Heavy metals in the soil of Kalmykia arid territories

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Abstract. In the composition of soils of the Republic of Kalmykia a large diversity of the gross content of heavy metals was found, which is explained by different genesis of top sediments and the leading role of fine particles in them. Several natural soil and geochemical provinces as well as technologically polluted territories were identified where an imbalance of chemical elements in food chains is observed. It shows promising use of the relationship between the gross amount of individual metals to study the genesis of soil-forming rocks and soils. The limits of the content of 23 elements were revealed, of which 5 elements are absent in the soil of the Republic of Kalmykia or are within the sensitivity of the instruments. In the south of the Republic of Kalmykia a soil and geochemical province with a high total As content was found. Its core is located in the southeastern part of the Black Lands. The arsenic content here ranges from 15 to 35 mg/kg. The province is polluted with oil. Besides, there is a uranium and phosphorite region, where, along with the phosphorus the arsenic was concentrated. The arsenic-rich rock destruction products were transferred to the neighboring plain and were part of sediments. However, toxicosis associated with a high content of arsenic was not observed in the described area, since soil As is immobile and its supply to food chains is limited. This can be judged by the number of elements in plant products: it remains environmentally friendly.

1. Introduction
The study of chemical elements in the natural objects is currently of great importance, since it helps to understand many biogeochemical and ecological events and, if they are negative, develop methods for eliminating them or mitigating their actions [1–5].

The soil cover of the Republic of Kalmykia (RK) has been formed for a long time and in different parts of it (in different environmental conditions). As our studies have shown all this is reflected in the regional and local specificity of the microelement composition of soil-forming rocks, as well as in the soils formed on them.

These circumstances make it possible to add some important details to the ideas about the history of the soil cover and the genesis of soils. It has to be admitted that the soil cover of RK has been insufficiently studied. New data may increase interest in the topic considered. Some approaches aimed to clarify the origin of light and loose sediments, on which most of the soil cover of RK is formed, are not purely regional.

The purpose and the objectives of this work is to study the gross content of trace elements in the soils of the arid territories of Kalmykia to identify their biogeochemical distribution in natural landscapes, to identify the deficiency or excess of trace elements.
2. Materials and methods

The Republic of Kalmykia is located in the south-east of the European territory of the Russian Federation between 44°40’ and 47°35’ north latitude and 40°10’ and 40°50’ east longitude. Kalmykia is the driest region of the European part of Russia. In terms of climate aridity this territory is the second after the deserts of Central Asia. In summer and winter, there is a small amount of precipitation here, which is explained not so much by the remoteness of the region from the ocean, as by the relatively rare penetration of cyclones. Due to its southern position the territory of Kalmykia receives a lot of heat. The sunshine duration here is 2180-2250 hours/year. The amount of total solar radiation entering the area varies from 115 kcal/cm² in the north and west and is up to 120 in the central and southeast regions [5–7]. The territory of Kalmykia belongs to the low-water-supplied regions of the country, as the hydrographic network here is poorly developed. Only the extreme northern section, bordering the Volgograd region, is characterized by a relative water content of about 0.5–1.0 l/s per 1 km². In the rest of the territory, it is even lower with a tendency to decrease in the direction from the north-west to the south-east and in the south is almost close to zero.

The Republic is located in the semi-desert zone, the distinctive feature of which is the complexity of the soil and vegetation cover, which manifests itself in a mosaic combination of steppe and desert areas. This combination is due to the abundance of salt and salt marshes that are widespread throughout the country [6]. The vegetation of the Caspian lowland repeats the variegated complexity of the soil cover. It is common to attribute associations and formations with the dominance of herbaceous perennial xerophytes, mainly turf grass and forbs to the steppe type of vegetation, and the dominance of halophytic and xerophytic semi-shrubs and half-shrubs to the desert type [7–9].

The average annual rainfall is small. In different parts of Kalmykia, it falls from 200 to 300 mm, and only on the western outskirts of the Manych valley it reaches 400 mm and more. The precipitation on the territory of the Black Lands is relatively little, i.e. 200–240 mm per year. More than half of the annual precipitation falls during the warm season, when the air temperature is high, and therefore a significant part of the precipitated rainfall evaporates, not having time to penetrate the soil.

The study of the geological and morphological conditions of the Caspian lowland proves the fact that the underlying rocks of the quaternary system are represented by the ancient Caspian sediments of the Khvalynsky stage. The lithological characteristic shows that the quaternary system is represented by clays and sands. The brownish gray and chocolate clay with thin lense sands. The gray and gray-green sands, fine-grained, slightly clayey, micaceous sands with the thickness from 30 to 130 m.

The soil survey of the North-West Caspian of the Russian territory and the Republic of Kalmykia was carried out. The features of the distribution of 25 elements in the soil and ecological Pre-Caspian District in the semi-desert soil-climatic region, where two districts (Chernozemelsky and Pri-Caspian) are studied. There are three administrative districts of Kalmykia and one district of Kazakhstan in this territory.

The semi-desert and soil-bioclimatic region is located on the flat territory of the southeast and the east of the republic. The Caspian province is characterized as a zone of light chestnut and brown soils, sodic complexes, sandy massifs and salt marshes.

The selection of soil samples for physicochemical and chemical analyzes and their subsequent cameral treatment was carried out according to the recommendations [10]. In accordance with the generally accepted agrochemical methods, the main physicochemical properties of soils were determined (the particle size distribution of soil, the content of organic matter, carbonates, exchangeable Ca+2 and Mg+2, pH, dry residue of aqueous extract and anion-cation composition).

The assessment of the ecological state of the studied soils was carried out according to the total content of chemical elements in the soil and in terms of metal retention by soils. The gross content of Mn, Cr, Ni, Cu, Zn, Pb, Cd, As in soils was determined by the atomic absorption method on an MGA-100 spectrometer with argon atomization.

An environmental load rationing was carried out by various methods: 1) while monitoring the content of heavy metals in soils, the soil pollution levels were compared over the natural background by MPC, clarke in the lithosphere and the background level; 2) biogeochemical load rationing. The concentration
coefficient was calculated by the ratio of the values of trace elements to clarke in the lithosphere according to A.P. Vinogradov [1] (Kk). The coefficient of background concentration of heavy metals in soils (anomaly coefficient) is calculated by the ratio of the values found to the background level (Kф).

3. Results

Chernozemelsky district is a district of brown, mostly solonized and slightly saline soils of light grain size: sandy, sabulous and loamy soils, as well as their irregularly spotted complexes with solonetzonthe sea and alluvium and marine sediments.

Brown semi-desert soils lack nutrients and humus. The alkaline reaction of the medium is up to pH 8.5–9.0. The absorption capacity is low. The alkalinity processes are ubiquitous. All the soils are complex with solonet and with salt marshes.

The limits of the content of heavy metals in the soils of the Chernozemelsky district are as follows:

- Al 400–1 107; Fe 1965.2 – 3015.6; Ti 17 – 45.0; V 32.3 – 90.5; Cr 16.2–37.3; Mn 30.4–174.1; Co 6.88 – 14.5; Ni 6.6–16.08; Cu 13.58 – 36.04; Zn 57.61 – 100.39; Ga 5.2–34.8; As 11.9 – 17.66; Sr 7.5– 12.7; Mo 0.05 – 0.19; Cd 0.01 – 0.16; Sn 0.10 – 0.42; Hg 0.001 – 0.013; Pb 1.85 – 8.84 mg/kg. Ba, Be, Li are absent.

The greatest variability is observed in Ti, Cr, V, Cu, Zn, As, Mo, Cd, Pb. The profile distribution of heavy metals differs insignificantly, since the soils have a light particle size distribution, vegetation is sparse, and the projective cover is less than 30%.

As far as the concentration range is concerned the picture is as follows: n*10³ – Al, Fe; n*10² – Ti, Mn; n*10 – Cr, Co, Ni, Cu, Zn; n – Pb; 0.1*n – As, Mo, Cd, Sn; 0.01*n – Hg. According to the concentration row the elements are arranged in a row: Al> Fe> Zn> Mn> Cu> Ni>Sr>Pb> Sn> Mo> Cd> As> Hg. The concentration coefficient indicates equal or close to 1 value of clarke - Cd (0.95), the excess of clarke for Co (1.6), Zn (4.2), Cu (1.2), below clarke - Fe (0.1), Ti (0.5) V (0.5), Cr (0.2), Mn (0.6), Ni (0.3), Sr (0.01), Mo (0.1), Sn (0.03), Pb (0.3), Al (0.5), Hg (0.003). For toxic metals the levels for Cd below clarke are 5 times, for Hg are 5–7 times, for Pb are 4-8 times.

Comparison with the background level of heavy metals in soils (Kf): below the background: Mn (0.2), Cd (0.15), Mn (0.2), Hg (0.05), Pb (0.4), As (0.4); equal to the background: Co (0.95), Mo (0.98); exceeds the background: Cr (1.1)Cu (1.6), Zn (1.7). Maximum permissible concentration is exceeded for Co (1.6), Zn (1.4).

The Primorsk part of the Pre-Caspian lowland of Kalmykia territory is a province of brown soils, sable complexes, sandy massifs and salt marsh spots. The studied soils have a light particle size up to marching sands on the marine sediments.

The limits of the content of heavy metals in the soils of the Lagansky district are as follows:

- Al 400–1 107; Fe 756.2–1895.6; Ti 24 – 147.1; V 30.0 – 64.5; Cr 7.5 – 20.3; Mn 75.1–206.0; Co 1.3–11.5; Ni 0.7– 18.6; Cu 6.2–34.12; Zn 17.5–42., 9; Ga 12.0–29.8; As 0.8–3.49; Sr 3.0–11.2; Mo 0.01–0.19; Cd 0.02–0.34; Sn 0.05–0.35; Hg 0.001–0.013; Pb 0.5–5.4 mg/kg. Ba, Be, Li are absent.

The greatest variability is observed in Ti, Cr, V, Cu, Zn, As, Mo, Cd, Pb. The large variability of such toxic heavy metals as Cd and Pb is due to confinement to sources of pollution, i.e. gas stations and heavy traffic. The whole territory of Laganicity is divided into microdistricts with canals. The sewage is mostly brought into canals, therefore pollutants are distributed throughout the city. This distribution is especially dangerous for toxic metals. The profile distribution of heavy metals differs insignificantly, since soils have a light particle size distribution, vegetation is sparse, and the projective cover is from 25 to 35%.

On the concentration range: n*10³ – Al, Fe, n*10² – Ti, V, Mn, n*10 – Cr, Co, Ni, Cu, Zn, Sr, n – As, Pb, 0.1*n – Mo, Sn, 0.01*n – Cd, Hg.

According to the concentration row the elements are arranged in a row: Al> Fe>Mn> V> Ti> Zn> Cu> Cr> Ni>Sr> Co>Pb> As> Cd> Hg.

The concentration factor (according to A.P. Vinogradov) indicates the levels: equal to clarke or with a slight excess of clarke - As (1.1), for Zn (1.5), Cu (0.98), Cd (1.8), other elements below clarke - Al (0.5), Fe (0.2), Ti (0.2), V (0.45), Cr (0.06), Mn (0.15), Co (0.5), Ni (0.25), Sr 0.03, Mo (0.06), Sn (0.2}
oils with neutral medium, and production rich in As around (MAC) for light soils is 2; - contours, - , and high saturation with many heavy metals of the main carriers of silt particles is typical. If we proceed from what has been said, it is easy to foresee that low and dropped down concentrations of metals should be confined to the soils of high terraces of rivers and valleys of ancient runoff, which are found in the southeast of the RK on the Black Lands.

In the south of the region there are vast territories, where redistribution of water-soluble salts between geomorphological structures and relief elements has been and is currently taking place, which has become one of the causes of soil salinity in low spaces of the steppe zone [5, 8, 9].

Compared to the natural soil-geochemical provinces, the polluted urban lands are not so extensive in the area and compact in configuration. Within such an area, the content of pollutant elements in soils is represented by a complex mosaic of contours, where along with the citywide pollutants the local ones (producers of individual industrial enterprises) may be present. Compared to natural soil-geochemical provinces, polluted urban lands are not so extensive in area and compact in configuration. Within such an area, the content of pollutant elements in soils is represented by a complex mosaic of contours, in which, along with citywide pollutants, local (producers of individual industrial enterprises) may be present.

In the south of the RK a soil-geochemical province with a high concentration of As was found. Its main part is located in the southeastern part of the Black Lands. The arsenic content here ranges from 15 to 35 mg/kg. One may correctly estimate these data if to take into account the fact that in the soils of the European part of the country the background content of arsenic varies between 0.8–8.6 mg/kg, and the domestic hygienic standard (MAC) for light soils is 2; for heavy soils with neutral medium –10 mg/kg. The products of rock destruction rich in As were transferred to the neighboring plain and were part of the loose sediments. However, the toxicosis associated with a high content of arsenic was not
observed in the described area. The fact is that the soil As is immobile and its supply to food chains is limited. This can be judged, in particular, by the amount of the element in plant production: it remains environmentally friendly.

Thus, we are dealing with a natural soil-geochemical province, enriched with the hygienic As standard, which, however, has no negative manifestation for the objective reasons. Similar cases when soils contain a large amount of inactive chemical element are possible in other places. They should be considered as potential biogeochemical provinces where the transition of sedentary forms of the element into mobile ones will occur when the properties of the soil change. In relation to As the alkalinity in soil must increase to pH of 9–10 in order for the element to become more mobile. The alkalinization of soil often occurs in case of its technogenic pollution. For example, now the pH is 8.5–9.0 in some soils of Elista. However, at the indicated values, the alkalinity becomes very toxic for plants, which makes it difficult or impossible to cultivate agricultural crops. In alkaline medium the mobility of Mo is increased. An increased gross quantity of this element was found in the soil cover in the south of the region. It is especially high (exceeds the MPC) in the soils in the south of the northwest of the Caspian Lowland, which are influenced by phosphorus-bearing rare-metal mineralization of rocks, of which Mo is a component. High concentrations of metal were found in marsh-saline and solonetz-saline vegetation on pastures and haymakings of the Caspian Sea [5, 8, 9].

Such (potentially dangerous) biogeochemical provinces can change their ecological status during other types of human activities. Therefore, the search, delineation, study of soil and geochemical features of such areas should be presented in the regional monitoring.

5. Conclusion

The study of heavy metals in the soil cover on the territory of Kalmykia has revealed a great diversity of their gross content due to the genesis of the surface sediments on which modern soils have been formed, as well as the unequal content in the soil-forming rocks of fine particles. The content of heavy metals in the air and soils of the cities and their suburbs is significant, which worsened the living conditions of the population and even made them dangerous.

1. The set of the excessive chemical elements contains not only well-known “priority” Pb, Cd, Zn, Cu, but also, judging by the soil cover in the city of Elista, not well studied Hg, Ga, Sn, Se, Ni, Mo and others.

2. The obtained information on the content and ratio of some elements in the soil cover made it possible to clarify the genesis of soil-forming rocks and soils. The role of aquatic migration and exogenous processes has been enhanced.

3. The aforementioned is reflected in the peculiarities of the microelement composition of soils in certain territories, which we consider as soil geochemical provinces. The deficiency or excess of chemical elements in soils typical for such provinces can negatively affect the life of plants, animals and humans through food chains.

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