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Temporal and Cross-Regional Variability in the Level of Air Pollution in Poland—A Study Using Moss as a Bioindicator

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Abstract: This study assessed recent (2015) and past (2001) levels of air pollution in four regions of Poland by moss monitoring. The surveyed regions encompassed, among others, copper and zinc-lead industrial districts, large urban agglomerations and an area away from pollution sources. Moss (*Pleurozium schreberi*) was sampled from 117 sites. In 2001, the concentrations of Cd, Cr, Cu, Fe, Ni, Pb, and Zn were determined. In 2015, 10 extra elements were analyzed in addition to these metals. The results showed that the regions substantially differed in the chemical profile of air pollution, which corresponded well with the type of industry and the degree of industrialization and urbanization. There was also a significant change in air pollution between the 2001 and 2015 surveys, but it was inconsistent: its magnitude and direction were both metal-dependent and region-dependent. Namely, while the levels of some metals (e.g., Cd and Pb) decreased, other metals (e.g., Cr and Ni) showed the opposite trend. Importantly, these decreases (or increases) were usually limited to regions of low concentrations of a given metal. The results suggest that air quality has not significantly improved recently, but the type of emissions has changed. It seems that the importance of non-industrial pollution sources has increased.

Keywords: biomonitoring; moss; *Pleurozium schreberi*; air pollution; trace metal; temporal pattern

1. Introduction

According to the World Health Organization (WHO), up to two-thirds of diseases resulting in premature death or permanent deterioration in the quality of human life can be the result of chronic exposure to broadly defined environmental contamination [1]. WHO lists polluted air at the forefront of the most harmful factors. Reports from the European Environment Agency (EEA) summarizing the results of many years of research on the concentration of airborne toxic substances e.g., [2] show that even in developed countries that invest heavily in environmentally-friendly solutions (e.g., Germany, Italy), the problem of low air quality exists and may not be eliminated in the near future. In the Central and Eastern European countries (CEECs), the situation is extremely difficult. For decades, many of these countries invested in the development of heavy industries regardless of their adverse environmental effects [3]. Poland is one such country. According to Karpiński et al. [4], in Poland, over 1500 large and medium-sized state-owned enterprises were built from scratch between 1949 and 1988. Among them, those of the smokestack industry, i.e., steelworks, non-ferrous metal works, coal-based power and cogeneration plants, chemical plants and mines, prevailed. They usually used outdated equipment and technology, which resulted in the release of large amounts of trace metals and other toxic substances into the atmosphere. This release was not restricted until the early 1980s, initially due to a lack of appropriate legal regulations, and later due to the lack of effective enforcement mechanisms [5,6]. Fortunately, after the 1989 political transformation, many environmentally troublesome plants were closed or modernized, and more effective air pollution abatement policies were implemented [7]. Nevertheless, Poland remains a highly industrialized region of Europe, with a relatively high level of pollution emissions [2], which can affect the environment of neighboring countries [8].

A prerequisite for developing long-term strategies to improve air quality is the knowledge of spatial variability and temporal trends in the emission (or deposition) of several toxic substances, including trace metals, particulate matter, persistent organic pollutants (POPs), nitrogen oxides, etc. Direct measurements of the concentrations of these substances in the air or precipitation are possible, e.g., using sensor-based instruments, but due to the high costs of this approach, satisfactory spatial resolution is rarely achieved. Therefore, other bioindicator-based methods are willingly employed to monitor air quality. Mosses are one of the longest and most commonly used bioindicators of atmospheric deposition. For the first time, they were used by Rühling and Tyler [9], who showed that these plants, thanks to some characteristics (carpet-like habit, high surface-area-to-volume ratio, lack of root nutrition, lack of cuticle, high cation exchange capacity of tissues), can efficiently capture trace metals from precipitation and dry deposition. The method developed by Scandinavian researchers quickly gained recognition and entered the canon of classic monitoring techniques [10–12]. It came to Poland in the 1970s [13] and became a standard tool for environmental monitoring. For a long time, mosses were used only to assess the level of trace metal pollution. Research in recent years has proved that they can also be successfully used to detect many other substances, e.g., POPs, nitrogen, radionuclides, particulate matter [14–17].

Although the spectrum of analyzed substances in mosses has increased substantially and the method itself has been improved over time (moss bag technique using devitalized cloned moss material as adsorbent is recommended [18]), most moss surveys are still conducted according to the old scheme: naturally growing mosses are sampled and trace metals are targeted elements in analyses [19]. The explanation is simple: this is the most cost-effective approach, and it is the only one possible when comparing the current level of pollution with that recorded in the past. This approach was also used in moss monitoring conducted in Poland and the results for 2001 and 2015 are presented in this paper. Our main goals were to characterize (1) the temporal change in the concentration of seven trace metals (Cd, Cr, Cu, Fe, Ni, Pb, and Zn) in moss between the 2001 and 2015 surveys, and (2) the differences in the chemical profile of atmospheric deposition (determined for 2015 based on 17 elements measured in moss, including trace and major elements) between four regions of the country differing in type of industry and the degree of urbanization.

2. Materials and Methods

2.1. Study Sites and Sampling

The 2001 and 2015 moss surveys were performed using *Pleurozium schreberi* (Willd. ex Brid.) Mitt.—a common moss species considered a good indicator of air quality [20,21]. These surveys were part of the European moss monitoring realized within the International Cooperative Programme on Effects of Air Pollution on Natural Vegetation and Crops [12,19]. Moss samples were collected at 117 sites (the same in both surveys) located in four regions of Poland differing in the type of industry and the degree of urbanization (Figure 1). The region in the west (LG; N = 31) encompassed the Legnica-Głogów copper district, with copper mines and smelters. The region in the south (SC; N = 29) mainly covered the Upper-Silesian agglomeration and Upper-Silesian and Cracow industrial districts—the most populated and heavily industrialized part of the country, with coal mines, coal-based facilities, zinc-lead ore mines and smelters, and steelworks. The region in the center of the country (CEN; N = 27) included parts of the Warsaw (the capital) and Łódź agglomerations, with power plants and chemical plants. The region in the northeast of the country (REF; N = 30), away from large cities and industry, was selected as the reference area. The sampling was conducted in summer according to the standard protocol developed for the European moss monitoring network [19]: at each site, several (usually 5–7) moss subsamples were taken from an area of approximately 200 m^2, from different moss carpets under gaps in the tree canopy (to reduce the influence of throughfall), and then bulked into one composite sample. Sampling sites were at least 300 m from highways and 100 m from other roads, and beyond the direct influence of local air pollution sources.

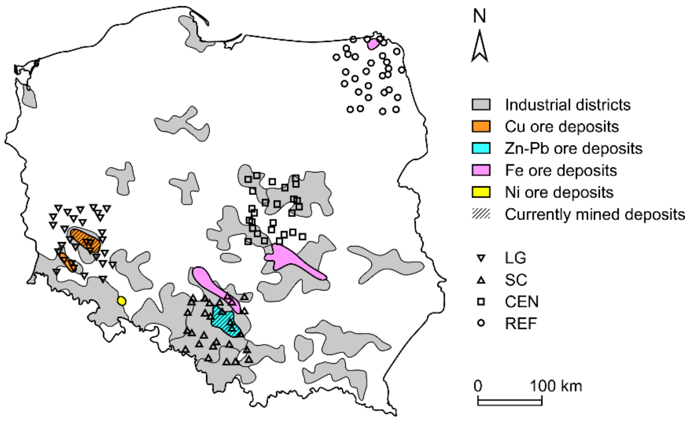

Figure 1. Location of sampling sites (see the text for explanation) in relation to industrial districts and major metal ore deposits in Poland.

2.2. Chemical Analysis

In the laboratory, moss material was cleaned carefully from macroscopic impurities (small litter fragments, soil particles, etc.). Then, its green parts, representing approximately the last three years' growth, were homogenized and dried to constant weight at 80 °C. In 2015, the concentration of 17 elements in moss was determined: As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mo, N, Ni, P, Pb, V, and Zn. For these elements except nitrogen, prior to chemical analysis, the moss material was digested in a mixture of concentrated HNO_3 and $HClO_4$ (4:1, v:v) using a hotplate (FOSS Tecator Digestor Auto, Germany). Elements were measured, depending on the concentration, by flame atomic absorption spectrometry (Varian AA280FS, Australia) or by graphite furnace atomic absorption spectrometry (Varian AA220FS, GTA 110, Australia) except for arsenic and mercury, which were measured using graphite furnace atomic absorption spectrometry (Varian AA280Z, GTA 120, Australia) and the Mercury Analyzer AMA 254 (LECO, USA), respectively. Nitrogen concentrations were determined by the Kjeldahl method using Kjeltec 2300 (Foss Tecator, Denmark). In 2001, only seven trace metals (Cd, Cr, Cu, Fe, Ni, Pb, and Zn) were analyzed. Moss material was prepared according to the same protocol, and the metals were measured by graphite furnace atomic absorption spectrometry (Varian AA220FS, GTA 110). The quality of analytical procedures was checked by analyzing certified reference materials: M2 and M3 [22] for most elements, and Spinach GWB 10015 for nitrogen (see Appendix A).

2.3. Statistical Analysis

Prior to statistical analysis, distributions of all variables were examined. Most distributions were positively skewed. Therefore, logarithmic functions were used to improve their normality or at least symmetry.

The temporal changes and cross-regional differences in the concentration of elements in mosses were examined using linear mixed-effects (LME) models. This method is recommended when the compared groups are unequal in terms of sample size, and the analyzed data are not completely independent [23], e.g., when there is a hierarchy in the data, such as repeated measurements (in the present study, two surveys at the same locations). In the case of elements measured in both surveyed years (Cd, Cr, Cu, Fe, Ni, Pb, and Zn), LME models included two fixed factors, year and region, along with their interaction (year × region), and one random factor—site identifier. The models were fitted in R 3.3.3 [24] with the "nlme" package [25]. The differences between two years and between four regions were tested by Tukey's method using the "multcomp" package [26]. In the case of elements measured once (in 2015), the same statistical methods were used, but only the effect of the region was determined.

For the purpose of interpreting the results of moss monitoring, the significance of the temporal and cross-regional variability of land-cover type was assessed using the LME approach. Land cover inventories in Europe are performed every few years within the CORINE (Coordination of Information on the Environment) program, and their outputs are freely available from the European Environment Agency and its partners (cooperating countries) in the form of thematic GIS layers. In this study, CORINE land cover (CLC) layers for 2000 and 2012 were used, as best corresponding to the 2001 and 2015 moss surveys. A single CLC variable was a percentage of the area occupied by a given CLC category within a 10-km radius of each sampling site. Four variables, representing CLC categories potentially relevant for air quality—urban fabric, industrial sites, agricultural area, and forest—were calculated using ArcMap 9.3 (ESRI Inc., Redlands, CA, USA) and analyzed using the same LME models as those built for the metals measured in the two surveyed years.

Multivariate data on the concentration of 17 elements in moss in 2015 was submitted to principal component analysis (PCA) to determine and visualize the chemical profile of air pollution for the four studied regions of Poland. Then, PCA-based factor analysis was performed for the same data to identify the main sources of air pollution. In this analysis, factors with eigenvalues >1 were varimax-rotated to improve the interpretability of the factor structure. Multivariate analyses were done using STATISTICA 9.1 (StatSoft Inc., Tulsa, OK, USA).

Table 1. The concentration of elements in moss in Poland (N = 117) in 2015 and its change between 2001–2015 expressed as percentage of the 2001 median (values below 100% represent a decline, values above 100% represent an increase in the study period; asterisks indicate statistically significant changes according to the LME analysis; cf. Figure 2). The change was calculated only for the seven elements that were measured in both years.

Variable	Median	Mean (SD [1])	Range	Change
As (mg kg^{-1})	0.33	0.34 (0.20)	0–1.10	–
Ca (g kg^{-1})	5.2	5.8 (3.1)	1.6–23.2	–
Cd (mg kg^{-1})	0.2	0.6 (1.3)	0.1–11.6	59% *
Co (mg kg^{-1})	0.22	0.26 (0.13)	0.06–0.74	–
Cr (mg kg^{-1})	1.6	2.4 (2.0)	0.7–11.3	180% *
Cu (mg kg^{-1})	7	11 (19)	3–197	92% *
Fe (g kg^{-1})	0.51	0.66 (0.49)	0.24–3.95	117% *
Hg (µg kg^{-1})	46	49 (14)	27–91	–
K (g kg^{-1})	6.18	6.20 (1.14)	3.76–9.44	–
Mg (g kg^{-1})	0.97	1.03 (0.36)	0.52–3.05	–
Mo (mg kg^{-1})	0.62	0.82 (0.90)	0.13–8.62	–
N (%)	1.44	1.48 (0.34)	0.68–2.38	–
Ni (mg kg^{-1})	2.8	3.1 (1.6)	1.2–13.7	178% *
P (g kg^{-1})	1.37	1.42 (0.35)	0.72–2.61	–
Pb (mg kg^{-1})	7	14 (27)	1–206	70% *
V (mg kg^{-1})	1.69	1.70 (0.64)	0.52–3.10	–
Zn (mg kg^{-1})	53	57 (36)	6–238	128%

[1] SD—standard deviation.

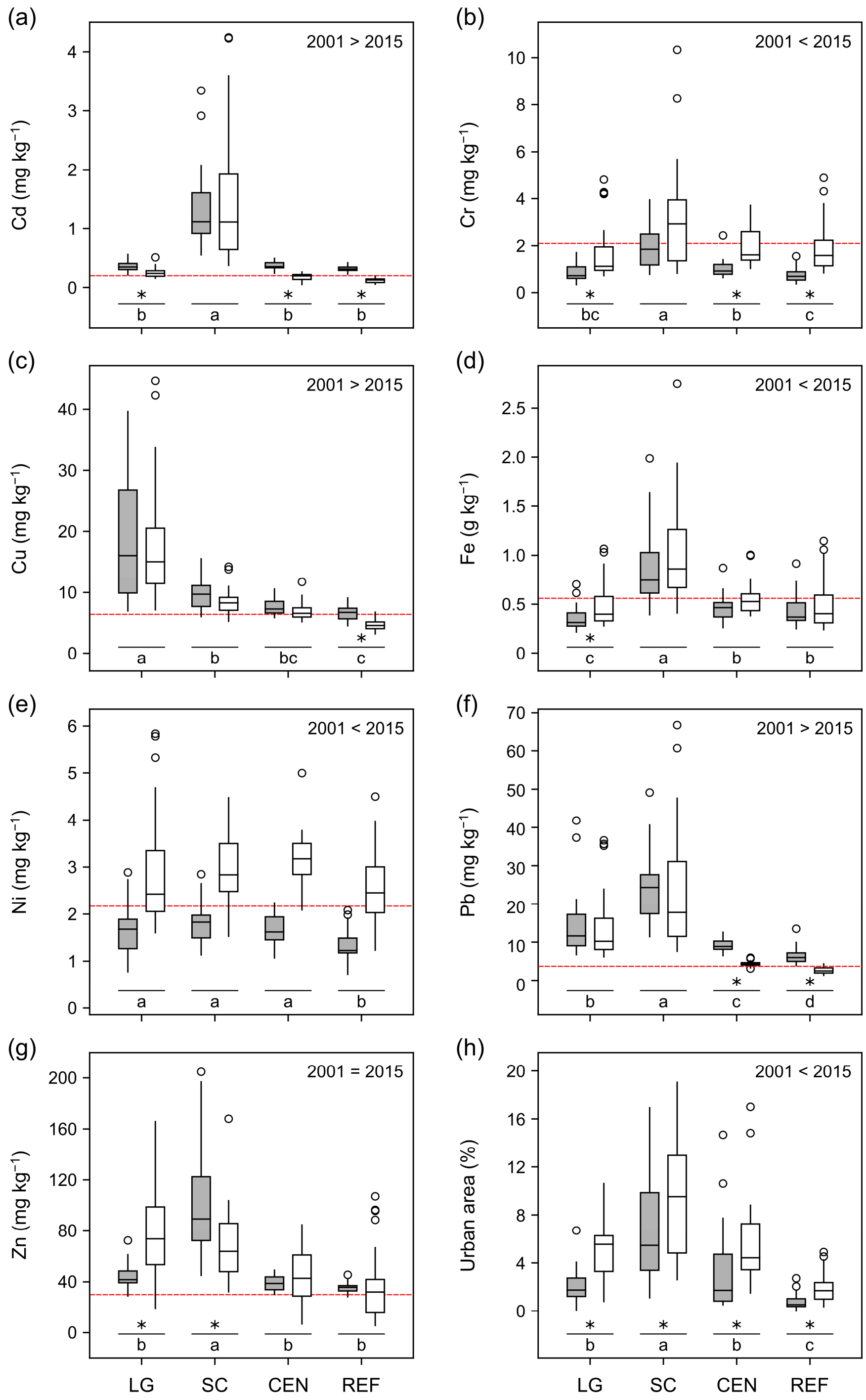

Figure 2. Changes in the concentration of trace metals in moss (**a**–**g**) and the percentage of the urban area (**h**) between 2001 (grey boxes) and 2015 (white boxes) in the four studied regions of Poland. Together with medians, quartiles, non-outlier range, and outliers (without extreme outliers) are shown. The red dashed-lines indicate the 2010 European median values [27]. The significant differences between years are marked with inequality expressions in the upper right corner of each panel, while the significant differences between regions are marked with different letters below the boxplots. Where there was a significant year × region interaction, the differences between years were tested separately for each region, and their statistical significance was denoted by asterisks. Between-group comparisons were performed (after significant LME results) using Tukey's test ($p < 0.05$). Note that while the boxplots present original values, statistical analysis was performed on transformed data.

3. Results

3.1. Changes in the Level of Trace Metal Accumulation in Mosses Between 2001 and 2015

The results of the LME analysis showed that the concentration of trace metals in moss changed significantly between the 2001 and 2015 surveys, but the direction of this change was inconsistent (Table 1, Figure 2). While the concentrations of Cd, Cu, and Pb in moss decreased, the concentrations of other metals (Cr, Fe, and Ni) increased or remained at the same level (Zn) when taking into account the country average. In addition, a significant interaction of survey and region was detected for all metals except Ni (Figure 2e), which means that the change was region dependent. In the case of Zn (Figure 2g), the interaction is most evident: the concentration of this metal in moss increased in the LG region, while it decreased in the SC region and remained unchanged in the CEN and REF regions. For other metals, the interaction is due to differences in the magnitude but not the direction of the change between regions. Typically, the change was significant only in regions with low concentrations of a given metal in moss (Figure 2a–d,f).

3.2. Changes in the Structure of Land Cover between 2000 and 2012

CLC data from 2000 and 2012 revealed that there was a significant shift in the structure of land cover in the study period (Figure 3). Urban and forest areas increased in all surveyed regions, while industrial areas increased only in the CEN region (Figure 2h; we chose to illustrate the temporal and cross-regional variability of the urban area since it was substantial and in line with the dynamics of some trace metals, for example, Cr, Fe, Ni). These increases took place at the expense of agricultural land, which shrunk everywhere.

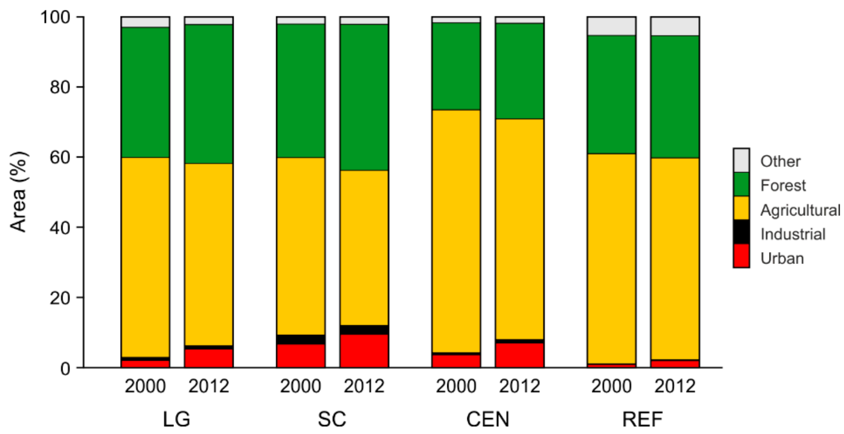

Figure 3. Change in the percentage of different categories of land cover between 2000 and 2012 in the four studied regions of Poland.

3.3. Cross-Regional Differences in the Level and Profile of Element Accumulation in Mosses in 2015

The 2015 concentrations of elements in moss are presented in Table 1. These concentrations significantly varied between the studied regions for all elements except Co (Figures 2 and 4). The most polluted regions were SC and LG. The former was characterized by high concentrations of all trace metals except Cu and Mo. In contrast, the latter was distinguished by high Cu-Mo pollution; concentrations of other metal pollutants were lower, but still exceeding those reported in REF, and even in CEN (e.g., Pb and Zn). The area beyond the reach of major sources of pollution (REF) was the cleanest. Interestingly, it was distinguished by high concentrations of major elements, Ca and Mg. The CEN region was intermediate between the industrial regions and the reference area. Its distinctive feature was the elevated concentration of P.

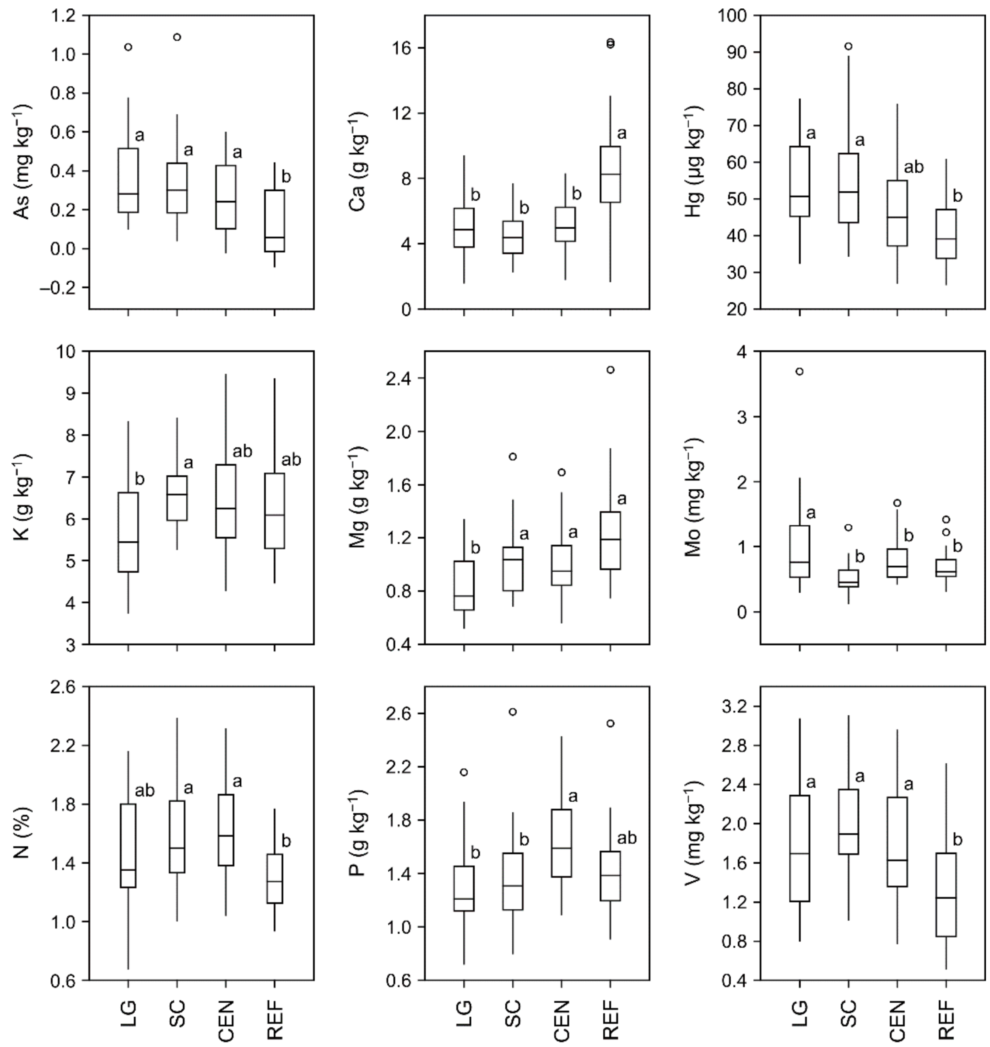

Figure 4. The concentration of major elements and trace elements (those measured only in 2015) in moss in the four studied regions of Poland (Co was omitted because it did not vary significantly between regions). Together with medians, quartiles, non-outlier range, and outliers (without extreme outliers) are shown. Boxplots marked with different letters significantly differ from each other by Tukey's test ($p < 0.05$).

The above picture is widely consistent with the results of multivariate analysis (Figure 5). In the PCA diagram, in which the first and second axes represent, respectively, the quantitative and qualitative shifts in the concentration of elements in moss, the largest between-region differences occur along the gradient being approximately diagonal to the PCA axes. The gradient starts from samples collected within the copper and zinc-lead industrial districts and ends with samples taken from unpolluted agricultural areas. The former was characterized by high atmospheric deposition of most elements, the main part of which were Pb, Cu, Cd, Zn, and Hg. The latter was characterized by low overall atmospheric deposition, in which major elements dominated.

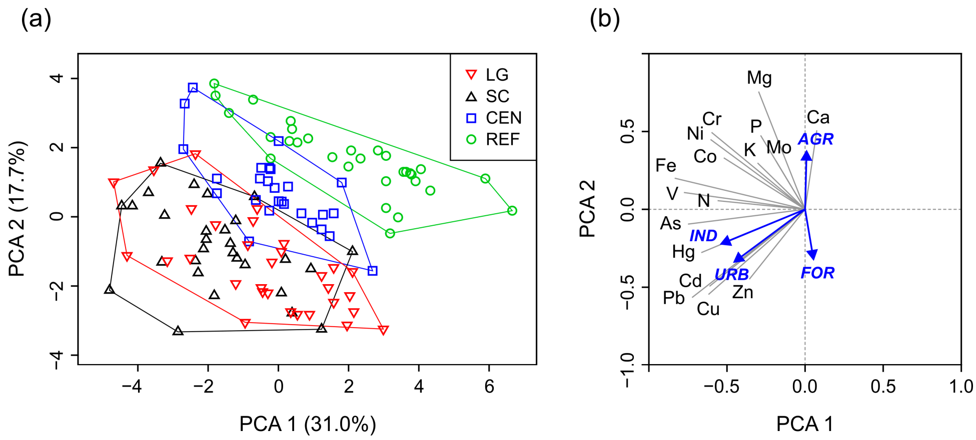

Figure 5. The results of principal component analysis (PCA) on the concentration of 17 elements in moss sampled at 117 sites in Poland. The PCA axes explain jointly 48.7% of the total variation in the data. For clarity, the sampling sites (marked according to the surveyed region; see the text for explanation) and elements are shown in separate diagrams, (**a**) and (**b**), respectively. In the right diagram, four land cover categories (URB—urban area, IND—industrial area, AGR—agricultural area, FOR—forest area) are passively projected in the ordination space.

In factor analysis performed on 17 elements, five factors were extracted (Table 2). These explained over 75% of the total variation in the data. Factor 1 represented trace metal pollution (only chalcophile elements: As, Cd, Cu, Hg, Pb, and Zn), whose emissions generally decreased during the study period. Factor 2 represented trace metal pollution (siderophile Co, Fe, and Ni, and lithophile Cr and V), whose emissions showed an upward trend. Factor 3 (lithophile K, Mg, and P, and atmophile N) and Factor 4 (lithophile Ca and Mg) represented major elements, while Factor 5 represented one trace metal (chalcophile Mo).

Table 2. Factor loadings (varimax-rotated) of element concentrations in moss determined by a factor analysis for 117 sampling sites in 2015. Loadings greater than 0.5 are in bold.

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
As	**0.584**	0.478	0.014	−0.053	0.334
Ca	−0.138	0.023	0.060	**0.898**	0.146
Cd	**0.746**	0.206	0.057	−0.075	−0.481
Co	0.129	**0.527**	0.150	0.055	0.386
Cr	−0.013	**0.924**	0.045	0.054	0.017
Cu	**0.823**	−0.015	0.064	−0.258	0.357
Fe	0.380	**0.836**	0.161	0.055	−0.169
Hg	**0.619**	0.169	0.371	−0.240	−0.008
K	0.076	0.018	**0.781**	0.212	−0.209
Mg	−0.193	0.414	**0.544**	**0.580**	−0.015
Mo	−0.019	0.192	−0.034	0.115	**0.836**
N	0.300	0.158	**0.684**	−0.264	0.070
Ni	0.016	**0.878**	0.018	−0.039	0.191
P	−0.089	0.058	**0.863**	0.081	0.127
Pb	**0.893**	0.204	−0.024	−0.126	−0.117
V	0.460	**0.504**	0.344	−0.011	0.184
Zn	**0.765**	−0.179	−0.095	0.456	−0.040
EV [1]	22.8	20.4	14.4	9.7	8.9

[1] EV—explained variance (%).

4. Discussion

4.1. Temporal Changes in Trace Metal Accumulation in Mosses

Since the establishment of the ICP Vegetation, six moss surveys were carried out. So far, the results of five of them covering the period 1990–2010 have been published. They showed that over two decades there was a significant decline in the amount of trace metals accumulated by mosses and that this decline was the largest for Pb (77%), V (55%), and Cd (51%), and the smallest for Hg (14% since 1995) and Cu (11%) [27]. The rate of decline was substantial at the beginning, i.e., between 1990 and 1995 (or 2000), becoming rather modest after 2000. In 2010, the trend ceased or even reversed for some countries (or within-country regions) and some elements [27]. The results of our study are in good agreement with the findings of the European moss monitoring. The declines we observed in the concentrations of trace metals in moss after 2000 were small, as evidenced by the fact that they were significant only for some regions (typically, those where a given metal showed slight exceedances of its European median; Figure 2). Moreover, the declines were found only for certain metals, i.e., those for which the downward trends in Europe were the steepest (Cd, Pb). For other metals, increases were recorded; they were either local (Zn, Fe) or countrywide (Ni, Cr).

The lack of a clear overall decrease in the concentration of trace metals in moss in recent years probably had many causes. One of them was that most of the conditions conducive to reducing metal emissions occurred in the past, i.e., before 2000. The first moss survey (1990) was carried out just after the collapse of the socialist bloc in 1989. The Central and Eastern European countries (CEECs) belonging to this bloc had been struggling with the economic collapse for years, which resulted in a gradual decrease in production [3]. After the fall of the Berlin Wall, these countries adopted the principles of the market economy, which meant the closure or privatization and restructuring of state-owned enterprises and a further decline in production. A side effect of political and economic transformation was a dramatic reduction of industrial emissions from CEECs [7,28]. Not only that but environmental policy also contributed to the improvement of air quality. In the 1980s and 1990s, air pollution control legislation and abatement technologies, including unleaded petrol and industrial dust collectors and other filtering systems, were widely introduced in Europe, resulting in much less release of trace metals into the environment [28]. After 2000, there were no breakthrough moments in Europe's environmental history to match those of preceding decades, which probably translated into slowing down the process of improving air quality. This slowdown is evident when the temporal patterns determined in this study are juxtaposed with the 1995–2010 patterns described elsewhere [29]. Between 1995 and 2010, pronounced decreases in Cu and Pb concentrations in moss were observed all over Poland (Pb) or at least in the industrial provinces of the country (Cu), while in the period 2001–2015, the concentrations of these two metals declined slightly and only in less polluted regions (REF, CEN). The latter result suggests that the current reduction of metal emissions is not necessarily due to restrictions imposed on the heavy industry but due to changes taking place in other sectors of the economy (e.g., transport, services).

Another highly probable reason for the lack of an overall improvement in air quality was the emergence of new sources of pollution or the increase in the importance of those that formerly had a relatively low impact on the atmospheric environment. Important components of emissions from these sources were Cr, Fe, and Ni, as evidenced not only by significant increases in the concentration of these metals in moss during the study period but also by their common origin (in factor analysis, these metals were combined in one factor). According to the latest ICP Vegetation report [30], the concentration of Cr, Fe, and Ni in moss generally showed a downward trend throughout Europe with a few exceptions: in Ukraine, the levels of Ni and Fe increased significantly between the 2005 and 2010 surveys (i.e., at the end of the monitoring period); the same was observed for Cr in Belarus and the Russian Federation. The authors of the report supposed that these increases were partly confounded by the fact that mosses were sampled from different regions in 2005 and 2010 in these countries. Our results, based on the same sampling scheme in both surveys, showed that the recent increase in Cr, Fe, and Ni concentrations in moss was not necessarily a methodological artifact. These metals, especially Cr and Ni, have many uses. They are used in steel-based industries, alloy and galvanic industries, and the tooling industry; they are needed for the production of refractory materials, pigments, batteries, fungicides, and many other necessary goods [31]. Likely, the demand for Cr/Ni containing products is currently growing. This is evidenced by the data collected by Statistics Poland [32] (formerly, the Central Statistical Office; Table 3) on metal emissions from large industrial plants estimated, among others, based on production volume. These data (available since 2005) show that emissions of Cr and Ni have increased in recent years, while emissions of other metals have changed inconsistently (they decreased, increased or remained at a constant level depending on the region).

Table 3. Atmospheric emissions of trace metals (kg year^{-1}) in 2005, 2010, and 2015 from industrial plants that are particularly harmful to the environment for voivodships most overlapping with the surveyed regions. Data obtained from Statistics Poland [32].

Voivodships	Year	Cd	Cr	Ni	Pb	Zn
Lower Silesian (LG)	2005	188	4	34	6347	5816
	2010	52	9	14	5507	878
	2015	43	156	234	4536	1789
Silesian (SC)	2005	622	3956	418	30,232	52,004
	2010	719	2981	1903	32,628	57,959
	2015	666	4427	2845	22,118	54,312
Mazovian (CEN)	2005	10	139	1447	172	5840
	2010	36	1288	3493	753	6612
	2015	27	1319	4399	1221	3578
Podlasie (REF)	2005	n/a	n/a	n/a	n/a	n/a
	2010	n/a	n/a	n/a	n/a	n/a
	2015	n/a	232	145	16	653

According to CLC data, there was a significant increase in the urban area between the 2001 and 2015 surveys in all the regions studied. This is a typical trend in many European countries [33,34]. This category of land cover is usually strongly correlated with the occurrence of small-scale (but very numerous) non-industrial sources of emissions. These emissions are generated, among others, by vehicular traffic, fuel combustion, and waste incineration [35–39], and contain a wide spectrum of elements, including trace metals from the first (factor 1) and second (factor 2) groups. It is possible that their increase over time undermined the effects of implementing pro-environmental solutions in the industrial sector, becoming another reason for the lack of a clear improvement in air quality in the period 2001–2015. It should be noted that the expansion of the urban area is preceded by construction works that cause mechanical disturbances to the ground surface. This is accompanied, especially in the case of large construction projects (motorways, housing estates), by the formation of substantial amounts of dust that can be transported in the air over long distances. Dust particles usually contain trace metals naturally occurring in soils (e.g., Fe) and those originating from historical atmospheric deposition of anthropogenic pollutants, and can significantly affect the content of elements in mosses [27]. This secondary emission may have been favored by drought episodes (making the ground surface susceptible to wind erosion), which have recently become increasingly severe in Poland.

4.2. Cross-Regional Differences in the Accumulation of Trace Metals and Major Elements in Mosses

The four regions selected for the study differ essentially in the type of industry and/or the degree of urbanization, and these differences are visible in the level of atmospheric deposition recorded by mosses and in its chemical profile.

The SC and LG regions are located in the southern part of the country, which has a variety of mineral resources. First of all, there are rich deposits of non-ferrous metals, mined for centuries (Pb, Zn) or decades (Cu) until the present day. The extraction of metal ores and their on-site processing (smelters are typically located near mines for greater profitability of metal production) are sources of huge emissions of trace metals, not only those that are the main goal of mining (Cu, Pb, and Zn) but also others that are components of ore minerals (e.g., chalcophile As and Cd) [40]. This is reflected by high concentrations of all these metals in mosses in both regions, SC and LG, or at least in one of them. The south of the country is also rich in non-metallic minerals. Hard coal and lignite are the most important. The deposits of the former are located mainly in Upper Silesia, and their distribution quite well coincides with the SC sampling area. The deposits of the latter are in the southwestern part of the country; those currently mined are situated near the LG region, at the meeting point of borders of three countries: the Czech Republic, Germany and Poland (so-called Black Triangle). Naturally, the occurrence of hard coal and lignite deposits and high energy demand (due to the high density of industry and high population density) determined the development of the energy sector in the south of the country. There are many large and small coal-fired power and cogeneration plants, which can be an important source of trace metal emissions. For example, increased Hg concentration in moss in LG and SC may be the result of emissions from electricity and heat production [41,42].

Moss monitoring showed that of the four regions studied, SC is the most polluted with trace metals. This is because it lies in the most industrialized and populated part of the country. It comprises the Katowice agglomeration, which is the largest urban agglomeration in Poland (about 3 million inhabitants), and many industrial facilities, including hard coal mines, Zn-Pb mines, steelworks, power plants, coke-oven batteries, cement plants, chemical plants, and others; the region is also characterized by heavy road and rail traffic. Only in terms of Cu pollution, SC is surpassed by another region, LG. Despite the obvious differences between SC and LG, PCA showed that the chemical profiles of atmospheric deposition determined (based on moss monitoring) for these two regions are very similar. This is not surprising, given that PCA was performed on transformed data. Transformation (logarithmic) functions significantly reduced the spread of high values, making the differences between the two industrial regions less spectacular than those indicated by the raw data.

According to the results obtained, the CEN region should be classified as moderately polluted. CEN is almost free of mineral resources, the extraction and processing of which could result in the release of large amounts of trace metals into the environment. Here, metal emissions can be generated by electromechanical, energy or chemical industries. A potentially important source of metal pollution is a large oil refinery and petrochemical complex located at the northern border of CEN. It may contribute to quite high concentrations of Ni in moss in the region [30]. Other sources are car traffic and the production of electricity and heat, which are concentrated in large cities (Warsaw, Łódź). Outside the cities, agricultural land dominates, a large part of which is occupied by orchards. Fertilization of crop fields and spraying of fruit trees may result in higher accumulation of some trace metals (e.g., Cr) and major elements (P, N, K) in moss [31]. Note that the latter are grouped in one factor (factor 3), which suggests a common origin.

The north-eastern part of Poland (REF), being away from large cities and industrial districts, is considered one of the cleanest areas of the country. In the REF region, mainly wood, paper, and food industries are located, which are minor sources of metal emissions. Moss monitoring confirmed that REF was a good reference area for other regions: the concentrations of most trace metals in mosses were the lowest here. Surprisingly, REF was distinguished by high concentrations of Ca and, to some extent, Mg in mosses (elements grouped in factor 4). Given that, apart from moderate agricultural activity, there are no significant anthropogenic (e.g., cement plants) and natural (e.g., calcite and dolomite minerals or calcium-rich soils) sources of these elements in the region (including the border zone of neighboring countries), Ca and Mg levels can be considered normal. This means that the levels of Ca and Mg recorded in other regions are low. This phenomenon might be explained by the competition of elements for binding sites [43,44]. In SC, LG, and CEN, where atmospheric deposition of pollutants is high to moderate, trace metals might use a large proportion of binding sites, thus limiting the adsorption of Ca and Mg on mosses.

5. Conclusions

The four regions studied were significantly different in the level and type of air pollution as indicated by moss monitoring. Industrial regions, located in the south of Poland, were characterized by high concentrations of many trace metals (Cd, Cu, Fe, Hg, Pb, Zn) in moss due to the presence of Zn-Pb and Cu mining and metallurgical industries and coal-based industrial facilities. The region in the center of the country was distinguished by elevated levels of Ni and P, which could be associated with the presence of the oil and petrochemical industry (Ni) and agricultural activities (P). The region in the northeast (reference area) was characterized by low (often lowest) concentrations of most elements. There was no clear improvement in air quality in Poland between 2001 and 2015. Concentrations of some metals in moss declined (Cd, Pb), continuing the trend from the previous decade, but the levels of others (Cr, Ni) increased at the same time. In addition, the changes were usually significant only in some of the regions studied. The results suggest that current air pollution abatement policies are becoming less and less effective. Probably the effects of implementing pro-environmental solutions in the industry are offset by the emergence of new non-industrial sources of pollution (e.g., related to the urban area, which has recently increased).

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Appendix A

The quality of analytical procedures was controlled based on the analysis of certified reference materials and blank samples. For most elements, moss reference materials M2 and M3 [22] were used. For the 2015 survey, M2 and M3 were analyzed in eight replicates (one analysis every 15 samples), except for Hg and P, for which one measurement was made. The percentage of recoveries are presented in Table A1. For the 2001 survey, M2 and M3 were analyzed once, and the recoveries were 85.2% and 82.5% (Cd), 91.8% and 88.1% (Cr), 86.5% and 85.4% (Cu), 92.1% and 93.1% (Fe), 81.9% and 86.3% (Ni), 94.0% and 91.0% (Pb), 89.0% and 84.8% (Zn), respectively. For nitrogen, another certified reference material—Spinach GWB 10015—was used. There were two measurements and the recoveries were: 97.9% and 98.6%.

Table A1. Percentage recoveries of the elements measured in 2015.

Variable	M2		M3	
	Mean	Range	Mean	Range
As	95.0	92.0–99.1	96.3	92.2–99.0
Ca	96.6	92.0–100.0	98.0	94.9–99.3
Cd	89.5	86.3–91.6	91.6	84.9–100.0
Co	94.1	88.2–99.7	95.1	90.6–99.0
Cr	96.6	93.4–100.2	96.3	93.1–99.3
Cu	89.6	88.1–95.1	90.0	87.8–92.0
Fe	93.3	90.9–94.9	95.2	87.3–99.0
Hg	95.3	–	95.4	–
K	96.9	94.4–99.2	96.8	93.6–99.6
Mg	98.1	96.6–99.6	97.1	95.5–98.8
Mo	91.6	82.5–96.3	91.7	81.5–101.1
Ni	94.8	89.5–100.1	94.1	89.0–100.2
P	96.0	–	98.0	–
Pb	97.8	94.5–99.8	97.4	94.0–100.1
V	92.8	83.7–102.3	90.2	86.4–97.9
Zn	95.7	93.9–99.1	94.7	88.2–98.6

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