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Peculiarities of the Accumulation of Chemical Elements by *Potentilla anserina* in the Impact Zone of Kuchiger Hydrotherms

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Abstract

The territories of discharge of ascending deep thermal waters are a unique object for studying the mineral composition of vegetation and soils under strong exposure to endogenous factors. The aim of this work was to determine the peculiarities of the accumulation of 25 chemical elements by *Potentilla anserina* L. in the impact zone of Kuchiger hydrotherms (Barguzin Depression, the Buryat Republic, Russia). The concentrations of Ca, K, Mg, P, S, and Zn in *P. anserina* plants did not vary significantly in the surveyed territory. In the zone of subaquatic discharge of ascending deep thermal waters, plants accumulated more Na, Sr, Li (near the discharge of high-temperature gryphons) and W, Mo (near the discharge of low-temperature gryphons). The maximum concentrations of Al, Mn, Ti, Cr, Ni, Co, La, and Y in the plants were found on the coastal diapir shaft with extremely high ascent activity of gas-hydrothermal mud fluids. Concentration of several elements in plant ash exceeded the clarke values for plants: Ca (K_c = 2.0–3.6), Na (K_c = 2.4–4.8), Sr (K_c = 3.5–9.5), Ba (K_c = 2.7–6.6), Li (K_c = 6.0–17.0), Sc (K_c = 6.0–21.0). The intensity of biological absorption was characterized by the biological absorption factor (BAF). The highest coefficients were found for P and S (BAF = 22.4–69.2). The elements of strong accumulation are Ca, Na, K, Mg, Mn, Sr, Zn, Cu, Li, Ni, Mo (BAF = 1.5–10.5); the rest elements were very weakly accumulated by plants (BAF = 0.1–0.9). The change in the intensity of element accumulation by plants under different conditions leads to a violation of the ratios between Fe/Mn, Fe/Zn, Cu/Mo, Ca/Sr, Ca/Ba, K/Ba, Sr/Ba.

Keywords: *Potentilla anserina*, elemental chemical composition, Kuchiger hotsprings zone

INTRODUCTION

Special attention is paid to the studies of the territories with discharges of hydrothermal waters. On the one hand, they are of great interest to determine the balneological, resort and recreation potential under the conditions of sustainable development of regions and reasonable management of natural resources [1], on the other hand, these territories serve as a unique object to study the changes of the chemical composition of vegetation and soils.

The Baikal rift zone is one of the largest active hydrothermal systems in the continental blocks of the Earth's crust. An essential sign of the manifestation of modern rift-driven processes in it is the presence of more than 600 sites of the discharge of mineral springs differing from each other in chemical composition, temperature and balneological characteristics [2–4]. Discharging waters have a substantial effect on the formation of landscapes [5, 6].

A large number of thermal water outlets are concentrated at the intersection of the Barguzin and Dyren faults in the north-eastern part of the rift zone (the north-western region of the Barguzin depression) [7]. One of the results of endogenesis manifested over this territory is a broad distribution of halomorphic ecosystems in the forest-steppe zone under the absence of salt-containing parent and sedimentary rocks. In addition, the exogenous mechanism of the formation of micro- and nano-relief, which is characteristic of floodland, is replaced by diapir, arising as a consequence of the pressure of ascending gas- and hydrothermal fluids from seismically active deep-seated faults [8, 9]. Specific features of the morphological structure [10], mineralogical composition and physicochemical properties of soils are detected [11]. The arrival of substantial amounts of sodium, sulphur, barium, strontium and rare earth elements in the soil of hydrothermal fields defines their geochemical features [12].

A complicated combination of exo- and endogenous factors of the formation of landscapes over this territory, along with the absence of any data on the biogeochemical migration of elements in the major landscape components, predetermined the relevance of the studies revealing the regularities of the accumulation of chemical elements by plants in various geochemical settings.

One of the end-to-end species growing at the regions with different kinds of gas- and hydrothermal fluid discharge in the zone affected by the Kuchiger hydrotherms is *Potentilla anserina* L. [9]. This is a monopodial rosellate vegetatively mobile plant with polyvariant ontogeny; it is characterized by increased morphological, anatomic and physiological plasticity, which allows it to grow under diverse ecological conditions [13]. This species is characterized by a broad ecological amplitude with respect to the degrees of wetting and salinization of the substrate: the plants frequently occur on floodplain, dry, alkaline meadows with different degree of bogginess, used for pasture and haying, along the banks of water reservoirs, in rarefied forest communities, and over waste lands [13, 14].

The goal of the present work was to study the effect of growing conditions on the content of macro- and microelements in the above-ground parts of *P. anserina* L. plants in the zone of discharge of thermal waters of the Kuchiger spring.

EXPERIMENTAL

The studies were carried out in the north-east of the Barguzin depression near Kuchiger ulus (Kucheger) in the Kurumkan District of the Republic of Buryatiya, at the site where the thermal waters of the Kuchiger springs are discharged (Fig. 1). The major gryphons of thermal waters have a group outlet at a distance of 25–30 m to the east from the course of a brook, which is a tributary of the Indikhen river. They are used for balneological purposes, so wooden structures intended for taking mud baths have been built above them. The chemical composition of the therms is fluoride sulphurous hydrocarbonate-sulphate (Kuldur type); these waters are characterized by low TDS, high content of silicic acid, alkaline medium (pH 9.28–9.90), increased temperature (40–50 °C) [1]. The waters of this type are distinguished by the high concentrations of a number of microelements – F, S, Si, Li, Sr, Ba [3].

Open gryphons are situated in a bog massif at a relatively large uplifted island. The bog and its peripheral parts contain many uplifted regions in the form of island and semi-island shafts having the diapir genesis and composed of the organogenous and mineral material pressed upwards. On the surface of shafts, depending on the vertical uplift, the bog-type vegetation is replaced by meadow-bog, meadow or even meadow-steppe vegetation. The surface of the alluvial plain in contact with the bog is also complicated by diapir shafts, hillocks, especially in the western part which is adjacent to the bog side. In the central part of the alluvial plain, there are many undulations in the form of fresh hillocks, subsidence sites in wetted hollows, as well as more mature, strongly flattened shafts on relatively dry positions. In the vegetation cover, the effect of endogenesis is exhibited in sharp local changes of associations, as well as in the formation of barrens that are completely or almost completely devoid of vegetation.

To collect the plants, the key plots (KP) 5–10 m^2 in size were settled at the territory under investigation (see Fig. 1). The plot KP-1 is situated at the edge of the diapir shaft formed in the bog massif in the zone of subaquatic seepage of thermal waters. A number of factors provide evidence that this region was the site of discharge of the high-temperature gryphon on top of which the therapeutic baths were arranged. This gryphon is not functioning at present. The diapir about 0.5 m high with respect to the water level in the bog is composed of rather friable fine ma-

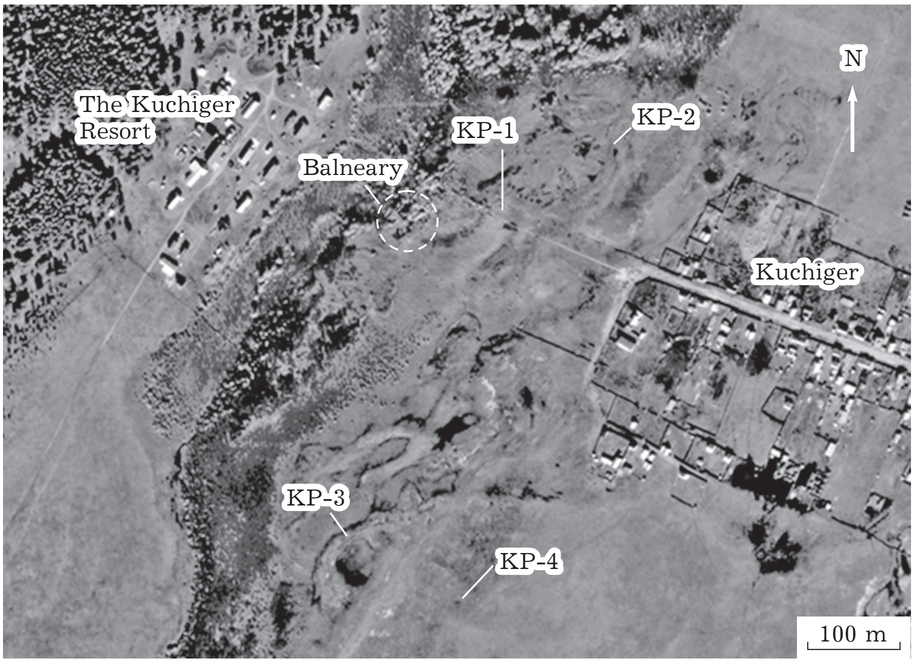

Fig. 1. An external view of the landscape, the geographic position of the Kuchiger hydrotherms and key plots (KP) in the satellite image (the cartographic service of Google).

terial; soil-like bodies were formed on its edges as a result of recent surface elevation. These bodies are composed of turbated layers of initial peat-gley and mull-gley soil on which *P. anserina* forms a monodominant community. The acidity of the upper layer of ground (0–20 cm) corresponds to pH 5.1, its humidity is 66.1 %.

The plot KP-2 is situated on the edge of the diapir shaft formed near the region where shallow lakes are accumulated in the bog, where numerous subaquatic discharges of low-temperature waters into the bog are observed as small lakes with clearly pronounced gryphons. The diapir shaft about 1 m high is characterized by higher nonuniformity of the ground substrate (mainly coarsely dispersed) and the vegetation in comparison with KP-1. The *P. anserina* L. plants form a monodominant community here. The acidity of the upper layer of ground is pH 8.3, and its humidity is 30.2 %

The plot KP-3 is located at the edge part of a high (1.5–2.0 m with respect to water level) coastal diapir shaft which is adjacent to the bog at a distance of 300–500 m downstream from open gryphons (bath site) and the plots KP-1 and KP-2. Extremely high activity of surface swelling is detected on the shaft, which is due to the ascending gas- and hydrothermal mud fluids, manifesting itself as fresh cracks on the shaft ridge, the formation of injective diapirs with extension, disruptions and turbation of host strata, as well as the formation of specific layers impregnated with oil bitumen. Here, too, *P. anserina* plants form monodominant communities on the material of initial peat-gley soil, elevated from the bog and strongly turbated. The acidity of the upper layer of ground is pH 5.7, humidity is 19.9 %.

The plot KP-4 is situated in the central part of the alluvial plain in a slightly subsiding site with closely occurring groundwater, where we assume latent subsoil and evaporative discharge of gas- and hydrothermal fluids to occur. Here *P. anserina* co-dominates in the meadow communities on wetted, strongly salinized turbated soil. The acidity of the upper layer of ground corresponds to pH 8.2, its humidity is 14.1 %.

The above-ground parts of 7 to 10 *P. anserina* plants were cut off over each KP using the square method. At the same time, the soil was sampled from a depth of 0–20 cm. The plant and soil samples were dried to the air-dry state under laboratory conditions, then the samples were ground and sieved. After that, the plant samples were mineralized in a SNOL 8.2/1100 L muffle furnace (AB UMEGA GROUP, Lietuva) at 450 °C for 3 h, the ash was dissolved in an 0.1 M solution of nitric acid. Soil samples were decomposed using a mixture of hydrofluoric, chloric and nitric acids (GOST PND F 16.1:2.3:3.11–98). The concentrations of 25 elements (Al, Ba, Ca, Ce, Co, Cr, Cu, Fe, K, La, Li, Mg, Mn, Mo, Na, Ni, P, S, Sc, Sr, Ti, V, W, Y, Zn) in the resulting solutions were determined by means of atomic emission with a SPECTRO ARCOS spectrometer (Spectro Analytical Instruments GmbH, Germany) in the certified laboratory at GKK GP RATs (Ulan-Ude, certificate No. ROSS RU.0001.511112). The analytical quality of the procedures was controlled using eth standard samples GSO RM 68, GSO 2508, GSO 2499, OSO 10235; the relative error of the method did not exceed 5–10 %.

The humidity of soil samples was determined using the gravimetric method, actual acidity (pH) was measured by means of potentiometry in water extracts with the mass ratio of soil to water 1 : 2.5 [15].

To evaluate the accumulating capacity of plants, we used the biological absorption factor (BAF), which is the ratio of element concentration in the ash of plants to its total concentration in soil. On the basis of BAF value, the elements were divided into groups: 1) vigorous accumulation (100 > BAF ≥ 10); 2) strong accumulation (10 > BAF ≥ 1); 3) weak accumulation and medium uptake (1 > BAF ≥ 0.1); 4) weak uptake (0.1 > BAF ≥ 0.01), 5) very weak uptake 0.01 > BAF ≥ 0.001 [16].

Statistical treatment of the results was carried out using standard methods [17] and a PAST v3.17 software package. The obtained data were tested for normality (Shapiro-Wilk's test, the level of significance (P) < 0.05) and equality of dispersions (Levene's test); the average values for elements (M) and the standard deviation (δ) were calculated. The differences between the key regions were estimated with the help of the several-sample tests package (ANOVA), for a significant result, the multiple comparison test (Tukey's test, $P \le 0.05$) was used.

RESULTS AND DISCUSSION

To reveal the features of the accumulation of chemical elements in *P. anserina* plants in the zone affected by thermal waters of the Kuchiger springs, a comparative analysis of the concentrations over KP was carried out, and the sequences of element accumulation in the descending order were plotted (Tables 1, 2).

Calcium and sodium dominate in the sequences of accumulation of ash-forming elements in the above-ground parts of *P. anserina* from all KP. The range within which calcium concentration varies depending on growing conditions was substantially smaller (variation coefficient (C_v = 12 %) than that for sodium (C_v = 33 %). In the zone of subaquatic discharge of thermal waters (KP-1, KP-2), sodium content in the plants increased by a factor of 1.6–1.9 in comparison with the coastal diapir shaft (KP-3) and the central part of the alluvial plain (KP-4). The concentrations of phosphorus, magnesium and potassium in the plants at the territory under study varied within narrow ranges (C_v = 11–16 %), and their order in the accumulation sequence was rather stable. The displacement of phosphorus to the last position in this group of elements was detected only in the plants from the coastal diapir shaft. The last position in the group of macroelements in the accumulation sequences for KP-2, KP-3, KP-4 is occupied by sulphur. In spite of a narrow range within which its concentration varies (C_v = 19 %), we observed a trend to an increase in sulphur content in the plants passing from the central part of the alluvial plain to the territory of subaquatic discharge of high-temperature gryphons (KP-1), which caused its shift to the third position in the accumulation sequence.

Results of the studies revealed a complicated manner of the changes of the concentrations (n, mg/kg of the dry substance) of microelements in plants. We conventionally divided microelements into four groups according to the absolute content in the above-ground parts of plants: 1) high-concentration elements (10 000 > n > 1000) – Al, Fe, Mn, Sr; 2) medium-concentration elements (1000 > n > 100) – Ba, Zn, Ti; 3) low-concentration elements (100 > n > 10) – Cu, Li, Cr, Ni, V; 4) elements that are present in very low concentrations (10 > n > 0.1) – La, Ce, Co, W, Mo, Sc, Y.

The content of the microelements of the first group in the plants at the territory under investigation varied within rather broad ranges (C_v = 62–71 %). The concentrations of aluminium, strontium and manganese at the coastal diapir shaft were 1.4–3.2 times higher, while iron concentration was 1.5 times lower than in the plants from the central part of the alluvial plain. At the territory of subaquatic discharge of hydrotherms, a decrease in aluminium and iron content in plants by a factor of 2.0–5.9 is observed, along with an increase in strontium concentration by a factor of 1.4–2.7 in comparison with the alluvial plain, especially at the site of the discharge of high-temperature gryphons, which causes the redistribution of these microelements in the accumulation sequence. In addition, manganese content in the plants at the territory of the dis-

TABLE 1

Content of macro- and microelements in the ash of *P. anserina* plants (M±δ, mg/kg) in the zone affected by the Kuchiger hydrotherms

Elements	Key plot				Clarke [[18]
	KP-1	KP-2	KP-3	KP-4	
	Macroelements				
Ca, 10^4	9.90±0.84	11.81±0.48	9.51±0.72	12.12±0.89	3.0
Na, 10^4	9.62^a±0.74	8.62^a±0.21	5.55^b±0.42	4.76^b±0.23	2.0
P, 10^4	3.60±0.24	3.46±0.14	2.89±0.22	3.97±0.22	7.0
K, 10^4	3.18±0.16	2.86±0.46	3.71±0.24	3.41±0.25	3.0
Mg, 10^4	3.19±0.20	3.09±0.12	4.13±0.36	2.94±0.28	7.0
S, 10^4	3.62±0.14	2.75±0.21	2.69±0.12	2.37±0.32	5.0
	Microelements				
Al	1500^d±112	4500^c±252	12 600^a±452	8900^b±356	1400
Fe	1500^c±94	2800^b±154	5100^a±256	7600^a±312	1000
Mn	2300^b±148	680^d±84	3700^a±248	1200^c±114	7500
Sr	2850^a±251	1440^b±116	1500^b±98	1050^c±100	30
Zn	585±84	560±72	756±128	491±52	900
Ba	310^c±36	270^c±28	510^b±25	660^a±58	100
Ti	100^d±18	160^c±24	470^a±42	370^b±39	1000
Li	187^a±19	66.32^c±9.42	119^b±18	89.32^b±7.56	11
Cu	55.40^b±9.82	101^a±12	97.84^a±10.40	79.91^a±6.54	200
Cr	8.91^c±1.21	23.43^b±2.36	36.72^a±4.22	24.12^b±1.42	25
Ni	13.42^c±1.98	19.62^b±1.84	51.51^a±10.12	18.45^b±1.14	50
V	1.93^c±0.19	5.68^b±0.48	14.31^a±3.28	14.11^a±1.08	61
Ce	1.92^c±0.06	5.74^b±0.39	9.96^a±1.24	8.24^a±1.12	0.1
La	2.09^c±0.11	5.28^b±0.12	7.91^a±0.23	6.01^b±0.24	0.1
Mo	8.39^b±0.42	16.04^a±1.26	5.69^c±0.52	6.08^c±0.46	20
W	5.01^b±0.52	9.51^a±1.18	4.88^b±0.23	5.41^b±0.42	0.2
Co	0.51^c±0.01	0.59^c±0.02	6.13^a±1.12	2.04^b±0.42	15
Sc	0.51^b±0.01	0.64^b±0.01	1.89^a±0.20	1.85^a±0.18	0.09
Y	0.51^d±0.01	0.99^c±0.02	2.55^a±0.45	1.63^b±0.12	1.0

Note. Letters in one row point to statistically significant differences between key plots ($P < 0.05$), where a > b > c > d.

TABLE 2

The series of element accumulation in *P. anserina* plants and in the soil in the zone affected by the Kuchiger hydrotherms

Key plot	Accumulation series	
	in plants	in soil
KP-1	Ca > Na > S > P > Mg > K > Sr > Mn > Al > Fe > Zn > Ba > Li > Ti > Cu > Ni > Cr > Mo > W > La > V ≥ Ce > Y ≥ Sc ≥ Co	Ca > Fe > Na > Al > S > Mg > K > P > Ti > Sr > Mn > Ba > Zn > Cu > Cr > V > W > Ce > La > Ni > Li > Mo > Sc > Y > Co
KP-2	Ca > Na > P > Mg > K > S > Al > Fe > Sr > Mn > Zn > Ba > Ti > Cu > Li > Cr > Ni > Mo > W > V ≥ Ce > La > Y > Sc > Co	Al > Ca > Na > Fe > K > Mg > Ti > S > Ba > Sr > P > Mn > Zn > V > Ce > La > Cr > Cu > Li > Ni > W > Co > Sc > Y > Mo
KP-3	Ca > Na > Mg > K > P > S > Al > Fe > Mn > Sr > Zn > Ba > Ti > Li > Cu > Ni > Cr > V > Ce > La > Co > Mo > W > Y > Sc	Al > Ca > Na > Fe > K > Mg > Ti > Ba > S > Sr > P > Mn > V > Zn > Ce > Cr > La > Cu > Ni > Y > Li > Sc > Co > W > Mo
KP-4	Ca > Na > P > K > Mg > S > Al > Fe > Mn > Sr > Ba > Zn > Ti > Li > Cu > Cr > Ni > V > Ce > La > Mo > W > Co > Sc > Y	Al > Ca > Na > Fe > K > Mg > Ti > Ba > Sr > P > Mn > S > V > Zn > Ce > Cr > La > Li > Y > Ni > Cu > Sc > Co > W > Mo

charge of low-temperature gryphons was 3.4 times lower than for the discharge of high-temperature gryphons.

Among the microelements of the second group, relatively low variation level was detected for zinc (C_v = 19 %), medium variation level was observed for barium (C_v = 42 %), and substantial variation level was detected for titanium (C_v = 63 %). A pronounced trend to a decrease in concentration in the zone of subaquatic discharge of thermal waters was established for barium and titanium: the content of these elements in plants was 2.1–3.7 times lower than at the alluvial plain. For all diapir shafts, zinc passes to the initial position in this group in the accumulation series.

A broad range of concentration variations was also observed for the microelements of the third group (C_v = 25–69 %). An increase in the concentration of lithium in the plants at the territory of the discharge of high-temperature gryphons and copper at the territory of the discharge of low-temperature gryphons leads to the transition of these elements into the group of higher content. Changes in the sequence of elements in the accumulation series are also due to an increase in nickel content (2.8 times) in the plants at the coastal diapir shaft, a decrease in vanadium concentrations (2.5–7.4 times) at the territory of subaquatic discharge of hydrotherms, and chromium (2.7 times) at the territory of the discharge of high-temperature gryphons.

The absolute values of concentrations of the elements from the very low concentration group vary greatly (C_v = 37–114 %), so do their positions in the accumulation series. For example, it was discovered that the plants growing at the coastal diapir shaft are distinguished by higher concentrations of cerium, lanthanum, cobalt, yttrium. In the zone of subaquatic discharge of hydrotherms, a decrease in the concentrations of scandium, cobalt and cerium by a factor of 3.0–3.8, 3.4–4.0 and 1.4–4.3, respectively, was detected in comparison with the concentrations found in the plants from the alluvial plain. At the territory of the discharge of low-temperature gryphons, the plants accumulate two times more molybdenum and tungsten.

It follows from the data obtained that *P. anserina* plants from all the studied sites have close elements compositions with respect to calcium, magnesium, phosphorus, sulphur, and zinc content. The plants growing in the zone affected by the subaquatic discharge of high-temperature waters (KP-1) accumulate more strontium, sodium and lithium; they are also distinguished by lower content of the III group elements (aluminium, scandium, yttrium, lanthanum), as well as iron, cobalt, barium, cerium, vanadium and titanium. Plants in the zone affected by low-temperature gryphons (KP-2) accumulate tungsten and molybdenum, while the plants at the coastal diapir shaft (KP-3) accumulate aluminium, manganese, titanium, chromium, nickel, cobalt, lanthanum, and yttrium.

The concentrations of the majority of the considered chemical elements (Mg, P, S, Al, Fe, Mn, Ti, Zn, Cu, Ni, Cr, V, Mo, Y) in the ash of aboveground parts of P. anserina were lower than the clarke level (concentration coefficient (K_c) < 1) established for plants in the world [18]. The clarke levels were exceeded for Ca (K_c = 2.0–3.6), Na (K_c = 2.4–4.8), Sr (K_c = 3.5–9.5), Ba (K_c = 2.7–6.6), Li (K_c = 6.0–17.0), W (K_c = 25.0–47.0), Sc (K_c = 6.0–21.0). Potassium concentration was within the clarke limits.

Taking into account the fact that soil is the major source from which chemical elements enter plants, accumulation series were also compiled over KP for the upper soil level (0–20 cm), and the absolute values of overall concentrations of elements were analyzed (see Tables 2, 3). It should be stressed that the series of element accumulation in the soil at KP-2, KP-3, KP-4 are rather similar to each other; some differences are observed in the shift of sulphur and copper to higher concentrations on diapirs. In addition, in the series of element accumulation characteristic of the territory of the discharge of low-temperature gryphons, a shift towards higher concentrations is exhibited by zinc, lanthanum, lithium, nickel, and tungsten.

The series of element accumulation is quite different for soil from the KP-1 plot, which is situated in the immediate vicinity from the site of the discharge of high-temperature gryphons. An increase in the concentrations of sulphur, tungsten and molybdenum by a factor of 16.9, 5.9 and 2.1, respectively, in comparison with the soil of the alluvial plain causes the shift of these elements in the accumulation series towards higher concentration. In addition, a substantial decrease in the content of a set of elements was detected in the soils, which also leads to the shift of these elements along the accumulation series. For instance, barium content decreased by a factor of 11.6, aluminium – 8.7, titanium –6.2, yttrium – 5.2, cerium – 3.7, sodium and scandium – 3.4, strontium – 2.9, cobalt – 2.8, iron – 2.5, chromium – 2.3, vanadium – 1.9, calcium – 1.7 in comparison with the soils of the alluvial plain.

TABLE 3

Content of macro- and microelements in soil (M±δ, mg/kg) in the zone affected by the Kuchiger hydrotherms

Element	Key plot				Clarke [19]
	KP-1	KP-2	KP-3	KP-4	
Macroelements					
Ca, 10^4	$2.08^b±0.22$	$2.46^b±0.34$	$2.96^{a,b}±0.12$	$3.58^a±0.31$	2.56
Na, 10^4	$0.92^c±0.14$	$2.15^b±0.11$	$2.62^a±0.21$	$3.11^a±0.30$	2.42
P, 10^4	$0.07^b±0.01$	$0.05^c±0.01$	$0.10^a±0.02$	$0.10^a±0.02$	0.07
K, 10^4	$0.19^b±0.16$	$1.85^a±0.46$	$1.81^a±0.24$	$2.07^a±0.25$	2.32
Mg, 10^4	$0.56^b±0.08$	$0.56^b±0.08$	$0.71^{ab}±0.06$	$0.99^a±0.12$	1.49
S, 10^4	$0.66^a±0.10$	$0.12^b±0.01$	$0.12^b±0.02$	$0.04^c±0.01$	0.09
Microelements					
Al	$9100^c±152$	$57\ 500^b±344$	$68\ 400^{ab}±512$	$79\ 600^a±481$	76 100
Fe	$9500^b±119$	$18\ 700^a±268$	$21\ 500^a±274$	$24\ 200^a±212$	40 600
Mn	$130^c±18$	$260^b±14$	$380^a±28$	$480^a±14$	770
Sr	$380^d±21$	$540^c±16$	$980^b±38$	$1120^a±150$	270
Zn	$30.60^b±8.40$	$67.61^a±2.27$	$38.86^b±2.88$	$51.10^a±3.52$	75
Ba	$120.00^b±3.61$	$1150.00^a±8.42$	$1240^a±25$	$1390^a±87$	628
Ti	$560^c±19$	$1870^b±74$	$2730^a±142$	$3470^a±309$	3900
Li	$8.41^b±0.99$	$18.22^a±1.42$	$8.31^b±0.78$	$15.94^a±0.56$	32
Cu	$14.92^b±0.82$	$27.72^a±1.21$	$18.42^b±1.44$	$10.51^c±1.84$	27
Cr	$14.10^b±1.71$	$26.33^a±1.36$	$30.81^a±2.24$	$32.34^a±1.42$	92
Ni	$10.54^b±2.28$	$17.14^a±1.24$	$13.90^b±1.12$	$11.26^b±1.10$	50
V	$39.25^b±1.19$	$48.44^b±4.48$	$64.82^a±5.81$	$73.92^a±10.08$	106
Ce	$11.92^b±0.64$	$38.72^a±0.34$	$38.12^a±0.24$	$44.31^a±0.12$	70
La	$11.26^c±0.11$	$30.35^a±0.14$	$19.69^b±0.13$	$23.15^b±0.24$	32
Mo	$4.27^a±0.42$	$2.05^b±0.26$	$2.43^b±0.42$	$2.04^b±0.56$	1.1
W	$29.81^a±3.52$	$10.26^b±1.80$	$5.73^c±0.27$	$5.01^c±0.62$	2.0
Co	$2.32^b±0.10$	$6.17^a±0.54$	$6.11^a±0.12$	$6.45^a±0.22$	18
Sc	$2.74^c±0.71$	$5.65^b±0.48$	$7.71^a±0.90$	$9.21^a±0.88$	10
Y	$2.71^c±0.12$	$9.21^b±0.82$	$12.52^a±1.45$	$14.07^a±2.26$	20

Notes. Letters in one row indicate statistically significant differences between key plots ($P < 0.05$), where a > b > c > d.

A distinguishing feature of the soil layer (0–20 cm) at the studied territory is a high content of sulphur with respect to the clarke of the lithosphere (K_c = 2.3–7.3) [19]. The maximal accumulation of this element is detected in the soils from the zones affected by high-temperature gryphons. Sulphur is not a typomorphous element of the landscapes of Transbaikalia and the Baikal Region, so its presence in soil may be evidence of the endogenous arrival within the dissolved salts and gases, and serve as a peculiar marker of the discharge of deep-seated fluids.

Along with sulphur, the root layer is also enriched with tungsten (K_c = 2.5–14.9), molybdenum (K_c = 2.2–3.9) and strontium (K_c = 1.4–4.1). An increased content of tungsten and molybdenum may be connected with W-Mo hydrothermal mineralization, which is confined to the zones of faults and crushing cracks [20]. High strontium content is characteristic of the Paleozoic granites of the Angara-Vitim batholith [21].

The content of the elements of iron (Fe, Mn, Co, Ni), as well as magnesium, zinc, lithium, chromium, vanadium, cerium, scandium and yttrium in the soil from all KP was below the clarke levels (K_c = 1.4–7.8). The concentrations of calcium, sodium, potassium, barium were below the clarke level in soils at the territories of the discharge of high-temperature gryphons, titanium – in the soil of diapir shafts, aluminium – in the soil of the coastal diapir and the central part of the alluvial plain.

Results of the correlation analysis of the data revealed the presence of reliable positive linear correlations between the content of iron, copper, lanthanum, sulphur, barium, titanium, chromium, aluminium, cerium, yttrium, vanadium and scandium in the ash of plants and soil (correlation coefficient $r = 0.51-0.97$, $P = 0.05$). The correlations were negative for sodium, strontium, and lithium ($r = (-0.79)-(-0.92)$, $P = 0.05$).

It was also discovered that an increase in the acidity of soil solution is accompanied by an increase in the content of magnesium, sulphur, zinc, lithium, manganese and strontium in *P. anserina* plants ($r = (-0.57)-(-0.91)$, $P = 0.05$), while the content of calcium, quite contrary, decreases ($r = 0.85$, $P = 0.05$). With an increase in soil humidity, the content of sulphur, sodium, lithium and strontium in plants increases ($r = 0.81-0.98$, $P = 0.05$), while the concentrations of copper, iron, barium, lanthanum, titanium, chromium, aluminium, cerium, cobalt, yttrium, vanadium, scandium decrease ($r = (-0.54)-(-0.91)$, $P = 0.05$).

The calculation of BAF showed that the elements most vigorously accumulated by plants are phosphorus and sulphur (BAF = 22.4–69.2) (Table 4). The elements strongly accumulated in *P. anserina* plants include calcium, sodium, potassium, magnesium, manganese, strontium, zinc, copper, lithium, nickel and molybdenum (BAF = 1.5–10.5). It should be stressed that the intensity of copper accumulation in plants decreases, while the intensity of calcium, sodium and strontium accumulation increases at the territory of the subaquatic discharge of hydrotherms. The BAF of sodium and strontium increased at the sites of the discharge of high-temperature gryphons (by a factor of 7.0–8.4). The intensity of the accumulation of manganese, zinc and lithium increased at the plots KP-1 and KP-3, molybdenum – at KP-2, nickel – at KP-3. Other elements (Al, Fe, Ba, Ti, Cr, V, Ce, La, W, Co, Sc, Y) belong to the group of weak accumulation and medium uptake (BAF = 0.1–0.9).

The changes in the intensity of element accumulation by plants from soil lead not only to differences in the absolute content of elements in plants but also to the distortions of ratios between the elements. The ratio of the concentrations of elements, especially those physiologically essential, is an important criterion to evaluate the misbalance in the elemental composition of plants [22]. It is known that Fe and Mn are interconnected in the metabolic processes in plants, and the efficiency of photosynthesis depends on the relations between these two elements. According to different data [23, 24], under natural conditions, the physiological norm of Fe/Mn varies within the range 1.2 (2.0)–2.5. According to our results, the lowest values of this ratio are observed at the territory of the discharge of high-temperature gryphons, which is evidence of the distortion of iron intake by plants (Table 5).

The Fe/Zn ratio in forage plants is 1.7, while in the steppe vegetation of Transbaikalia it is much higher (9.5) due to very high iron content [25]. For the alluvial plain, this ratio in the *P. anserina* plants reaches 15.4, while at the diapir shafts it decreases by a factor of 2.2–6.0.

The Ca/Sr ratio in plants is essential for the determination of biogeochemical provinces with high strontium content and related endemic diseases. In spite of the fact that the toxicity of strontium compounds is weak, the high level of the element in the environment is connected with the risk of the development of a number of pathologies (osteochondrodystrophy (Kashin-Bek disease), strontium rickets, and fragility of bones) due to the possibility of calcium replacement by strontium in bones. In animals and humans, this causes skeletal deformations and dwarfism [26].

TABLE 4

Biological absorption factors in the zone affected by the Kuchiger hydrotherms

Element	Key plot			
	KP-1	KP-2	KP-3	KP-4
		Macroelements		
Ca	4.80	4.80	3.20	3.40
Na	10.50	4.00	2.10	1.50
P	51.40	69.20	29.30	41.40
K	16.70	1.50	2.10	1.60
Mg	5.70	5.50	5.80	3.00
S	5.50	22.80	22.40	60.70
		Microelements		
Al	0.17	0.08	0.18	0.11
Fe	0.16	0.15	0.24	0.31
Mn	17.60	2.60	9.70	2.40
Sr	7.60	2.70	1.50	0.94
Zn	19.10	8.30	19.50	9.60
Ba	2.50	0.23	0.41	0.47
Ti	0.18	0.09	0.17	0.11
Li	22.20	3.60	14.30	5.60
Cu	3.70	3.70	5.30	7.60
Cr	0.63	0.91	1.20	0.74
Ni	1.30	1.20	3.70	1.60
V	0.05	0.12	0.22	0.19
Ce	0.16	0.15	0.26	0.19
La	0.19	0.17	0.40	0.26
Mo	2.00	8.00	2.30	3.00
W	0.17	0.93	0.87	1.00
Co	0.20	0.09	1.00	0.32
Sc	0.18	0.11	0.24	0.20
Y	0.18	0.11	0.20	0.12

TABLE 5

Element ratios in *P. anserina* plants from the zone affected by the Kuchiger hydrotherms

Element ratio	KP-1	KP-2	KP-3	KP-4
Fe/Mn	0.7	4.1	1.4	6.5
Ca/Sr	34.7	81.9	63.3	116.0
Ca/Ba	319.0	437.0	186.0	183.0
Sr/Ba	9.2	5.3	2.9	1.6
K/Ba	102.0	106.0	72.6	51.6
Cu/Mo	6.6	6.2	17.1	13.1

Judging from the criteria established for plants, the values of the ratio Ca/Sr ≥ 100 point to a satisfactory ecological situation, while Ca/Sr < 10 point to the emergency [27].

As mentioned above, the calcium content in the plants of *P. anserina* in the region under investigation did not exhibit substantial variations, while strontium content was 2.7 times higher at the territory of the discharge of high-temperature gryphons; in addition, BAF of strontium at that territory increased by a factor of 8.4. This caused substantial changes in the Ca/Sr ratio: it decreased from 115 (in the central part of the alluvial plain) to 35 (at the territory of the discharge of high-temperature gryphons). The data obtained by us are in agreement with the results of previous investigations on the basis of which geochemical provinces with anomalously high strontium concentrations in soil were revealed in the region of the Kuchiger springs [12].

A decrease in the Cu/Mo ratio in forage plants may lead to urolithiasis in agricultural animals. High molybdenum concentrations enhance the activity of xanthine oxidase, which causes the formation of uric acid and the formation of bioliths. Also, molybdenum substitutes copper and phosphorus in compounds thus causing a decrease in the activity of phosphatases and copper-containing enzymes, which distorts the protein metabolism [25]. An optimal ratio of these elements in plants is 12–16 [23], it is frequently much lower in the steppe vegetation of Transbaikalia (3.8) [25]. In the region under investigation, the Cu/Mo ratio in plants corresponded to the optimal values at the alluvial plain and on the coastal diapir shaft, while it was 2.0–2.8 times lower at the territory of subaquatic discharge of hydrotherms.

Barium content in soil-forming rocks, soils and vegetation in Transbaikalia exceeds the clarke, which leads to the distortions of its relations with other elements (first of all with calcium) and to the endemic diseases of animals (for example, osteodystrophy) [28]. Barium forms poorly soluble phosphates $Ba_3(PO_4)_2$ in plants, which also causes metabolic disorders. In the zone of subaquatic discharge of hydrotherms, the Ca/Ba ratio was nearly two times higher than at the rest of the territory. Increased concentrations of barium salts have a negative effect on the assimilation and metabolism of potassium [29]. According to our data, conjugated changes in the concentrations of these elements are observed in *P. anserina* plants ($r = 0.74$, $P = 0.05$), however, the K/Ba ratio in plants in the zone of subaquatic discharge of hydrotherms was 1.5–2.0 times higher than at the alluvial plain and the coastal diapir shaft. If the concentration of barium ions is increased, they occupy a larger number of adsorption binding sites in the root system, so the intake of some elements into the above-ground parts decreases [30]. Our data provide evidence of the possible competitive interaction of Sr/Ba. This ratio increases 1.8–5.8 times in the plants growing on diapir shafts where a decrease in barium concentrations both in plants and in the soil is detected.

CONCLUSION

It was established as a result of the investigation that *P. anserina* plants in the zone affected by the Kuchiger hydrotherms insignificantly differ by calcium, potassium, magnesium, phosphorus, sulphur and zinc content. In the zone of subaquatic discharge of thermal waters, these plants accumulated higher amounts of strontium, sodium and lithium (near the discharge of high-temperature gryphons), as well as tungsten and molybdenum (near the discharge of low-temperature gryphons). The concentrations of aluminium, manganese, titanium, chromium, nickel, cobalt, lanthanum, yttrium in the plants were maximal at the coastal diapir shaft, where the extremely high activity of the uprise of gas-hydrothermal mud fluids was detected.

In the ash of *P. anserina* plants grown at all key plots, the clarke values established for plants in the world were exceeded for the following elements: Ca (K_c = 2.0–3.6), Na (K_c = 2.4–4.8), Sr (K_c= 3.5–9.5), Ba (K_c = 2.7–6.6), Li (K_c = 6.0–17.0), W (K_c = 25.0–47.0), Sc (K_c = 6.0–21.0).

For the established range of element concentrations, close correlations were revealed between the soil and plant contents of S, Fe, Al, Sc, Ba, Ti, Cu, La, Cr, Ce, Y (r = 0.51–0.97, $P = 0.05$), as well as Na, Sr, Li (r = (–0.79)–(–0.92), $P = 0.05$).

The elements vigorously accumulated by plants include P and S (BAF = 22.4–69.2); strongly accumulated elements are Ca, Na, K, Mg, Mn, Sr, Zn, Cu, Li, Ni and Mo (BAF = 1.5–10.5). Other elements (Al, Fe, Ba, Ti, Cr, V, Ce, La, W, Co, Sc, Y) relate to the elements of weak accumulation and medium uptake (BAF = 0.1–0.9). The intensity of element accumulation from soil varied substantially depending on growing conditions, which may be one of the reasons for the distortion of the ratios of Fe/Mn, Fe/Zn, Cu/Mo, Ca/Sr, Ca/Ba, K/Ba, Sr/Ba and the development of endemic diseases in animals and humans at the territory.

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