

## Abstract

Bioindicators are one of the most popular and useful tool for assessing anthropogenic impacts on air quality. The main objective of this study was to evaluate the possibility of creating a useful and reliable tool for characterizing and evaluating the environmental state (both qualitatively and quantitatively) of a given study area using correlations existing between compounds analysed both in the atmosphere and in lichens. Moreover, it was tried:

- i. to identify potential sources of contaminants;
- ii. to verify whether atmospheric gaseous pollutants can be inferred from the analysis of bioindicators composition;
- iii. to investigate if certain characteristics of the investigated area, such as elevation, human presence or road traffic, influence the variability of the analyzed compounds.

To fulfill these purposes two sampling seasons were selected: 1) the heating season (winter - February 2013, when higher anthropogenic inputs were expected) and 2) the vegetative season (summer - July 2013, with no heating and thus a lower anthropopressure stress expected). Depending on availability, samples of *Hypogymnia physodes* (1-20 g of dry mass) were collected in 20 locations in the Swietokrzyski National Park (ŚNP; 18 samples) and in its vicinity (2 samples). Three of the sampling points were located along roads, and another three were taken at the highest elevation of the park. Lichens were collected from trunk and branches of *Abies alba* trees at approx. 2 m height above the ground.

The analysis of the main gaseous pollutants presented the following average concentration values for winter and summer, respectively: NO<sub>2</sub> 7.5 and 2.7 μg·m<sup>-3</sup>; SO<sub>2</sub> 7.2 and 0.8 μg·m<sup>-3</sup>; CO<sub>2</sub> 512 and 468 ppm. The concentrations for the investigated elements in lichen samples showed the following average values for winter and summer, respectively: %C<sub>org</sub> 43.5 and 46.4%; %N<sub>org</sub> 1.9 and 1.9%; %S<sub>adsorbed</sub> 0.041 and 0.048%; %S<sub>org</sub> 0.045 and 0.118%. Their corresponding average isotope compositions for winter and summer campaign were as follow, respectively: δ<sup>13</sup>C<sub>org</sub> -26.6 and -26.8‰; δ<sup>15</sup>N<sub>org</sub> -9.0 and -9.6‰; δ<sup>34</sup>S<sub>adsorbed</sub> 3.4 and 2.6‰; δ<sup>34</sup>S<sub>org</sub> 2.6 and 1.3‰. Metal (Cd, Cu, Zn, Pb, Mn, Mg, Fe) concentrations and free radical concentrations were also measured in the lichen samples.

Results yielded important information about the ŚNP local environmental conditions:

- i. Concentrations of the main gaseous pollutants were higher during winter than during summer, and higher at the highest elevations (SO<sub>2</sub>) and along roads (NO<sub>2</sub>);
- ii. It was identified an approximately six months delay between emissions of the contaminants in the air and their incorporation into bioindicators, revealed by the study of both the contaminant concentrations as well as their corresponding isotope compositions;
- iii. It was showed that variations in the isotope compositions of the investigated elements in bioindicators were controlled by fossil fuel combustion from road traffic and the industry as well as by natural factors such as elevation (related to O<sub>3</sub> concentration, precipitation and lightening levels);

The Principal Component Analysis (PCA) which was operated on the generated dataset identified that the variability in air quality at the Świętokrzyski National Park was controlled by two main independent factors: 1) long distance transport of pollutants and 2) local emissions from fossil fuel combustion.