Հայաստանի Հանրապետության գիտությունների ազգային ակադեմիա
Երիտասարդ գիտաշխատողների հոդվածների ժողովածու
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BIOGEOCHEMISTRY OF LICHENS IN CONDITIONS OF URBAN POLLUTION

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The study aimed at clarification of biogeochemistry of widely distributed ubiquitous and tolerant lichen *Parmelia saxatilis* in conditions of contamination of Yerevan agglomeration by heavy metals (HMs). It is found out that with increase in air pollution, *P. saxatilis* shows decreased number of apothecial thallomes and increased number of isidiosic individuals. The lichen shows a sharp increase in biogeohemical activity of HM accumulation in urban territory compared with background, but individual metal-selective properties in relation to the row of pollutants (Mo, Cr, Ni, Pb). A decreasing row of HM accumulation in lichen (Mo>Ag>Pb>Cu>Cr>Ni, Co, Zn) reflects in quantitative terms a geochemical row of atmospheric pollutant flow.

***Արևշատյան Ս.*, Քարաքոսների կենսաերկրաքիմիան քաղաքային աղտոտման պայմաններում:** Հետազոտության նպատակն էր Երևան քաղաքի ծանր մետաղներով (ԾՄ) աղտոտման պայմաններում *Parmelia saxatilis* լայն տարածված և դիմացկուն քարաքոսի կենսաերկրաքիմիայի ուսումնասիրությունը: Բացահայտված է, որ աղտոտման աճին զուգընթաց *P. saxatilis* նվազում է ապոտեցիալ թալոմների քանակը և ավելանում է իզիդիոզ նմուշների թիվը: Հավաքագրված նյութը ենթարկված է ԾՄ-ի տարալուծման, որի արդյունքում բացահայտվել է, որ *P. saxatilis* մոտ քաղաքային աղտոտման պայմաններում` ֆոնի համեմատությամբ կտրուկ աճում է ԾՄ-ի կուտակման կենսաերկրաքիմիական ակտիվությունը: Սակայն դիտվում է մի շարք աղտոտիչների վերաբերյալ (Mo, Cr, Ni, Pb) անհատական ընտրասեռում: Բացահայտված է, որ քարաքոսում ԾՄ-ի կուտակման նվազող շարքը (Mo>Ag>Pb>Cu>Cr> Ni,Co,Zn) որակապես արտացոլում է մթնոլորտային աղտոտման երկրաքիմիական շարքի հոսքը:

***Аревшатян С.* Биогеохимия лишайников в условиях городского загрязнения.** Целью исследования было изучение состояния биогеохимии космополитного и толерантного лишайника *Parmelia saxatilis* в условиях загрязнения г.Еревана тяжелыми металлами (ТМ). Выявлено, что с ростом загрязнения у *P. saxatilis* уменьшается количество апотециальных талломов и возрастает число изидиозных экземпляров. Собранный материал проанализирован на содержание ТМ, в результате чего выяснено, что у *P. saxatilis* в условиях городского загрязнения в сравнении с фоном резко возрастает биогеохимическая активность накопления ТМ, однако отмечается индивидуальная металлонакопительная селективность в отношении ряда поллютантов (Mo, Cr, Ni, Pb). Выявлено, что убывающий ряд накопления ТМ в лишайнике (Mo>Ag> Pb>Cu>Cr> Ni, Co, Zn) качественно отражает геохимический ряд потока атмосферного загрязнения.

Introduction. International experience in bioindication of environmental pollution with heavy metals (HMs) claims that the lichens hold the highest levels of metal accumulation [12, 14, etc.]. Methodology of biogeochemical lichen-indication (BGChL-indication) in relation to HMs is widely verified for all types of man-made pollution [7, 10, 18, etc.], but predominantly for forest areas with plain relief. For the mountainous areas, such works are lacking [16]. In Armenia, we first perform verification of this technique in Yerevan City [3, 4]. This paper aims at studying biogeochemistry of ubiquitous lichen *Parmelia saxatilis (L.) Ach.* in conditions of Yerevan pollution by HMs.

Material and Methods. The studies were conducted by transect geobotanical observations and ecologo-geochemical verification of the area which became sparser in potentially clean places (Forest Park zones) and became denser near factories and adjacent lands. The lichen thallomes were collected from 4 sides in each sampling point strictly according to the maps, air dried, ground, ashed ($t=500^0C$) and analyzed for HM contents by quantitative spectral analysis. The quantitative characteristics of HM accumulation by lichens were determined by comparison of actual material with data from background areas using a number of geochemical parameters:

– Coefficient of concentration [6] – $$CC = C_i / C_b \quad (1),$$
where C_i – concentration of a chemical element in the sample, C_b – background concentration;

– Polynov-Perelman's coefficient of bioaccumulation [15] – $$A_x = C_x / N_x \quad (2),$$
where C_x – concentration of a chemical element in the sample, N_x – clark of a chemical element in lithosphere;

– Coefficient of biogeochemical activity of the species [2] – $$CBGChA_x = \Sigma A_x / n \quad (3),$$
where ΣA_x – sum of A_x, n – number of studied chemical elements.

Results and Discussion. It is found from transect geobotanical observations of Yerevan depression that the basic part of this territory (up to 1250-1300 *m* elevations) is deprived of lichen cover, only the lichen *Prosa sp.* occurs sometimes on limy substrates (pH ≥ 7) from northern exposure in Hrazdan riverside. The pattern of lichen flora distribution in urban agglomeration is similar to other large industrial centers in Europe: from periphery towards the center. According to R. Sernander's [19] classification, the central and southern portions of the city belong to the *lichen* desert, followed by the Kanaker slopes having the trivial acidophilic epiphytes (*Xanthoria parietina* (L.) Th. Fr., *Physcia pulverulenta* (Schreb.) Hampe.) and epilites (*Parmelia saxatilis* (L.) Ach., *Xathoria elegans* and others). The results of these studies do not allow to carry out the lichen indication of Yerevan city through the distribution areas of individual species, as most ubiquitous species have disjunctive pattern of distribution, the lichen flora and ecology of species are unequally studied [1, 5]. Hence, our research was oriented towards the method of BGChL-indication. The ubiquitous and tolerant species *Parmelia saxatilis* was chosen by us among the most common species in Yerevan area as an indicator species which is widely verified in indication of environmental HM pollution, particularly in South Baikal region

[21, 22]. Besides, we took into account that epilites and epiphytes accumulate HMs more intensely that epigeic lichens [16].

Representatives of urban lichen flora (compared with background areas) if not disappear forever then undergo some morpho-anatomical distortions of thallome structure, as shown by data on ratio between apothecium and isidium specimens of thallomes in *P. saxatilis* in different pollution zones of the city (*Fig. 1*).

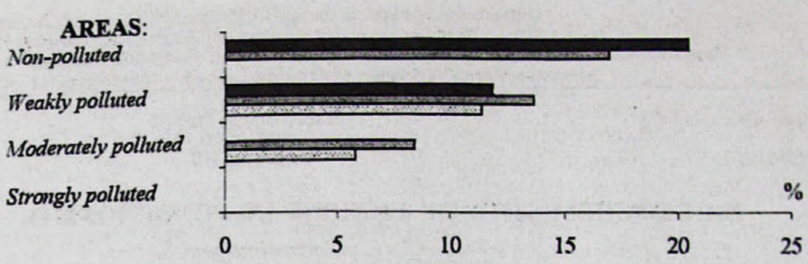

Fig. 1. The ratio of quantities of apothecium and isidium specimens of *Parmelia saxatilis* in different pollution zones, %.
Thallome forms: - isidium, - isidium-apothecium, - exclusively apothecium.

In background regions, the two types of thallomes have been found: apothecium and isidium-apothecium ones; the role of isidium-apothecium and isidium specimens increases with pollution; the lichens are absent in most polluted areas. These distortions are most frequently observed in samples collected close to the center and south of the city where the synergism in HM contamination takes place in surface atmosphere. The whitish cover appears along the thallome edges, together with chlorosis and necrosis of phycobiont (up to destruction of algal stratum), thallome size diminishes and deforms; apothecia and fans sterilize and the number of isidia changes. All this tends to complicate identification of most species.

Universality of lichens as accumulating bioindicators of HMs is caused by evolutionary adaptability od these *pioneers of extreme habitats* (especially xerophylic ones): immediate capture-loss of aqueous aerosols from the air (150-300% of dry weight), year-round interaction with ambient environment by whole thallome surface, presence of huge sorption surface per weight unit and other properties [8, 11, 18]. This entails the effect of cumulating (under chronic accumulation, for relatively short term ~15 months) of HMs, whose concentrations are adequate to mean gross contents in the environment. The lichen thallomes act as the passive cation-exchangers; active accumulation may occur during nutritional deficiency [20] what is facilitated by sorption surface.

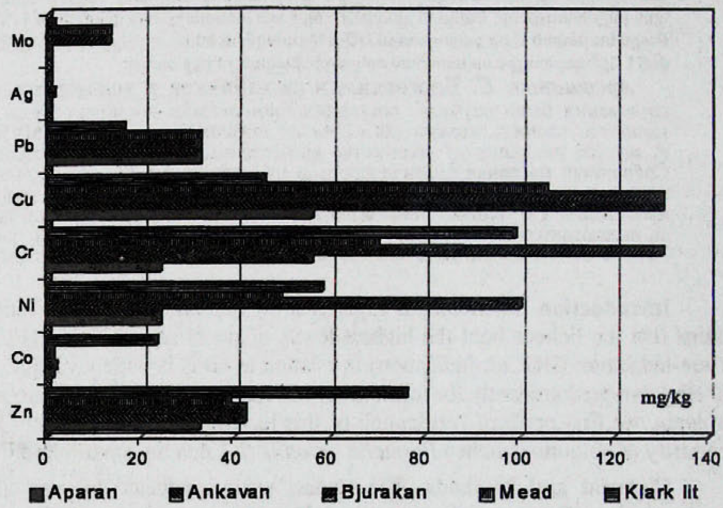

Fig. 2. **The background concentrations of heavy metals in thallomes of *P. saxatilis*.**

To identify the biogeochemistry of *P. saxatilis* in conditions of pollution, quantitative parameters of HMs in lichen are studied in background areas. It is found out that HM contents differ individually, but are close in most elements to their clarks in lithosphere (*Fig. 2*).

For calculations we accepted it most rational to use the mean parameters in all elements. Using the obtained background characteristics, we have calculated the level of anomality (LA) of HM distribution in the studied species (*Formula 1*). In *Table 1*, the anomalous concentrations of chemical elements are given for Kanaker aluminum plant (KAP) and Yerevan botanical garden (YBG) in relation to background. As we may see, the principal portion of elements belongs to man-produced ones.

Table 1. Exceeding of HMs over background concentrations in *P. saxatilis* in the city.

Area	HMs										
	Mo	Ag	Co	Cr	Sn	Ni	Pb	Cu	Zn	V	Zn
Kanaker aluminum plant	42	10	18	10	1,8	5,6	3,1	4,2	2,3	1,8	1,3
Yerevan botanical garden	24	24	13	5,6	13	4,2	3,1	4,2	4,2	1,8	1,3

In *Table 1* it is shown a distinct difference in HM accumulation by thallomes of *P. saxatilis* in background areas and in the city. The most obvious anomalies are found in Kanaker ravine of Hrazdan River near the KAP. The territory of YBG is peculiar by its closeness to the central part of the city and to the big Miasnikian motorway what leaves its trace in lichen geochemistry whose bogeochemical activity is higher than in the KAP. Besides, the lichen flora of YBG is absolutely immigrant as it is absent in the nearby areas. The HM concentrations differ from background $BGChA_x$ by 4.65 times for the YBG and by 4 times for the KAP. The most prominent anomalous diversions over the background are observed in **Mo** - in 42 (KAP) and 24 (YBG) times; **Ag** - 10 and 24 respectively; **Co** - 18 and 13; **Cr** - 10 and 5.6; **Sn** - 1,8 and 13.

Molybdenum is known to be frequently accompanied by copper, which correspond to each other in ratio 1.75:10 (KAP) and 1:10 (YBG). Similar pattern was also noted in chemical composition of Kadjaran copper-molybdenum province [13] where decreased concentrations of **Mo** are explained by high amounts of **Cu**.

For identification of biogeochemistry and metal-accumulating capacities of *P. saxatilis* the coefficients of bioaccumulation (**A_x**) were calculated for individual HMs (*Formula 2*).and additive biogeochemical activity (**$BGChA_x$**) of HM accumulation (*Formula 3*). As shown by data of *Table* 2, urban *P. saxatilis* sharply increases bioactivity of the following HMs: **Ag**, **Mo, Sn, Pb, Cu, Cr** and **Ni**.

Table 2. Intensity of heavy metal accumulation by *P. saxatilis* under air pollution: **A_x**:□ – 0,n and less; ▒ – n; ■ – 10n.

Areas		A_x HMs								$BGChA_x$
		Ag	Mo	Pb	Cu	Cr	Ni	Co	Zn	
Background		▒	▒	▒	▒	□	□	□	□	2,24
Yerevan city	KAP	■	■	▒	▒	▒	▒	□	□	8,77
	YBG	■	■	▒	▒	▒	▒	□	□	8,17

Based on analysis of *P. saxatilis* thallomes, we can conclude that this bioindicator is selective for a number of HMs, which are divided by us into 3 groups by their accumulative intensities:

1) Chemical elements of strong accumulation (10n): **Mo, Ag**;
2) Chemical elements of moderate accumulation (n): **Pb, Cu, Cr, Ni**;
3) Chemical elements of weak accumulation (0,n and less): **Co, Zn**.

As shown here, **Mo** and **Ag** are main contributors; concentrations of other elements (**Pb, Cu** and others) increases not so sharply and sometimes stays constant (**Co, Zn**). Given the generalized data, the descending rows of HMs accumulation are composed for background and polluted areas:

Background – **Ag, Mo, Cu, Pb** (n) - **Ni, Cr, Zn, Co** (0,n);
KAL – **Mo, Ag** (10n) - **Pb, Cu, Cr, Ni** (n) - **Co, Zn** (0,n);
YBG – **Ag, Mo** (10n) - **Pb, Cu, Ni, Cr** (n) - **Co, Zn** (o,n).

The lichens do reflect the HM distribution in different points of surface air more precisely than the vascular plants, even such photophytes as *Picea, Abies* and others, would do [9], and this phenomenon depends on thallome age, species and exposure time in a polluted site. Numerous observations in industrial regions in different countries have displayed a direct correlation between air pollution and impoverishment in specific composition of lichens. As primarily air-borne transfer of toxic matter causes environmental pollution of Yerevan City, pollutant concentrations should be determined simultaneously in lichens and air.

A strong dependence of HM accumulation in *P. saxatilis* upon aerial pollutant loads is found out (*Fig. 3*).

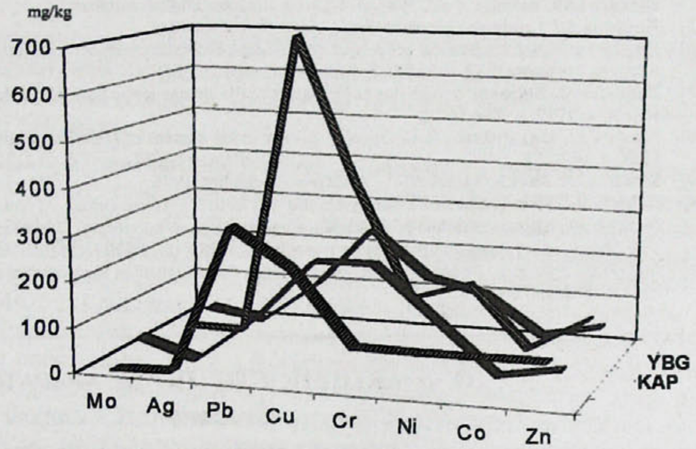

Fig. 3. Dependence of HM accumulation by *P. saxatilis* upon the level of air pollution.
LEGEND. Pollution level: lichen, air.

The general consecutive row of HMs in lichen – **Mo>Ag>Pb>Cu>Cr>Ni, Co, Zn** – is a middle link between the rows of heavy metal flows in air pollution processes:

Mo>Cu,Ni>Cr>Pb>Co,Zn (1991), **Ag>Pb>Cu,Ni>Mo>Zn>Co,Cr** (1995).

However, selective accumulation of HMs by lichens takes place and its mechanism is still unknown. Likely, this results from morpho-physiological properties of individual species. The forest lichens and epiphytes are the richest in mineral elements, as the forest itself serves as a filter of precipitation. The species studied by us was selective for a number of HMs (**Mo, Cr, Ni** and **Pb**) what allows employing them as bioindicators of environmental pollution with these elements and their complexes.

Thus, *P. saxatilis* may serve a reliable bioindicator just for the HMs.

Conclusion. The lichens growing in urban conditions fix strongly the man-induced fluctuations and express higher sensitivities than the vascular plants due to lacking physiological and anatomo-morphological barriers of HM accumulation.

Being one of the first links in biogeochemical chains in ecosystems, the lichens have adequately been reflecting the quantitative pattern of air pollution. Selective and relatively non-barrier metal-accumulating property of *P. saxatilis* makes it a good candidate for complex bioindication of the effect of man-made activities on the landscapes in study area and other industrial regions of Armenia and large-scale network of monitoring for active sources of air pollution. The methodology of BGChL-indication may be especially valuable and informative for hardly studied highland areas and those having little precipitation.

The lichen indication as a method of studies of the modern status of surface atmosphere allows to functionally differentiate, coupled with quantitative characteristics of HM accumulation by lichens, a given territory and reveal the trends in distribution of pollution, as well as the relationships of their accumulation in natural accumulating biosubstrate (lichens) regardless of pollution source.

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О β–АКТИВНОСТИ ПОЧВ АРАРАТСКОЙ РАВНИНЫ

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В статье приводятся результаты анализа данных по суммарной β-активности почв в ряде пунктов Араратской равнины. Измерения показали, что уровень β-радиоактивности находится в основном в пределах естественного уровня: от 512 до 651*Бк/кг*. Повышение уровня β-активности почв отмечается в г.Ереване.

Նալբանդյան Ա., Անանյան Վ., **Արարատյան հարթավայրի հողերի β-ակտիվության մասին:** Դիտարկվում է հողերի գումարային β-ակտիվությունը Արարատյան հարթավայրի մի շարք կետերում: Չափումները ցույց են տվել, որ β-ռադիոակտիվության մակարդակը հիմնականում բնական մակարդակի սահմաններում է՝ 512-ից 651 Բկ/կգ: β-ակտիվության մակարդակի բարձրացում նշվում է Երևան քաղաքում:

Nalbandyan A., Ananyan V. **On β–activity of the soils of the Ararat plain.** The cumulative β–activity of soils in a number of sites of Ararat valley has been considered. The measurements have shown that the level of β–activity of soils is mainly within the natural background: from 512 to 651 Bq/kg. Increase in the level of β–activity of soils has been documented in Yerevan City.

ВВЕДЕНИЕ. Радиоактивность окружающей среды характеризуется естественным и техногенным фоном излучения. Естественный фон создается космическим излучением и содержанием естественных радионуклидов в породах, почвах, водах, атмосфере, продуктах питания. Техногенный фон – естественный фон излучения, измененный в результате деятельности человека. Быстрый рост атомной энергетики влечет за собой значительное увеличение радиоактивных отходов, определенная часть которых, даже при нормальной работе предприятий ядерного топливного цикла, может проникать в окружающую природную среду.

В результате испытаний ядерного оружия произошло загрязнение природной среды искусственными радионуклидами в глобальном масштабе. За 1959-1963гг. наблюдалось повышение