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## Ecological and Geochemical Characteristics of the Landscapes of Western Tuva.

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### ABSTRACT

We have performed ecological and geochemical evaluation of the landscapes of the Khemchik depression (western Tuva). We have calculated values of total soil pollution with heavy metals, as well as the coefficient of biogeochemical transformations indicating changes in microelement composition of vegetation. We have found that the investigated area slightly contaminated in ecological and geochemical terms. Mapping of ecological and geochemical environment has demonstrated the difference between the chemical composition of vegetation and soils. Evaluation of intraregional patterns of substance migration in the main components of the landscape of the depression has shown that the composition of the vegetation is less dependent on their content in the pedosphere.

**Keywords:** landscape geochemistry, total soil pollution, coefficient of vegetation biogeochemical transformation, ecological and geochemical mapping

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## INTRODUCTION

Percentage abundance of chemical elements reflects the basic patterns of their redistribution between the components of natural environments. Regional percentage abundance of chemical elements shows natural and geochemical diversity of these environments. Being a product of the interaction of abiotic and biotic natural environments, the soil has a decisive influence on these environments, which in turn determines its global ecological role. Communication between the system of chemical elements of the biosphere components is performed by different groups of their compounds specific to each environment. Chemical pollution further complicates these interactions. This fact determines the increasing attention to the compounds of the chemical elements of soil. Therefore, the analysis of the pollutant concentration in soils is an important segment of ecological and geochemical evaluation of the components of terrestrial ecosystems and of the comprehensive assessment of the territory, as well as its determining factors. This assessment shows the condition of the components of landscape and biocenotic structure upon study and allows making both qualitative and quantitative evaluation of the state of soil cover and the anthropogenic influence thereon (Shchiptsova, 2014).

## OBJECT OF RESEARCH

Landscapes of Khemchik depression have differentiated under the influence of contrasting natural conditions and the most complex territorial geology that have stipulated a variety of soils and diversity of vegetation. However, both altitudinal and latitudinal climate manifestation has determined the heterogeneity of landscape-geochemical conditions that gives them the form and classifies as follows:

1. *High-mountain landscapes* are represented by rock-talus high mountains with thin loam-gravelly cover with alpine and sub-alpine meadows and shrubs, patches of tundra and woodlands on mountain meadow soils. The highland steppes are mainly represented by cryophytic-grass steppes, herb meadows on the alpine tundra and alpine steppe soils with rock placers. Open woodlands of cedar and larch and subalpine tall-grass meadows, shrubs on mountain meadow soils and patches of tundra on peat-humus soils represent Forest areas.
2. *Middle-mountain landscapes* are represented by mountain chestnut and mountain forest soils with the dominating coniferous and deciduous forests, as well as by larch forests on mountain meadow soils in combination with dry steppe communities on mountain-chestnut soils. Steeper slopes are covered with typical rocky steppe.
3. *Steppe landscapes* are represented by intermountain hollow steppes, usually with bunchgrass sagebrush-grass vegetation, and better moisture conditions are favorable for growth of herb feather-grass meadow communities on the variable chestnut soils.
4. *Anthropogenic landscapes* have been demarcated in the zone of residential complexes: footprint of "Proton" carrying missile (alpine landscapes), mining and processing plant "Tuvaasbest" and Chadan open-pit coal mine (steppe landscapes). It is important to note the presence of ruderal and halophytic flora in the vegetation of steppe anthropogenic landscapes identified as the communities of *Artemisia frigida* and *Stipakrylovii* with admixed *Potentilla acaulescent* and *Agropyronrepens*.

## RESEARCH TECHNIQUE

Identification of ecological and geochemical conditions of Khemchik depression was carried out by testing soils, dominant vegetation communities and surface water. Sampling of environmental components was performed by the sequence (catena) approach: the sampling points were laid in the valleys of major rivers, on the tops and the slopes of the mountain range of different hypsometric levels, the terraces at various levels, taking into account the landscape organization of ecosystems.

Soil samples were taken from the root zone at a depth of 5-20 cm; water samples were collected from the water column at a depth of at least 1 m; samples of plant material were collected from the sampling point of soil samples with an area of 1 m<sup>2</sup> by mowing the aboveground plants.

The samples of air-dry soil, dry plant material, and surface water had Cu, Mn, Co, Zn, Pb, Cd, Ni, Al and other elements determined.

We performed analysis of the samples in the agrochemical laboratory "Tuvinskaia", Republic of Tuva, in the Common use Center of Siberian Federal University and the Scientific and Educational Common Use Center of Tuva State University (accreditation certificate No. AAC.A.00162). To determine the elemental composition of environmental objects we used: atomic absorption spectrometers Analyst 600 and Analyst 800 by Perkin-Elmer, and Sollar 6M by Thermo scientific; atomic emission spectrometers Optima 5300 by Perkin-Elmer and ICAP 6500 by Thermo scientific. To determine and/or identify the organic matter of different origin we used: gas chromatography-mass spectrometer by Agilent, spectrophotometers Cary 100, Cary 5000 Eclipse by Varian, IR spectrometer Nicolet by Thermo scientific, spectrofluorometers LS 55 and spectrophotometers Lambda 950 by Perkin-Elmer.

We processed the obtained results by statistical methods using Microsoft Office Excel, which calculated the mean and standard deviations of the elements in the surface waters, soils and plants.

To identify the geochemical habit of the territories, we compared the soil and surface water composition with lithospheric percentage abundance (Vinogradov, 1962), and the composition of plants - with an average concentration of chemical elements in the annual increment of terrestrial plants (Dobrovolskii, 2003). We reflected typical geochemical characteristics of the soil, plants and water in the formula, which numerator contains the concentrating elements with their concentration coefficients ( $C_c$ ), and denominator contains elements deconcentrating with scattering coefficients ( $C_s$ ).

Total pollution index  $Z_c$  reflects polyelement load on soil:

$$Z_c = \sum_1^n C_c - (n - 1),$$

where  $n$  – the number of heavy metals with  $C_c > 1.5$ .

For sanitary hygienic assessment of soil pollution, we used maximum allowable concentrations (MAC) (sanitary standard ГН 2.1.7.2042-06).

Changes in microelement composition of plants indicate a complex indicator - the coefficient of the biogeochemical transformation  $Z_v$ , proposed by Kosheleva N.E., Kasimov N.S., Sorokina O.I., Gunin P.D., Bazha S.N. and Enkh- Amgalan in their paper (2013), which is calculated by the formula:

$$Z_v = \sum_1^{n_1} C_c + \sum_1^{n_2} C_s - (n_1 + n_2 - 1),$$

where  $n_1, n_2$  – the number of microelements with  $C_c > 1.5$  and  $C_s > 1.5$ , respectively.

We performed ecological and geochemical mapping by using the package ArcGIS 9.3.1. by inversed distance weights. Individual samples with extremely high concentrations of heavy metals, many times exceeding the average level in the territory of the depression were excluded from analysis to prevent overestimation of territorial contamination upon data interpolation (Methodological guidelines ...; 1999).

## RESULTS AND DISCUSSIONS

We have evaluated the intensity of the ecologically significant factors for each type of landscape: the content of chemical elements in soils and plant communities.

In our ecological and geochemical research, we placed a priority on the investigation of partitioning behavior of Mn, Cu, Zn, Co, Pb, Ni, Cd, I and other components in the environment.

When using a landscape approach, both the functioning of basic natural systems and the "geometry" of migration real and energy flows assume great importance in the geoecological simulation (Koshkarev, 1997). Indices of inter- and intralandscape migration of substances are the main values in the evaluation of the geochemical resistance. The main factors determining the resistance of landscapes to pollution (geochemical resistance), according to M.A. Glazovskaia (1988), are the decomposition rate of pollutants and the intensity of their removal out of the geosystem. Removal of pollutants depends on local terrain, degree of drainage and dissection of the territory, as well as hydrological regime. The decomposition rate is determined by the soil

microbial activity and generally decreases with the decrease in annual accumulated temperatures, and depends also on azonal factors (mesorelief, moisture conditions). Analysis of these factors allows ranking the landscape areas according to their resistance to anthropogenic pollution.

Ecological and geochemical assessment of the findings was carried out based on the integrated use of geochemical, sanitary and hygiene, and biogeochemical parameters.

Geochemical data on the individual components such as soil, plant communities and surface waters of the depression have served as the basis for the integrated assessment of the main landscape types of the area under study. The trace element composition of soil and plant cover provided information about both the intensity and specialization of contamination sources.

Estimation criteria for the level of contamination of soils and their corresponding environmental hazards (acc. to Davydova, Volkova, 1988 as amended by Kosheleva et al., 2013):

- low / non-hazardous –  $Zc < 16$ ;
- average / moderately hazardous –  $Zc 16-32$ ;
- high / hazardous –  $Zc 32-64$ ;
- very high / very hazardous –  $Zc 64-128$ ;
- maximum / extremely hazardous -  $Zc > 128$ .

To characterize the soil contamination in Khemchik depression we calculated general indices for both the main types of background landscapes, and individual hazard categories of elements for technologically transformed territories. In case of anthropogenic load, a specific feature of heavy metals contained in the landscape components is their multielemental ability (Kosheleva, Kasimov et al., 2013).

Table 1: Assessment of total pollution of the landscape components of Khemchik depression

Key areas	Values of total pollution indices					
	Soil Zc			Plant community Zv		
Edegey township	2.8			28.2		
The Khemchik river valley (left bank)	5.5			25.1		
Ulug-Khovu township	3.7			31.9		
The Ustuu-Ishkin river valley	2.3			29.1		
Neighborhoods of Khondelen village	3.0			25.7		
The Adar-Tosh ridge (the spur of Western Tanu-OI)	2.3			27.4		
Neighborhoods of lake Sut-Khol	2.8			22.3		
Neighborhoods of lake Kara-Khol	3.0			22.0		
Neighborhoods of the plant "Tuvaasbest"	23.1			31.3		
	7.3*	16.6**	2.2***	10.5*	14.5**	8.6***
Footprint of "Proton" carrying missile	27.1			18.4		
	14.1*	13.3**	2.4	4.1*	6.8**	9.6***
Neighborhoods of Chadan coal deposit	1.7			16.6		
	2.5*	3.4**	0	5.5*	2.1**	11.0***

Notes:

\* - elements of hazard category I

\*\* - elements of hazard category II

\*\*\* - elements of hazard category III

We have determined the area of carrying missile footprint based on the maximum values of the total soil pollution with elements of hazard category I, with the level of 14.1 (Table 1). Halo of increased value Zc in this zone is associated with the presence of increased amounts of Pb. Minimum indices Zc for these elements are observed in the neighborhoods of Chadan coal deposit ( $Zc = 2.5$ ). Generally, the major pollutants are lead and zinc, besides of that, there is relatively increased amounts of arsenic.

Elements of hazard category II are concentrated in the vicinity of the mining and processing plant "Tuvaasbest" ( $Z_c = 16.6$ ), that is rated according to the assessment criteria of the level of soil contamination as average, and according to the environmental hazard - as moderately hazardous. Copper and nickel play leading role in the formation of these halos, and cobalt - in a lesser degree. The lowest indices of total pollution as well as of the elements of hazard category I were determined in soil of the affected zone of Chadan coal deposit (3, 4).

The considered technologically transformed landscapes are scarcely contaminated with elements of hazard category III and their  $Z_x$  is at 2.4 and 2.2 in the area of carrying missile footprint and the affected zone of the plant "Tuvaasbest", respectively.

Generally, the average index  $Z_c$  for soils of the Khemchik depression is 7, which indicates a low level of their contamination. It is known that anthropogenic pollution of soils is of areal nature (Saksin, Bubnova, 2006), in connection therewith we have calculated the contaminated areas of the territory under study. For example, more than 80% of the depression - mostly all natural ecosystems - are characterized by a very low pollution level ( $Z_c < 8$ ). Moderately hazardous pollution ( $Z_c > 16 < 32$ ) is observed in 18% of the territory being a part of the technologically transformed landscapes (the neighborhood of the mining and processing plant "Tuvaasbest" and the area of "Proton" footprint).

The comparison of the element contents in soils of industrial areas with the MAC (ГН 2.1.7.2042-06) has revealed the exceedance of statutory limits for Cu, Co, Pb, Ni and As. The territories with exceeded MAC level, which decreases in the row Co (100%) > Pb (67%) > Ni (67%) > Cu (33%) > As (33%), reflect the environmental hazard of heavy metals.

The ecological condition of plant formations in the depression was evaluated by the degree of heavy metal rationing in mature plant tissues by comparing them with known concentrations of trace elements by Melsted (1973). We have revealed the excessive content of Ni in 100% of vegetable formations of the depression, and an excessive level of Pb in more than 50% of phytocenoses. The excessive contents of Co and Cr were observed in plants growing in the human-impacted territories. The concentration of Cd approaches the upper optimum limit. We have revealed a lack of such essential element as Mn in the plant cover of the accumulative steppe and middle-mountain transit ecosystems.

It is known (Kabata-Pendias, Pendias, 1989; Dobrovolskii, 1998; Bargagli, 2005), plants respond to environmental deterioration by accumulating and deconcentrating the trace elements, which is due to changes in the intensity of biological processes. Therefore, the coefficient of the biogeochemical transformation ( $Z_v$ ) reflects the disruption of normal ratios of elements in plants specific to their phylogenetic and ontogenetic specialization, as well as quantitatively describes an imbalance of essential chemical elements resulting from the increased anthropogenic load.

Thus, we have calculated the average coefficient  $Z_v$  for plant cover of Khemchik depression that is 23.9 (Table 1), which is defined as a relatively low level of biogeochemical transformation (Kosheleva, 2013). Generally,  $Z_v$  of plant communities is poorly differentiated to different types of landscapes of the depression; the strongest changes have been recorded in the foothill levelled steppe ( $Z_v = 31.9$ ) and in the vicinity of the mining and processing plant "Tuvaasbest" ( $Z_v = 31.3$ ). The plant communities growing in other human-affected areas are characterized by weak biogeochemical transformation, which indicates their tolerance to anthropogenic press and the ability to function normally under considerable emission of pollutants.

To assess intra-regional laws of composition and migration of the substance in the main components of the landscape, which act as objects of monitoring and environmental prediction - soil cover and plant communities, we performed zoning in accordance with the peculiarities of geomorphological, bioclimatic differentiation, as well as orographic conditions that determine the intensity of chemical elements migration. Since the altitudinal zonation is essential in the differentiation of landscape structure in the area studied, the most convenient way of zoning is to divide the territory into the orographic complexes. Thus, we have defined high-mountain, middle-mountain and steppe landscapes. We further determined their biochemical specialization of soils, plants and surface waters. The main indicators of the chemical composition are presented in the form of equations (Figure 1), where the numerator shows the elements of the worldwide

average, and the denominator - quantities below the percentage abundance. Brown color shows the contents of elements in soils, and green - in plant communities. An explication legend to the map is shown in Table 2.

**Table 2: Main types of landscape of the Khemchik depression**

Sampling points		Landscapes and main plant communities (ecosystems)	Dominant types of soil
No.	Topological names		
1	The levelled steppe to the north-west of the city of Ak-Dovurak, Edegey township	Accumulative, interdepression, steppe-type (the leveled interdepression steppes at the bottom of the depression)	Chestnut steppe
2	Sub-valley steppe on the left bank of the river Khemchik, neighborhoods of Sug-Aksy, Kara-Chyraa and Kyzyl-Taiga villages		Light-chestnut steppe
3	Foothill levelled steppe to the north-east of Chadan city, Ulug-Khovu township		Light-chestnut steppe
4	The Ustuu-Ishkin river valley down from Ara-Oi township to the north-west of Ishkin village	Transit middle-mountain (the Alash plateau 1000-1500 meters above sea level, dissected with the deep river valleys and mixed forest)	Mountain-steppe chestnut
5	Rocky herb steppe on the slopes of the southern exposition (neighborhoods of Khondelen village)		Mountain-steppe chestnut
6	Range spur of Western Tannu-Ola (Adar-Tosh mountain pass)		Mountain-forest dark chestnut
7	Neighborhoods of lake Sut-Khol	Eluvial high-mountain (spurs of Western Saian with absolute elevation of up to 2400-2800 m)	Dark meadow-chestnut
8	Neighborhoods of lake Kara-Khol		Chernozem-like mountain-meadow
9	The affected zone of the mining and processing plant "Tuvaasbest"	Anthropogenic landscapes (the structure of plant communities includes ruderal and halophytic flora. Identified often as <i>Artemisia frigida</i> and <i>Stipa</i> communities)	Light-textured light chestnut steppe soils
10	Middle reach of the high-mountain river Monagy (the basin of lake Kara-Khol)	Anthropogenic landscapes (dark coniferous forests with subalpine meadows, shrubs, and alpine tundra)	mountain-meadow soils with peat-humus patches
11	Chadan open-pit coal mine (10 km to the east of Chadan city)	Anthropogenic landscapes (herb and wheat grass and sheep fescue real steppe, with patches of pea shrub and herb and low-bunchgrass real steppe)	Chestnut and light chestnut

The depression soils are characterized by high, with respect to percentage abundance, content of Cd, Zn and Pb in all natural landscapes, and the amount of As above the worldwide average in the highlands (Figure 1). With decrease in absolute elevations there is an increase in the content of manganese and copper, which were characterized by deconcentration in the transit and eluvial landscapes. Anthropogenic soils are enriched with respect to the worldwide average value with almost all elements in question, which is likely due to the influence of anthropogenic factors. Ni, Cu and Pb are most prone to the accumulation. In turn, lead is highly technophile (the ratio of annual production of the element in tonnes to its percentage abundance in the lithosphere (Perelman, Kasimov, 1999)) emitted to the environment by various industrial facilities and transport. In contrast to the natural landscapes, the considered territories are cadmium-depleted.

Plant communities, especially in high-mountain areas, are characterized by concentration of multiple elements (Figure 1). Thus, cadmium plays a leading role both here and in the respective soils. The high-mountain vegetation is distinguished by deficit of such vital elements as Mn in large amounts ( $C_s = 13.7$ ), and Zn in a relatively minimal amount ( $C_s = 1.5$ ). The vegetation of middle-mountain and accumulative landscapes has deficiency of many elements. They are characterized by accumulation of Cd and Ni, and the same with Cr in the steppe floristic complexes. Plant communities growing in the zone of influence of anthropogenic factors, as well as alpine plants have lack of manganese and zinc, and accumulate the rest of the elements in question.

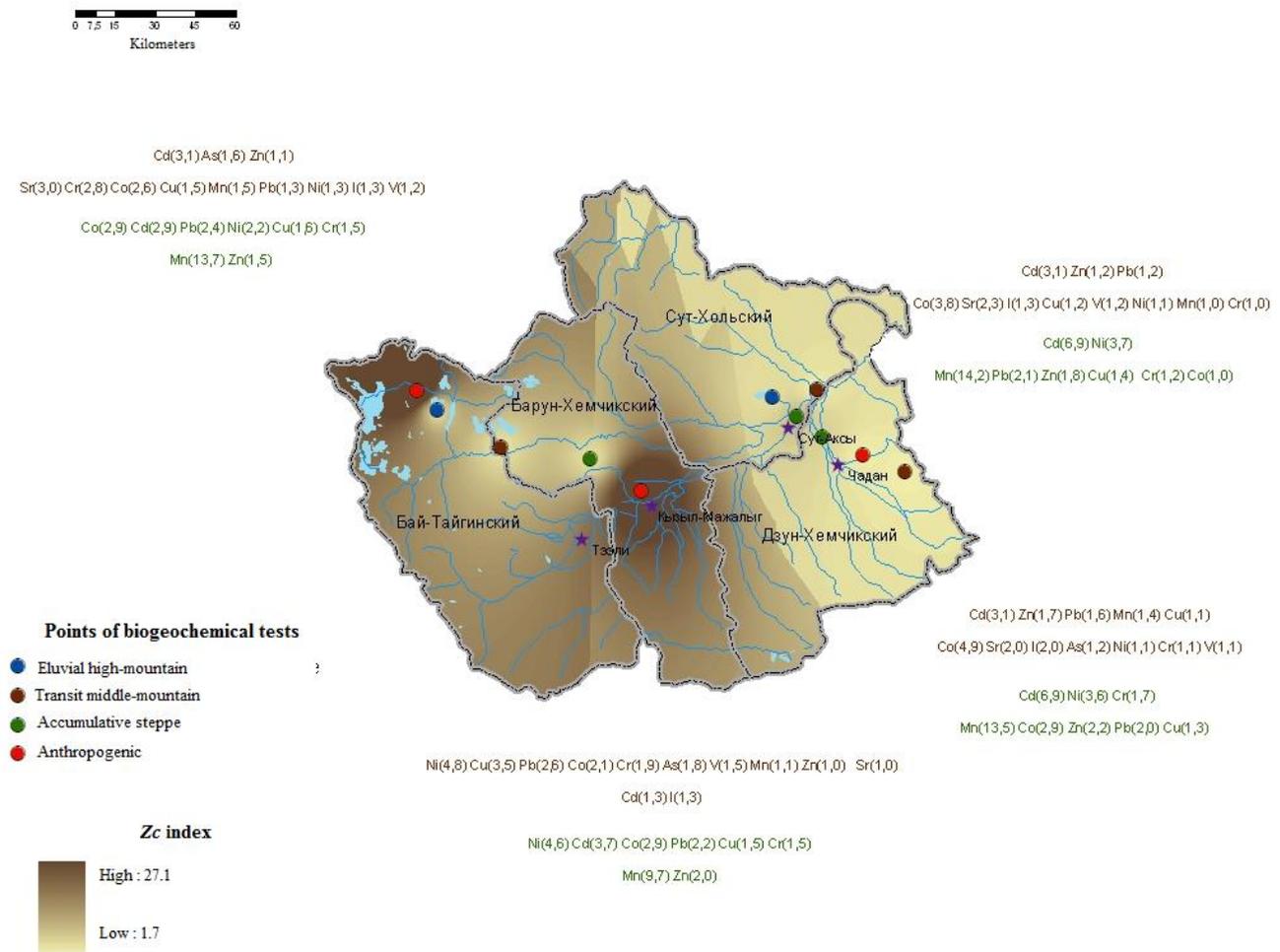


Figure 1. Ecological and geochemical map of the Khemchik depression

Generally, we can assess the soils of landscape and ecological systems of the Khemchik depression as slightly polluted, since the calculated value of the total pollution index is less than  $Z_c < 8$ , which allows us to classify their state as satisfactory. Low- and medium-contrast anomalies of heavy metals are confined mainly to anthropogenic landscapes, with the exception of the affected zone of the Chadan coal deposits, where virtually no pollution was observed. At the same time, plants are also characterized by weak biogeochemical transformation, which indicates also the environmental "purity".

#### SUMMARY

In general, we can conclude that there is a low overall level of contamination of soils and plant communities in all investigated samples, including those from the technologically transformed landscapes. All samples feature an extreme shortage of essential trace elements, except for the soils of high-mountain landscape formations and vegetation. This is especially true of manganese, iodine, and some other trace elements. This may be due to the fact that manganese binds strongly to soil organic matter, thus becoming unavailable to plants. As a result, the plant of the plain landscapes, where the processes of organic matter decomposition are slowed down, and with manganese in the inactive state, often have a physiological deficiency of this element.

It is known that the communities in the surface layers of soil and in vegetative plant organs indicate the sources and the general similarity of the behavior of pollutants in different landscape-geochemical conditions (Kosheleva, Kasimov et al., 2013). Our ecological and geochemical mapping has otherwise demonstrated a clear difference between the chemical composition of vegetation and soils, except for cadmium only. Evaluation of intraregional patterns of substance migration in the main components of the landscape of the depression has shown that the composition of the vegetation is less dependent on their content in the pedosphere.

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