Toxic element concentrations in lichen *Platismatia interrupta* around the geothermal power station on Kunashir Island

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Abstract. The results of the study of the gross content of 14 chemical elements in lichen *Platismatia interrupta* collected around the geothermal power station “Mendeleevskaya” on Kunashir Island are presented. The highest exceedance was noted for As in the research area. The gross content of As varies from 0.8–2.6 mg/kg in control areas and up to 5–9 mg/kg in the impact zone, i.e. the maximum excess in lichen is noted by 11.6 times. For other elements, there were no strong exceedances in the impact zone compared to the control areas. According to the results of regression analysis, a statistically reliable inverse exponential relationship between the content of As and the distance to the power station (adjusted R2: 0.86, p-value: 0.001) is traced. The average value of the enrichment coefficient for As exceeds 100, which indicates the non-substrate origin of this element.

1. Introduction

Industrial development of geothermal fields is one of the most economical and promising methods of power generation. However, operations carried out on geothermal fields can destroy local ecosystems, including mechanical damage to natural landscapes, water and air pollution [1, 3]. Geothermal steam often contains a large amount of salts and among them are very often ions of F, B3+, As3+, 5+ and heavy metals. Geothermal steam also contains from 0.5 to 6 % by weight non-condensable gas, mostly CO2, H2S, CH4, NH3 [7]. Concentrations of H2S in natural steam range significantly from 30 mg/l and up to 500-1000 mg/l as per the particular deposit.

The content of hydrogen sulfide in the air above 50 mg/l paralyzes a human, and death occurs at higher concentrations. Such accumulations of hydrogen sulfide occur on geothermal fields [4]. A toxic substance – ammonium in high concentrations – 88 mg/l was found in the condensate of the steam discharged into the environment by the geothermal power plant on the Iturup Island [5]. The release of carbon dioxide into the atmosphere together with the evaporation of a large amount of water can lead to thermal pollution of the environment and local changes in climatic conditions, especially in the areas with big power stations [7]. In the areas of modern volcanism of the Kuril region, all uses of thermal waters are possible. There are high regional average values of deep heat flow – up to 92 mW/m² and there are many thermic anomalies – natural hydrothermal outputs of a wide variety of composition and temperature [7].

The purpose of this work is to assess the gross content of a number of toxic elements in thalluses of the lichen *Platismatia interrupta* W.L. Culb. et C.F. Culb. and to determine the spatial distribution of toxic chemical elements around the geothermal power station “Mendeleevskaya” on Kunashir Island. Research on lichen accumulation of pollutants in the area of operation of the geothermal power station “Mendeleevskaya” on Kunashir Island is performed for the first time. There is not much research on the
impact of geothermal power plants on the environment by lichenoidication methods, due to the specifics of production and the difficult access to facilities. There are two such geothermal power stations on Kuril Islands. The first researches of impact of geothermal power stations and geothermal wells on lichens were carried out in Italy and Mexico [16, 8, 10]. Laboratory studies of lichens collected on geothermal fields in Italy showed an increased level of toxic elements such as S, B, As, Hg and others [2, 6, 9].

2. Research area
Research was performed around the geothermal power station “Mendeleevskaya” in the vicinity of the town of Yuzhno-Kurilsk at the foot of the Mendeleev volcano (figure 1). Mendeleev volcano shows intense fumarolic activity. The “Mendeleevskaya” geothermal power station operates on the basis of the geothermal field “Goryachiy Plyazh” since 2002 year and provides an electricity to Yuzhno-Kurilsk town. The power of the station at the moment is 3.6 MW. The steam-water mixture is discharged from the pipes in the vertical and horizontal directions, in windless weather, the steam tail of the vertical pipe can reach a height of more than 10 m and extends tens of meters around the power plant. The vegetation of the research area is typical for the island of Kunashir and is represented by coniferous forests formed by Picea glehnii (F.Schmidt) Mast., P. jezoensis (Siebold & Zucc.) Carrière and Abies sachalinensis (F.Schmidt) Mast. with the dominance of the first. The grass layer is formed by representatives of the genus Sasa Makino & Shibata. The average age of coniferous trees in the surveyed forest areas is 100–150 (200) years.

![Map of Kuril Islands showing the location of Mendeleevskaya geothermal power station and Goryachiy Plyazh village.](image)

**Figure 1.** Research area: a – geothermal power station “Mendeleevskaya”, b – Goryachiy Plyazh village, c – north-eastern sulphatric field of the Mendeleev volcano.

3. Materials and Methods
The widespread lichen *Platismatia interrupta* from the bark of *Picea glehnii* was used for chemical analyses. Samples of the lichen were collected in August 2015 in the vicinity of the geothermal power station “Mendeleevskaya” from 9 sites remote from the power plant at different distances in all directions. Thalluses of the lichen were investigated on the content of 14 chemical elements – Al, S, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Mo, Cd, Pb, Hg by a mass spectrometry method with inductively connected plasma on the Agilent 7500a device by the technique FR.1.31.2009.06787. The required amount of test substance is 1 g of dry weight of lichen material. Samples were taken from at least 6 tree trunks per site in each study area on 1.2–1.8 m above the level of soil cover, as described in the “Monitoring with Lichens” manual [13].

To assess the effect of the composition of the Earth’s crust on the elemental composition of samples [17, 12, 15], widely used calculated enrichment factors were used for each element (X) with respect to
the content of this element of the reference material and the content in the sample and reference material of the reference element by the formula:

\[ EF = \frac{\left( \frac{X}{\text{reference element}} \right) \text{in lichen}}{\left( \frac{X}{\text{reference element}} \right) \text{in reference material}} \]

For reasons described [17, 11], the upper continental crust [18] was chosen as the reference material, and aluminum is chosen as the reference element (Fe, Ti and Sc are also often used as the reference element).

4. Results and discussions

Gross content (mg/kg) of chemical elements in the lichen *Platismatia interrupta* (except Cd, the contents of which were obviously smaller than the detectable values) are shown in the Table 1.

| №  | Al   | S    | Cr | Mn  | Fe   | Co | Ni | Cu   | Zn   | As | Mo | Hg | Pb |
|----|------|------|----|-----|------|----|----|------|------|----|----|----|----|
| 1  | 752.0| 763.5| 1.5| 204.2| 577.4| 0.5| 1.4| 4.0  | 32.4 | 8.6| 0.3| 0.0| 3.5|
| 2  | 401.6| 517.1| 3.3| 240.6| 407.4| 0.4| 0.8| 5.1  | 28.7 | 5.0| 0.3| 0.0| 3.8|
| 3  | 507.3| 806.8| 3.5| 99.7 | 473.4| 0.5| 2.0| 4.8  | 35.1 | 9.0| 0.3| 0.0| 6.1|
| 4  | 1397.1| 797.4| 3.4| 160.6| 984.1| 0.5| 1.5| 5.0  | 40.5 | 7.5| 0.3| 0.0| 5.8|
| 5  | 547.2| 674.9| 1.8| 76.3 | 536.4| 0.5| 2.1| 4.9  | 29.0 | 1.3| 0.4| 0.0| 5.1|
| 6  | 627.8| 933.7| 5.4| 99.9 | 593.4| 0.6| 1.6| 5.0  | 37.5 | 2.6| 0.4| 0.1| 5.9|
| 7  | 690.8| 659.6| 3.5| 162.7| 620.0| 0.4| 1.1| 3.7  | 33.4 | 1.5| 0.2| 0.1| 5.2|
| 8  | 605.7| 577.0| 1.4| 133.7| 542.3| 0.5| 1.4| 3.9  | 28.6 | 0.8| 0.3| 0.0| 4.5|
| 9  | 660.8| 757.5| 3.5| 168.2| 524.7| 0.4| 1.3| 4.7  | 34.0 | 1.1| 0.2| 0.0| 5.3|

Geothermal power plant steam is discharged through two pipes located in the northern and southern parts of the station. Plots 1–4 are located in forest areas most exposed to steam. Their distance from the pipes is 122–242 m. They are in the impact zone. Damaged lichens were noted on trees in the impact zone. The trees themselves on the edge of the forest are strongly damaged or dead (figure 2).

Figure 2. Damaged fir trees in impact area of the geothermal power station “Mendeleevskaya” on the Kunashir Island (left picture), geothermal steam discharge (right picture).
Sampling plots 5–9 are remoted from pipes by distance 468–1028 m; they are less exposed to emitted vapors. They represent control areas. For most of the elements, the gross content in the impact and control zones do not have statistically significant differences. Data for all sites are uniform – the coefficient of variation does not exceed 33.5% for all elements except Al (39%) and Cr (40%). The main exception is As. In control areas, its content is 0.8–2.6 mg/kg, and in the impact zone – 5–9 mg/kg, the coefficient of variation is 78%. The maximum excess relative to the minimum is 11.6 times.

Based on the results of regression analysis for As only, a statistically reliable inverse exponential relationship between its content and the distance to power station (adjusted R² 0.86, p-value: 0.001) is traced. Mapping of As content in the lichen *Platismatia interrupta* by inverse distance weighting method was also performed. The scattering diagram and spatial distribution map are shown in figure 3.

![Figure 3](image-url)

**Figure 3.** Scatter plot of gross content of As in the lichen *Platismatia interrupta* (y axis, mg/kg) at various distances from power station discharge pipes (x axis, m) and spatial distribution of elements (IDW interpolation). Full circles indicate the places of discharge of vapors (pipes), hollow circles – sampling areas, isolines on the map show the content of As in lichen thalluses in mg/kg.

For the remaining elements, the "zero" hypothesis was confirmed – no statistically significant correlations between the gross content in the lichen and the distance to the used predictors were noted. As predictors, the distance to pipes, access road and power station border were used. The spatial distribution of the gross content of these elements does not show patterns and general trends.

An enrichment factor (EF – enrichment factor) was calculated to estimate the ratio of anthropogenic to natural lithogenic sources of chemical elements entering the environment. The EF values are shown in figure 4.

It is generally accepted that EF values up to 5 indicate that the accumulation of elements in lichen thalluses comes from a reference material – the Earth's crust [17, 12, 11]. Thus, it can be concluded that Fe, Co, Ni and Cr (as well as the reference material Al) have a generally lithogenic occurrence. The next group of elements – Cu, Mn, Mo, Pb, Zn – have average EF values from 21.6 to 63.9 with minimum values from 10.4 to 35.3. Moreover, their spatial distribution is relatively uniform – the coefficient of variation is 11–17% for all these elements, except Mn (33.4%).

The gross content of S is characterized by average homogeneity (coefficient of variation 16.7%). At the same time, the average EF is 149.4 (74.9–208.8), which indicates the unsubstantiated nature of its origin. We can assume that the high S content is associated with the activity of the Mendeleev volcano – 2 km southwest of the power plant is the northeast solfataric field, on which sulfur was mined in significant quantities in the past. In addition, the Kisliy stream flows from the solfataric field. Its channel approaches the power station up to 450 m. Along the stream there are three groups of thermal springs. Their waters also contain H₂S [19].
As is the only element characterized by high EF (average value is 111, ranging from 21 to 302) and high sample heterogeneity – a coefficient of variation of 77.5 %. In addition, as mentioned earlier, the gross content of As in lichen thalluses correlates closely and statistically reliably with the distance to the pipes.

As is a toxic substance and has an adverse effect on plants. The increased content of As in the soil leads to the dumping of needles and the death of thin roots of coniferous trees, reduces the growth of plants and development of mycorrhiza [14]. This is probably one of the reasons for the damaged trees and necrosis of lichens in the research area.

5. Conclusion
The results of the analysis of the content of toxic elements in the thalluses of the lichen *Platismatia interrupta* in the vicinity of the geothermal power station “Mendeleevskaya” show a mostly homogeneous distribution. In accordance with the values of the accumulation coefficient, Cu, Mn, Pb, Zn, As and S have a non-substrate origin.

For most elements, the relationship between their content and the predictors considered was not confirmed. The spatial distribution of their gross content does not show patterns and general trends and requires further study.

The high value of EF for S in combination with the average uniformity of distribution suggests that the source of S compounds is the solphataric activity of the Mendeleev volcano.

High EF value for As, non-uniformity of distribution and high correlation coefficient of gross content of As with distance to power station discharge pipes are noted. Due to usually increased content of As in geothermal products, it is very likely that the source of As supply to lichen thalluses is a steam discharged by a geothermal power plant. Apparently, As is one of the reasons for the noted necrosis of lichen thalluses and the damaged trees in the impact zone. The impact of power station on the surrounding ecosystems was noted at a distance of up to 400 m from steam discharge pipes.

References
[1] Ármannsson H and Kristmannsdóttir H 1992 Geothermal environmental impact *Geothermics* 21 56 pp 869–880
[2] Bargagli R and Barghigiani C 1991 Lichen biomonitoring of mercury emission and deposition in mining, geothermal and volcanic areas of Italy *Environmental Monitoring and Assessment* 16 3 pp 265–275
[3] Belousov V I and Belousova S P 2002 Natural disasters and environmental risks (on the example of the development of geothermal energy) (Petropavlovsk-Kamchatsky: Publishing House of KSPU)
[4] Ellis A J 1977 Geothermal fluid chemistry and human health Geothermics 6 3 pp 175–182
[5] Ezhkin A K, Zharkov R V and Kordyukov A V 2015 Assessment of the impact of the Okeanskaya geothermal power plant (Baransky volcano, Iturup Island) on the environment by the lichenoinidication method Bulletin of the FEB RAS 2 pp 109–117
[6] Ferrara R, Maserti B E, Andersson M, Edner H, Ragnarson P, Svanberg S and Hernandez A 1998 Atmospheric mercury concentrations and fluxes in the Almadén district (Spain) Atmospheric Environment pp 3897–3904
[7] Kononov V I 1983 Geochemistry of thermal waters of the regions of modern volcanism (rift zones and island arcs) (Publishing House “Science”) p 379
[8] Loppi S 1996 Lichens as bioindicators of geothermal air pollution in central Italy Bryologist 99 1 pp 41–48
[9] Loppi S and Bonini I 2000 Lichens and mosses as biomonitors of trace elements in areas with thermal springs and fumarole activity (Mt. Amiata, central Italy) Chemosphere 41 9 pp 1333–36
[10] Loppi S and Nascimbene J 1998 Lichen bioindication of air quality in the Mt. Amiata geothermal area (Tuscany, Italy) Geothermics 27 3 pp 295–304
[11] Loppi S, Pirintsos S A and De Dominicis V 1999 Soil contribution to the elemental composition of epiphytic lichens (Tuscany, central Italy) Environmental Monitoring and Assessment 58 2 pp 121–131
[12] Nash T H and Gries C. Lichens as indicators of air pollution in The Handbook of Environmental Chemistry (New York: Springer-Verlag) Ed O Hutzinger 4 Part C pp 1–29
[13] Nimis P L, Scheidegger C and Wolseley P A 2002 Monitoring with lichens—monitoring lichens in Monitoring with Lichens—Monitoring Lichens (Springer Netherlands) pp 1–4
[14] Ormrod D P 1978 Pollution in Horticulture (Elsevier, Amsterdam, The Netherlands) p 260
[15] Paoli L, Munzi S, Gutтовá A, Senko D, Sardella G and Loppi S 2015 Lichens as suitable indicators of the biological effects of atmospheric pollutants around a municipal solid waste incinerator (S Italy) Ecological Indicators 52 pp 362–370
[16] Peralta M G and Carmona A C 1995 Líquenes como indicadores biológicos en el campo geotérmico Los Azufres, Michoacáan, México Geotermia 11 pp 137–143
[17] Puckett K J and Finegan E J 1980 An analysis of the element content of lichens from the Northwest Territories, Canada Canadian Journal of Botany 58 19 pp 2073–89
[18] Rudnick R L and Gao S 2003 Composition of the continental crust Treatise on geochemistry 3 pp 1–64
[19] Zharkov R V 2014 Thermal springs of the South Kuril Islands (Vladivostok: Dalnauka) p 378