Geochemical state of vegetation in the north-east of the Republic of Tyva

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Abstract. The article considers the geochemical features of vegetation in the area of the planned construction of the Ak-Sug copper-porphyry deposit. In the Todzha basin in the north-east of the Republic of Tuva, the practice of using mining and processing plants has an initial cycle (since 2015), so research is needed for further monitoring, forecasting and restoration of natural geosystems. It should be noted that to date, no specialized study of the material composition of raw materials and the impact of mining waste on the environment has been conducted in the study area. The presented materials can be used to manage the state of the environment and optimize the use of natural resources in the areas of activity of mining enterprises of the republic, which will help to reduce the anthropogenic impact on the geosystems of the region.

1. Introduction

The north-eastern part of Tuva is an ecotone zone, forming the boundary between the arid and humid regions of the Asian subcontinent, located in the strip of the ultracontinental and continental sectors of North Asia [1].

The vegetation cover of the study area is characterized by the most humid type of vertical zonation of the vegetation cover of the mountain systems of Tuva [2]. The main pattern of vegetation distribution is altitudinal zonation, which is caused by changes in climatic conditions depending on the height of the area above the ocean level. Its nature also depends on the geographical location and height of the mountain ranges. The features of the altitudinal zonation also depend on the humidification conditions associated with the formation of cyclonic and continental provincial variants of its structure. The landscapes of the mountain-taiga belt, which occupy almost 3/4 of the territory, are the most typical for the study area. The landscapes of the mountain-tundra belt are more monotonous, as rare-coniferous forests of Siberian larch with alpine and subalpine vegetation dominate almost everywhere. The peaks of the mountains are occupied by stony placers, the spread of modern snowfields in the char belt.

2. Material and Methods

The study of vegetation in the area of the Ak-Sug deposit, which is located in the southern spurs of the Eastern Sayan at its junction with the Western Sayan, was carried out in the seasons of 2009, 2013,
Vegetation cover in the area of the Ak-Sug deposit develops in a typically mountainous and humid climate. The relief is highly dissected, the absolute marks of the peaks in the area of the deposit vary significantly from 1800 to 2400 m, reaching 2783 m. There are many small car lakes, where the rivers originate. The axial parts of the ridges are composed of effusive rocks belonging to the Proterozoic. Fluvialglacial deposits of the Cenozoic are developed. All the watershed ridges at the base are covered with powerful accumulations of deluvium, consisting of large and small debris and rubble. The soils are mountain-tundra, mountain-meadow, mountain-taiga, formed on various rocks [3].

In the surveyed area, two vegetation zones are well defined: mountain-forest and high-mountain-tundra.

The main research method was the method of specific floras in combination with a detailed route survey (figure 1). As a result of the conducted research, a herbarium was collected, geobotanical descriptions were made in accordance with generally accepted methods. The selection of plant samples was carried out in accordance with the requirements for sampling for general and local contamination [4-5]. The determination of the content of heavy metals in plant samples was carried out in an ash solution after mineralization of the plant material with an atomic absorption spectrophotometer SPECOL-11 (in the laboratory of the Federal State Station of the Agrochemical Service "Tuvinskaya"). The background content of heavy metals in plants is calculated for the air-dry mass. The plants were salted in a muffle furnace at 450-500°C.

Figure 1. Layout of key sites in the study area.
3. Results and Discussion
For the biogeochemical analysis of plant composition, we examined the dominant plant species in the study area to identify exactly which fraction accumulates most of the heavy metals and which organs play an important role in the biogeochemical cycle of substances in these ecosystems.

Maximum allowable concentrate (MAC) of $\text{Pb}$ in plant feeds is 5.0. Normal concentrations for plants are from 0.1 to 5.0 mg/kg, critical – 10.0 mg/kg, phytotoxic-more than 60 mg/kg [6]. According to our data, the lead content in green mosses ($\text{Polytrichum commune}$ Hedw., $\text{P. stictum}$ Brid.), the Pb concentration is at the normal level and is 0.914 in the P 1311006 site (table 1). The average Pb value higher in $\text{Betula rotundifolia}$ Spach. leaves was 0.762 mg/kg in the plot of P 1370002 mg/kg (table 2).

On average, the Pb content in the plant samples of the studied sites ranges from 0.06 to 0.762 mg/kg. In total, the Pb content in the studied areas corresponds to the II class of ecosystem risk.

Table 1. Heavy metal content in green mosses.

|                | Plots        | Cd   | Pb    | Ni    | Zn    | Cu    | Hg    | As    | Co   | Fe    |
|----------------|--------------|------|-------|-------|-------|-------|-------|-------|------|-------|
| P 1305001      | 0.103        | 0.473| 0.433 | 45.45 | 14.57 | 0.013 | 0.039 | 0.081 | 50.46|
| P 1301001      | 0.189        | 0.604| 0.807 | 60.63 | 14.25 | 0.017 | 0.048 | 0.093 | 45.79|
| P 1310004      | 0.156        | 0.442| 0.777 | 78.31 | 17.45 | 0.02  | 0.066 | 0.127 | 149.6|
| P 1310006      | 0.158        | 0.47  | 0.791 | 80.85 | 20.43 | 0.023 | 0.062 | 0.178 | 162.4|
| P 1310008      | 0.145        | 0.526| 1.102 | 67.31 | 14.35 | 0.019 | 0.055 | 0.126 | 125.82|
| P 1330004      | 0.187        | 0.829| 1.368 | 282.9 | 63.95 | 0.027 | 0.076 | 0.183 | 88.47|
| P 1330006      | 0.175        | 0.77  | 0.792 | 125.91| 29.99 | 0.024 | 0.068 | 0.164 | 77.03|
| P 1370002      | 0.131        | 0.784| 0.685 | 84.94 | 15.88 | 0.015 | 0.047 | 0.11  | 174.8|
| P 1370004      | 0.157        | 0.811| 1.032 | 1352.62| 398.23| 0.034 | 0.095 | 0.205 | 398.98|
| P 1370006      | 0.133        | 0.649| 0.909 | 149.59| 41.7  | 0.015 | 0.042 | 0.162 | 234.12|
| P 1370008      | 0.136        | 0.641| 0.655 | 74.27 | 17.06 | 0.014 | 0.046 | 0.153 | 212.46|
| P 1390005      | 0.21         | 0.808| 0.777 | 193.28| 59.99 | 0.02  | 0.058 | 0.136 | 202.74|
| P 1390007      | 0.255        | 0.88  | 1.27  | 127.17| 33.37 | 0.017 | 0.06  | 0.13  | 178.43|
| P 1390009      | 0.229        | 0.661| 0.749 | 78.88 | 18.3  | 0.014 | 0.044 | 0.11  | 167.08|
| P 1311000      | 0.244        | 0.563| 1.301 | 72.24 | 16.03 | 0.014 | 0.046 | 0.203 | 108.57|
| P 1311002      | 0.284        | 0.644| 1.093 | 105.61| 23.67 | 0.018 | 0.064 | 0.13  | 43.47|
| P 1311004      | 0.216        | 0.787| 0.83  | 91.18 | 20.31 | 0.019 | 0.06  | 0.116 | 128.13|
| P 1311006      | 0.255        | 0.914| 0.881 | 109.84| 28.96 | 0.021 | 0.07  | 0.128 | 150.68|
| P 1311008      | 0.178        | 0.456| 0.652 | 44.81 | 7.74  | 0.011 | 0.026 | 0.098 | 30.59|
| P 1313005      | 0.252        | 0.759| 0.713 | 152.91| 41.93 | 0.019 | 0.062 | 0.134 | 144.63|
| P 1313007      | 0.244        | 0.445| 1.254 | 79.08 | 17.52 | 0.016 | 0.044 | 0.146 | 130.31|
| P 1313009      | 0.236        | 0.429| 0.491 | 66.32 | 15.54 | 0.015 | 0.039 | 0.128 | 122.79|
| P 1315002      | 0.207        | 0.579| 0.783 | 49.14 | 8.15  | 0.012 | 0.027 | 0.121 | 35.63|
| P 1315004      | 0.19         | 0.567| 0.776 | 89.59 | 21.83 | 0.017 | 0.054 | 0.146 | 99.18|
| P 1315006      | 0.174        | 0.561| 0.785 | 85.14 | 20.48 | 0.017 | 0.049 | 0.142 | 81.17|
| P 1317003      | 0.186        | 0.706| 0.685 | 60.48 | 11.56 | 0.016 | 0.053 | 0.121 | 90.13|
| P 1317005      | 0.227        | 0.893| 0.906 | 104.56| 23.22 | 0.023 | 0.067 | 0.152 | 136.06|
| P 1319002      | 0.226        | 0.82  | 1.642 | 57.95 | 9.77  | 0.016 | 0.05  | 0.164 | 29.48|
| mean           | 0.196        | 0.66  | 0.891 | 141.8 | 36.7  | 0.018 | 0.054 | 0.139 | 128.5|

MAC of $\text{Cd}$ in plant feeds is 0.3 mg/kg [7], the critical concentration is 0.5–10 mg/kg [8], and the toxic concentration for plants is 100 mg/kg and higher [6]. The average Cd value in green mosses was 0.196 mg/kg, which is lower than the MAC. The maximum concentration of Cd is contained in the leaves of $\text{Betula rotundifolia}$ from the plot P 1319002 – 1.32 mg/kg (exceeding the MAC by 4 times).
Table 2. The content of heavy metals in higher vascular plants.

| Plots      | Cd     | Pb       | Ni   | Zn    | Cu     | Hg    | As     | Co     | Fe     |
|------------|--------|----------|------|-------|--------|-------|--------|--------|--------|
| P 1305001 | 0.126  | 0.684    | 0.529| 62.5  | 0.016  | 0.053 | 0.096  | 71.1   |
| P 1301001 | 0.157  | 0.728    | 0.513| 47.67 | 0.012  | 0.036 | 0.064  | 30.68  |
| P 1310004 | 0.137  | 0.4      | 0.658| 73.01 | 0.014  | 0.046 | 0.114  | 113.9  |
| P 1310006 | 0.132  | 0.669    | 0.529| 15.36 | 0.007  | 0.049 | 0.118  | 120.9  |
| P 1310008 | 0.087  | 1.042    | 0.788| 62.82 | 0.018  | 0.044 | 0.119  | 165.45 |
| P 1310009 | 0.136  | 0.487    | 0.669| 73.01 | 0.015  | 0.046 | 0.114  | 113.9  |
| P 1311000 | 0.189  | 0.472    | 1.064| 69.76 | 0.013  | 0.037 | 0.242  | 74.67  |
| P 1311002 | 0.526  | 0.224    | 0.703| 51.28 | 0.011  | 0.029 | 0.071  | 21.5   |
| P 1311004 | 0.51   | 0.154    | 0.523| 63.67 | 0.013  | 0.038 | 0.098  | 104.55 |
| P 1311006 | 0.581  | 0.169    | 0.605| 89.4  | 0.014  | 0.044 | 0.107  | 108.29 |
| P 1311008 | 0.623  | 0.202    | 0.744| 90.48 | 0.018  | 0.051 | 0.112  | 60.35  |
| P 1313005 | 0.414  | 0.157    | 0.396| 77.51 | 0.014  | 0.037 | 0.099  | 73.64  |
| P 1313007 | 0.396  | 0.22     | 1.052| 72.93 | 0.194  | 0.041 | 0.129  | 58.88  |
| P 1313009 | 0.378  | 0.215    | 0.372| 65.27 | 0.013  | 0.036 | 0.112  | 54.15  |
| P 1315002 | 0.708  | 0.241    | 0.927| 101.34| 0.019  | 0.059 | 0.148  | 70.5   |
| P 1315004 | 0.484  | 0.156    | 0.708| 81.4  | 0.149  | 0.043 | 0.8   | 55.05  |
| P 1315006 | 0.468  | 0.142    | 0.719| 79.06 | 0.013  | 0.035 | 0.088  | 54.49  |
| P 1317003 | 0.634  | 0.163    | 0.439| 56.75 | 0.014  | 0.039 | 0.098  | 76.94  |
| P 1317005 | 0.74   | 0.172    | 0.592| 68.11 | 0.016  | 0.05  | 0.086  | 88.18  |
| P 1319002 | 1.321  | 0.31     | 1.771| 91.43 | 0.019  | 0.064 | 0.208  | 49.22  |
| mean      | 0.36   | 0.39     | 0.71 | 96.29 | 0.05   | 0.04  | 0.11   | 84.9   |

MAC of Ni in plant feeds is 3.0 mg/kg, the critical concentration in plants is in the range of 20–30 mg/kg, the phytotoxic concentration for plants is more than 80–100 mg/kg. The maximum Ni concentrations were found in the plot P 1319002 (1.771 mg/kg) and P 1311000 (1.064) in the ash of *Betula rotundifolia* and *Pinus sibirica* Du Tour., *Bergenia crassifolia* L. in the plot P 1311004, it accumulates metal 800 times less. On average, the Ni content fluctuates in the range from 0.040 to 0.867 mg/kg in the plots.

MAC of Zn in plant feeds is 50 mg/kg, and in human plant foods – 10–50 mg/kg, the phytotoxic concentration is 400 mg/kg. The maximum Zn content was found in the plot P 1370004 and P 1330004 plots in *Pinus sibirica* and *Betula rotundifolia* conifers from 706.96 and 111.05 mg/kg, which is much higher than the MAC norm. The average Zn content in green mosses in all areas was 141 mg/kg.

MAC of Cu in plant feed is 30 mg/kg, and the phytotoxic concentration is 20 mg/kg. The average Cu content in the green mosses of the plots is 36.7 mg/kg with a maximum permissible concentration of 30 mg/kg. High Cu concentrations were observed in the plot P 1370004 – 398 mg/kg. *Betula rotundifolia* accumulates Cu on average 23 mg/kg, The maximum accumulation was found in the same plot P 1370004 and was 210 mg/kg. The average Cu content in *Pinus sibirica* conifers is 5.83 mg/kg.
MAC of As in plant foods is 0.2 mg/kg. The phytotoxic concentration of As has not been established. Aquatic plants, mosses and lichens are more actively absorbed by As. It also accumulates in the bottom sediments, which confirms the active migration in humid landscapes. *Betula rotundifolia*, green mosses accumulate As in concentrations much higher than other plants. Minimum As content in *Bergenia crassifolia*.

MAC of Co in plants is in the range of 10 to 20 mg/kg. Critical concentration – 5 mg/kg, phytotoxic – more than 80 mg/kg. Like other metals, it is accumulated by mosses and lichens. In humid landscapes, it is relatively mobile. Weak accumulation by plants does not prevent its removal from the upper horizons of podzolic and sod-podzolic soils. The concentration of Co in green mosses, *Pinus sibirica* conifers, and *Betula rotundifolia* in the studied areas is below the MAC.

MAC of Fe content is considered normal for different plants from 20 to 300 mg/kg [9]. Green mosses in the studied areas contain an average of 128 mg/kg, the maximum content in the plot P 1370004 – 399 mg/kg. The average content in *Betula rotundifolia* was 84.9 mg/kg, the minimum amount was observed in the plot P 1211002 – 21.5 mg/kg.

4. Conclusion

The results of geochemical analysis of plants in the area of the Ag-Sug copper-porphyry deposit in the north-east of the Republic of Tuva indicate a more intensive accumulation of Cu, Zn, Mn, Fe, and As by individual plants. The high concentration of Cu is due to the presence of a copper ore deposit. The same applies to As, which is an accompanying component in the deposit. The high Zn content is due to the presence of this element in the pyritization zone that borders the main deposit. The degree of natural contamination with heavy metals decreases as they move away from their main source – the ore field.

The geochemical state of vegetation in the area of the deposit shows a high adaptability of plants to the high content of certain chemical elements. It should be noted that plants have a certain resistance to soil contamination. There are two ways to adapt plants to high concentrations of heavy metals – the use of specific protective mechanisms (barriers), the nature of which is not at all clear, and inactivation of incoming metals, the transport of these substances to less affected cell compartments. Despite the increased content of some heavy metals in plants-plants have a surprisingly stable, thanks to which, even growing directly in the field, they take from the soil only the right amount of the required norm of chemical elements, while perfectly performing their functional role in the cycle of substances and energy and there are no anatomical and morphological deviations in the structure of plants.

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