increase in the mercury concentration in soils, it shows increased concentrations of other HM in anthropogenically disturbed soils. In native soils, there is the inverse nature of the relationship, with a direct connection between the remaining HM.

The group of siderophile elements has very strong bonds in the accumulation of Fe, Ni, Co, and Hg both in disturbed and natural soils. However, in native landscapes, mercury decreases as the remaining elements increase (figure 2).

Elements of the lithophilic and biophilic groups are more dependent on each other in the accumulation in soils of different landscapes of the Tunka basin (figure 3). At the same time, it is worth noting both the direct and reverse nature of the relationship.

In soil samples from native landscapes, among the elements of the lithophilic group, Si, Al, Ti, Ca, Mg, and K are most associated with other elements of the group. Moreover, the nature of the relationship is different. Sodium was found to be the most autonomous by the nature of its accumulation in the soils of natural landscapes. With an increase in the intake of manganese and potassium, the sodium concentration also increases. In disturbed soils, the bonds among the elements of the lithophilic group are less strong and, as a rule, negative. Mutual accumulation of silicon is mostly disturbed. There is a connection only in the intake of manganese and potassium.

Among the elements of the biophilic group in native soils, K, Ca, Mg, Mn, and Zn have the greatest relationships. Copper and iron are the most autonomous by the nature of accumulation. In soils of disturbed landscapes, the nature of the relationship between the elements of the biophilic group is opposite to that described above. The elements of this group are the most important for plant nutrition; hence, they affect the diversity of flora (and indirectly fauna) of the studied region.

Some researchers distinguish a separate group, a group of plant nutrients. In this group, the number of elements is obviously lower than in the biophilic one. Among them, in the soils of natural landscapes,
potassium, manganese, zinc, and magnesium are the most associated. Moreover, the nature of the relationship is positive. Phosphorus and copper are the least associated with elements of the group. Mercury concentrations increase with increasing phosphorus and decrease with increasing magnesium, copper and iron, although, in disturbed soils, mercury has a stable positive relationship with these elements. Additionally, in the soils of disturbed landscapes, phosphorus, potassium and calcium are least associated with the elements of the plant nutrition group, which is the opposite tendency in the accumulation of elements in comparison with the soils of native landscapes. However, magnesium, manganese and zinc also remain the most bound elements in the group, but the nature of the bond changes.

![Diagram](image)

**Figure 2.** The interrelation of mercury with elements of groups of geochemical classifications in soils of natural landscapes of the Tunka basin.

The nature of the accumulation of chemical elements of different groups from geochemical classifications with mercury differs depending on the degree of the landscape disturbance. Thus, with an increase in the concentration of mercury in native soils, the accumulation of elements of the lithophilic, biophilic and plant nutrition groups also increases. At the same time, in disturbed soils, the nature of their accumulation is the opposite. However, the reverse relationship of mercury with heavy metals is observed in all groups of geochemical classifications.

In anthropogenically disturbed soils, with an increase in mercury concentration, elements of lithophilic, biophilic and plant nutrition elements also increase. This is due to the high biophilicity of mercury and the tendency to form strong mercury-organic complexes that, in turn, are easily accessible to plants. Moreover, these complexes, along with high bioavailability, are also highly toxic.

It should also be noted that the distribution of chemical elements in the soil profile is different. In native soils, the concentrations of chemical elements decrease with depth. In disturbed soils, there is no such tendency because the anthropogenic impact is mainly reduced to the use of land in agriculture (arable land), and there is a mixing of the soil layer in the upper 50 cm layer [8]. Therefore, the distribution of the concentration of chemical elements with depth in such soils is chaotic, and there are no definite patterns.

The concentrations of chemical elements do not exceed the standard values in all studied soils regardless of the degree of anthropogenic load, soil type and depth. However, Cr, Ni and Pb are higher than the MPC standards for soils mainly in disturbed soils. It should be noted that in native soils, there was the excess in the upper horizon, whereas, in disturbed soils, it was with depth.
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Gross mercury concentrations in the studied soils do not exceed the maximum permissible concentration (Efficiency Limit) but are elevated relative to the regional background (table 1) [8]. The multiplicity of mercury exceeding the relative regional background (Kf) averages 1.16 (0.05-6.2). The calculated geoeocological parameters of the mercury load on the soil in the Tunka basin revealed the multiplicity of excess mercury concentrations in the upper soil horizon above the Clark of the Earth's crust (K_{EC}) to an average of 0.29 (0.01-1.55) and above the Clark of the Earth's soils (K_{SS}) – to 2.32 (0.10-12.40) [9].

### Table 1. Mercury load on the soils in the Tunka basin.

| Soils            | K_a  | K_{MPC}^a | K_{EC}^a | K_{SS}^a |
|------------------|------|-----------|----------|----------|
| Anthropogenic    | 1    | 0.009     | 0.25     | 2        |
| Anthropogenic ledge | 0.8  | 0.008     | 0.20     | 1.6      |
| Natural          | 1.45 | 0.014     | 0.36     | 2.9      |
| Natural slope    | 2.05 | 0.02      | 0.51     | 4.1      |
| Forest K_{SS}    | 2.15 | 0.02      | 0.54     | 4.3      |
| Bog K_{SS}       | 1.15 | 0.11      | 0.29     | 2.3      |

^a K_B – concentration factor relative to the background, K_{MPC} – concentration coefficient relative to the maximum permissible concentration, K_{EC} – concentration coefficient relative to the earth’s crust, K_{SS} – concentration factor relative to soil.

### 4. Conclusion

We evaluated the distribution of chemical elements in the soil of the Tunka basin (the Republic of Buryatia, Tunka National Park). To do this, we studied their gross concentration in natural and agrogenically transformed soils: arable land, fallow lands, hayfields, and pastures. The distribution of chemical elements in the soils of the Tunka basin is extremely uneven, except for Fe, Al, Mg, P, Sr, Zn, and Co. The concentrations of chemical elements, as a rule, do not exceed standard values, except for Cr, Ni and Pb. The nature of the interaction of mercury with chemical elements of groups of different
geochemical classifications has opposite patterns, depending on the degree of anthropogenic load. In natural soils, the concentration of mercury increases with an increase in the concentration of silicon and phosphorus and a decrease in other heavy metals: Fe, Pb, Cu, Co, Ti, Ni, V, Cr as well as aluminum and magnesium. In disturbed soils, Hg is directly proportional to all of the listed elements, except for manganese. In general, the type of soil, the genetic horizon, the degree and type of anthropogenic load on the soil of the Tunka basin affect the concentration, degree of distribution and the nature of the relationship of the studied chemical elements.

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