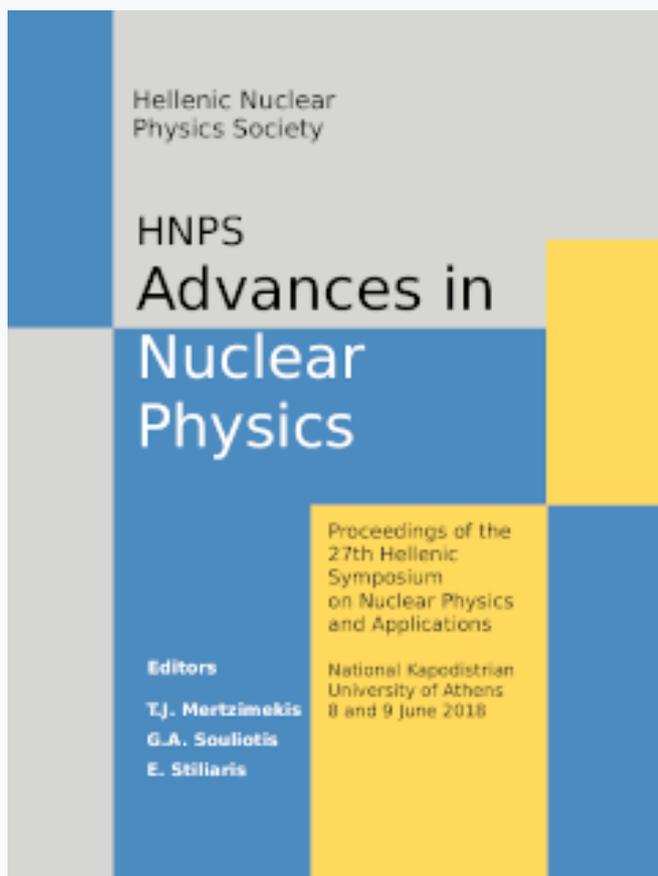


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# Heavy metals and radionuclides concentrations in mosses from the region of Northern Greece

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**Abstract** Mosses can be used as biomonitors for investigating the atmospheric deposition of radionuclides and heavy metals. They receive most of their nutrients directly from wet and dry deposition. During the 2015/2016 European moss survey, ninety-five samples of *Hypnum cupressiforme* Hedw. were collected in Northern Greece. They were analyzed to the content of heavy metals using INAA. The concentrations of <sup>137</sup>Cs, <sup>40</sup>K, <sup>7</sup>Be and <sup>210</sup>Pb radionuclides were determined using gamma spectrometry. Differences have been observed in the activity concentrations between mosses collected from ground surface, rocks, branches and near roots. Finally, a high sampling density was achieved, providing information for the elemental and radionuclides deposition from the atmosphere to terrestrial systems over the region of Northern Greece.

**Keywords** biomonitoring, moss, radionuclides, heavy metals

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## INTRODUCTION

Since the late of 60's, a lot of European countries have used bryophytes as bioindicators in national and multinational studies of the atmospheric deposition of heavy metals and radionuclides [1-10]. The use of the moss technique for the determination of atmospheric deposition in different geographical areas is based on the fact that the heavy metals concentrations in mosses, especially in the carpet-forming species, are associated to atmospheric fallout [6,10]. Using biological indicators in monitoring of the environment is a successful, effective and low cost method compared to the direct ambient air measurements [1-6]. A large number of sampling sites can be achieved needing no special instrumentation, while simultaneous measurements of heavy metals and radionuclides are carried out. The absence of roots indicates that nutrients, heavy metals and radionuclides are accumulated in

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carpet-forming mosses due to wet and dry deposition [10]. These properties make mosses an ideal medium for metals and airborne radionuclides deposited from the atmosphere [11].

Naturally occurring radionuclides  $^7\text{Be}$  and  $^{210}\text{Pb}$  together with the artificial  $^{137}\text{Cs}$  are a useful tool in studying the environmental processes.  $^7\text{Be}$  and  $^{210}\text{Pb}$ , right after their formation in the atmosphere, they are attached to aerosol particles and follow their path [12-13].

$^7\text{Be}$  is formed by spallation reaction between cosmic rays and nuclei of oxygen and nitrogen in the stratosphere and upper troposphere [14-15]. The concentrations of  $^7\text{Be}$  in surface air are decreasing with the increase of latitude [12,13,15].

The radionuclide  $^{210}\text{Pb}$  is widely found in the terrestrial environment. It is a member of  $^{238}\text{U}$  decay series. Lead-210 is present in the atmosphere due to the decay of  $^{222}\text{Rn}$  diffusing from the ground [16]. Once  $^{210}\text{Pb}$  is formed in the atmosphere, it is attached to aerosol particles and follows their path. So it can be used for tracking the aerosols deposition and their residence time in the atmosphere.

The artificial radionuclide  $^{137}\text{Cs}$  was mostly released in the atmosphere due to atmospheric nuclear weapon tests and Chernobyl nuclear accident. After that, there were no other significant  $^{137}\text{Cs}$  emissions, and the atmospheric  $^{137}\text{Cs}$  was exposed to physical decay as well as wet and dry deposition [17]. In recent years the Fukushima accident contributed to the release of  $^{137}\text{Cs}$  in the atmosphere but with minor influence in regions far from Japan.

The aim of this study is to measure the elemental concentrations and the activities of the radionuclides  $^{137}\text{Cs}$ ,  $^7\text{Be}$ ,  $^{210}\text{Pb}$  and  $^{40}\text{K}$  in mosses and investigate their possible variabilities between different places in Northern Greece.

## EXPERIMENTAL DETAILS

Ninety five (95) samples of *Hypnum Cupressiforme* Hedw. were collected in the North part of Greece. The samples were collected from different altitudes, from 30 m to 1450 m above the mean sea level. All samples of fresh plant material were collected in a short time interval during the end of summer 2016, according to ICP Vegetation Protocol [18]. After sampling, mosses were dried at  $105^\circ\text{C}$  for 2 hours to a constant weight. Soil and all other mechanical impurities were removed manually. After the preparation, each sample of mosses were put in two cylindrical plastic containers, diameter 67 mm and height 31 mm.

All samples were analysed to the content of radionuclides concentrations in the University of Novi Sad in Serbia. Low-background extended range HPGe detector equipped with a Be window was used in order to get evidence about  $^{210}\text{Pb}$ . Relative efficiency of detector is 32%. The detection efficiency was established using NIST Standard Reference Material 4350B (Columbia River sediment) packed in same geometry. Accuracy of efficiency calibration was tested using IAEA source made from dry grass [11]. The concentrations of  $^{210}\text{Pb}$ ,  $^{137}\text{Cs}$ ,  $^7\text{Be}$  and  $^{40}\text{K}$  were determined by their gamma-line in 46.5 keV, 661.7 keV, 477.6 keV and 1460.8 keV, respectively.

The concentrations of 33 elements were determined in all moss samples by using INAA performed in Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia [19,20].

## RESULTS AND DISCUSSION

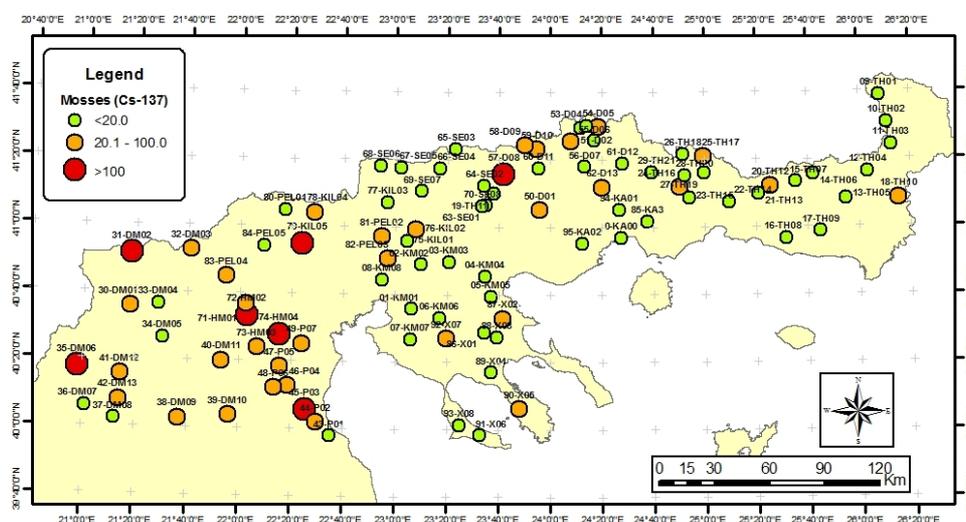
The activity concentrations of the radionuclides  $^{137}\text{Cs}$ ,  $^7\text{Be}$ ,  $^{210}\text{Pb}$  and  $^{40}\text{K}$  were calculated. The min and max concentrations in  $\text{Bq kg}^{-1}$  of the above radionuclides as well as the mean value are presented in Table 1.

**Table 1.** The min and max concentrations of  $^7\text{Be}$ ,  $^{137}\text{Cs}$ ,  $^{40}\text{K}$ ,  $^{210}\text{Pb}$ . In parenthesis the mean activities of the above radionuclides are presented.

Radionuclides	Range (mean value) $\text{Bq kg}^{-1}$
$^7\text{Be}$	69-1280 (388)
$^{137}\text{Cs}$	0-425 (35)
$^{210}\text{Pb}$	147-1920 (817)
$^{40}\text{K}$	120-750 (269)

Differences have been noticed in the activity concentrations between mosses collected from different surface types such as ground surface, rocks, branches and roots.  $^7\text{Be}$  and  $^{210}\text{Pb}$  activity concentrations are higher in moss samples from the ground surface and rocks than those near roots.  $^{137}\text{Cs}$  concentrations are higher in mosses collected near roots and rocks than those collected on the ground surface.  $^{40}\text{K}$  concentrations are higher in mosses collected from branches and near roots than those collected from rocks.

The cosmogenic radionuclide  $^7\text{Be}$  and the natural occurring radionuclide in the Earth's crust  $^{40}\text{K}$  are not correlated. The long-living radionuclide  $^{40}\text{K}$  was transferred to mosses due to the re-suspension and the decayed plant matter covering mosses [21]. The majority of  $^{210}\text{Pb}$  in mosses has arrived through aerosol deposition (e.g. dust that contains  $^{238}\text{U}$  daughters). The activity of  $^{210}\text{Pb}$  in mosses can vary from region to region due to the different soil structure. In Fig. 1 the concentrations of  $^{137}\text{Cs}$  in moss samples is presented. The majority of  $^{137}\text{Cs}$  in mosses has arrived through aerosol deposition (re-suspension).



The concentrations of 33 elements were determined in moss samples by using INAA. The min and max concentrations ( $\mu\text{g g}^{-1}$ ) of 7 elements are presented in Table 2 below. Higher concentrations of Al and V are observed in regions where metal industries exist and in regions close to coal fired power plants. Areas with manufacturing industries, as well as electricity production activities, present also a rise in concentrations of As, Cr and Ni elements.

**Table 2.** The minimum and maximum concentrations of Al, As, Cr, Fe, Ni, V, Zn in Greek moss samples ( $\mu\text{g g}^{-1}$ ).

	<i>Al</i>	<i>As</i>	<i>Cr</i>	<i>Fe</i>	<i>Ni</i>	<i>V</i>	<i>Zn</i>
Min	1350	0.52	2.04	1010	1.72	2.61	14.60
Max	46100	17.90	222.00	28700	138.00	33.40	282.00

## CONCLUSIONS

Moss biomonitoring is an effective and economic technique for the detection of  $^{137}\text{Cs}$ ,  $^7\text{Be}$ ,  $^{210}\text{Pb}$  and  $^{40}\text{K}$  radionuclides especially for measurements in large areas. Ninety-five sampling sites were covered and details were provided for the spatial distribution of the above radionuclides and heavy metals over Northern Greece. Mapping of  $^7\text{Be}$  and  $^{210}\text{Pb}$  activity in mosses provides information about aerosols deposition and helps tracking their pathway. Finally, regional differences in the atmospheric deposition of several elements can be achieved.

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