Response of lichens to heavy metal and SO_2 pollution in Poland – an overview

K. Sawicka-Kapusta, M. Zakrzewska, G. Bydłoń & A. Sowińska
Environmental Monitoring Research Group,
Institute of Environmental Sciences, Jagiellonian University,
Kraków, Poland

Abstract

Epiphytic lichen Hypogymnia physodes (L) Nyl. from the natural environment and transplanted was used for ten years (1997–2006) to estimate air contamination in Poland. Lichens from natural environment were collected from the Base Station of the Integrated Nature Monitoring System and from Polish National Parks. Transplantation was carried out in Cracow city, small forest sites near Cracow conurbation and industrial areas in the Małopolska district. Hypogymnia physodes showed the changes in air pollution in Poland but also confirmed the presence of some areas still being contaminated. They are located near heavy industry, near large cities like Cracow and also in some areas located far from industrial sources.

Keywords: Poland, biomonitoring, air pollution, heavy metals, sulphur dioxide, lichens, Hypogymnia physodes.

1 Introduction

Biological monitoring can be defined as the measurement of the response of living organisms to changes in their environment [1, 2]. It is a very useful and sensitive method for estimating air and environment quality. This method has been successfully used for more than fifty years [3–5]. Lichens are very good bioindicators of air pollution as they accumulate contaminants as the function of their concentration in the air. This accumulation undergoes the passive way [6, 7]. Another advantage of lichens as an excellent bioindicator is that many species have a wide geographical distribution and are very common. Therefore they can be used at a local, regional and national scale [5, 8, 9]. Air pollution originates mainly from industrial manufacturing and energy production, coal and oil

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combustion, vehicular traffic and also small local sources. In Europe the main sources of air pollution have been increasing urbanisation and heavy traffic [10–12]. In the last ten years of 20th century Poland was one of the most polluted countries in Europe [13, 14]. The country was heavily affected by gaseous (SO_2, NO_X, CO, CO_2), particulate emissions (including heavy metals and polycyclic aromatic hydrocarbons) and other organic compounds. The situation has significantly improved in the last few years, but still high concentrations of these pollutants are being measured. Poland became a member of the European Union in 2004 and according to Environmental Protection Law showed adherence to standards of air quality. In 2005, Poland emitted 457 thousands tonnes of dust, 1222 thousand tonnes of sulphur dioxide, 811 thousand tonnes of nitrogen dioxide and 326 511 thousand tonnes of carbon dioxide. Heavy metal emissions also decreased when compared with the early nineties but in 2005 Poland emitted 1350 metric tonnes (t) of Zn, 536 t Pb, 46 t Cd, 20 t Hg, 54 t Cr, 237 t Ni and 356 t Cu [14]. At the present time the main sources of emissions are not heavy industry but large conurbations, heavy traffic and an abundance of local sources, located in small towns and villages.

The aim of this paper is to show the changes in air pollution in Poland in ten years using *Hypogymnia physodes* as a bioindicator.

2 Material and methods

Epiphytic lichen *Hypogymnia physodes* (L) Nyl. from the natural environment and transplanted were collected all over Poland over a ten year period (1997–2006). The investigated areas were located in different polluted parts of the country, around the heavy industry: steelworks, metal smelters, coal and metal mining, chemical factories, busy roads, small urban areas and Cracow conurbation. Samples were also taken from different forest areas, national parks, and Base Stations of the Integrated Nature Monitoring System for Poland. *Hypogymnia physodes* from unpolluted areas (Borecka Forest or Bory Tucholskie Forest) were transplanted to 7 small forest sites near Cracow agglomeration, 11 sites in Cracow city, and to 4 industrial sites in the Małopolska district. The transplants were exposed to a six month long period of winter and summer seasons. Unwashed lichen was digested in 4:1 nitric and perchloric acid. Concentration of heavy metals (Cd, Pb, Cu, Zn, Fe, Cr, Ni) were determined using IL 250 flame AAS [15], whereas sulphur content was determined using turbidimetric Butters-Chenry's method [16]. Simultaneously reference materials (SRM) were also analysed. Data are presented in $\mu g \cdot g^{-1}$ dry weight. Statistical analysis was carried out to determine the potential differences between the concentration of contaminants between sites and period of time.

3 *Hypogymnia physodes* the useful bioindicator of air pollution

Lichens are the symbiotic association between fungus and alga or cyanobacterium. Epiphytic lichens growing on the tree stems and branches use them only as a substrate. Instead lichens get nutrients from rainwater and deposited dust. They absorb substances for growth and survival through the exposed surface of the thallus [6, 7]. Lichens can accumulate trace metals (both essential and non essential) to levels far greater than their expected physiological needs [7, 17] Therefore they are used as sensitive bioindicators of heavy metals in the air [5, 8, 17]. Lichens have been shown to be highly sensitive to gaseous air pollution, particularly to sulphur dioxide. SO_2 caused high concentration of sulphur and acute injuries of lichen thalli [3, 4, 18, 19]. Lichens show the concentrations of metals and sulphur, also organic compounds and radionuclides as a function of atmospheric deposition amount. Thus it makes them widely used in monitoring of air pollution [4–7]. Lichens could be collected from natural environment or transplanted from clean area to the polluted sites [5, 15, 17, 21, 22].

During 1997 and 2006 several investigation using epiphytic lichens *Hypogymnia physodes,* collected from the natural environment or transplanted were carried out to estimate air pollution in different parts of Poland [12, 15, 23–27].

4 Investigation of air pollution in some areas in Poland

4.1 Monitoring of air pollution by heavy metals and SO_2 in the Base Stations of the Integrated Nature Monitoring System between 2001-2005

Heavy metals and sulphur concentration in H*ypogymnia physodes* collected from natural environment in the areas of seven Base Station of the Integrated Nature Monitoring System were determined [25]. In July 2001, 2003 and 2005 lichen samples were collected in Szymbark, Św. Krzyż, Pożary, Storkowo, Koniczynka, Puszcza Borecka and Wigry. The highest concentration of all heavy metals and sulphur was found in 2001 in Koniczynka Base Station situated 5 km north-east from Toruń agglomeration. Also high concentrations of cadmium, lead, zinc, iron and sulphur were noticed in lichens collected in Św. Krzyż and Szymbark Base Stations in 2001. The lowest level of investigated metals was found in Wigry and Storkowo Base Stations. Sulphur concentration ranged from 1200 $\mu g \cdot g^{-1}$ in Puszcza Borecka to 2889 $\mu g \cdot g^{-1}$ in Koniczynka Base Station. In the year 2003 the concentration of cadmium, lead, zinc, iron and sulphur increased in almost all Base Stations while copper remained at the same level. In 2005 a decrease of all investigated metals was noticed, with the exception of cadmium in Puszcza Borecka Base Station. In the case of sulphur, a higher concentration was noticed in Puszcza Borecka and Storkowo Base Station, lower in Pożary, Św. Krzyż and Szymbark (fig. 1). No changes were found in Wigry Base Station. The results of the following study confirmed air contamination by heavy metals and sulphur dioxide in three of the investigated Base Stations (Koniczynka, Św. Krzyż, Szymbark). Generally Base Stations located on the North of Poland were less contaminated by heavy metals (Cd, Pb, Cu, Zn, Fe) and SO_2 than Stations situated on the South. No statistical differences between years were found in all Base Stations. The sources of emissions which caused contamination are different in each of the investigated Base Stations [25–27].

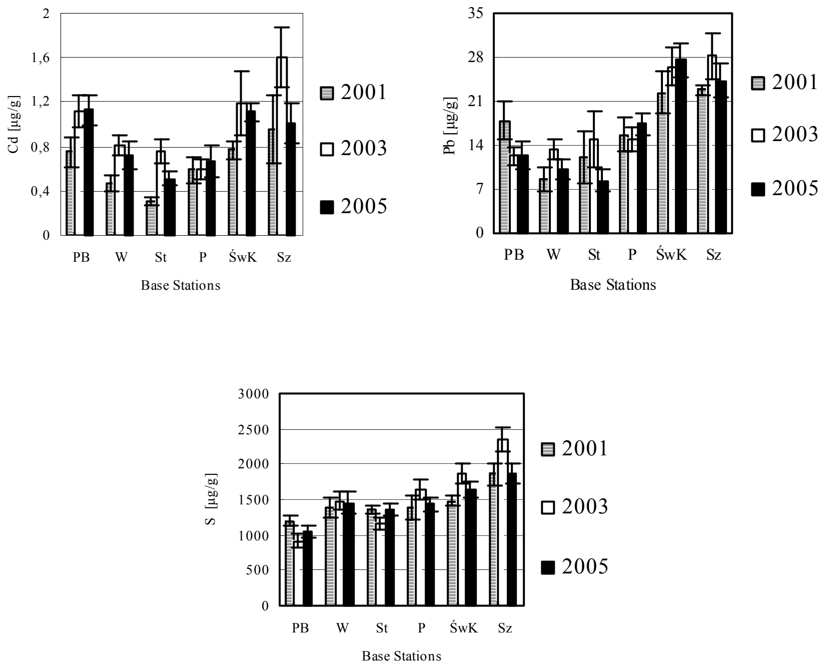


Figure 1: Lead, cadmium and sulfur concentrations ($\mu g \cdot g^{-1}$ d.w.) in the air of the Base Station of the Integrated Nature Monitoring System.

4.2 Changes in air pollution in Polish National Park

The first estimation of heavy metal contamination of the environment in Poland on a national scale, based on metal concentration in lichen *Hypogymnia physodes* were conducted in 1990 in 13 national parks [15]. The investigations were repeated in 1998 and 2005 in all Polish National Parks [23].

Samples of *Hypogymnia physodes* from natural environment were collected in July 1998 and 2003 from 23 Polish National Parks. The aim of this study was to estimate air pollution by heavy metals (Pb, Cd, Cu, Zn, Fe) (fig. 2) and sulphur dioxide and to compare the contamination over period of 5 years [22]. In 1998 and 2003 *Hypogymnia physodes* from Ojcowski National Park had the highest concentration of all heavy metals. In 1998 the lowest Cd and Pb concentration were found in Bory Tucholskie NP and in Woliński NP, respectively. The lowest Cu and Zn amount was observed in lichens from Białowieski NP while the concentration of Fe was lowest in Woliński NP. In 2003 the lowest content of Cd, Pb and Zn were determined in Drawieński NP while the concentration of Cu and Fe were found in Białowieski NP. The highest concentration of S in 1998 was detected in lichens from Świętokrzyski NP while in 2003 in lichens from Warta River Mouth NP. When comparing the concentration of heavy metals in lichens collected in 1998 and in 2003 it was found that the same twelve national parks were classified as relatively clean. They are: Woliński, Drawieński, Słowiński, Wigierski, Białowieski, Narwiański, Biebrzański, Bory Tucholskie NPs situated in the north of Poland and Kampinoski, Poleski, Roztoczański, Wielkopolski NPs located in the central part of the country. Warta River Mouth NP established in 2001 also belongs to relatively clean. Moderately polluted areas were represented by nine national parks (Świętokrzyski, Karkonoski, Góry Stołowe, Gorczański, Babiogórski Pieniński, Tatrzański, Bieszczadzki and Magurski NPs. Ojców NP situated in heavily industrialised region, remained heavily polluted. As far as SO_2, nine national parks were classified as clean; seven were recognized as moderately polluted, fifth as polluted and two were heavily polluted.

Sulphur dioxide concentration in the lichens from national parks has not decreased compared to 1998 as sulphur concentration is much higher than 5 years ago. Comparison of air pollution by heavy metals was not much lower as was expected. Cadmium concentration was even higher than 5 years ago [23]. Generally, national parks located in the southern part of Poland were more contaminated by heavy metals than those in the north of the country. Contamination by $S0_2$ is much more uniform across the country as high sulphur concentrations were noticed in national parks located in different parts of Poland. Air contamination in national parks originated from industrial sources, long distance transport but mainly from local sources located close to national parks border.

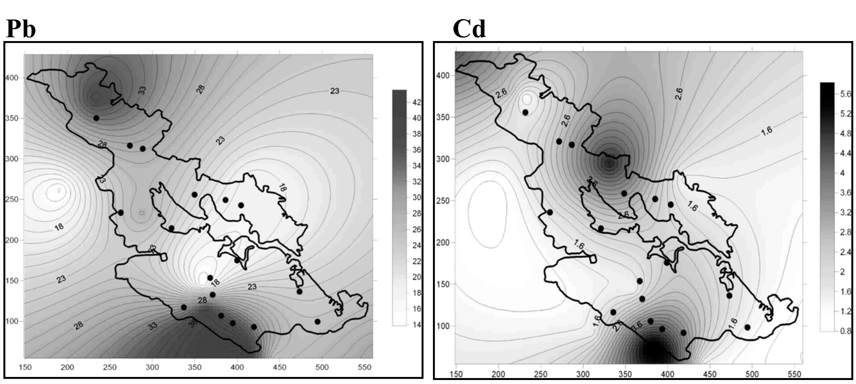
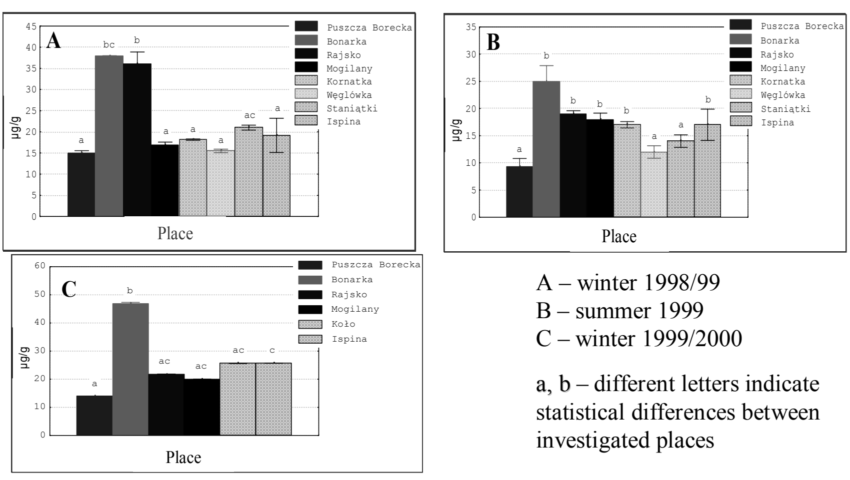


Figure 2: Lead and cadmium concentration ($\mu g \cdot g^{-1}$ d.w.) in the air of the Magurski National Park.

4.3 Lichens as bioindicators of urban pollution

Seven small forest sites located at different distance from Cracow conurbation and from busy road and along the prevailing wind direction were selected. Five sites were located along southern transect (Bonarka located 3 km from the town centre, Rajsko - 8 km, Mogilany - 14 km far from the city, Kornatka near Dobczyce reservoir - 26 km from Cracow and Węglówka - 35 km from agglomeration. Along the eastern transect only two sites: Koło (25 km from steelworks and 30 km from Cracow) and Ispina (30 and 35 km respectively) were located. *Hypogymnia physodes* from unpolluted area (Borecka Forest, north-eastern Poland) were transplanted to each of investigated sites for a six-month period. The transplants were exposed for two winter seasons 1998/1999 and 1999/2000 and for summer 2000. Observation for macroscopic injuries appearing on lichen thalli surface was performed monthly in each site. After transplantation concentrations of Cd, Pb, Cu, Zn, Fe and S in lichens were determined [12]. The highest metal concentration in *Hypogymnia physodes* was found in sites located close to Cracow conurbation. Generally concentrations of heavy metals and sulphur were higher after winter transplantations. The highest lead concentration (48 $\mu g \cdot g^{-1}$) was in Bonarka after winter 1999/2000 and in Bonarka and Rajsko (36 $\mu g \cdot g^{-1}$ on average) after winter 1998/1999 (fig. 3). The highest iron concentration (4200 $\mu g \cdot g^{-1}$) was found in Bonarka after winter 1998/1999 and in Koło and Ispina (2700 $\mu g \cdot g^{-1}$on average) after in winter 1999/2000. High metal concentrations and acute injuries on lichen thalli observed during the winter transplantation were caused by high SO_2 emission from Cracow. High heavy metal and sulphur concentrations in *Hypogymnia physodes* confirm impact of Cracow conurbation (including steelworks emission) on small forest areas [12].



A – winter 1998/99
B – summer 1999
C – winter 1999/2000

a, b – different letters indicate statistical differences between investigated places

Figure 3: Lead concentration ($\mu g \cdot g^{-1}$ d.w.) in transplanted lichens *Hypogymnia physodes*.

4.4 *Hypogymnia physodes* identified metal pollution from industrial sources in Małopolska district

Lichen *Hypogymnia physodes* from Borecka Forest (unpolluted area) were transplanted in the middle of April 2002 for a six-month period to four forest sites located near industrial sources [27]. The following sites were chosen: **1**. Bukowno situated in the immediate vicinity of the "Bolesław" Zn-Pb smelter, **2**. Młoszowa located close to "Trzebinia" refinery and "Siersza" power plant, **3**. Jankowice affected by emission from the chemical industry "Dwory" in Oświęcim and **4**. Alwernia located close to the "Alwernia" chemical industry. After exposition, concentrations of heavy metals (Cd, Pb, Zn, Cr, Ni, Cu, Fe) and S in lichens were analysed. Statistical highest concentrations of Cd, Pb and Zn were detected in Bukowno as the result of zinc-lead smelter manufacturing. Extremely high Cr concentration in lichens was determined in Alwernia because of chromium compounds production. S concentration was rather uniform in all investigated sites with highest concentration in Młoszowa and Jankowice as the result of emission from power plant (based on coal) using coal and H_2SO_4 production in chemical industry [27].

Table 1: Average concentration (± SD) of elements in *Hypogymnia physodes* transplanted to the Cracow-Silesia industrial region.

	Elements (μg^{-1} d.w.)			
Locations	Cadmium	Lead	Copper	Zinc
Borecka Forest	0.54 ± 0.02^{a}	9.0 ± 0.4^{a}	3.7 ± 0.4^{a}	55 ± 7^{a}
Bukowno	7.70 ± 0.47^{d}	123.7 ± 20.0^{b}	10.8 ± 0.3^{d}	583 ± 56^{c}
Młoszowa	1.37 ± 0.05^{c}	11.2 ± 1.5^{a}	7.5 ± 0.4^{bc}	68 ± 6^{ab}
Jankowice	1.02 ± 0.12^{b}	11.3 ± 1.2^{a}	5.9 ± 0.3^{b}	55 ± 4^{a}
Alwernia	1.29 ± 0.10^{bc}	12.7 ± 3.1^{a}	9.9 ± 1.8^{cd}	77 ± 5^{b}

	Elements (μg^{-1} d.w.)			
Locations	Iron	Nickel	Chromium	Sulphur
Borecka Forest	350 ± 47^{a}	1.08 ± 0.19^{a}	0.22 ± 0.04^{a}	1237 ± 33^{a}
Bukowno	1306 ± 164^{c}	1.91 ± 0.12^{b}	0.79 ± 0.06^{b}	1842 ± 397^{b}
Młoszowa	720 ± 106^{b}	1.36 ± 0.19^{ab}	0.48 ± 0.06^{b}	1960 ± 109^{b}
Jankowice	597 ± 38^{b}	1.38 ± 0.06^{ab}	2.89 ± 0.54^{b}	1999 ± 242^{b}
Alwernia	1202 ± 368^{c}	9.18 ± 1.42^{c}	75.85 ± 4.62^{c}	1665 ± 109^{ab}

[a, b, c, d] – means within a column with different letters are statistically different in the element levels between studied sites at $P < 0.05$ for $N = 5$. Data from Białońska and Dayan [27].

5 Conclusions

1. Air contamination in Base Stations of the Integrated Nature Monitoring System was not improved during the 2001-2005 period
2. National parks located in the southern part of Poland were more contaminated by heave metals than those in the north of the country. $S0_2$ is much more uniform across the country as high sulphur concentrations were noticed in national parks located in different parts of Poland.
3. High metal and sulphur concentrations and acute injuries on *Hypogymnia physodes* thalli confirmed impact of Cracow conurbation (including steelworks emission) on small forest areas.
4. Transplanted *Hypogymnia physodes* is the excellent tool to identify metal emission from industrial sources.

References

[1] Burton M.A.S., *Biological Monitoring of Environmental Contaminants (Plants)*. MARC Rep. 32, Monitoring and Assessment Research Centre, King's College London, University of London, London, 1986.

[2] Martin, M.H. & Coughtrey, P.J., *Biological Monitoring of Heavy Metals Pollution - Land and Air*. Applied Science Publisher, London, 1982.

[3] Haksworth D.L.& Rose F., Qualitative scale for estimating sulphur dioxide air pollution in England and Wales using epiphytic lichens. *Nature* **227 (254)** pp. 145–148, 1970.

[4] Kranner I., Beckett R.P. & Varma A.K., (eds.) *Protocols in Lichenology. Culturing, Biochemistry, Ecophysiology and use in Biomonitoring*. Springer Lab Manual, Berlin, Heidelberg, New York, 2002.

[5] Conti, M.E. & Cecchetti, G., Biological monitoring: lichens as bioindicators of air pollution assessment - a review. *Environmental Pollution*, **114**, pp. 471–492, 2001.

[6] Tyler, G. Uptake, retention and toxicity of heavy metals in lichens. *Water, Air and Soil Pollution*, **47**, pp. 321–333, 1989.

[7] Puckett, K. J., Bryophytes and lichens as monitors as metal deposition. Lichens, Bryophytes and Air Quality. *Lichenologist*, **30**, pp. 231–267, 1988.

[8] Jeran, Z., Jacimovic R., Batič, F., Smodis B. & Wolterbeek H. Th. Atmospheric heavy metal pollution in Slovenia derived from results of epiphytic lichens. *Frasenius J Anal. Chem.*, **354**, pp. 681–687, 1996.

[9] Giordani P., Is the diversity of epiphytic lichens a reliable indicator of air pollution? A case study from Italy. *Environmental Pollution,* **146**, pp. 317–323, 2007.

[10] Cotrufo, M.F., De Santo, A.V., Alfani, A., Bartoli, G. & De Cristofaro, A., Effects of urban heavy metal pollution on organic matter decomposition in *Quercus ilex* L. woods. *Environmental Pollution*, **8**, pp. 81–87, 1995.

[11] Monaci, F., Moni, F., Lanciotti, E., Grechi, D. & Bargagli R., Biomonitoring of airborne metals in urban environments: new tracers of

www.witpress.com, ISSN 1743-3541 (on-line)

vehicle emission, in place of lead. *Environmental Pollution*, **107**, pp. 321–327, 2000.
[12] Sawicka-Kapusta K., Gdula-Argasińska J., Zakrzewska M., Budka D. & Szpakowska K., The influence of Cracow urban pollution on small forest areas. *J.Phys. IV France* **107,** pp**.** 1197–1200, 2003.
[13] Nowicki, M., *Environment in Poland. Issues and Solutions*. Kluwer Academic Publishers. Dordrecht/Boston/London. Dordrecht, 1993.
[14] *Environment*. Central Statistical Office, Warsaw, Poland, 2007.
[15] Sawicka-Kapusta, K. & Rakowska, A., Heavy metal contamination in Polish national parks. *The Science of the Total Environment, Supplement, Part 1,* pp. 161–166, 1993.
[16] Nowosielski, O., *Metody oznaczania potrzeb nawożenia*. PWRiL. Warszawa, 1968.
[17] Jeran Z., Jacimovic R., Batic F. & Mavsar R., Lichens as integrating air pollution monitors. *Environmental Pollution*, **120**, pp. 107–113, 2002.
[18] Seaward M.R.D., Lichens and sulphur dioxide air pollution: field studies. *Environmental Reviews*, **1,** pp. 73–91, 1993.
[19] Takala K., Olkkonen H., Ikonen J., Jaaskelainen L & Puumalainen P., Total sulphur content of epiphytic and terricolous likens in Finland. *Ann. Botanici Fennici*, **2**, pp. 91–100, 1985.
[20] Pilegaard, K., Heavy metals in bulk precipitation and transplanted *Hypogymnia physodes* and *Dicranoweisia cirrata* in the vicinity of a Danish steelworks. *Water, Air and Soil Pollution*, **11**, pp. 77–91, 1979.
[21] Jeran, Z., Byrne, A.R. & Batič, F., Transplanted epiphytic lichens as biomonitors of air-contamination by natural radionuclides around the Žirovski Vhr uranium mine, Slovenia. *Lichenologist*, **27**, pp. 375–385, 1995.
[22] Van Dobben, H.F., Wolterbeek, H.T., Wamelink, G.W.W. & Ter Braak, C.J.F., Relationship between epiphytic lichens, trace elements and gaseous atmospheric pollutants. *Environmental Pollution*, **112 (2)**, pp. 163–169, 2001.
[23] Sawicka-Kapusta, K., Zakrzewska, M., Gdula-Argasińska, J. & Stochmal M., *Ocena narażenia środowiska obszarów chronionych. Zanieczyszczenie metalami i SO_2 parków narodowych*. Centrum Doskonałości Unii Europejskiej IBAES, Instytut Nauk o Środowisku, Uniwersytet Jagielloński. Kraków, 2005.
[24] Sawicka-Kapusta K., Zakrzewska M., Gdula-Argasińska J. & Bydłoń G., Air pollution in the base stations of the environmental integrated monitoring system in Poland. *Air Pollution XIII*, ed. C.A. Brebbia, WIT Transaction on Ecology and the Environment. WIT Press, Vol. 82, pp. 465–475, 2005.
[25] Sawicka-Kapusta K., Zakrzewska M. & Bydłoń G., Biological monitoring – the useful method for estimation air and environment quality. *Air Pollution XVI*, eds. C.A. Borrego &C.A. Brebbia, WIT Transaction on Ecology and the Environment. WIT Press, Vol 101, pp. 353–362, 2007.

[26] Sawicka-Kapusta K., Zakrzewska M. & Bydłoń G. Monitoring of air pollution by heavy metals and sulphur dioxide in the Base Stations of Integrated Nature Monitoring System using lichen *Hypogymnia physodes*. Biblioteka Monitoringu Środowiska, pp.217–226. Warszawa, 2007.
[27] Białońska D., Dayan F.E., Chemistry of the lichen Hypogymnia physodes transplanted to an industrial region. *Journal of Chemical Ecology*, **31,** pp. 2975–2991, 2005.