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Identification of the Degree of Air Pollution by Heavy Metals using Moss Bioindicators

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ABSTRACT

The article presents data on the detection of the degree of atmospheric air pollution with metal ions using moss bioindicators. For the purpose of air bioindication, moss and soil samples were examined to identify the bioindicator properties of moss. Concentrations of heavy metals were determined on an Agilent Technologies 7500 Series ICP-MS (7500cx) instrument using inductively coupled plasma mass spectrometry (ICP-MS, USA).

The content of metal ions in the studied samples collected from the least polluted territory of the city of Baku, which amounted for moss samples: Cd (0.19689), Cu (59.19030), Ni (18.746), Pb (62.40856), Zn (50.11554) and Hg (0.060154); for soil samples - Cd (1.07352), Cu (23.24958), Ni (20.33940), Pb (27.45685), Zn (12.11554) and Hg (0.059426) mg/kg, respectively.

The content of heavy metals in the studied samples collected from the most polluted area near the city of Baku was experimentally determined and for samples of mosses, they were Cd (0.53978), Cu (63.19252), Ni (20.557), Pb (63.40856), Zn (161.20163) and Hg (0.061379); for soil samples, Cd (0.27662), Cu (25.51854), Ni (23.466), Pb (27.456), Zn (85.00345) and Hg (0.060578) mg/kg, respectively.

Keywords: Moss, Pollution, Heavy metals, Mass spectrometry, Bioindicators

INTRODUCTION

Rapid industrialization in cities and the contributory relationships with the original pollution sources can cause serious environmental problems within cities [1-4].

Currently, methods based on the use of natural plates, which include mosses, are actively developing to assess the degree of air pollution by heavy metals and other toxic elements. Mosses are efficient accumulators of heavy metals contained in the atmosphere.

Biomonitoring of atmospheric pollution with heavy metals and other chemical elements using moss is one of the simplest, most promising and effective methods for monitoring, detecting and evaluating changes in air quality. One of the most important ecological features of mosses as a tool for biomonitoring is that mosses have a high accumulation capacity and a large surface, are widely distributed, have a long life cycle (from 1 year to 15 years) and survive in a highly polluted environment.

The method of moss biomonitors is based on a comparative analysis of the concentrations of chemical elements in mosses, selected at different points of the studied or background area. The method allows determining the most polluted zones, monitoring the dynamics of air pollution and with known background concentrations, it makes possible to quantify the average pollution levels without determining the MAC.

Mosses are living organisms of the plantae kingdom and classified in the phylum bryophyta. They grow in forests, on rocks, on trees, bare soil, cracks of concrete side walls, on

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burnt bricks on abandoned automobiles and uncompleted buildings [5].

Previous research works have shown that mosses have proven to be better bioindicators of pollution because they are more sensitive to atmospheric pollution [6].

Meanwhile, atmospheric metals pollution in Nigerian cities has been reported Ojiodu et al. [7] reported that the atmosphere of Owode - Onirin in Lagos state, Southwestern, Nigeria is highly polluted with the heavy metals: Zinc, Zn (66.01%), Lead, Pb (15.99%), Copper, Cu (12.79%), Chromium, Cr (2.89%), Nickel, Ni (2.25%).

Autors analyses the level of antioxidants (water-soluble antioxidants, carotenoids and anthocyanins) in plants under the conditions of environmental cadmium pollution. The authors emphasise excessive background concentration of cadmium in plant samples collected in Kaliningrad and note a positive correlation between cadmium concentration and traffic intensity. A negative correlation between the Cd content and the anti-oxidative status of plants and a positive one with the anthocyanin content were established in the course of research [8].

Mosses are comparatively more effective at accumulating elements and heavy metals than other plant species. Therefore, moss biomonitoring was used as a complementary technique alongside classic instrumental methods in air pollution detection and control [9-13].

Mosses plants have proven to be excellent indicators of atmospheric pollution, as they reflect metals concentration gradient and sources of deposition. The concentrations of heavy metals were analyzed by Atomic Absorption Spectrophotometer (AAS) Perkin Elmer AA 200. Results show that the average concentrations of the heavy metals at Yaba College of Technology Campus were Zn 12.711 µg/g, Pb 1.174 µg/g, Cu 9.095 µg/g, Ni 3.626 µg/g and Cd 0.086 µg/g. The most polluted site is Students affairs unit (6.532 µg/g) while the least polluted is Bakassi hostel (1.031 µg/g). The levels of some of the heavy metals were present in concentrations greater than WHO threshold limiting values [14].

Based on the foregoing, the purpose of this work was a qualitative and quantitative assessment of atmospheric air pollution with heavy metals to study regional and local pollution of both atmospheric air and the soils of the studied area by environmental pollutants during biomonitoring of biosphere pollution.

In experimental studies as a bioindicator for air bioindication and determining the degree of contamination of the biosphere with environmental pollutants, we used moss collected in the vicinity of Baku and Baku.

MATERIALS AND METHODS

We have carried out experimental studies and collecting samples of moss, soil from the environs of Baku and from a relatively unpolluted zone of Baku.

During the analysis of samples of soils and mosses, the process of sample preparation was carried out, the basis of which was the preliminary cooking of the studied samples in the microwave oven of the Milestone STARTD company (Microwave Digestion System) according to the DG-EN-45 SoilandCrudeoil procedure. A certain part of the samples was dried in a drying oven at a temperature of 35-40°C, followed by grinding and homogenizing the samples. According to the method of DG-EN-45 “Soil and Crude oil”, samples were taken with a mass of 0.2 ÷ 0.25 g and reagents were added; 10 ml of 65% HNO_3, 1 ml of 1% HCl, 1 ml of 30% H_2O_2.

RESULTS AND DISCUSSION

To determine the concentration of metal ions in the samples of the studied samples, calibration curves were constructed **(Figure 1)**.

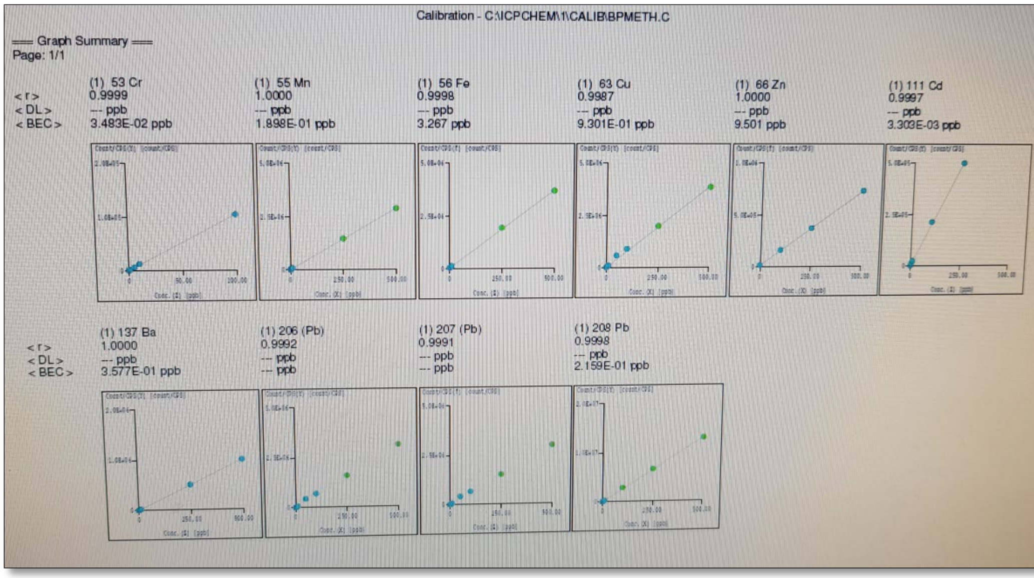

Figure 1. Calibration curves for standard samples of heavy metals by mass spectrometry with inductively coupled plasma.

The physical parameters of the cooking process samples (temperature, time and power) are presented in **Tables 1 and 2**. The concentration of heavy metals was determined on an Agilent Technologies 7500 Series ICP-MS instrument (7500cx) inductively coupled plasma mass spectrometer (ICP-MS, USA).

Table 1. Physical parameters of the oven Milestone STARTD for DG - EN - 45 "Soil and Crude oil".

Step	Time (min)	Temperature (°C)	Power (W)
1	10	220	1000
2	20	220	1000

Table 2. Physical parameters of the oven Milestone STARTD for DG - EN - 45 "Soil and Crude oil".

Step	Time (min)	Temperature (°C)	Power (W)
1	5.5	175	1000
2	10	175	1000

In the investigated samples, the determination of metals in water was carried out within the limits of ppb and for soil and moss in ppm. Agilent Technologies standard solutions were used to calibrate the equipment.

The data of quantitative determination of metal ions in moss and soil samples collected from the most polluted territory near Baku using inductively coupled plasma mass spectrometry are presented in **Tables 3 and 4**.

Table 3. The results of the analysis of moss samples collected from the most polluted areas near the city of Baku (moss samples of 0.2319 g were taken for analysis of moss).

Metals	ppm (mg/kg)	%
Cd	0.53978	$53978*10^{-5}$
Cu	63.19252	0.0063
Ni	20.557	0.0021
Pb	63.40856	0.0063
Zn	161.20163	0.016
Hg	0.061379	$61379*10^{-6}$

Table 4. The results of the analysis of soil samples collected from the most polluted area near the city of Baku (samples of soil in the amount of 0.2121 g were taken for analysis).

Metals	ppm (mg/kg)	%
Cd	0.27662	$27662*10^{-5}$
Cu	25.51854	0.0026
Ni	23.466	0.0023
Pb	27.456	0.00275
Zn	85.00345	0.0085
Hg	0.060578	$60578\text{-}10^{-6}$

The content of heavy metals in moss and soil samples collected from the most polluted areas near the city of Baku, which amounted to samples for mosses: Cd (0.53978), (Cu (63.19252), Ni (20.557), Pb (63.40856), Zn (161.20163) and Hg (0.061379); for soil samples, Cd (0.27662), (Cu (25.51854), Ni (23.466), Pb (27.456), Zn (85.00345) and Hg (0.060578) mg/kg, respectively **(Figures 2 and 3)**.

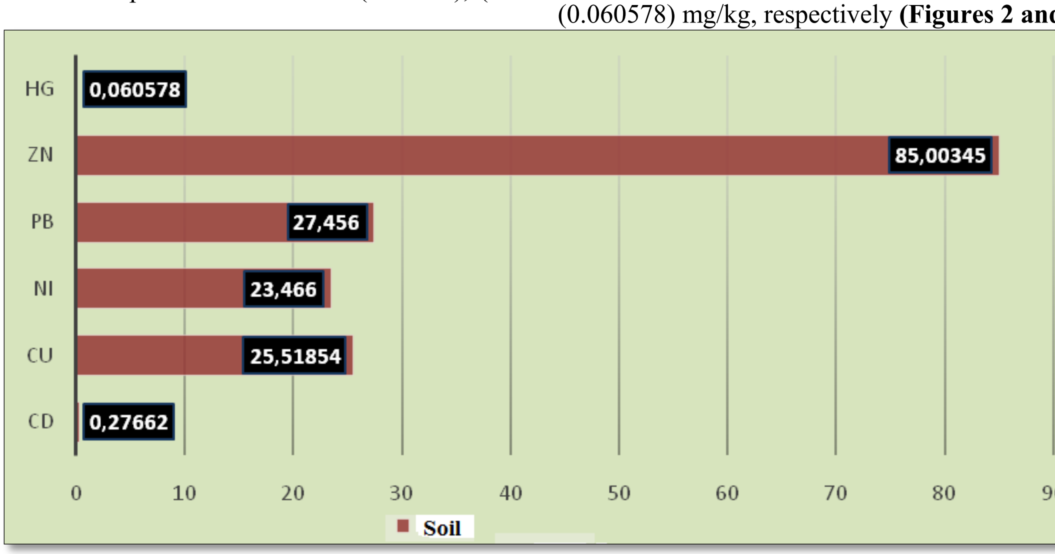

Figure 2. Data on the content of metal ions in the studied soil samples collected from the most polluted territory near Baku.

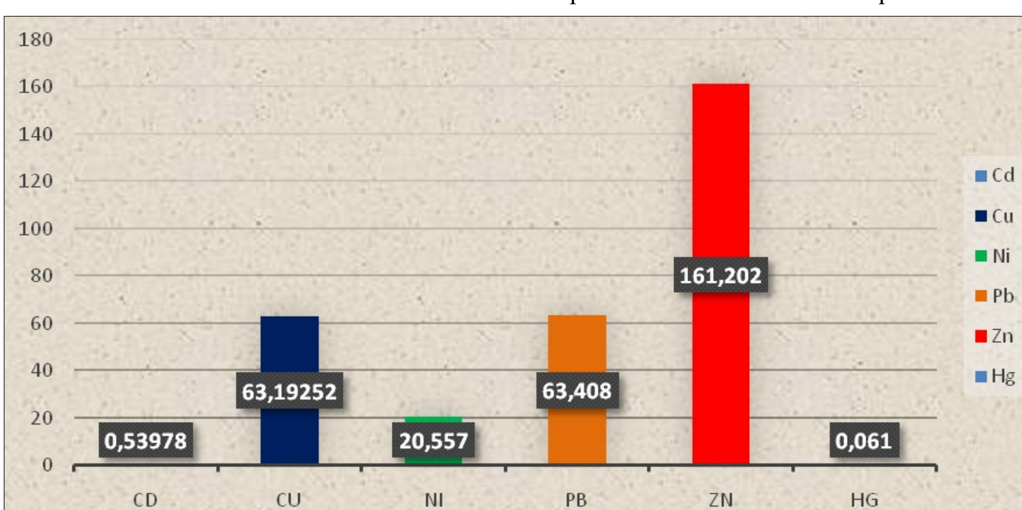

Figure 3. Comparative data on the content of metal ions in the studied samples of moss collected from the most polluted area near the city of Baku.

The data of quantitative determination of metal ions in moss and soil samples collected from the least polluted territory of Baku by mass spectrometry with inductively coupled plasma are presented in **Tables 5 and 6**.

Table 5. Data of quantitative determination of metal ions in moss samples by mass spectrometry with inductively coupled plasma collected from the least polluted territory of Baku (moss samples for the analysis in the amount of 0.2411 g.

Metals	ppm (mg/kg)	%
Cd	0.19689	$19689*10^{-5}$
Cu	59.19030	0.0059
Ni	18.746	0.0019
Pb	62.40856	0.0062
Zn	50.11554	0.005
Hg	0.060154	$60154*10^{-6}$

Table 6. Data of quantitative determination of metal ions in soil samples by the method of mass spectrometry with inductively coupled plasma, collected from the least polluted territory of Baku (for the analysis samples of soil were taken in the amount of 0.2369 g).

Metals	ppm (mg/kg)	%
Cd	1.07352	0.00011
Cu	23.24958	0.0023
Ni	20.33940	0.002
Pb	27.45685	0.00270
Zn	12.11554	0.0012
Hg	0.059426	$59426-10^{-6}$

As a result of the analyzes, the content of metal ions in moss and soil samples collected from the least polluted territory of Baku was found, which amounted for samples of moss: Cd (0.19689), Cu (59.19030), Ni (18.746), Pb (62.40856), Zn (50.11554) and Hg (0.060154); for soil samples, Cd (1.07352), Cu (23.24958), Ni (20.33940), Pb (27.45685), Zn (12.11554) and Hg (0.059426) mg/kg, respectively **(Figures 4 and 5)**.

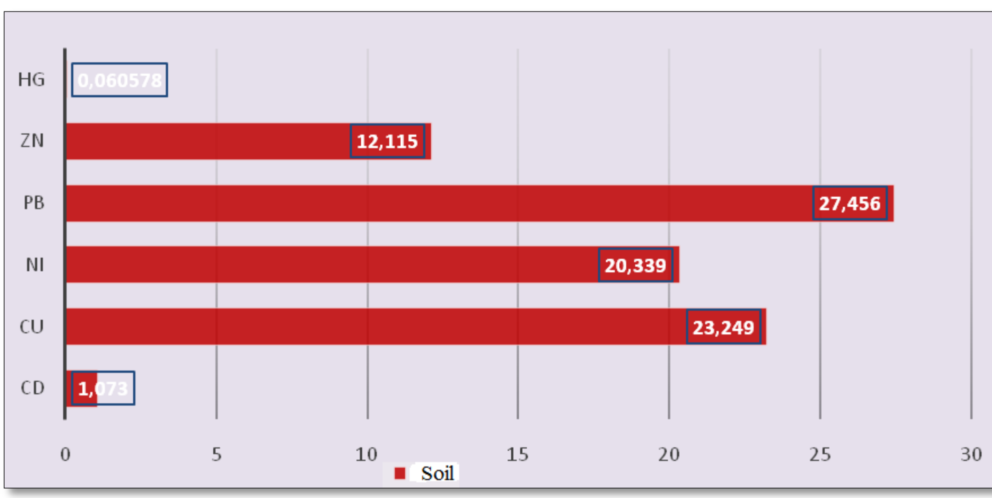

Figure 4. Data on the content of metal ions in the studied soil samples collected from the least polluted territory of Baku.

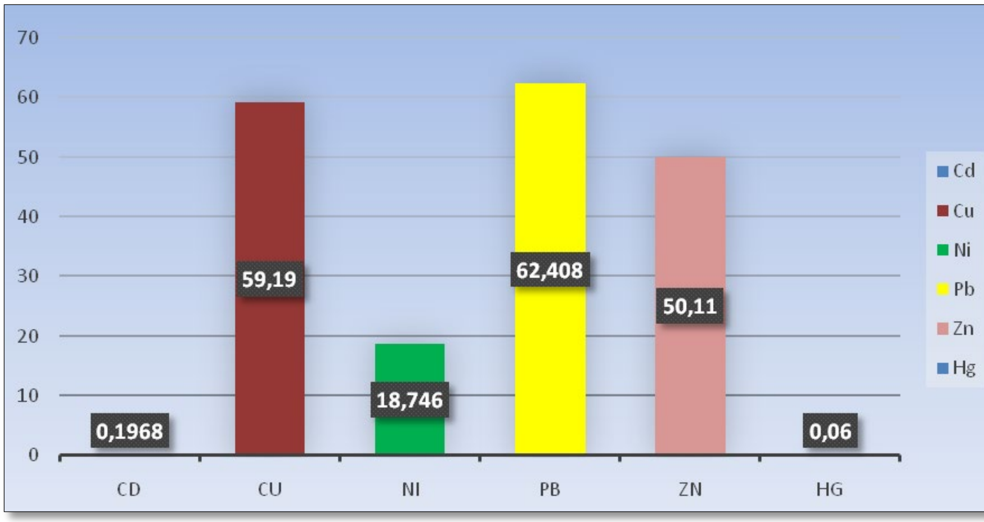

Figure 5. Data on the content of metal ions in the studied moss samples collected from the least polluted territory of Baku.

CONCLUSION

Thus, when comparing the concentration of metal ions in the samples under study, we can assume that mosses are subject to anthropogenic impact; these data provide the basis for the use of mosses as bioindicators to identify the degree of contamination of the biosphere by pollutants.

Based on the experimental data obtained, it can be stated that the method of mass spectrometry with inductively coupled plasma provides the necessary data on the degree of contamination of the atmosphere with toxic substances, which is reflected in the elemental composition of mosses. Analysis of these data showed that mosses are informative plant species indicating the ecological state of the environment.

Limits of the content of metal ions in moss and soil samples collected from the environs and from the territory of the city of Baku were revealed. The obtained data on the content of metal ions in moss and soil samples provide valuable information for ecosystem biomonitoring.

The content of metal ions in the studied samples collected from the least polluted territory of Baku was determined experimentally. For samples of mosses, they amounted to Cd (0.19689), Cu (59.19030), Ni (18.746), Pb (62.40856), Zn (50.11554) and Hg (0.060154); for soil samples - Cd (1.07352), Cu (23.24958), Ni (20.33940), Pb (27.45685), Zn (12.11554) and Hg (0.059426) mg/kg, respectively.

The content of heavy metals in the studied samples collected from the most polluted area near the city of Baku was experimentally determined, and for samples of mosses, Cd (0.53978), Cu (63.19252), Ni (20.557), Pb (63.40856), Zn (161.20163) and Hg (0.061379); for soil samples, Cd (0.27662), Cu (25.51854), Ni (23.466), Pb (27.456), Zn (85.00345), and Hg (0.060578) mg/kg, respectively.

The content of heavy metals in the series is decreasing for mosses and soil samples: Pb>Zn>Cu>Cd>Hg and Pb>Cu>Ni>Zn>Cd>Hg. Thus, the activity values of the detection limits of heavy metals in moss, soil and water samples provide valuable information for the biomonitoring of the ecobiosystem.

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