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Original Research

Determination of Heavy Metal Concentration in Mosses of Słowiński National Park Using Atomic Absorption Spectrometry and Neutron Activation Analysis Methods

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Abstract

The aim of this study was to (i) determine environmental pollution in Słowiński National Park on the basis of Zn, Fe, Ni, Cd and Cr concentrations in *Pleurozium schreberi* gametophores, (ii) draw a map of heavy metal concentrations in the area and (iii) compare the results with previous reports. Samples of *Pleurozium schreberi* were collected from 27 locations in Słowiński National Park in 2002. Cd concentration was determined by atomic absorption spectrometry (AAS), and Zn, Fe, Ni and Cr concentrations were determined using neutron activation analysis. The results of our research suggest a reduction of heavy metal contamination in the area of Słowiński National Park over the last 27 years and confirmed that the area is one of the cleanest in Poland and may still serve as a reference background for determining pollution in other areas.

Keywords: heavy metals, moss monitoring, *Pleurozium schreberi,* Słowiński National Park

Introduction

Słowiński National Park (18,619 ha) is situated in the central part of the Polish Baltic coast. It was founded in 1967 to protect local ecosystems: dune, lake, peat bog and forest. Due to its special environmental value, shifting sand dunes and eolic processes unique on the European scale, the Park was registered in 1977 as one of the UNESCO World Biosphere Reserves. Słowiński National Park is also included in the RAMSAR Convention on Wetlands, whose protection includes the habitats of water and marsh birds [1, 2].

With only one thousand permanent residents, the area is lightly inhabited; however, each year 500,000 tourists visit the Park. There are no large towns, factory plants or high traffic roads within many kilometers, but due to the dominant wind direction, pollutants do reach the area. Most

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Table 1. Results obtained by Grodzińska et al. [5, 6, 9, 10] and our own results concerning heavy metal concentration in the mosses (*Pleurozium schreberi*) within Słowiński National Park.

Year	Concentration [µg/g d.m.]					References
	Zn	Fe	Ni	Cd	Cr	
1975	70	1250	3.5	0.9	4.9	[5, 6]
1986	35	760	2.5	0.6	2.8	[9]
1995	40	250	1.5	0.25	1.5	[10]
2002	38	233	0.9	0.25	0.8	-

of this pollution comes from long-distance transport of air pollution from western and south-western Poland and from Germany. Local pollution only slightly contributes to the deterioration of the aerosanitary situation [3, 4].

Studies on heavy metal content in mosses, carried out in Polish national parks in 1975 and repeated in 1986, 1990 and 1995, showed that Słowiński National Park is one of the least polluted areas in Poland [5-10]. However, because it is constantly exposed to industrial pollution from long-distance transport, it is absolutely necessary to monitor the Park's status. Such studies are essential for securing the main function of national parks, namely the protection of ecosystem biodiversity in its most intact form [3].

Mosses are commonly used as indicators of heavy metal pollution. It is based on their specific morphological and physiological properties [8, 11, 12], i.e.:

(i) they have no epiderms or cuticule – their cell walls are easily penetrable by metal ions;
(ii) they have no organs for the uptake of minerals from the substrate – they obtain these mainly from precipitation and dry deposition;
(iii) they accumulate metals in a passive way, acting as ion exchangers.

The aim of this study was to

(i) determine environmental pollution in Słowinski National Park on the basis of Zn, Fe, Ni, Cd and Cr concentrations in *Pleurozium schreberi* gametophores,
(ii) draw a map of heavy metal concentrations in the area, and
(iii) compare the results with previous reports.

Material and Methods

Material and the Research Area

Samples of *Pleurozium schreberi* were collected from 27 locations in Słowiński National Park in 2002. The samples were taken from clearings within the coniferous forest. Each location was at least 300 meters from main roads and built-up areas, and at least 100 meters from minor roads and individual houses. The area of moss sampling was 2500 m^2 for each location. The geographic coordinates were determined using GPS. Four zones were established to determine the significance of differences in heavy metal concentrations in the Park area (central zone: sites 1-6, western coastal zone: sites 7-14, middle coastal zone: sites 15-19 and eastern coastal zone: sites 20-27).

Each site was subject to at least 3 samplings. Each sampling included 5 to 10 subsamples taken within a few meters radius. Their total capacity was about 2 dm^3. The sampled moss was packed into airtight bags and transported to a laboratory. In the laboratory the samples were prepared by removing irrelevant material, such as leaves, twigs, conifer needles and dead shoots. The samples were then dried to reach a constant weight of about 20 g at 40°C.

Heavy Metal Concentration Analysis

Cd concentration was measured by atomic absorption spectrometry – AAS (Solar 969), in air-acetylene flame [13]. Zn, Fe, Ni and Cr concentrations were determined by neutron activation analysis [14, 15].

For neutron activation analysis moss samples of about 0.3 g dry mass (d.m.) were heat-sealed in polyethylene foil bags for short-term irridation and packed in aluminum cups for long-term irradiation. Neutron activation analyses were performed in the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna (Russia). This method allows quantitative analysis of high precision for about 40 chemical elements simultaneously. In this paper results of analyses of four metals are presented: Zn, Fe, Ni, Cr. Neutron activation analysis is one of the instrumental neutron analysis methods. It consists of activation of atomic nucleus due to absorption of a fundamental particle, mostly neutron, and then investigating gamma radiation spectrum emitted by radioisotopes which came into being in the sample. Reactor IBR-2 in the Joint Institute for Nuclear Research in Dubna is a pulsed fast-neutron source, in which periodic reactivity change takes place, within a very wide range of states: from subcritical to supercritical. In this reactor supercritical state is gained by periodic directing of neutron beam to the reactor active zone by reflecting them from rotating neutron reflectors filled with helium [15].

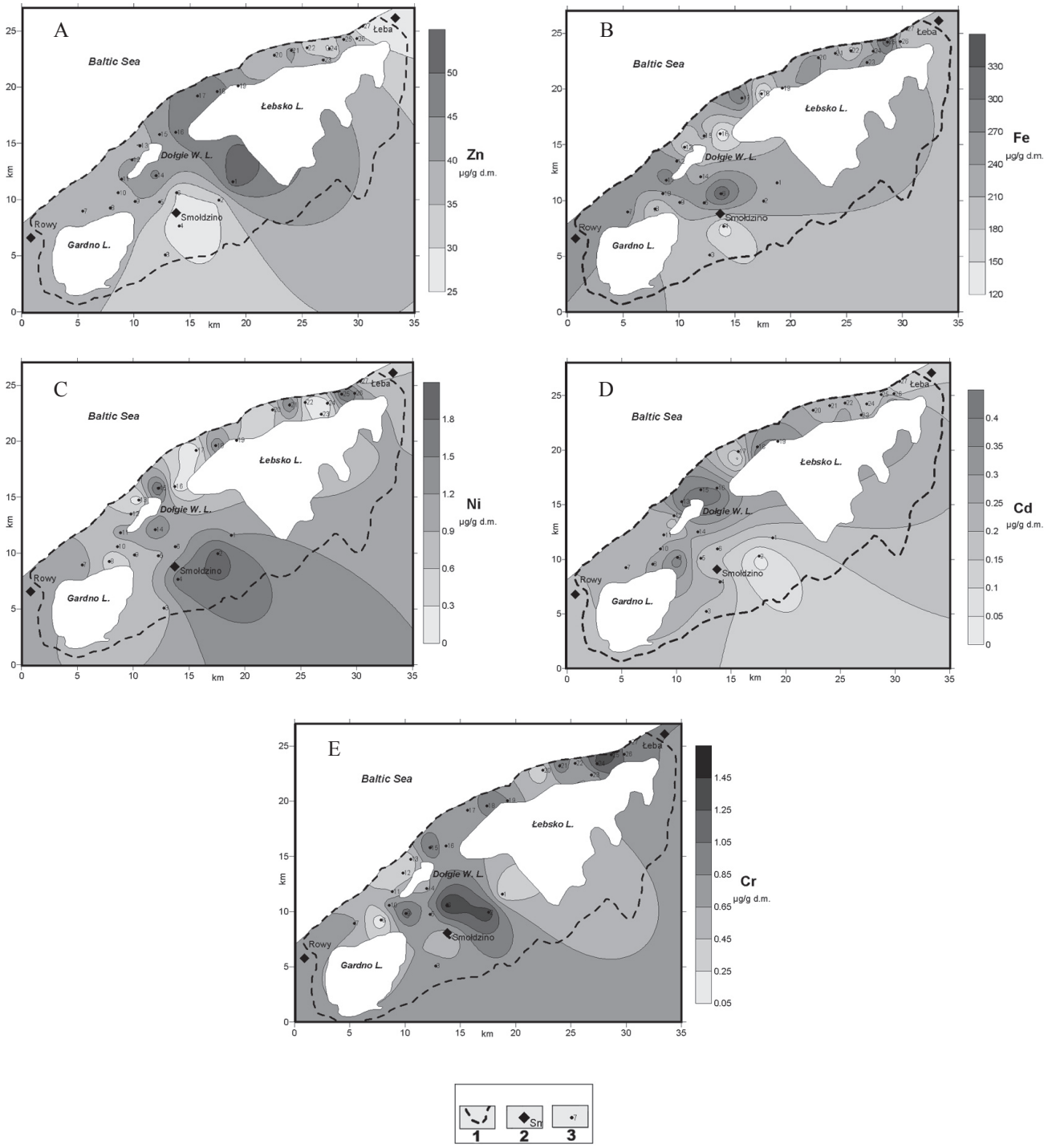

Fig.1. A-E. Metal concentrations within Słowiński National Park area. (A – Zn, B – Fe, C – Ni, D – Cd, E – Cr). Maps were drawn using the Krigging method (Surfer 8.0 software). Pollutant concentrations were directly determined from measurements of heavy metal concentrations in samples of *Pleurozium schreberi* moss, taken at 27 sampling sites in the northern and central parts of Słowiński National Park. In the southeastern part of the park, a lack of sampling points made it impossible to use interpolation to analyze the pollution data in the area. Definitions: 1 - Słowiński National Park borders, 2 - towns and villages, 3 - sampling sites

Determination of Heavy Metal Concentrations Across the Park Area

Maps were drawn using the Krigging method (Surfer 8.0 software). Contamination of the investigated area was evaluated with regard to the distribution of pollutants. They were directly determined from measurements of heavy metals concentrations in samples of *Pleurozium schreberi* moss taken at 27 sampling points in the northern and central part of Słowiński National Park. In the

southeastern part of the park, a lack of sampling points made it impossible to use interpolation to analyze the pollution data in the area.

Statistical Analysis

Statistical analysis was conducted using v.6.0 of Statistica software. Non-parametric ANOVA Kruskal-Wallis rank and U-Mann Whitney tests were used to check the significance of difference ($p<0.05$). A test for Spearman rank correlation coefficient (rs) was used to check the statistical significance of observed correlations.

Results

The analysis of heavy metal concentrations (Zn, Fe, Ni, Cd, Cr) in *Pleurozium schreberi* gametophores served as a basis for the evaluation of environmental pollution in Słowiński National Park. The spatial distribution of the heavy metal pollutants in the mosses in Słowiński NP is illustrated in Figs. 1. A-E. For each element, concentration classes were distinguished. Areas where concentrations of a specific metal in the moss were within a given range, were drawn on the maps as distinct zones.

Mean Zn concentration in the area was 38.0 μg/g d.m.(min. 24.8 μg/g d.m. – max. 53.3 μg/g d.m.) (Fig. 2. A). It had the highest mean value (45.5 μg/g d.m) in the middle coastal zone and the lowest mean value in the central zone (34.8 μg/g d.m) (Fig. 3. A). Significant differences between the zones were observed between the central zone and both western and eastern coastal zones ($p<0.0046$ and $p<0.0293$, respectively), between the western coastal zone and the middle coastal zone ($p<0.0108$), and between the middle coastal zone and the eastern coastal zone ($p<0.0031$).

Mean Fe concentration in the area was 233.9 μg/g d.m. (min. 123.0 μg/g d.m. – max. 335.0 μg/g d.m) (Fig. 2. B). The highest mean Fe concentration was reported in the eastern coastal zone (243.6 μg/g d.m.), and the lowest in the middle coastal zone (201.3 μg/g d.m) (Fig. 3. B). Differences in Fe concentrations between all the zones were not significant.

Mean Ni concentration in the area was 0.90 μg/g d.m. (min. 0.09 μg/g d.m. – max. 2.02 μg/g d.m) (Fig. 2. C). The highest mean Ni concentration was observed in the central zone (1.23 μg/g d.m), and the lowest in the eastern coastal zone (0.73 μg/g d.m) (Fig. 3. C). Differences in Ni concentrations between all the zones were not significant.

Mean Cd concentration in the area was 0.24 μg/g d.m. (min. 0.03 μg/g d.m. – max. 0.42 μg/g d.m) (Fig. 2. D). The highest mean Cd concentration was reported in the middle coastal zone (0.34 μg/g d.m.), and the lowest in the central one (0.15 μg/g d.m) (Fig. 3. D). Significant differences in Cd concentrations were only observed between the central zone and the western and eastern coastal zones ($p<0.0173$ and $p<0.0123$, respectively).

Mean Cr concentration in the area was 0.78 μg/g d.m. (min. 0.05 μg/g d.m. – max. 1.53 μg/g d.m) (Fig. 2. E). The highest mean Cr concentration was observed in the eastern coastal zone (0.90 μg/g d.m.), and the lowest in the western coastal zone (0.60 μg/g d.m) (Fig. 3. E). Differences in Cr concentrations between all the zones were not significant.

A significant correlation between the metal concentrations was only found between Cd and Fe ($rs = - 0.47$; $p<0.01$).

Discussion

Słowiński National Park is under relatively little threat from gas and dust pollution compared with other national parks in Poland. This is due to its location in a lightly inhabited area of the Baltic coast, far from industrial centers. Despite the industrial emissions and dust from long-distance transport still present in the area, the natural environment of Słowiński National Park is relatively unaffected – which is why it could serve as a reference area for determination of pollution in other areas in Poland [5-10].

Mean heavy metal concentrations in mosses collected in 1995 across Poland were: Zn – 43.0 μg/g d.m., Fe – 362.0 μg/g d.m., Ni – 1.4 μg/g d.m., Cd – 0.44 μg/g d.m. and Cr – 1.50 μg/g d.m. [16]. Concentrations of heavy metals in *Pleurozium schreberi* were, as a rule, highest in southern Poland, where industrial plants turn out approximately 31% of the national production and release to the atmosphere approx. 40% particulate pollutants. For example, a 1998 comparison of mosses collected in Silesia-Kraków Industrial Region and control area in northeastern Poland showed that the concentrations of metals in *Pleurozium schreberi* from industrial regions are several fold higher than in the mosses from sparsely industrialized control area (respectively: for Zn – 150 μg/g d.m. and 37.4 μg/g d.m.; for Fe – 1226 μg/g d.m. and 298 μg/g d.m.; for Ni – 2.5 μg/g d.m. and 1.4 μg/g d.m.; for Cd – 2.2 μg/g d.m. and 0.1 μg/g d.m.; for Cr – 6.2 μg/g d.m. and 0.8 μg/g d.m.) [8, 17].

This study shows a decrease in heavy metal concentrations (Zn, Fe, Ni, Cd and Cr) in *Pleurozium schreberi* gametophores compared with values reported by other studies in previous years [5, 6, 9, 10]. Table 1 shows results of studies carried out by Grodzińska et al. [5, 6, 9, 10] in the same area in 1975, 1986, 1995, and also results of our own study carried out in 2002.

Our results concerning heavy metal concentration in the mosses within Słowiński National Park area are similar to measurements taken in northeastern Poland, usually used as the control area for pollution studies in Poland [8, 17]. Differences in the distribution of the metals were significant only for Zn and Cd.

The results strongly suggest a reduction of heavy metal contamination in the area of Słowiński National Park over the last 27 years. However, a direct comparison with previous studies is not possible due to different analysis methods (for Zn, Fe, Ni, Cr) and the number of sampling sites. In the stated studies [5, 6, 9, 10], heavy metal concentrations were determined in all the national parks in

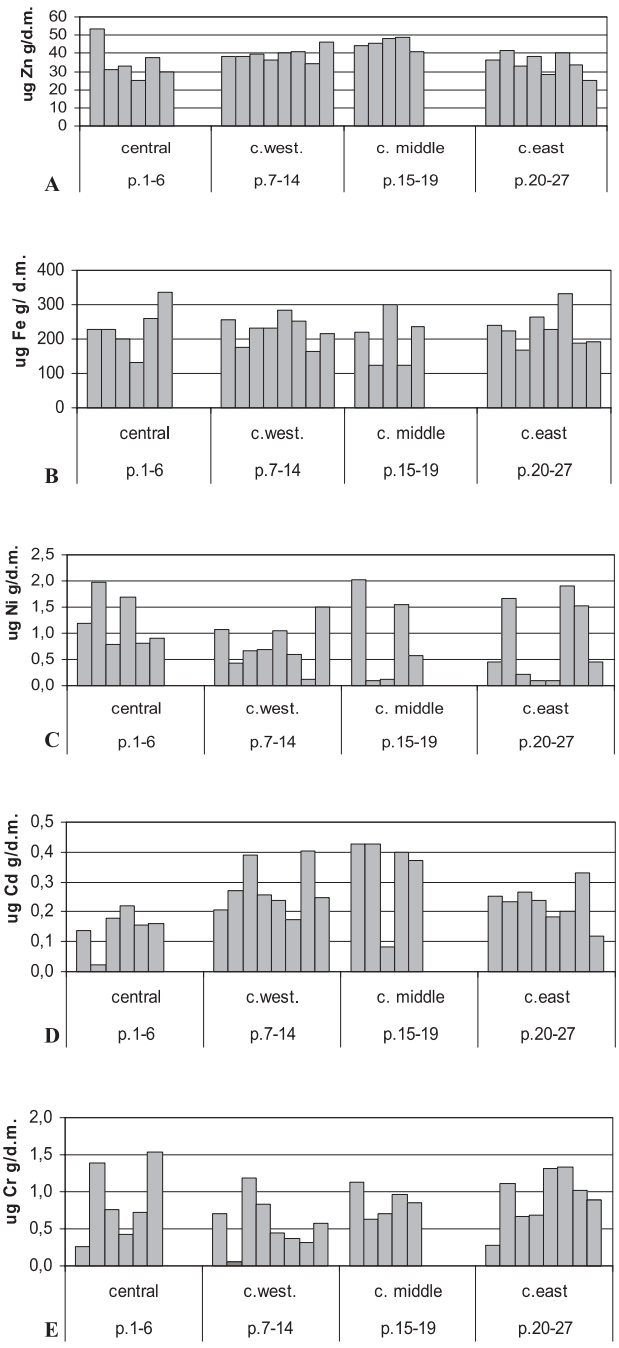

Fig.2. A-E. Mean metal concentrations (µg/g d.m) in *Pleurozium schreberi* gametophores in individual sampling sites (n= 27 locations) across the Park in 2002. Each site was subject to at least 3 samplings. Each sampling included 5 to 10 subsamples taken within a few meters radius. (A – Zn, B – Fe, C – Ni, D – Cd, E – Cr).

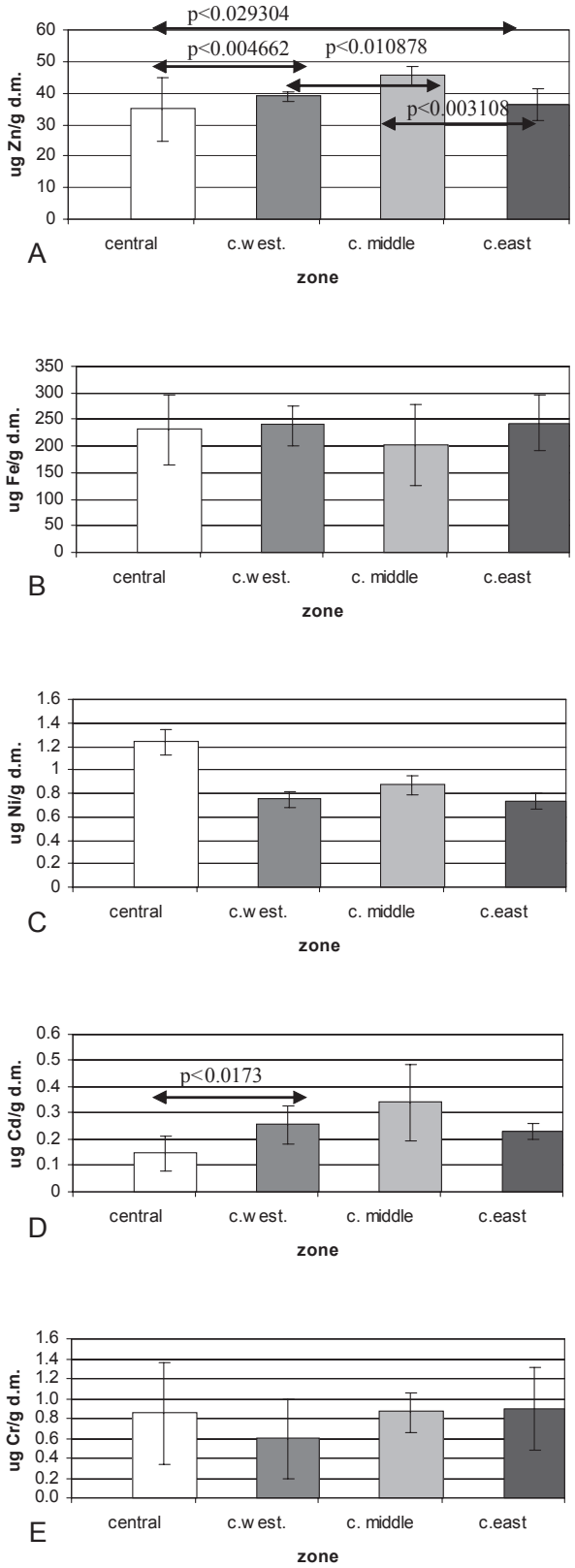

Fig.3. A-E. Mean metal concentrations (µg/g d.m) in Pleurozium schreberi gametophores determined in four zones established within Słowiński National Park area in 2002 (central zone: sites 1-6, western coastal zone: sites 7-14, middle coastal zone: sites 15-19 and eastern coastal zone: sites 20-27). (A – Zn, B – Fe, C – Ni, D – Cd, E – Cr).

Poland, and the samples were taken from two sites (in central and peripheral areas). Heavy metal concentrations were determined only by atomic absorption spectrometry analysis.

In this study of contamination, the samples were taken from 27 sites (3 samples per each site, comprising from 5

to 10 sub-samples). More precise results (for Zn, Fe, Ni, Cr) were obtained thanks to the neutron activation method of analysis.

Changes in the contamination of the Słowiński National Park with heavy metals, recorded by the mosses, correlate with a decrease in dust emission levels in 1975-2002 in Poland (by 38%, from 225.6 thousand tonnes in 1975 to 140.0 thousand tonnes in 2002) [18, 19]. The decrease in concentrations of metals is mainly caused by better control of dust emission, advanced filter technology and the closure of polluting industrial plants [10].

Conclusions

The studies on heavy metal concentrations (Zn, Fe, Ni, Cd, Cr) in *Pleurozium schreberi* gametophores, carried out in Słowiński National Park in 2002, showed a gradual reduction of pollution, and confirmed that the area is one of the cleanest in Poland. They prove that the park may still serve as a reference background for determination of pollution in other areas.

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