Accumulation of heavy metals with the lichen thalli of *Cladonia rangiferina* L. at the roadside phytocenoses of the West Siberian Subarctic

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Abstract. The article reflects the results of a comparative analysis of the content and accumulation of heavy metals such as chromium, lead, nickel, zinc in the thalli of *Cladonia rangiferina* L. in the anthropogenic phytocenoses of the West Siberian Subarctic, Russia. The next series of accumulations of heavy metals in descending their concentrations in soils is Zn > Pb > Cr > Ni. Analysis of the results showed that among the factors affecting the accumulation of elements, the most significant was the distance from the highway. The content of most elements is significantly (p <0.05) related. *Cladonia rangiferina* L. accumulates heavy metals depending on the location of the sampling point relative to the source of pollution. The coefficient of biological absorption, as well as the biogeochemical activity of the species, varies in different areas but has the greatest value in areas close to the source of anthropogenic load.

1. Introduction

The *Cladonia rangiferina* L. belongs to a group of lichens that grow well in warm and cold types of climate, but the tundra is still the ideal place. Possessing high resistance to large frosts, the plant is indispensable in the diet of many animals. In appearance, the reindeer lichen is a branched tubular sinuous overgrown, which is very soft and pleasant to the touch. However, it is very fragile when dry, it crumbles easily. The plant is of great national economic importance. As is known, it serves as one of the most important forage plants for deer in the tundra.

The when dry makes up to 1/3 of the reindeer ration. The value of moss is high nutritional value, it is rich in carbohydrates, well absorbed by deer. Playing the role of the basis of the diet for reindeer in the winter, lichens serve as a source of pollutants in trophic chains [1], [2].

Among the many environmental pollutants of technogenic origin, heavy metals are the most common and toxic. Therefore, their effect on plant objects has been actively studied for many years. Pollution of the environment near the roads leads to a change in the roadside soil [3-6].

Lichens are the edificators of many plant communities of northern phytocenoses. There is a known increased sensitivity of this group of organisms to various forms of anthropogenic impact and the absorptive capacity of thalli with respect to a number of chemical elements, including heavy metals. However, in the conditions of the North, research devoted to the issues of the distribution and accumulation of heavy metals in the environment were developed only in recent decades.

Based on the foregoing, the purpose of this work is to study the characteristics of the
accumulation of heavy metals in the thalli of *Cladonia rangiferina* L. growing on the territory of the West Siberian Subarctic.

2. Materials and Methods

2.1. Selecting sites

To determine the degree of anthropogenic impact, observational sites with different intensities of technogenic load were selected.

Section 1. The watershed ridge near the highway is located 30 km north of the city of Novy Urengoy, Yamalo-Nenets Autonomous Okrug, Russia. The view of the natural area is the northern taiga-forest-tundra (N 66°05'131, E 76°19'897).

Section 2. The natural zone type is the sedge-cotton grass-sphagnum tundra-shrub tundra; a road near the town of Nadym, Yamalo-Nenets Autonomous Okrug, Russia (N 75°56'823, E 75°16'475).

Section 3. The natural zone type is the northern valley taiga, the highway is located 20 km from the town of Pangody, Yamalo-Nenets Autonomous Okrug, Russia (N 66°48'420, E 76°24'522).

Section 4. (7E, 7A, 7B). This is a highway near the village of Tazovsky, Yamalo-Nenets Autonomous Okrug, Russia (N 67°29'358, E 78°44'469).

2.2. Soil sampling

Soil sampling and sample preparation for quantitative chemical analysis were carried out in accordance with [7], [8]. Five samples taken from each site. Samples were taken at a distance of 10, 25, 50 meters from the roadway.

2.3. Sampling Cladonia rangiferina L.

Sampling of plant material, their preparation for quantitative chemical analysis, was carried out from areas of 20 × 20 cm, in accordance with [9], [10]. The composition of lichen syusus was divided, and a homogeneous sample without dead parts was left for analysis.

2.4. Sample preparation

Sample preparation was carried out using the speedwave MWS-2 microwave decomposition system from Perkin Elmer (USA). A soil sample of m=4.0 g was placed in a plastic tube, then HNO₃:HCl=1:3 was added. The tube was placed in a microwave oven to decompose the sample using the program recommended by the furnace manufacturer, using the following heating mode: raising the temperature to 200°C for 5 min, keeping for 5 min at 200°C, cooling to 45°C. The dissolved sample was transferred to a 15 ml tube, adjusting the volume to 10 ml with distilled water, and the analysis was performed.

For the decomposition of plant samples, it (m = 0.3 g) was placed on a tube, then was added H₃SO₄:H₂O₂=1:3. The following decomposition steps were carried out in the same manner as previously described.

Quantitative chemical analysis of the accumulation of trace elements and heavy metals Zn, Pb, Cr, Ni in soil and plant samples was carried out by inductively coupled plasma on an OPTIMA-7000DV atomic emission spectrometer (Perkin Elmer, USA). For calibration, standard solutions from Perkin Elmer (USA) were used.

2.5. Biological absorption coefficient

To assess the efficiency of absorption of heavy metals, the coefficient of biological absorption ($A_x$) is used. It is the content of the trace element in the ash of plant material for its content in the root zone of the soil [1]:

$$A_x = I_x / n_x$$ (1)
Where $I_i$ is the content of the $i$-th heavy metal in plant ash, mg / kg; $n_i$ is the content of the $i$-th heavy metal in the soil, mg / kg. An index value from 1 to 10 indicates an intense accumulation of the element by the plant; from 0.1 to 1 is an average accumulation; from 0.01 to 0.1 is a weak absorption; from 0.001 to 0.01 means absence of biological accumulation of the element [11].

2.6. Biogeochemical activity of species (BCA)

The biogeochemical activity of the species expresses the general ability of the species to concentrate microelements, it is an integral characteristic allowing to quantify the ability of plants to accumulate trace elements [12].

Statistical processing of the results was carried out in the software package Statistica 10.0. Arithmetic averages (X), standard arithmetic mean (SD) errors, estimates of the significance of differences in arithmetic averages by Student’s t-test were calculated.

3. Results

The concentration of chromium in the soils of the studied areas varied from 0.001 to 0.01 mg / kg; Zn (ave. 14.78 ± SD, 12.69 ± SD for Pb (ave. 13.68 ± SD); 0.35-12.30 for Ni (ave. 6.32 ± SD); 4.78-28.30 for Zn (ave. 16.54 ± SD). According to the average content, the studied elements are presented as the next row (in decreasing concentration): Zn > Pb > Cr > Ni.

To study the accumulation of heavy metals in plant objects, their accumulation was determined in the thalli of Cladonia rangiferina L. (Table 1).

**Table 1.** The content of heavy metals ($I_i$), the coefficient of biological absorption ($A_i$), and the biogeochemical activity of the species (BCA) in the thalli of Cladonia rangiferina L.

| $L$, m | Cr   | Pb   | Ni   | Zn   | BCA |
|-------|------|------|------|------|-----|
|       | $I_i$ (mg / kg) | $A_i$ | $I_i$ (mg / kg) | $A_i$ | $I_i$ (mg / kg) | $A_i$ |
| Section 1 |       |      |      |      |     |
| 50    | 7.61±0.04* | 0.6  | 10.23±0.09* | 0.5  | 4.03±0.03* | 0.6  | 4.47±0.02* | 0.6  | 2.3  |
| 25    | 9.32±0.08* | 1.1  | 14.69±0.08 | 1.1  | 6.78±0.02 | 1.2  | 6.09±0.04* | 1.1  | 4.5  |
| 10    | 11.36±0.07 | 1.6  | 18.25±0.09 | 1.3  | 9.12±0.03* | 1.6  | 7.17±0.03* | 1.5  | 6.0  |
| Section 2 |       |      |      |      |     |
| 50    | 4.69±0.02* | 0.5  | 11.23±0.09 | 0.3  | 3.69±0.01* | 0.3  | 6.00±0.02* | 0.6  | 1.7  |
| 25    | 6.35±0.04* | 1.0  | 12.36±0.08 | 0.9  | 5.69±0.02 | 1.0  | 7.71±0.04* | 1.1  | 4.0  |
| 10    | 9.21±0.05 | 1.6  | 16.02±0.06 | 1.5  | 8.96±0.04 | 1.8  | 12.48±0.03 | 1.3  | 6.2  |
| Section 3 |       |      |      |      |     |
| 50    | 7.04±0.03* | 0.7  | 8.36±0.06* | 0.8  | 4.70±0.09* | 0.8  | 6.89±0.02 | 0.6  | 2.9  |
| 25    | 10.36±0.04 | 0.8  | 9.36±0.07* | 0.9  | 6.41±0.09* | 0.9  | 7.48±0.02* | 0.8  | 3.4  |
| 10    | 13.02±0.07 | 1.2  | 13.20±0.09 | 1.6  | 11.52±0.08 | 1.3  | 8.40±0.03* | 1.4  | 5.5  |
| Section 4 |       |      |      |      |     |
| 50    | 8.03±0.09* | 0.4  | 12.69±0.08 | 0.8  | 8.34±0.10* | 0.7  | 8.49±0.02* | 0.3  | 2.2  |
| 25    | 12.69±0.08 | 1.6  | 14.32±0.09 | 1.5  | 10.58±0.12 | 1.2  | 9.78±0.06* | 0.7  | 5.0  |
| 10    | 14.78±0.09 | 1.9  | 17.36±0.09 | 1.9  | 17.39±0.10 | 1.9  | 12.89±0.07 | 1.6  | 7.3  |

Note: * differences from control are significant at p <0.005.

Analyzing the results obtained on the content of heavy metals in the thalli of Cladonia rangiferina L. shows that their greatest accumulation is observed on the sections nearest to the highway (10 meters). The content of Cr in all the studied sites varied at 4.69-14.78 (9.74 ± SD on average), 8.36-18.25 for Pb (ave. 13.31 ± SD), 3.69-17.39 for N (ave. 10.54 ± SD), 4.47-12.89 for Zn (ave. 8.68 ± SD) mg / kg.

The average concentration of heavy metals in the soil significantly exceeds their concentration in the Cladonia rangiferina L. thalli in areas remote from the source of anthropogenic load, but their accumulation in lichens increases in areas close to the highway.
The high correlation between the metal content of *Cladonia rangiferina* L. thalli and the soil of the studied areas is noted \((r = 0.95-0.99)\).

To characterize the intensity of the absorption of elements by *Cladonia rangiferina* L. thalli from the soil, the biological absorption coefficient \((A_x)\), as a ratio of the metal content in the plant to its gross content in the soil, is calculated. The transfer of heavy metals from soil to lichen occurs through biological absorption of elements by biomass. The danger of pollution is higher, the greater the number exceeds 1. The highest coefficient of biological absorption is in the areas 1, 2, 3, 4 (10 meters from the highway) in relation to Cr, Pb, Ni and Zn. Also, the highest rate of biological absorption coefficient \((A_x > 1)\) is in areas 1, 2, 4 (Cr, Ni), 1, 4 (Pb), 1.2 (Zn) (25 meters from the highway).

In all areas, the coefficient of biological absorption is from 0.1 to 1 (an average accumulation is \(A_x \leq 1\) for Cr, Pb, Ni, and Zn (50 meters from the highway), with the exception of the following sections: 2 \(A_x = 0.9\) (Ni); 3 \(A_x = 0.8-0.9\) (Cr, Pb, Ni, Zn); 4 \(A_x = 0.7\) (Zn) (25 meters from the highway).

The magnitude of the biogeochemical activity of the species (BCA) depends mainly on the quantity and composition of the pollutants most vigorously absorbed by plant objects, and to a lesser extent on the elements that are poorly captured. The biogeochemical activity of the species in the plots varied from 1.7 to 7.3, the highest value was noted at plots 1 (6.0), 2 (6.2), 4 (7.3) 10 meters from the highway.

4. **Discussion**

A number of authors note that the content of heavy metals in lichen thalli correlates with the intensity of anthropogenic activity, with vehicle emissions, first of all. The spatial distribution of elements has a direct relationship with the sources of emissions. The maximum content is observed near the highways, the minimum is in green areas \([1],[13],[14]\). In our studies, the biological absorption coefficient \((A_x)\) is calculated. It showed the movement of heavy metals by bioabsorbing elements through biomass. The highest result was found at the nearest point, 10 meters from the highway.

Many researchers note that the degree of biological absorption of heavy metals by the lichenbiota is inversely proportional to their concentration in the environment. Lichens absorb heavy metals not only from the soil but also from the atmosphere, sometimes they absorb up to half of the elements they contain \([2],[15],[16]\). Studies have shown that in less polluted areas, an average concentration of heavy metals in the soil significantly exceeds their concentration in *Cladonia rangiferina* L thalli. In areas close to the highway, their accumulation increases.

5. **Conclusion**

The analysis of the obtained data allowed us to construct the next elemental series of the accumulation of heavy metals according to their decreasing concentrations in soils: Zn > Pb > Cr > Ni. The intensity of biological absorption and the magnitude of the biogeochemical activity of the species were assessed. A direct relationship between the content of heavy metals in the thalli of *Cladonia rangiferina* L. and their habitat was found.

The degree of accumulation of pollutants in the thalli of *Cladonia rangiferina* L. is determined by the distance of the latter from the point of emission. The highest concentrations of heavy metals were recorded at a distance of up to 10 km from the source, which the biogeochemical activity of the studied species confirms.

Epiphytic lichens are distinguished by the ability to accumulate various chemical elements in thalli, which serves as the basis for using them in monitoring environmental pollution. Initiated studies should be continued in the direction of determining the content of pollutants in various components of ecosystems. By increasing the content of heavy metals in lichens, roadside phytocenoses, we can judge the deterioration of the environment.
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