Mercury and its bonding forms in the Soil of the Tunka Depression

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Abstract. The work evaluates the general distribution of mercury in the soil cover of the Tunkinskaya depression (the Republic of Buryatia, the national park "Tunkinsky"). For this purpose, its gross contents in natural and agrogenically transformed soils were studied: plowlands, fallow lands, hayfields and pastures. The physico-technical characteristics of soils, the content of organic carbon, the group composition of humus are determined. The method of processing the results included the calculation of the ecological and geochemical parameters: the concentration coefficient relative to the background, MAC, Clark concentration relative to the Earth's crust, the Earth's soils, the identification of the relationship with the physical and technical characteristics of the soil, and the content of CO₂, CO₂ carbonates, fulvic and humic acids. In soils, the largest part of mercury is in free form (>41%). The proportion of physically and chemically related mercury accounts for 9-16% of all mercury in the soil. The least amount of mercury in the soils is in the form of sulfides and chemically bound forms of mercury (<10%). It should be noted that this feature is noted both in native soils and in anthropogenically disturbed soils. The proportion of chemically and strongly bound mercury increases with depth, and the content of free and sulphide forms decreases.

1. Introduction

Soil is an important component of biosphere. It has several main functions, such as geological, geoeconomical, biocological, bioenergetic, hydrological, and meteorological. Soil is an intermediate for regulation of the water and air chemical composition, and for energy and matter exchange in many elements of the global biogeochemical cycles. All these functions determine many interrelations in the global mechanism of geographical environment functioning [1].

Mercury is pervasive, compound, and hydro- and sulfophilous. It is present in all types of ecological environment and has many occurrence forms, which complicate the process of its study. Even in very low concentrations mercury is supertoxic and superpathologic. It is found in the lithosphere in the form of solid compounds, in various gaseous phases and dispersed forms, each of which predominates in concrete physical-chemical conditions, but easily changes from one form to another [2].
2. Methods and research objects
This study aims to evaluate the general allocation of mercury in the soil mantle of the Tunka Depression (Republic of Buryatia, Tunkinskii National Park). For that purpose, a total mercury concentration in natural and agrogenically transformed soil samples was examined [1]. Those samples were taken from arable land, set-asides, hay-fields, and pastures. Soil samples had been collected during the summer periods of 2015 and 2016, using two methods: envelope method according to [3] and method of study of genetic horizons including soil materials. In total, 26 sites were chosen and 77 soil samples were collected. Under laboratory conditions the samples were got to the air-dried state at a room temperature and screened (sieve size is equal to 1 mm).

The Tunka depression is a continuation to the west of the Baikal rift zone. Its length from east to west is 190 km (figure 1). From the south it is bounded by the Khamar-Daban Mountains and the spurs of the Khangarul ridge, from the north by the Tunkinsky louches, from the west by the southeastern chain of the Great Sayan. In the basin there are six separate basins, separated by narrowings of the bed of the Irkut-Bystrinskaya, Torskaya, Tunkinskaya, Turanskaya, Khoytogolskaya and Mondina.

The sample analysis was conducted in the laboratories of International innovative academic center «Uranium Geology», Geocology and Geochemistry Department, Tomsk Polytechnic University. Mercury content in the earth samples was detected on the Atomic Absorption Spectrometer RA-915+ with pyrolyzer PYRO-915 (pyrolysis method). Precision is equal to 5 ng/g. Mercury concentration was calculated on 1 gram of dry basis. Forms of mercury in soil samples were determined by thermal desorption using a modification of the attachment to the mercury analyzer RA-915 +. Besides, there were determined physico-technological characteristics of the soil samples, Corg concentration, and humus group composition. Results processing technique included calculation of ecological-geochemical indexes: concentration coefficient with reference to the background, maximum permissible concentration, percentage abundance with reference to the Earth crust and soil, identification of interrelations with physico-technological characteristics of the soil, and also content of Corg, CO₂ carbonates, and fulvic and humic acids.

![Figure 1. Map of the location of the Tunka depression.](image-url)
3. Results and discussion

Average mercury concentration in the soil of the Tunka Depression is equal to 23 ng/g, assuming spread from 1 to 124 ng/g (table 1). All depth profiles of mercury concentration in studied soil cross-sections look similar: maximum values appear in the upper part of the profile with subsequent decrease. Acquired data corresponds to principles of mercury allocation in the soil in many other countries [4]. In addition, it is worth mentioning that the highest mercury concentrations are detected in upper horizons in the interval from 0 to 0.2 meters (figure 2). However, a depth of detection of the highest mercury concentrations is inhomogeneous: 26% of the highest mercury concentrations are found at a depth of 0-5 cm, 21% - at a depth of 10-15 cm, and 19% - at a depth of 5-10 cm.

![Figure 2. Distribution of mercury with depth in the soils of the Tunka depression.](image)

It is found that upper horizons of the soil hold higher total mercury concentrations than lower horizons. Maximum values are detected in the detritus, peat, humus, and topsoil horizons. Relatively lower mercury concentrations are found in the vegetable and agrohumus horizons. In the soils of alfehumus (podbur and sod podbur soil) and texture-differentiated (sod brown podzolic soil) sections, which are widespread on the studied territory, it is clearly observed that there is a certain increase of mercury concentration in accumulation-illuvial horizons (BHF and BT). It can occur due to a downward migration of a mercury in the form of organo-mineral complexes from overlying humus and eluvial horizons [5].

In the studied soil profiles, two kinds of relation between mercury concentration and soil pH are revealed: positive one (r=1 when P=0,02) in transformed soil and negative one (r=-0,9 when P=0,04) in natural soil. There is a negative relation between mercury, Corg and CO₂ of carbonates in natural soil (r=-0,76 when P=0,05 for Corg; r=-0,88 when P=0,04 for CO₂ of carbonates). Also there is a positive relation between mercury, Corg and CO₂ of carbonates in transformed soil (r=0,82 when P=0,05 for Corg; r=0,99 when P=0,03 for CO₂ of carbonates). Interrelation between mercury concentration, and fulvic and humic acids on the studied territory is not identified. However, there is a steady interrelation between mercury and undissolved residue (r=0,5 when P=0,02).

Average mercury concentration in natural and agrogenically transformed soils is varied significantly from 20ng/g in transformed soil to 29 ng/g in natural soil. It is worth mentioning here that...
mercury concentration in transformed soil is lower and conforms to regional geochemical background (20 ng/g) [6]. It can be linked to blending of soil layers when plowing: thin humus horizons and detritus containing the highest mercury concentration are blended with underlying mineral horizons with considerably lower mercury concentrations [7].

Total mercury concentrations in the studied soil samples do not exceed maximum permissible concentration, but are higher than those of the regional background are. Average rate of this excess over regional background is equal to 1.16 (0.05-6.2). Calculated geocological parameters of the mercury load on the soil of Tunka Depression reveal the rate of excessive mercury concentrations in the upper layer of the soil. It exceeds abundance of mercury in Earth mantle (up to 0.29 in average (0.01-1.55)) and in Earth soils (up to 2.32 (0.10-12.40)).

Table 1. The content of mercury, depending on the physical and chemical characteristics of the soils of the Tunka depression.

| Soil                | Soil horizons [11] | Capacity, sm | CHg, ng/g | pH  | Corg, % |
|---------------------|--------------------|--------------|-----------|-----|---------|
| Anthropogenic       | P, rr, W, Pw       | 0-37         | 20        | 8.0 | 1.21    |
| Anthropogenic ledge | AU, W, A0          | 0-30         | 16        | 7.3 | 1.56    |
| Natural             | AH, AU             | 0-13         | 29        | 6.6 | 4.31    |
| Natural slope       | AY, Aye            | 0-17         | 41        | 6.2 | 6.58    |
| Forest              | T, Th, mr          | 0-14         | 43        | 6.4 | 15.64   |
| Bog                 | T1, T2h            | 0-12         | 23        | 7.7 | 53.80   |

According to the results of determining the forms of mercury in soils, it should be noted that in most of the soil samples studied, the largest part of mercury is in free form (Table 2), the share of which is over 41%. The proportion of physically and chemically bound mercury accounts for 9 to 16% of all mercury in the soil. This is due to the presence of organic matter in soils in the form of humic and fulvic acids [8], as well as with the activity of a number of microorganisms that transfer mineral forms of Hg into organic forms. These forms of mercury are most accessible to living organisms, and are more toxic. The second place in the investigated soils is the share of physically and firmly bound mercury compounds (5-56%). The lowest amount of mercury in soils is in the form of sulfides and chemically bound forms of mercury, less than 10%. It should be noted that this feature is noted both in native soils and in anthropogenically disturbed soils. The proportion of chemically and strongly bound mercury increases with depth, and the content of free and sulphide forms decreases.

Table 2. Forms of mercury thermoforms in soils [9].

| T°, C | Form of mercury | Chemical compound |
|-------|----------------|-------------------|
| 150-160| Free           | HgO               |
| 250-290| Physically sorbed | HgCl2           |
| 310-320| Chemically sorbed  | Hg2Cl2          |
| 350-410| Sulphide       | HgS               |
| 500-1000| Isomorphic     | HgSO4             |

4. Conclusion
As a result of the study, the total content of mercury in various types of both natural and anthropogenically disturbed soils was determined. At the same time, the average content in natural soils exceeds the concentration in soils experiencing anthropogenic impact. In this case, it is worth noting an increase in the content of mercury in natural soils associated with more acidic soil conditions. In disturbed soils, the concentration of mercury increases in more alkaline conditions. In
addition, natural soils are characterized by an increase in mercury content at lower Corg values and CO$_2$ of carbonates. In disturbed soils the picture is the opposite. Calculations of geoecological indicators revealed an excess of mercury in the upper horizons above the background and Clarks.

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