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“Adaptation of Forest Ecosystems to Air Pollution and Climate Change”
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Heavy metal (Zn, Pb, Cd) concentration in soil and moss (*Pleurozium schreberii*) in the Brynica district, southern Poland

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The atmospheric heavy metal pollution (lead, cadmium and zinc) of the Brynica district (one of the most polluted regions of Poland) was assessed in the top layer of soils (0-20 cm), organic layer and in tissues of the common woodland moss *Pleurozium schreberii*. Samples were taken in July 2008 at 31 points distributed over a 1500 x 1500 m grid. The concentration of trace elements changed depending on analysed material, distance from the metallurgic complex “Miasteczko Slaskie” and type of metals. The highest concentrations were close to Miasteczko Slaskie. The highest values were in the organic layer. Moss samples were useful as biomonitors. The analyses confirmed a considerable contamination with heavy metals of the forest environment in the Brynica district.

Keywords: Air pollution, Heavy metals, *Pleurozium schreberii*, Biomonitors, Trace elements

Introduction

Contamination of the natural environment is currently a global problem. Heavy metals, beside sulphur dioxide, nitrogen oxides and ozone, constitute primary sources of threat to environment (Serengil et al. 2011). They constitute the universal and generally used sign of environmental pollution, particularly if we consider the top layer of soil and selected species of plants, mosses and lichens (Panek 2000). The toxicity of heavy metals depends on their biochemical role in metabolic processes. Zinc, lead and cadmium, when introduced into ecosystems in large amounts, have a great potential of disturbing the chemical balance (Kabata-Pendias & Pendias 1979). The present knowledge of natural concentrations of trace metals in soil and plant tissues is poor due to a lack of ecosystems without anthropogenic pressure. Forest soil is particularly suitable for investigating trace metal pollution because the soil structure is not deformed (Panek 2000). In Poland, analysis of trace elements in the soil was performed by many authors (Zwolinski 1995, Zwolinski 1999, Tokarz & Turzanski 1999, Korzeniowska & Stanislawska-Glubiak 2003, Gancarczyk-Gola & Palowski 2005, Rusek et al. 2005, Pajak & Jasik 2010).

Mosses are very accurate and sensitive bioindicators of heavy metal deposition in the environment (Tyler 1970, Rühling et al. 1987, Türkan et al. 1995, Grodzinska et al. 1999, Szarek-Lukaszewska et al. 2002, Szczepaniak & Biziuk 2003, Zechmeister et al. 2003, Dmuchowski & Bytnerowicz 2009). In central and northern Europe the moss species *Pleurozium schreberii* and *Hylocomnium splendens* are most popular as biomonitors of heavy metals (Harmens et al. 2008, Migaszewski et al. 2009). *Plerozium schreberii* is recommended for use in European surveys (Berg 1997, Grodzinska et al. 1999).

The aim of this research was to determine the level of heavy metal (Zn, Pb, Cd) pollution in the Brynica district, on the basis of the concentration of these metals in selected components of the forest ecosystem. An additional purpose was to describe the relation between the concentration of metals in individual components and its changes with the distance from the likely source of emission, *i.e.*, a metallurgic complex.

Material and Methods

The investigation site was located in the Brynica district, forest inspectorate Swierklaniec. The Brynica district is part of a large forest complex situated in the northern part of the Upper-Silesian Industrial Region (southern Poland - Fig. 1). Sampling sites were located in the dominant habitat types in pine tree stands, east of the source of emission (“Miasteczko Slaskie”), according to the direction of prevailing winds. Samples

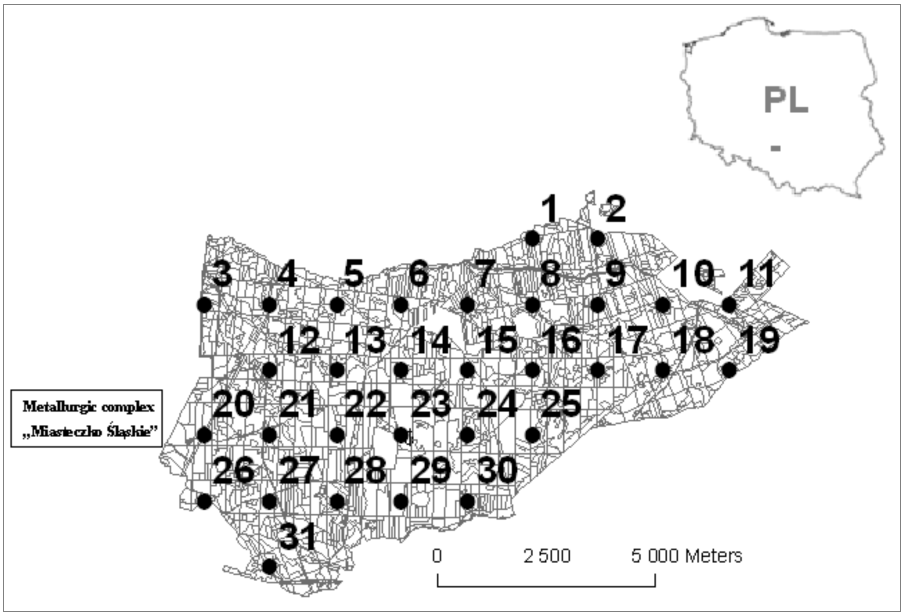

Fig. 1 - Location of the study area in Poland and sampling sites in Brynica district.

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Tab. 1 - PH and concentrations of heavy metals in the moss *Pleurozium schreberii,* organic layer and top layer of soil [mg kg^{-1}]. (*): lack of moss samples.

Sampling site	Distance from metalurgic complex [km]	Moss			Organic layer				Soil (0-20 cm)			
		Zn	Cd	Pb	pH 1M KCl	Zn	Cd	Pb	pH 1M KCl	Zn	Cd	Pb
20	1.8	*	*	*	3.80	2542.00	83.00	2108.35	3.40	524.46	11.45	709.05
26	2.2	*	*	*	4.12	1261.00	60.30	1333.35	3.76	173.56	3.20	56.05
21	3.3	969.10	37.50	810.55	3.04	730.75	24.80	833.35	3.04	348.86	6.50	473.05
27	3.5	699.60	27.60	856.05	3.02	1017.00	24.25	828.35	3.24	47.91	1.20	84.30
3	3.7	467.65	24.50	657.05	3.17	666.75	15.90	683.35	3.02	89.91	3.45	90.55
12	3.7	641.10	30.85	683.05	3.26	776.25	29.15	830.85	3.21	72.26	1.95	108.60
31	4.3	334.85	16.85	433.55	3.26	391.40	13.40	481.35	3.69	149.56	2.75	155.65
4	4.6	523.90	26.75	746.05	2.97	908.00	22.20	1225.85	2.94	40.86	1.50	118.05
22	4.8	464.35	20.65	421.55	3.64	881.75	21.25	635.85	3.32	284.71	4.00	706.55
28	4.9	*	*	*	3.14	368.80	8.05	190.35	3.87	96.21	2.00	198.55
13	5.1	371.95	14.75	385.05	3.18	659.50	15.45	504.35	2.60	395.31	8.05	465.55
5	5.8	368.15	16.90	653.05	3.11	389.55	14.00	476.85	2.61	273.26	6.70	282.05
23	6.3	289.40	14.30	322.55	3.00	271.50	9.75	384.35	3.34	38.31	0.65	121.95
29	6.4	368.35	21.55	517.55	2.87	365.60	10.35	444.85	3.17	91.71	3.45	155.70
14	6.5	344.95	9.30	192.45	3.06	320.75	7.90	155.35	3.74	19.06	0.50	78.10
6	7.0	279.05	8.70	191.40	3.46	721.00	11.20	266.85	3.08	85.41	2.00	79.85
24	7.8	75.10	14.95	116.10	3.05	326.15	6.30	427.85	3.14	47.66	1.20	97.10
30	7.9	261.50	11.75	265.85	3.05	342.25	8.55	363.35	3.05	33.66	1.45	161.45
15	7.9	196.80	8.05	191.90	2.85	293.75	7.80	508.85	2.81	84.26	4.05	161.60
7	8.4	236.10	8.20	199.05	3.01	335.45	7.85	307.35	2.63	238.71	7.15	220.05
25	9.3	199.35	8.35	178.65	2.94	251.60	6.60	334.35	3.06	26.71	0.35	75.00
16	9.4	170.55	6.60	121.35	2.95	238.25	5.70	247.85	3.10	83.56	2.10	117.20
8	9.8	190.80	5.10	148.15	3.21	281.90	6.40	187.85	2.93	53.41	1.55	84.50
1	10.4	155.75	6.75	168.10	2.95	137.75	3.75	190.35	3.06	11.06	0.45	32.05
17	10.9	162.35	6.00	128.55	3.04	273.95	5.20	585.85	2.89	71.36	2.60	170.05
9	11.2	187.90	5.05	124.25	3.12	329.25	6.25	246.35	3.18	23.31	0.85	39.70
2	11.8	192.10	6.85	165.20	4.23	587.00	17.00	623.35	3.62	38.86	1.60	104.55
18	12.4	162.80	5.55	134.75	2.96	231.30	4.85	263.35	2.79	107.61	5.10	115.05
10	12.7	149.70	3.90	97.80	2.87	203.55	3.75	151.85	2.89	32.66	1.25	51.40
19	13.9	241.40	4.05	117.90	3.10	249.30	5.70	291.85	2.94	36.46	1.05	129.40
11	14.1	*	*	*	3.19	166.65	3.30	231.85	3.07	19.71	0.80	33.05

were taken from the top layer of mineral soils (0-20 cm), organic layer and the tissue of common woodland moss *Pleurozium schreberii*, at 31 systematically located points on a 1 500 x 1 500 m grid. The sampling period was in July 2008. Five subsamples were collected within 100 m^2 area and mixed to form a composite sample. Soil samples were dried and passed through a 2 mm sieve to remove roots and stones. Samples of the organic layer were ground to powder. The pH of the organic layer and soil samples was measured in 1M KCl and distilled water (10 g of soil or 5 g of organic layer mixed with either 50 ml KCl or water). Samples of *Pleurozium schreberii* were taken from 27 sampling sites. All samples were transported to the laboratory in polyethylene bags. After removing other debris, green and brown parts of unwashed tissues were dried at 60 °C and ground to powder. Each soil, organic layer and moss sample was digested in a spectral pure concentrated acid mixture (HNO_3 and $HClO_4$). Concentration of heavy metals (Zn, Pb Cd) in the moss tissues, mineral soil and organic layer was measured by AAS (AA Varian 20) by atomization in air-acetylene flame.

The relationship between concentration of metals in mosses and distance from the potential source was described by the non-linear equation (eqn. 1):

$$concentration = a \cdot \exp^{\left(\frac{b}{x}\right)}$$

where a and b are parameters of the equation, e is the base of the natural logarithm, x is the distance.

Due to different distributions of the compared variables correlations among concentrations of metals in mosses, organic layer and soil were described by Spearman rank. All statistical analyses were carried out with the STATISTICA® 8.0 software.

The graphic representation of the pollution with heavy metals in the Brynica district was obtained by the ARCMAP software. This statistical image of the dependence adequately represents spatial interactions between the measurement points. The method could be used for predicting values at the interpolation surface.

Tab. 2 - Parameters of eqn. 1 and basic statistics.

Elements	Parameter	Value	Error	t-value	P	R^2	R
Pb	a	90.95	17.8599	5.092429	0.000029	0.8018	0.8955
	b	7 518.21	797.3783	9.428659	0		
Cd	a	3.907	0.5889	6.63438	0.000001	0.8586	0.9266
	b	7 268.11	616.8116	11.78336	0		
Zn	a	92.271	12.5227	7.36831	0	0.8687	0.932
	b	7 158.03	557.5065	12.83937	0		

Results and discussion

The highest concentrations were at sampling site 21 (soil and organic layer) and 20 (moss), *i.e.*, the closest sites to the Metal-

Fig. 2 - Cadmium (Cd) concentration (mg kg^{-1}) in organic layer in Brynica district.

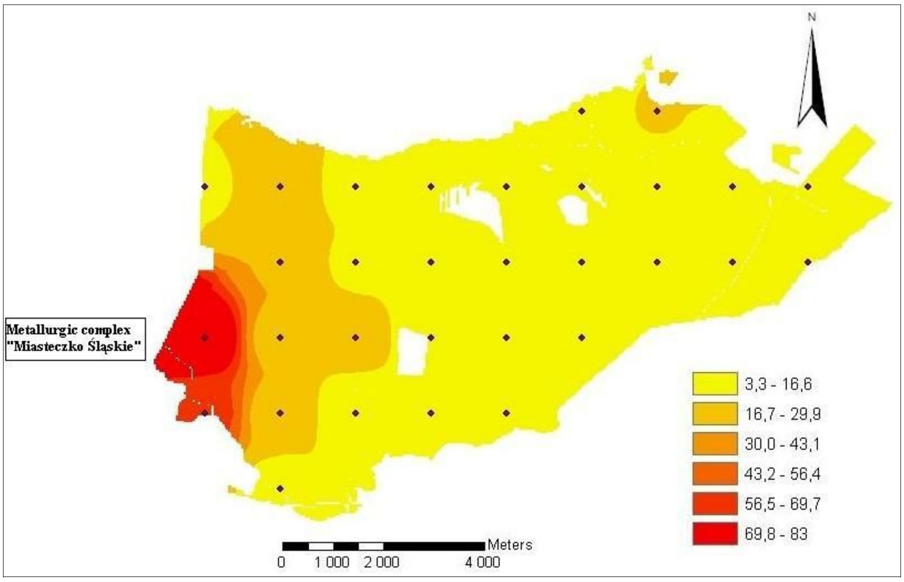


Fig. 3 - Lead (Pb) concentration (mg kg^{-1}) in organic layer in Brynica district.

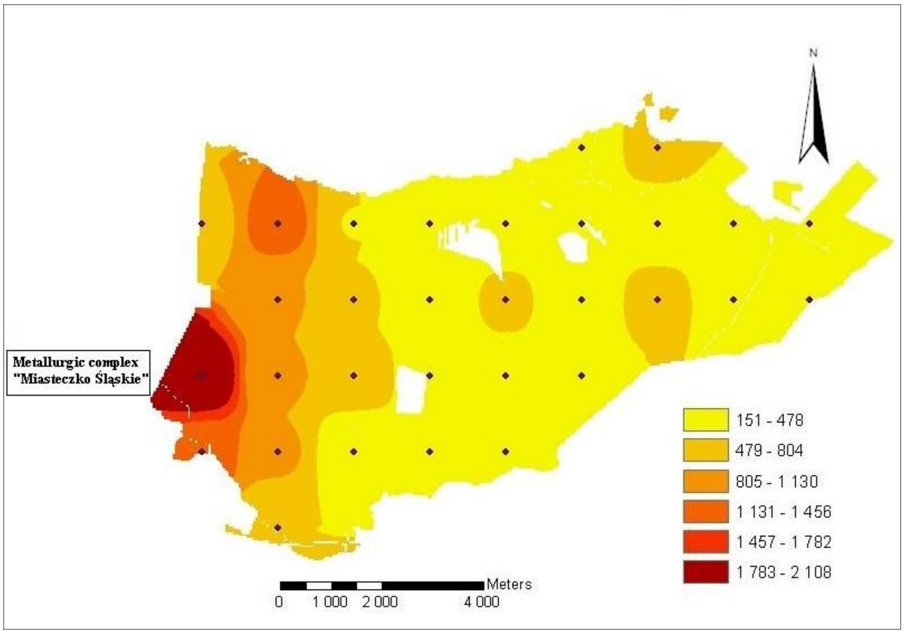
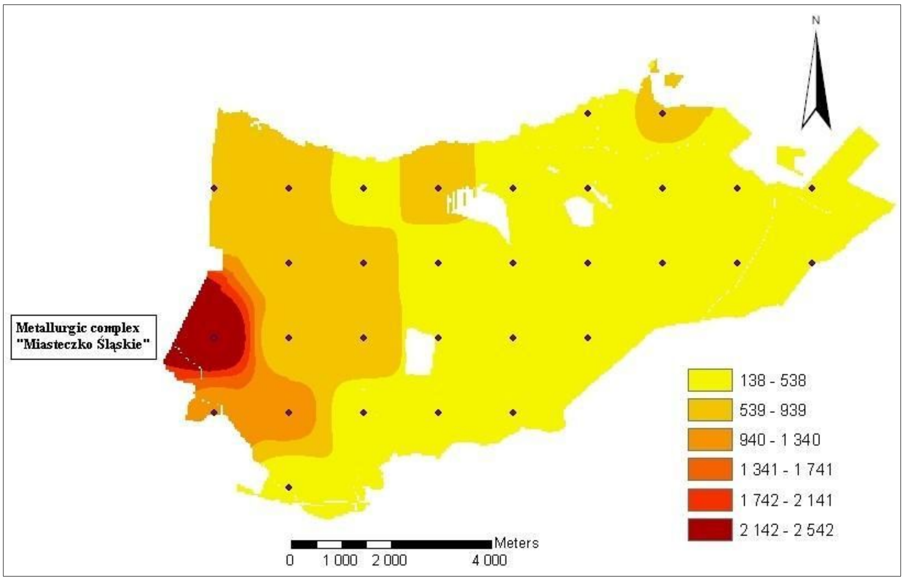


Fig. 4 - Zinc (Zn) concentration (mg kg^{-1}) in organic layer in Brynica district.



Tab. 3 - Correlation matrix in Spearman rank model. Values labelled with an asterisk (*) are significantly correlated.

-	Element	Moss			Organic layer			Soil		
		Zn	Cd	Pb	Zn	Cd	Pb	Zn	Cd	Pb
Moss	Zn	1.000	0.840*	0.922*	0.823*	0.940*	0.697*	0.432*	0.291	0.379
	Cd	0.840*	1.000	0.895*	0.813*	0.905*	0.792*	0.438*	0.269	0.347
	Pb	0.922*	0.895*	1.000	0.794*	0.914*	0.742*	0.454*	0.344	0.382*
Organic layer	Zn	0.823*	0.813*	0.794*	1.000	0.948*	0.781*	0.602*	0.473*	0.383*
	Cd	0.940*	0.905*	0.914*	0.948*	1.000	0.812*	0.607*	0.445*	0.435*
	Pb	0.697*	0.792*	0.742*	0.781*	0.812*	1.000	0.618*	0.501*	0.529*
Soil	Zn	0.432*	0.438*	0.454*	0.602*	0.607*	0.618*	1.000	0.936*	0.729*
	Cd	0.291	0.269	0.344	0.473*	0.445*	0.501*	0.936*	1.000	0.728*
	Pb	0.379	0.347	0.382*	0.383*	0.435*	0.529*	0.729*	0.728*	1.000

lurgic complex (Tab. 1). The minimum and maximum concentrations in soil differed among sites by over 20- (Cd), 30- (Pb) to almost 50-fold (Zn). Differences in the moss and organic layer concentrations were also very large (over 20-fold difference in the organic layer and 8- to 13-fold in the moss). Although most European countries have been showing a reduction in trace element deposition (Rühling & Tyler 2004, Harmens et al. 2008), a very high concentration of Zn, Cd and Pb was still present in the Brynica district.

Such a high level of heavy metals was attributed to the activity of the metallurgic complex "Miasteczko Slaskie", as confirmed by the very high coefficients of correlation of the Zn ($R = 0.932$), Pb ($R = 0.895$) and Cd ($R = 0.927$) concentration in moss tissue with the distance (Tab. 2). The spatial distribution of heavy metal concentrations in the organic layer in the Brynica district confirmed the metallurgic complex as the main source of heavy metal pollution (Fig. 2, Fig. 3 and Fig. 4).

A very high correlation was found between the concentration of heavy metals in the moss tissue and their concentrations in the organic layer (Tab. 3). The heavy metal concentrations in mineral soil and in other showed either a not-significant or very weak correlation with the other components of the forest ecosystem. This suggests that mosses and soil organic layer are better biomonitors of heavy metal pollution than the mineral soil.

In comparison with analyses conducted for the entire Poland (Grodzinska et al. 1997), the Brynica district belongs to the areas which are the most polluted with cadmium. While cadmium concentrations above 2 mg kg^{-1} were determined only in 0.8 % of the area of Poland, in the analysed samples of mosses in the Brynica district all the concentrations exceeded this threshold. In the case of lead in moss tissues, almost the entire territory of the Brynica district (except one site) belongs to the areas of Poland most polluted with this metal (1.5 % area of the country). In the case of zinc, 90 % of the surface of the analysed area belongs to the most polluted areas of Poland (*i.e.*, 1% of Poland). Considering the great value of mosses as biomonitors of heavy metal contamination (Grodzinska et al. 1997, Chakrabortty & Paratkar 2006), the Brynica district is seriously polluted with Zn, Pb and Cd. The concentrations found in the moss *Pleurozium schreberii* in the Brynica district were much higher than those determined in the Small Pieniny Mountains (150 km on south-east from the analysed area) by Panek and Szczepaska (Panek & Szczepanska 2005): in the case of zinc these concentrations were 20-fold, and for lead and cadmium over 80-fold. Zwolinski (1995) emphasized that the total concentration of all heavy metals in forests is overwhelming among adverse effects. A total concentration of about 500 mg kg^{-1} of heavy metals in the organic layer of forest soil constitutes a critical threshold. In the Brynica district, on 80 % of sampling sites, the total concentration of Zn, Cd and Pb was found to be higher than 500 mg kg^{-1}.

In conclusion, trace element (Zn, Pb, Cd) pollution in the Brynica district suggests this area as one of the most polluted of Poland. The best biomonitors were the soil organic layer of soil and the moss tissues of *Pleurozium schreberii*. The metallurgic complex "Miasteczko Slaskie" was confirmed as a significant source of heavy metal pollution, which may affect ecosystem vitality.

References

Berg T (1997). Use of mosses (*Hylocomium splendens* and *Pleurozium schreberi*) as biomonitors of heavy metal deposition: from relative to absolute deposition values. Environmental Pollution 98 (1): 61-71. - doi: 10.1016/S0269-7491(97)00103-6

Chakrabortty S, Paratkar GT (2006). Biomonitoring of trace element air pollution using mosses. Aerosol and Air Quality Research 6: 247-258. [online] URL: http://www.ieecas.cn/qrjweb/qr-jxh/AAQR/2006%20(Volume%206,%20No.%203)/2006%20(Volume%206,%20No.%203)/2_cjt06049_247-258.pdf

Dmuchowski W, Bytnerowicz A (2009). Long-term (1992-2004) record of lead, cadmium, and zinc air contamination in Warsaw, Poland: determination by chemical analysis of moss bags and leaves of Crimean linden. Environmental Pollution 157: 3413-3421. - doi: 10.1016/j.envpol.2009.06.019

Gancarczyk-Gola M, Palowski B (2005). Metale ciezkie i pH powierzchniowych warstw gleby wokol centrow przemyslowych oraz na terenach wolnych od zanieczyszczenia. Roczniki Gleboznawcze, Warszawa, 56 (1-2): 59-66.

Grodzinska K, Szarek-Lukaszewska G, Godzik B, Braniewski St, Budziakowska E, Chrzanowska E, Pawlowska B, Zielonka T (1997). Ocena skazenia srodowiska Polski metalami ciezkimi przy uzyciu mchow jako biowskaznikoów. Biblioteka Monitoringu Srodowiska, Warszawa (Poland).

Grodzinska K, Szarek-Lukaszewska G, Godzik B (1999). Survey of heavy metal deposition in Poland using mosses as indicators. The Science of the Total Environment 229: 41-51. - doi: 10.1016/S0048-9697(99)00071-6

Harmens H, Norris DA, Koerber GR, Buse A, Steinnes E, Rühling A (2008). Temporal trends (1990-2000) in the concentration of cadmium, lead and mercury in mosses across Europe. Environmental Pollution 151: 368-376. - doi: 10.1016/j.envpol.2007.06.043

Kabata-Pendias A, Pendias H (1979). Pierwiastki sladowe w srodowisku biologicznym. Wydawnictwo Geologiczne.

Korzeniowska J, Stanislawska-Glubiak E (2003). Fitotoksyczne zawartosci niektorych metali ciezkich w glebie. Zesz. Probl. Post. Nauk Rol. 493: 167-173.

Migaszewski ZM, Ga1uszka A, Crock JG, Lamothe PJ, Dolegowska S (2009). Interspecies and interregional comparisons of the chemistry of PAHs and trace elements in mosses *Hylocomium splendens* (Hedw.) B.S.G. and *Pleurozium schreberii* (Brid.) Mitt. from Poland and Alaska. Atmospheric Environment 43: 1464-1473. - doi: 10.1016/j.atmosenv.2008.11.035

Pajak M, Jasik M (2010). Poziom akumulacji cynku, kadmu i olowiu w wierzchniej warstwie gleb lesnych w sasiedztwie Huty Cynku "Miasteczko Slaskie". Zeszyty Naukowe Uniwersytetu Zielonogorskiego nr 137, Inzynieria Srodowiska 17: 112-122.

Panek E (2000). Metale sladowe w glebach i wybranych gatunkach roslin obszaru polskiej czesci Karpat. IGSMiE PAN, Krakow, Poland.

Panek E, Szczepanska M (2005). Metale sladowe i siarka w wybranych gatunkach roslin w Malych Pieninach. Gospodarka Surowcami Mineralnymi tom 21 (1): 89-109.

Rusek A, Kabala C, Drozdowska J (2005). Zawartosc olowiu, cynku i miedzi w wybranych typach prochnic lesnych Dolnego Slaska. Roczniki Gleboznawcze 56 (1-2): 137-146.

Rühling A, Rasmussen L, Pilegaard K, Mäkinen A, Steinnes E (1987). Survey of atmospheric heavy metal deposition in the Nordic countries in 1985 monitored by moss analyses. NMR, Copenhagen, Denmark, pp. 44.

Rühling A, Tyler G (2004). Changes in the atmospheric deposition of minor and rare elements between 1975 and 2000 in south Sweden, as measured by moss analysis. Environmental Pollution 131: 417-423. - doi: 10.1016/j.envpol.2004.03.005

Serengil Y, Augustaitis A, Bytnerowicz A, Grulke N, Kozovitz AR, Matyssek R, Müller-Starck G, Schaub M, Wieser G, Coskun AA, Paoletti E (2011). Adaptation of forest ecosystems to air pollution and climate change: a global assessment on research priorities. iForest 4: 44-48. - doi: 10.3832/ifor0566-004

Szarek-Lukaszewska G, Grodzinska K, Braniewski S (2002). Heavy metal concentration in the moss *Pleurozium schreberi* in the Niepolomice Forest, Poland: changes during 20 years. Environmental Monitoring and Assessment 79: 231-237. [online] URL: http://www.ncbi.nlm.nih.gov/pubmed/12392161

Szczepaniak K, Biziuk M (2003). Aspects of the biomonitoring studies using mosses and lichens as indicators of metal pollution. Environmental Research 93: 221-230. - doi: 10.1016/S0013-9351(03)00141-5

Tokarz M, Turzanski KP (1999). Ocena stanu zanieczyszczenia gleb wojewodztwa malopolskiego metalami ciezkimi i siarka. Oficyna Wydawnicza TEXT, Krakow, Poland.

Türkan I, Emür H, Ümmühan C, Kivilcim S (1995). Comparison of moss and bark Samales as biomonitors of heavy metals in highly industrialised area in Izmir, Turkey. The Science of the Total Environment 166: 61-67. - doi: 10.1016/0048-9697(95)04518-6

Tyler G (1970). Moss analysis - a method for surveing heavy metal deposition. In: Proceedings of the "2nd International Clean Air Congress", Washington, DC, USA, pp. 129-132.

Zechmeister HG, Grodzinska K, Szarek-Lukaszewska G (2003). Bryophytes. In: "Bioindicators and biomonitors. Principles, concepts and applications" (Markert BA, Breure AM, Zechmeister HG eds). Elsevier, Amsterdam, The Netherlands, pp. 329-375.

Zwolinski J (1995). Effects of emissions from non-ferrous metal Works on forest environment - the role of heavy metals in forest degradation. Journal of the Forest Research Institute, Series A 809: 1-86.

Zwolinski J (1999). Zmiany zawartosci metali ciezkich oraz aktywnosci mikrobiologicznej w glebach borow sosnowych na terenie Polski poludniowo-zachodniej w latach 1988-1997. Prace IBL seria A. 872: 104-118.