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Using moss and lichens in biomonitoring of heavy-metal contamination of forest areas in southern and north-eastern Poland

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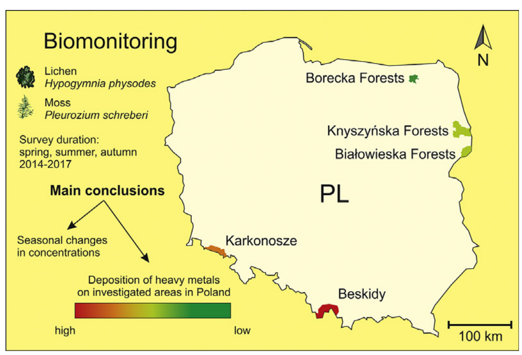
HIGHLIGHTS

- Mn, Ni, Cu, Zn, Cd, Hg and Pb content in moss and lichens samples collected in Poland
- Periodical sample collection during 3 years
- Seasonal changes in metal concentrations in moss and lichens
- An increase in cadmium concentration at the beginning of the growing season

GRAPHICAL ABSTRACT



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ABSTRACT

In the years 2014–2016 biomonitoring studies were conducted in the forest areas of south and north-eastern Poland: the Karkonosze Mountains, the Beskidy Mountains, the Borecka Forest, the Knyszyńska Forest and the Białowieska Forest. This study used epigeic moss *Pleurozium schreberi* and epiphytic lichens *Hypogymnia physodes*. Samples were collected in spring, summer and autumn. Approximately 500 samples of moss and lichens were collected for the study. In the samples, Mn, Ni, Cu, Zn, Cd, Hg and Pb concentrations were determined. Based on the obtained results, the studied areas were ranked by extent of heavy-metal deposition: Beskidy > Karkonosze Mountains > forests of north-eastern Poland. Some seasonal changes in concentrations of metals accumulated in moss and lichens were also indicated. There was observed, i.a., an increase in Cd concentration at the beginning of the growing season, which may be related to low emissions during the heating season. Analysis of the surface distribution of deposition of metals in the studied areas showed a significant contribution of nearby territorial emissions and unidentified local emission sources. The contribution of distant emission to Zn, Hg and Pb deposition levels in the Karkonosze and Beskidy region was also indicated.

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1. Introduction

In studies of the elemental composition of environmental matrices, particular attention is paid to heavy metals, most of which are harmful to human health. Among them are distinguished the metals known to have strongly toxic properties: Cd, Hg and Pb. Heavy metals are originally extracted from the lithosphere, intentionally by planned extraction and incidentally in the process of obtaining other raw materials – mainly fuels. Industrial emissions associated with fuel combustion are considered to be the main source of atmospheric pollution. In many countries, including Poland, one of the most important sources of heavy-metal emissions is uncontrolled low emission during the heating season (Olszowski and Bożym, 2014). It should be noted that heavy metals are also released into the atmosphere through natural processes, *e.g.* due to volcanic exhalation (Loppi et al., 1999). Heavy metal emission, followed by deposition, increases contamination of the lithosphere and hydrosphere. Heavy metals introduced into ecosystems are involved in the exchange of matter between biocenosis and biotope, and by integrating into the subsequent trophic chains they often reach the human body (Ping et al., 2009).

Today, methods using bioindicators and biomonitors are increasingly being used to assess environmental quality. Compared to the classical monitoring of environmental pollution, the main advantage of this type of method is that it is inexpensive and does not require any collection of training samples, the advantages of which include allowing free planning of the number of measurement sites (Markert et al., 2003; Markert, 2007). The most frequently used biomonitors of atmospheric aerosol pollution with heavy metals and radioisotopes are mosses and lichens (Szczepaniak and Biziuk, 2003; Wróbel et al., 2015; Dołhańczuk-Śródka et al., 2015). Due to their anatomical structure and the way they absorb nutrients, these organisms effectively accumulate atmospheric pollutants, especially heavy metals. Their use in biomonitoring studies allows for assessment of the contamination levels of studied areas (Cucu-Man and Steinnes, 2013) and identification of the sources and directions of spread of pollutants (Kolon et al., 2015). Biomonitoring studies are conducted on all continents, including the Arctic (Riget et al., 2000; Wojtuń et al., 2013) and Antarctica (Colabuono et al., 2015). The largest project so far to use mosses for biomonitoring research is ICP Vegetation which covers most European countries. In 1990, 21 European countries contributed to the first session of the project (Harmens et al., 2007). Since 1990, moss samples have been collected every 5 years.

Much information is also provided by biomonitoring studies conducted on a local scale to assess emissions from point (Suchara and Sucharová, 2008), linear (Zechmeister et al., 2005) and territorial (Liiv and Kaasik, 2004) emission sources. A frequent topic of biomonitoring research is the assessment of heavy-metal contamination of forest ecosystems and changes taking place there (Cucu-Man and Steinnes, 2013). In this case, the important tools for assessing the origin of pollutants are statistical methods, such as factor analysis (Frontasyeva et al., 2004), cluster analysis (Dragović and Mihailović, 2009) and compositional data analysis (Ziembik et al., 2013). The results of the study, intended to distinguish primary from secondary effects (*e.g.* raising of dust from the soil), are often interpreted by the designation of the *Enrichment Factor* (*e.g.*, Gandois et al., 2014). The enrichment factor enables comparison to be made between standard proportions (of Sc, Al and rare earth metals) and the proportions of analytes accumulated in the biomonitor and in the soil.

Another approach presented in this paper is to interpret the results by determining the *Comparison Factor*, which compares the concentration of analytes accumulated in lichens and moss (Kłos et al., 2010; Kłos et al., 2011). Studies show that, due to the different transport mechanisms of analytes from the soil, significantly higher concentration of analytes accumulated in lichens than in moss may indicate primary and relatively recent deposition of these analytes.

The aim of the presented study was to compare the contamination of forests in southern and north-eastern Poland with the heavy metals Mn, Ni, Cu, Zn, Cd, Hg and Pb – including in terms of seasonal changes – and to identify the potential sources of these metals.

1.1. Materials and methods

The study used epigeic moss *Pleurozium schreberi* and epiphytic lichens *Hypogymnia physodes*.

1.2. Study areas

Fig. 1 shows the location of the study areas on the Polish map, differing in level of anthropogenicity, and also shows the location of the sampling sites within the studied areas.

1.3. Method

Samples of lichens were collected from horizontal branches of spruce or larch at a height of 1.5–2.0 m from the ground, from sites not affected by sub-crown precipitation, located at least 300 m from busy roads. For each session, moss and lichen samples were collected within a period 2–3 days. Samples of moss were also collected from around the trees from which lichen samples were collected. At each site 6 subsamples of similar abundance were collected and were then mixed to obtain a sample of plant material. The actual positions of the sites differed to varying degrees for each session. Geographical coordinates were determined to an accuracy of 1″, which approximately corresponds to 30-m square. The approximate location and number of sampling sites is illustrated in Fig. 1. From each of 56 sites, samples of moss and lichen were collected 9 times. The total number of the plant samples was 1008. Samples were collected in 2014–2016. The sampling dates are set out in Table 1. The table also lists the metals that were determined in samples collected in subsequent sessions.

After manual removal of impurities and drying of samples at 323 K, the collected material was homogenized in an agalite mortar and stored in closed polyethylene containers. The 0.4 g of subsamples taken from homogenized material was mineralised in a mixture of nitric acid and hydrogen dioxide in an iCE microwave oven (Thermo Electron Corporation, USA). To determine Hg concentrations in plant samples, an AMA 254 analyser was used.

1.4. Quality control

In the Supplementary Materials (SM) additional data concerning quality of determinations are presented. In Table 2 of SM, the instrumental detection limits (*IDL*) and instrumental quantification limits (*IQL*) for the spectrometer, iCE 3500 and AMA 254 are presented. The results were converted into 1 g of sample.

Calibration of the spectrometer was performed with a standard solution from ANALYTIKA Ltd. (Czech Republic). The values of the highest concentrations of the models used for calibration (2 mg/dm^3 for Cd, 5 mg/dm^3 for Cu, Zn, Pb, 7.5 mg/dm^3 for Mn and 10 mg/dm^3 for Fe) were approved as linear limits for signal dependence on concentration.

In Table 3 SM, concentrations of heavy metals in certified reference materials BCR 414 *plankton* and BCR-482 *lichen*, produced at the *Institute for Reference Materials and Measurements, Belgium*, are shown.

Interlaboratory comparison of determination results was included in quality assurance procedures. The measurements were carried out in Opole University (UO) labs and in an accredited lab at ZWP EMITOR (Opole, PL). For the comparison, the samples of moss and lichen collected in sites 2 and 8 (Karkonosze, Session II) were taken. Concentrations of metals were determined in solution after mineralisation and dilution to 25 cm^3. The measurement results are collected in Table 4 SM.