JOINT INSTITUTE FOR NUCLEAR RESEARCH
Frank Laboratory of Neutron Physics
Sector of Neutron Activation Analysis and Applied Research

FINAL REPORT ON THE SUMMER STUDENT PROGRAM

Atmospheric deposition of lead, cadmium and copper in the Donetsk agglomeration studied by moss biomonitoring

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Participation period:
August 11 – October 5, 2019

Dubna, 2019

Content

Abstract

The method of moss biomonitoring of atmospheric deposition of trace elements was applied in the Donetsk-Makeevka agglomeration to assess the environmental situation in this region.

Our study was carried out in the framework of the UNECE ICP Vegetation (https://icpvegetation.ceh.ac.uk/).

The 113 moss samples were collected in May 2019. Concentrations of Cd, Cu, and Pb determined by atomic absorption spectrometry in the moss samples are reported. Distribution maps (ArcGis software) of these elements was used for assessing pollution sources of the Donetsk-Makeevka agglomeration. Median values of the studied elements were compared with the data obtained for the other countries in Europe. The increase in concentrations for all three elements in comparison with the other countries was observed.

1 Introduction

Donetsk agglomeration is one of the most economically developed regions of the Eastern Europe. The main cross-industry complexes are power, ferrous and non-ferrous metallurgy, machine-building, chemical-industrial, transport and recreational.

The Donetsk region is characterized by steppe and forest types of vegetation. The steppes are located in the south and east of the region, in the north and the Donetsk ridge - steppes and gully forests.

Donetsk's climate is moderate continental. It is formed by influence of the western transport of air masses from the Atlantic Ocean and periodic invasions of air masses from the Arctic and Siberia.

The moderately continental climate is characterized by reduced air humidity throughout the year in Donetsk.

Industrial facilities. 22 coal mines have been operating in Donetsk. The heaps (artificial mounds of waste rock) are located in the immediate vicinity of the residential areas.

PrAO «Donetskstal» is a large metallurgy plant (ironworks) in the central part of the city.

There are chemical (plastics production, chemical reagents production, leather processing) and by-product coke industries. Metallurgy companies are located in Donetsk, Mariupol, Enakiev, Makeevka, Alchevsk. Non-ferrous metallurgy is represented by the production of zinc (Konstantinovka), mercury (Nikitovka), copper and rolled brass products (Bakhmut). The chemical-industrial complex include production of nitrogen (Severodonetsk, Gorlovka) and phosphate fertilizers (Konstantinovka), soda (Lysychansk, Slavyansk), organic synthesis products (Severodonetsk, Donetsk, Lisichansk, Stakhanov, Rubezhnoye).

The centers of mining (heating) equipment production are Donetsk, Lugansk, Gorlovka, Yasinovataya. The centers of agricultural engineering are Lugansk, Pervomaisk. The center of instrumentation is Severodonetsk. Diesel locomotives are produced in Lugansk, railway cars in Stakhanov.

The emissions of the city's enterprises form steady smog (dark purple haze) in small area along with the enterprises of the Donetsk agglomeration, which bangle year-round.

We used the method of passive moss biomonitoring in this work [1-3].

The most important property of mosses, that make them suitable to assess heavy metal pollution on a large time scale, is related to the fact that they do not have roots, and uptake nutrients directly from wet and dry deposition. Thus, the mineral adsorption occurs over their entire surface [4, 5].

The main objectives of this work:

- to determine the level of heavy metal pollution of the Donetsk-Makeevka agglomeration and comparison this results with other countries of Eastern and Western Europe;

- to describe local sources of pollution (mines, ferrous / non-ferrous metallurgy and mechanical engineering).

2 Experimental

2.1 Sampling

Sampling was performed in May 2019 at a total of 113 sampling sites in Donetsk-Makeevka agglomeration in accordance with the CLRTAP (2015) manual for moss sampling [6].

We have chosen *Ceratodon purpureus* (Hedw.) Brid for this study (Fig.1).

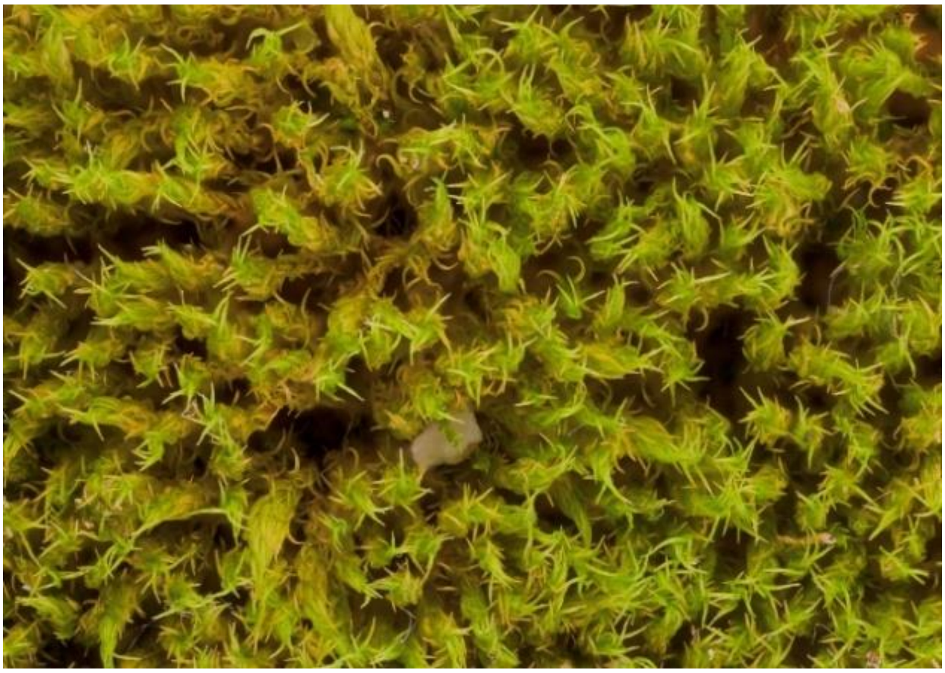

Fig. 1 *Ceratodon purpureus* (Hedw.) Brid

However, in the North Azov Sea the *Hylocomium splendens, Pleurozium schreberi, Hypnum cupressiforme, Pseudoscleropodium purum* [7] are not distributed widely throughout the territory. Therefore, we had to choose available moss species found in the Donetsk Region as the objects of our study.

2.2 Materials and Methods

The 113 moss samples was collected in May 2019.

Collected samples were cleaned from extraneous materials adhered to the surface of the samples such as tree bark, lichens, soil dust, and dead materials and then dried at 30-34°C to a constant weight.

The samples were homogenized using agate mill. Due to the dense sampling network, we had possibility to consider mosses in each square as subsamples of one sample taken from an area of 15 × 15 and 7 × 7 km (Fig. 2).

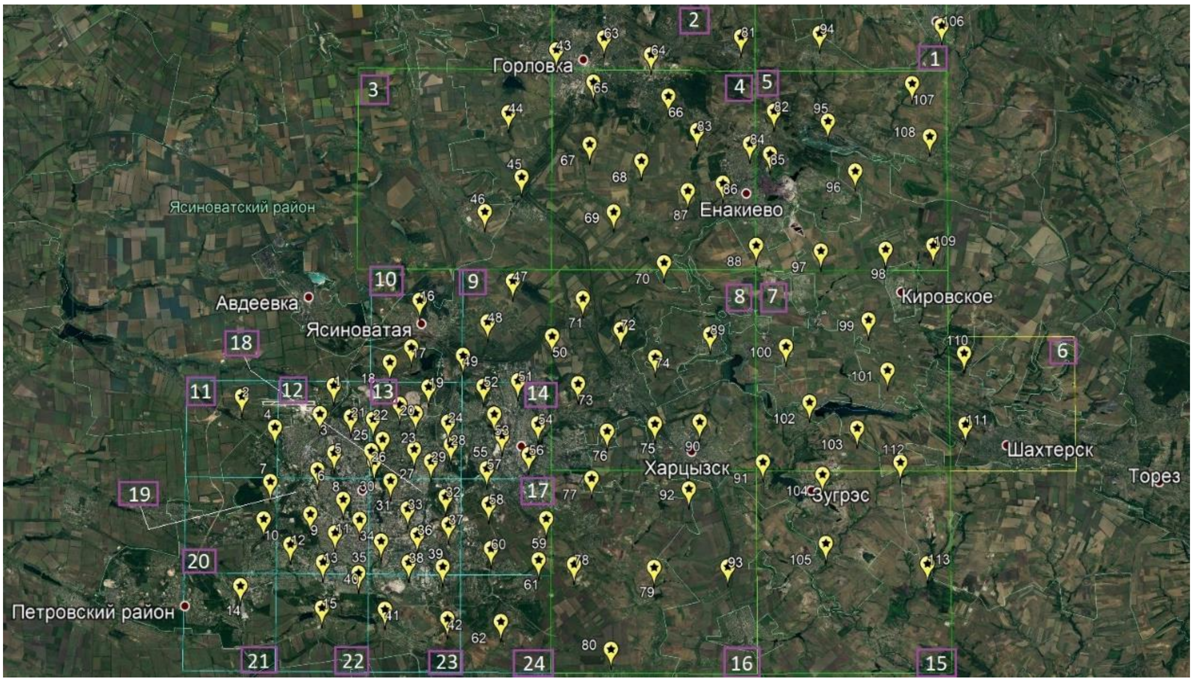

Fig. 2. The locations of sampling sites in Donetsk-Makeevka agglomeration

2.3 Analysis

The concentrations of Cd, Cu and Pb in the moss samples were determined by atomic absorption spectrometry (AAS) using iCE 3300 AAS Atomic Absorption Spectrometer with electrothermal (graphite furnace) atomization (Thermo Fisher Scientiic, Waltham, MA, USA).

For AAS, approximately 0.2 g of moss from each sample was placed in a Telon vessel and treated with 5 mL of concentrated nitric acid (HNO_3) and 1 mL of hydrogen peroxide (H_2O_2).

The moss material was introduced in a microwave digestion system (Mars; CEM, Matthews, NC, USA) for complete digestion. Digestion was performed in two steps: (1) ramp: temperature 160°C, time 15 min, power 400 W, and pressure 20 bar; (2) hold: temperature 160°C, hold time 10 min, power 400 W, and pressure 20 bar. Digests were quantitatively transferred to 100-mL calibrated lasks and made up to the volume with bi-distilled water. All of the reagents used for this study were of analytical grade: nitric acid; trace pure (Merck, Darmstadt, DE); hydrogen peroxide, p.a. (Merck); and bi-distilled water.

The concentration of Cd, Cu and Pb in the moss samples was determined by means of an Thermo Scientific™ iCE™ 3000 Series AA spectrometers with electrothermal (graphite furnace) atomization. The calibration solutions were prepared from a 1 g/L stock solution (AAS standard solution; Merck, Germany).

In the case of AAS, quality control was performed by using the NIST certified reference materials SRM 1570a (spinach leaves) and SRM 1575a (pine needles).

In both cases, the experimentally measured contents were in good agreement with the recommended values. The difference between certified and measured content of elements of the certified material varied between 1% and 10%.

3 Results and Discussion

Based on the results of atomic absorption determination, the diagram of concentration distribution (Fig. 3) was constructed for the location of the sampling points. The maximum concentrations of all elements (Pb, Cd, Cu) are observed at 8, 10, 13, 16, 17, 18, 22 points.

Distribution maps (ArcGis software) of these elements was used for assessing pollution sources of the Donetsk-Makeevka agglomeration (Figs. 4, 5, 6).

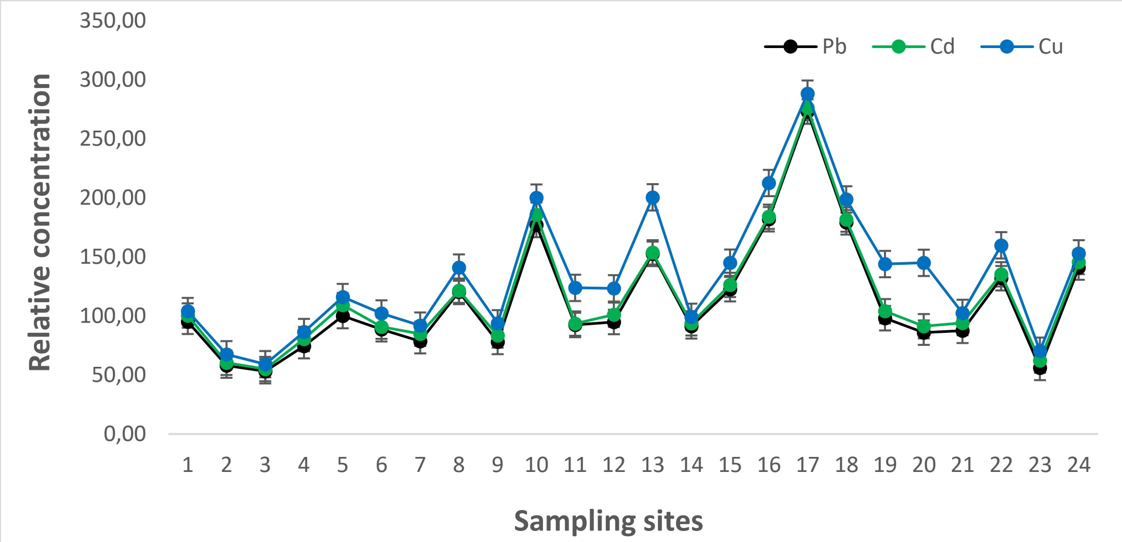

Fig. 3 The diagram of concentration distribution sampling points

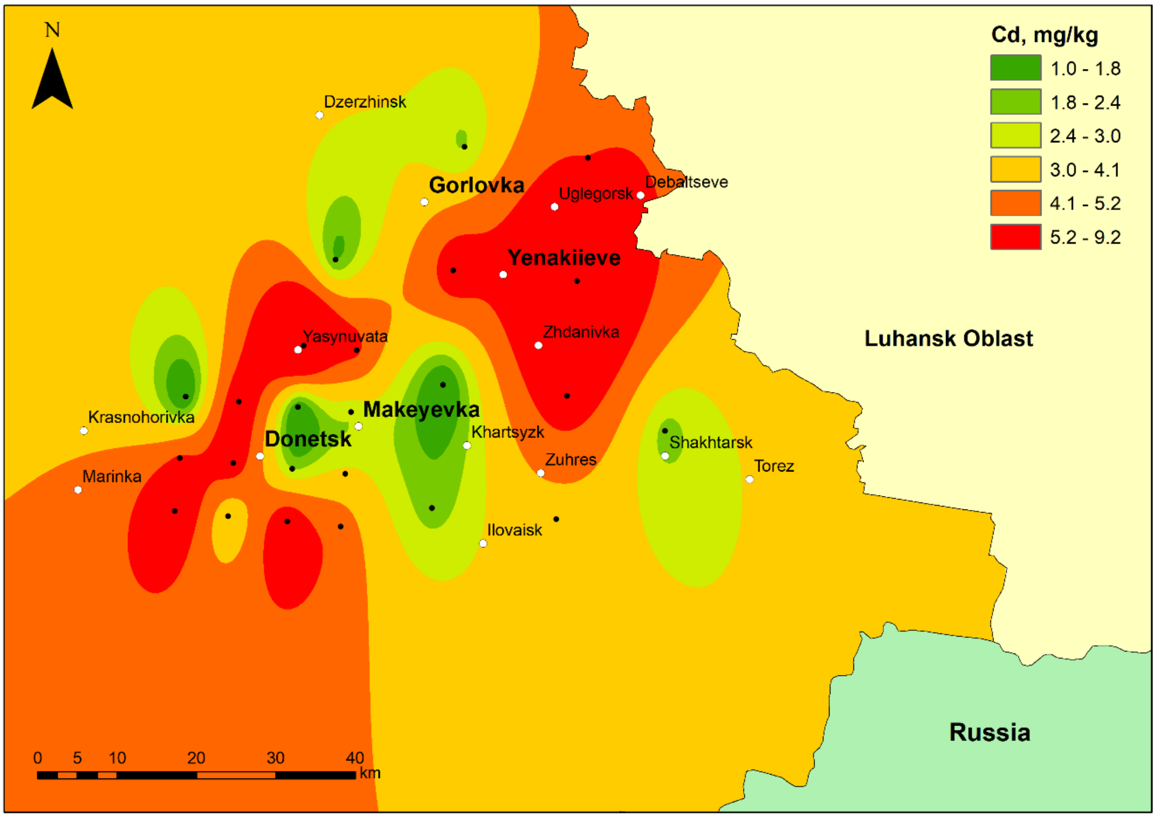

Fig. 4 The geographical distribution of Cd in the Donetsk-Makeevka agglomeration

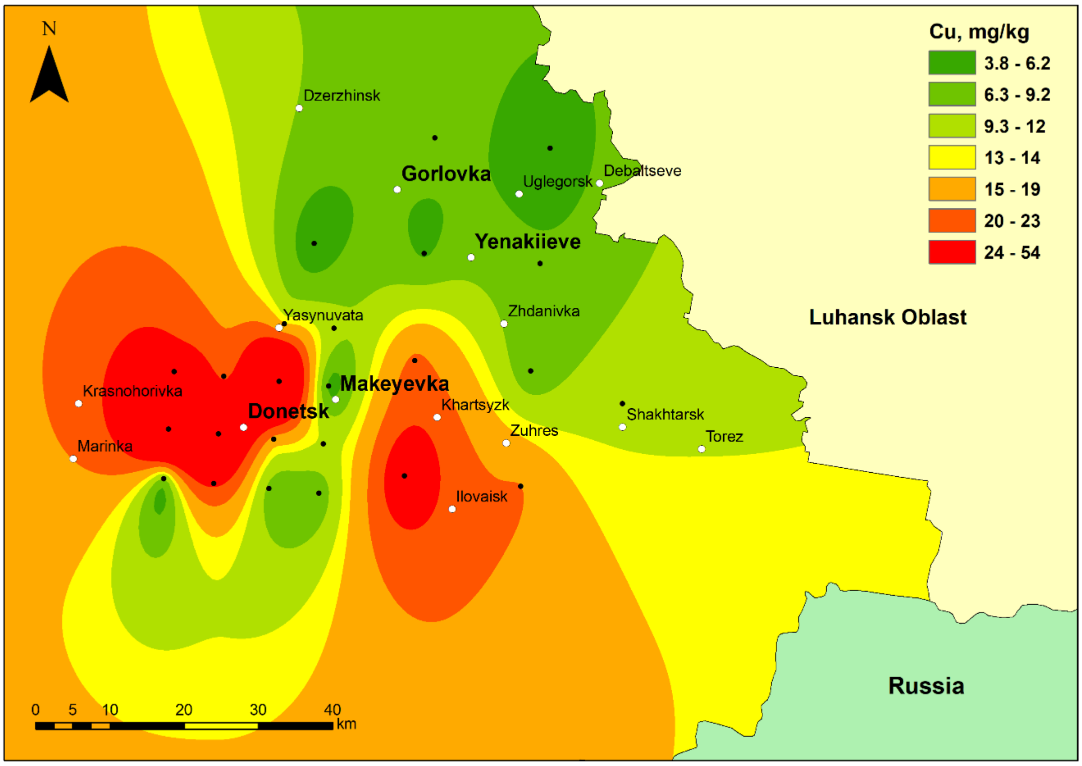

Fig. 5 The geographical distribution of Cu in the Donetsk-Makeevka agglomeration

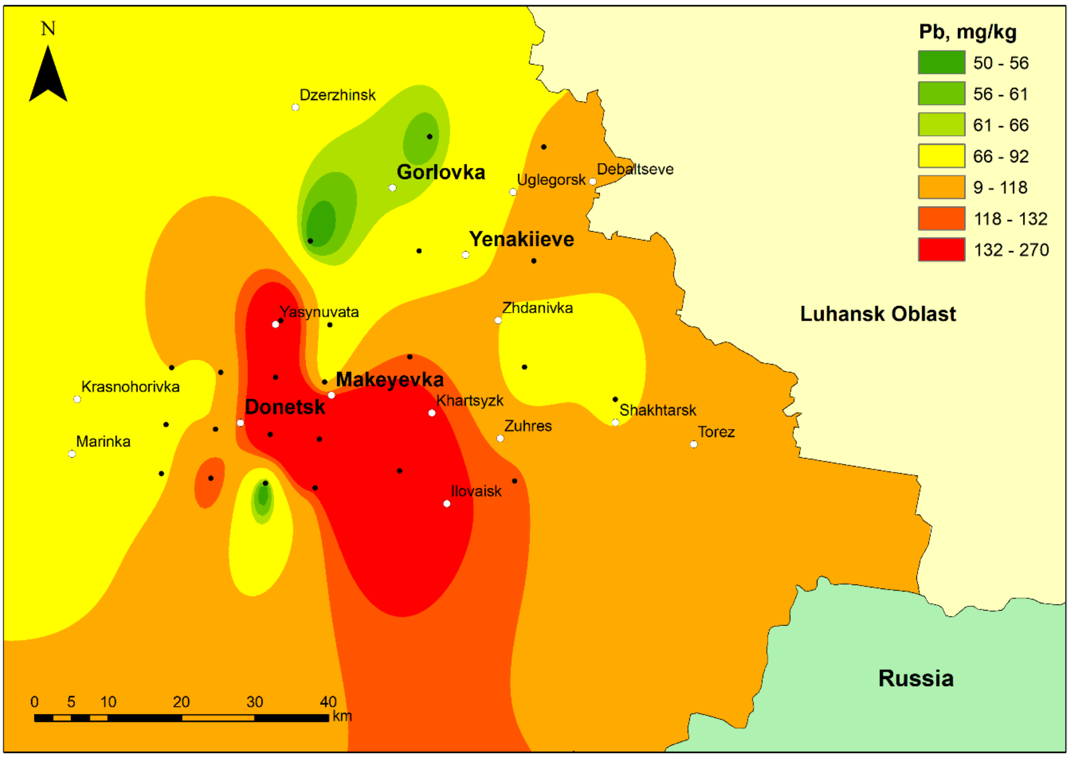

Fig. 6 The geographical distribution of Pb in the Donetsk-Makeevka agglomeration

The study area of the Donetsk-Makeevka agglomeration in Figs. 4, 5, 6 shows the geographical distribution of elemental concentrations of Cd, Cu, and Pb by interpolation method.

The distribution of the heavy metals (Cd, Cu, and Pb) was very similar and all had high concentrations in the moss.

Non-ferrous metal mining and smelting activities are the biggest contributors of heavy metal pollution as they result in large discharges of wastewater, waste gas and solid waste into the environment.

In the same way, industrial activities including leather and cement factories, non-metallic mining and smelting activities that include coal and oil exploration, rare earth element and regular ore mining release high amounts of heavy metal elements into the environment also release high amounts of heavy metals.

As for spatial distribution of Cu and Pb (Figs. 5, 6), it was observed that the highest levels of contamination by heavy metals were localized in the central area (Donetsk) and South East (Ilovaisk). The elevated concentrations of Cd in moss were recorded in the North East of the Donetsk-Makeevka agglomeration (Yenakiive).

Table 1 Median contents of heavy metals in moss of the Donetsk agglomeration compared with the other countries [8].

Country	Concentration, mg/kg		
	Pb	Cd	Cu
Albania	2.42	0.11	3.96
Austria	2.40	0.13	5.00
Belgium	3.87	0.30	6.50
Bulgaria	8.00	0.21	7.01
Donetsk	94.99	4.17	11.57
Spain	2.13	0.16	4.70
Macedonia	4.61	0.22	3.54
Poland	4.93	0.30	6.04
Russia	-	0.068	7.22
Romania	30.8	1.20	17.8
Slovenia	5.01	0.27	5.42
Croatia	3.21	0.43	6.55
France	3.29	0.17	6.06
Estonia	2.41	0.14	3.67

The highest values for copper in the Romanian moss are due to the well-known copper mines in this western part of the country.

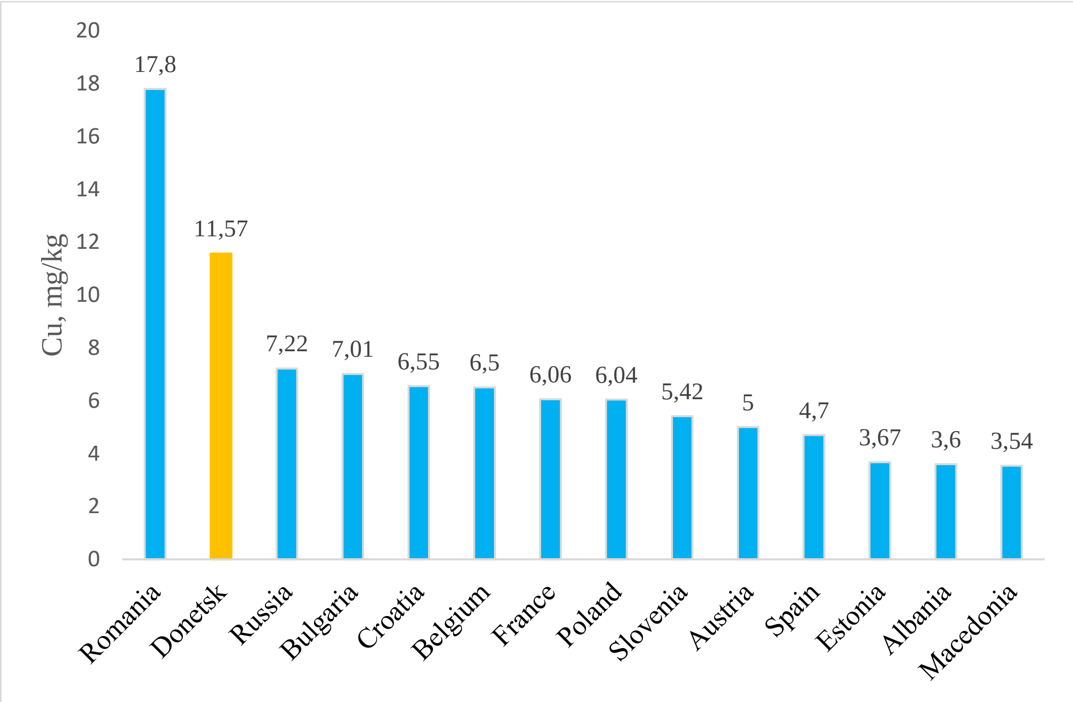

Fig. 7 Medial values of copper in samples of bryophytes in different countries

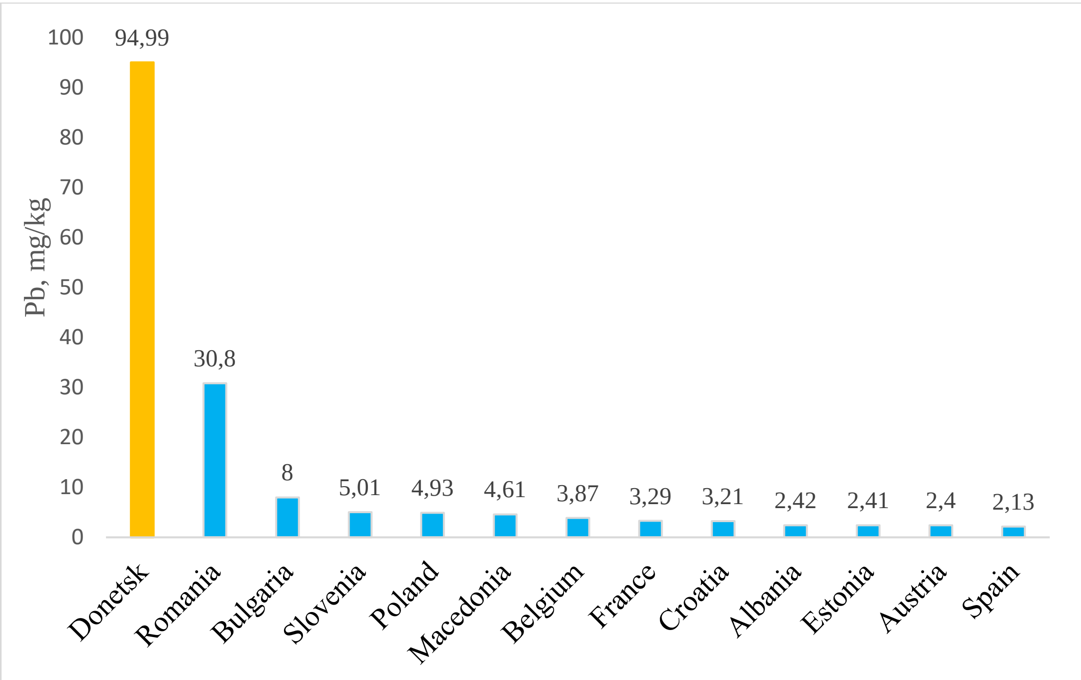

Fig. 8 Medial values of lead in samples of bryophytes in different countries

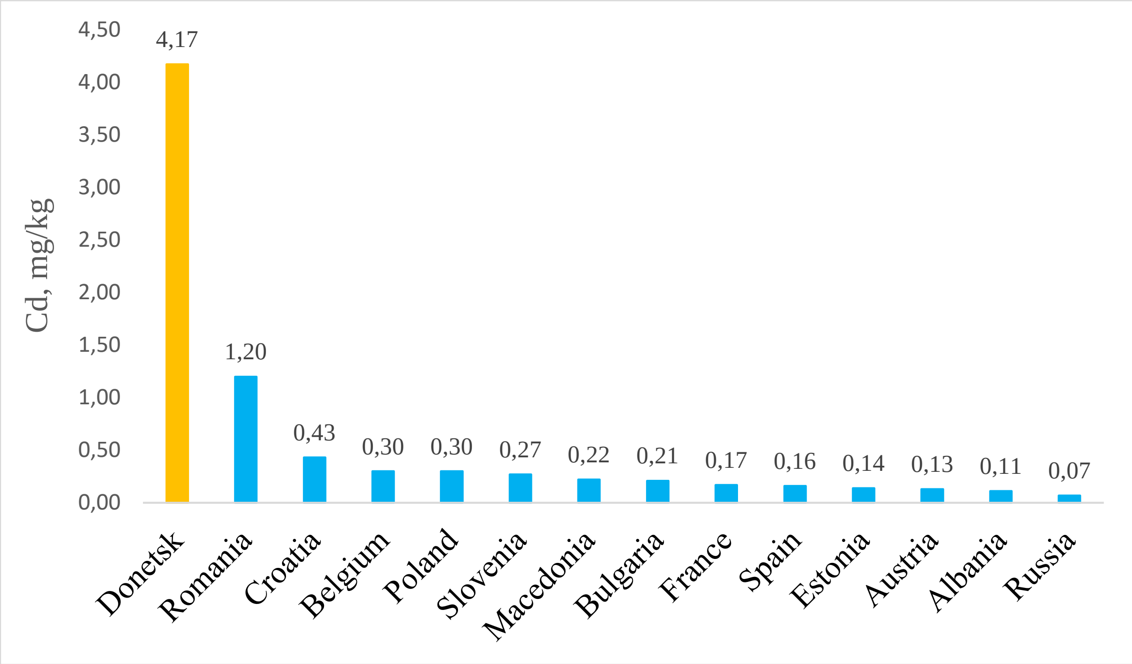

Fig. 9 Medial values of cadmium in samples of bryophytes in different countries

The total content of heavy metals in question in the moss samples collected at the territory of Donbass exceeds the concentration of those in bryophytes from the other European countries (Table 1).

These concentrations are most obvious for lead content: 94.99 mg/kg, which exceeds the concentration in the Romanian moss (30.8 mg/kg) by more than 3 times (64.19 mg/kg), cadmium (4.17 mg/kg), which exceeds the concentration of the Romanian moss (1.20 mg/kg) by 2.97 mg/kg. The content of copper (11.57 mg/kg) exceeds the values from the other countries, but lower than the medial content of these elements in moss of Romania.

Acknowledgements

The authors would like to thank some members of the staff of the Department of Activation Analysis and Applied Research of FLNP JINR for handling analysis of the moss samples. I am also grateful to my supervisor, Prof. Marina V. Frontasyeva, for her support and advices.

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