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TWO SPECIES OF LYCOPODIACEA AS A TOOL FOR MONITORING ENVIRONMENTAL HAZARDS

Abstract. The thermal decomposition of species of Lycopodiaceae were carried out. The weight loss steps (TG) and thermal effects (DSC) were measured. The values of the reaction heat of thermal decomposition have been determined. Also atomic absorption spectroscopy of species of Lycopodiaceae were carried out. Studies of the thermal decomposition of Lycopodiaceae revealed a increased thermal stability with distances from Zaklady Górniczo-Hutnicze "Boleslaw". The content of heavy metals determined in samples of plants and land taken from places localized in different distances from Zaklady Górniczo-Hutnicze "Boleslaw".

Keywords: Lycopodiaceae, heavy metal ions, soil, thermal decomposition

Introduction

In the recent years there have been more and more frequently signalized phenomena of decreasing the number of club-mosses positions and acreage of their cenopopulations [1]. Even if the positions of protected species are localized in the nature reserve, it doesn't guarantee their stability. At the same time there is observed their occurrence at anthropogenic habitats which are headings of a sand mine, and in the forests situated relatively not far from the emitters of the pollution. The South part of Kraków-Czestochowa Upland is strongly industrialized and exposed to industrial imission [2]. Despite mentioned threat, there were 84 legally protected species affirmed on this area [3]. Among them were 4 species of Lycopodiaceae [4]. Populations of Lycopodium annotinum and Diphasiastrum tristachyum are menaced because of changes of habitat (i.e. drying) as well as economic usage of forests. All species of Lycopodiaceae are under legal protection in Polan but they are also destroyed by illegal pulling out their shoots for Easter decorations[5]. All species of Lycopodiaceae are under legal

protection in Poland. Lycopodium annotinum is a long-term perennial, clonal plant with crawling shoots. Vertical bifurcally forked shoots grow out of horizontal shoots. The shoots have one strobil. Narrow leaves (up to 1 cm long) sprout from the shoots. The width of the shoot along with leaves is 10–15 mm. Diphasiastrum tristachyum is a long-term perennial, clonal plant with crawling shoots. Vertical bifurcally forked branches grow out of horizontal shoots. Small, squamous leaves sprout from the shoots. The shoots reach 1,6 mm of width. Strobli sprout in number of a few from bifurcally forked stalks [6–9]. A common source of contamination of the environment are the means of transport, communication and industry. Industry emit many harmful substances such as carbon oxides, nitrogen oxides, sulfur dioxide, soot, heavy metals that are components of exhaust gases and particulates, and hydrocarbons [10–12]. Of the heavy metals on the merit of lead compounds (toxic lead tetrachloride) as well as zinc, cadmium, chromium [13].

Metals contained in dust enter the soil and plants, together with atmospheric precipitation, dry fallout and go to different up the food chain. In addition to transport, the environment in industry areas soil is contaminated with dust emitted by various plants, and in winter a major source of pollution are heating devices. Because heavy metals migrate very free in the soil, are the lasting pollutants [14].

Experimental

Thermal analysis

Thermogravimetric (TG) and calorimetric (DSC) studies of species of *Lycopodium annotinum* and *Diphasiastrum tristachyum* were carried out. The weight loss steps (TG) and thermal effects (DSC) were measured using DSC–TG NETZSCH STA 409C apparatus. The thermal decomposition was studied over a temperature range of 293–723K at a heating rate of 5K/min. All samples (about 20 mg) were heated in corundum crucible covered with no hermetic lids. Weight loss steps (TG) and thermal effects (DSC) were determined.

Heavy metal determination

Atomization absorption spectrometry studies of species of *Lycopodium annotinum* (J) and *Diphasiastrum tristachyum* (S) were carried out. In order to prepare samples of mineralization have been in the microwave oven MarsX-press company CEM method increased the wet pressure. Used for digestion, nitric acid 65% cz.d.a. of 10 cm^3 to 0,5 g sample. Determination of metals content (Zn, Cd, Pb and Cu) was made using the method of atomic absorption spectrometry with electrothermal device on AA The Varian 240 companies. The

applied method uses a series of external benchmarks. Used as a modifier palladium standard solution 1000 mg/dm^3.

Results and discussion

The analyzed stands of *Lycopodium annotinum* (J) and *Diphasiastrum tristachyum* (S) are localized in a timber fresh pine coniferous forest (*Leucobryo – Pinetum)* at the Forest Inspectorate Superdivision Olkusz. Administratively the areas are situated in the Małopolskie Province, Polish administrative unit Olkusz. This area is exposed to industrial imission (among others heavy metals). The stands of club mosses are localized in various distance from Zakłady Górniczo-Hutnicze "Bolesław" in Bukowno emitting compounds of sulphur, zinc, lead and cadmium. The sample vertical modules of *Lycopodium annotinum* (J) and *Diphasiastrum tristachyum* (S), were collected from four study plots, localized in a fresh timber pine forest similar to *Leucobryo – Pinetum* (Fig. 1).

Fig. 1. Localization of the study plots. E – Emitter Zaklady Górniczo-Hutnicze "Boleslaw" in Bukowno; P – study plot Pomorzany (PS and PJ), Z – study plot Zurada (ZJ); K – study plot Kolbark (KS, KJ AND KJK); Ch – study plot Chrzastowice (ChJ and ChS)

The thermogravimetric studies responded to some questions: 1) what is the stability studied species? 2) how will it affect stability species localized at different distances from Zakłady Górniczo-Hutnicze "Bolesław"? 3) why is changed a stability of studied species? 4) which species provide the highest stability? 5) change stability of species in time line?

The DSC traces for *Lycopodium annotinum* and *Diphasiastrum tristachyum* show, that the thermal stability of studied species increase with distances from Zaklady Górniczo-Hutnicze "Boleslaw" (Fig. 2 and 3).

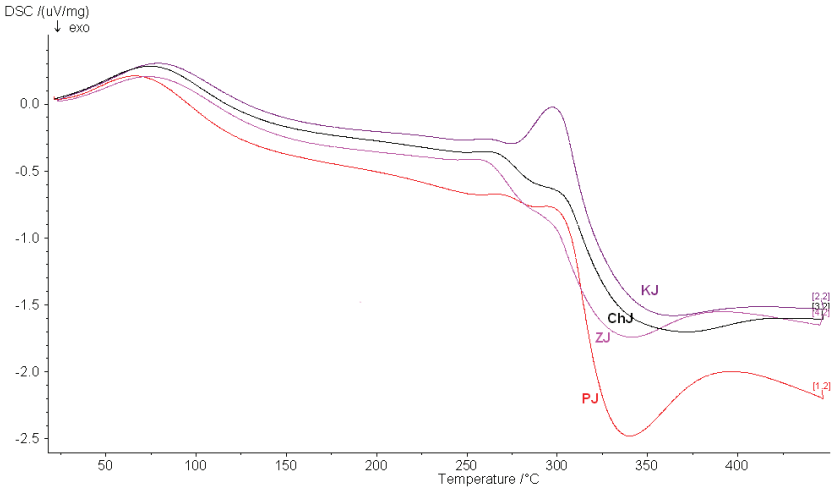

Fig. 2. TG/DSC/DTG curve of Lycopodium annotinum localized at different distances from Zaklady Górniczo-Hutnicze "Boleslaw" in Bukowno

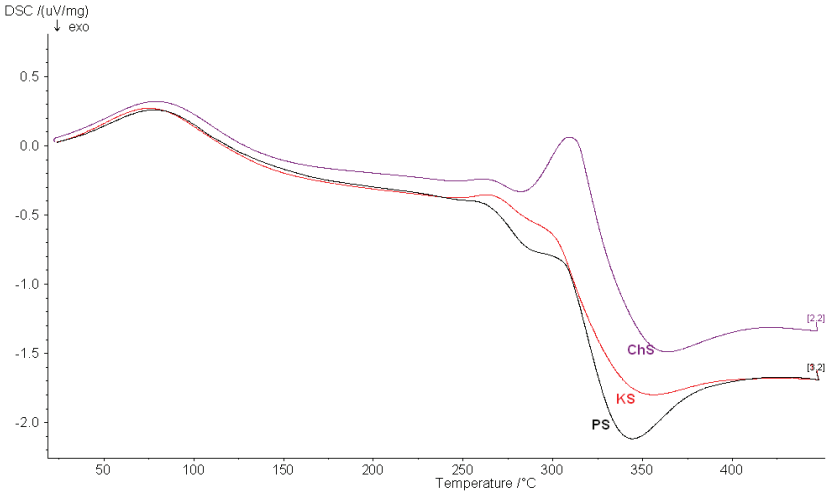

Fig. 3. TG/DSC/DTG curve of Diphasiastrum tristachyum localized at different distances from Zaklady Górniczo - Hutnicze "Boleslaw" in Bukowno

All studied species of *Lycopodiaceae* after loosing adsorbed and included water began to decompose around 300°C. As it seen on Figure 2 and 3, the thermal effects of decomposition of investigated species at low temperature consists of evolution of crystalline and hydroxilic water.

The DSC measurements within the range of 250–400°C revealed two transitions steps. The first step were endothermic and the two transition at about 340°C was strongly exothermic. This exothermic step moved into high temperature at different distances from Zakłady Górniczo-Hutnicze "Bolesław".

Simultaneously, the decomposition rate given as tgα of the slope of the TG curves is localized at the same temperature range and equals 3,60.

Thermal stability, in our opinion, depends on the content of heavy metal ions. Thermal analysis shows the different content of heavy metal ions depending on the distance from the source of contamination.

The diagrams of the thermal decomposition of *Diphasiastrum tristachyum* lokalized in Kolbark from year 2008 and 2009 and localized in Pomorzany from year 2007 and 2009 are very similar (Fig. 4 and 5). The small shift of the main peak of decomposition is observed. Little changes of thermal stability over the time are associated with the processes of oxidation and reduction caused probably by heavy metal ions *i.e.* Zn (II) and Cu (II).

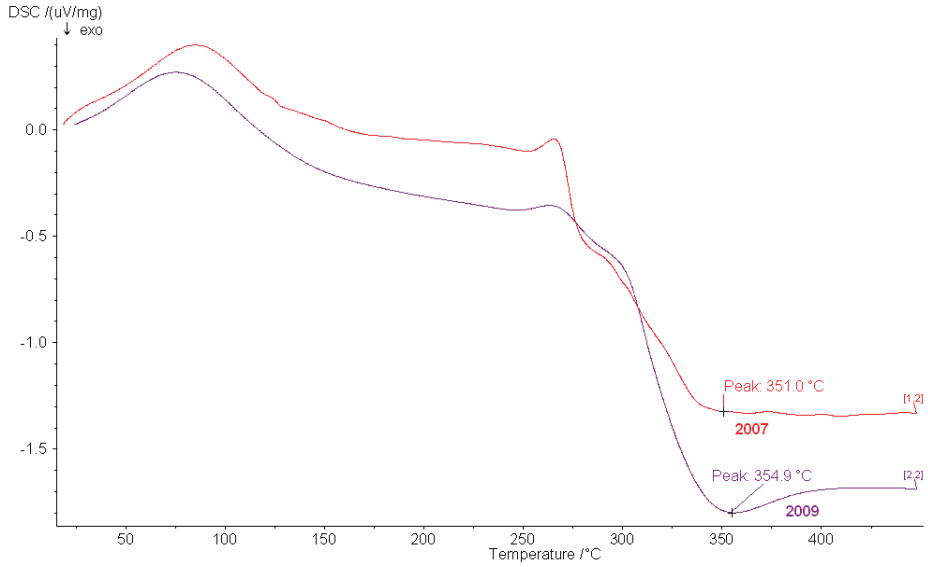

Fig. 4. The DSC curve of Diphasiastrum tristachyum localized in Pomorzany in 2007 and 2009 year

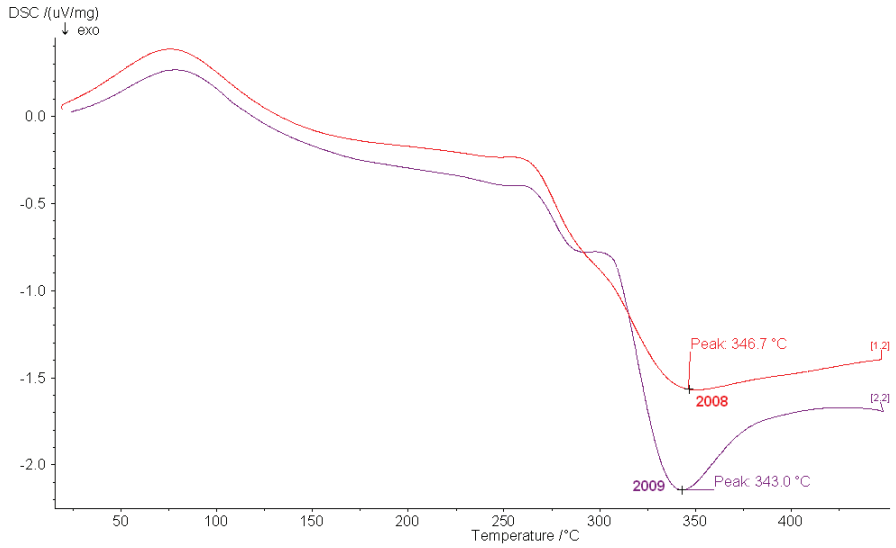

Fig. 5. The DSC curve of Diphasiastrum tristachyum localized in Kolbark in 2007 and 2009 year

The DSC grams of ears (KJK) and green vegetative parts of plant (KJ) show changes in metal ions accumulation. Main peak of decomposition was moved from 371 to 338°C. Lower thermal stability of ears probably inform, that heavy metal ions accumulate mainly in ears (Fig. 6).

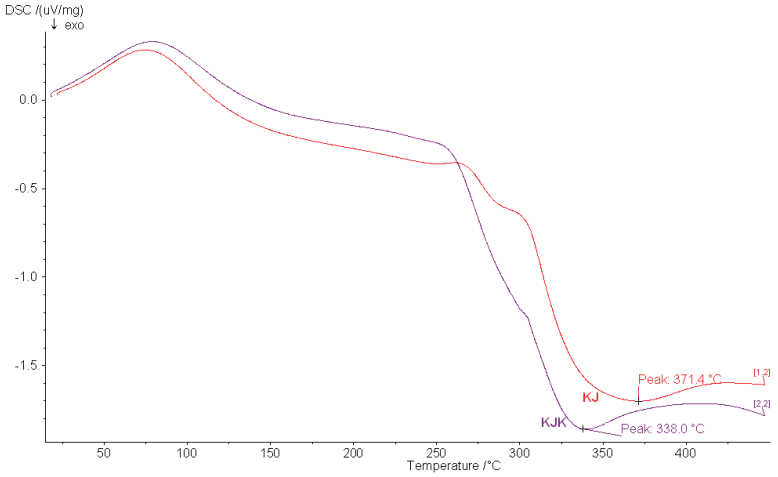

Fig. 6. The DSC curve of Lycopodium annotinum of ears (KJK) and green vegetative parts of plant (KJ) of species localized in Kolbark in 2009 year

Dispersed in air spores of *Lycopodium annotinum* are very explosive. When a lighted match is dropped into a pile of this powder, it does not burn. However, when the powder is dispersed into a fine mist near a candle flame, it ignites into a spectacular fireball. This results from an increasing the available surface area for combustion: when the powder is dispersed into a mist, the particles are surrounded by enough oxygen to support a combustion reaction.

The DSC of spores of studied species are destroyed in low temperature (Fig. 7).

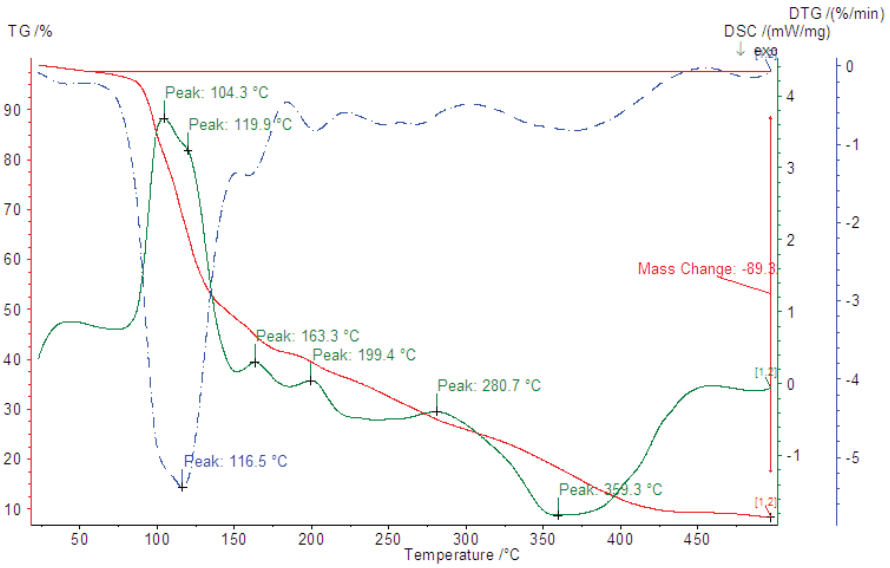

Fig. 7. TG/DSC/DTG curve of spores of Lycopodium annotinum

Spores are highly flammable (contain essential oils), formerly used to cause the special effects in theaters, and to chimney cleaning.

One might see that after loss of approximately 4% water, reflected by a decrease of the TG line and peaks on the DTG and DSC lines (small endothermic effect) in the low-temperature part of the line, there is a plateau on the TG line. In temperature 98°C begin the weight loss of sample.

In temperature range from 100 to about 150°C weight loss is about 50% in one-step decomposition. The decomposition is very fast (slope – tgα = 3.74). It is probably caused by explosion of spores and release of essential oils). In the temperature range from 150 to 300°C loss weight is 25%. In this range are observed three endothermic effects. They are due to further decomposition of organic compounds contained in spores. In the 359,3°C is localized main exothermic peak of decomposition. In this temperature is observed further weight

loss (15%) with slope 0,98. Form abou temperature 400°C on the course of the TG line a plateau is observed.

Variation in size of the test positions of *Lycopodiaceae* is collected in literature [10].

The content of heavy metals in the land adjacent to the station showed a large variation.

The atomization absorption spectrometry studies responded to some questions: 1) what is the content of metals in studied species? 2) how will it influence on stability species localized at different distances from Zakłady Górniczo-Hutnicze "Bolesław"?

The tested areas were characterized by neutral or alkaline reaction for up to a pH in the range from 6,98 to 7,88. Is well known that the acidic soil reaction clearly increases assimilate of heavy metals by plants. Due to the high pH, the reaction was not a factor in the increased mobility of metals in the test area.

According to Kabata-Pendias et al. [8] limit the content of metals in soils with contamination of anthropogenic origin of Pb is 70 mg, 150 mg Zn, 25 mg Cu, and 1 mg Cd kg^{-1}. While taking into account of the Minister of the Environment (2002) [9] for soil quality standards and quality of land, may be the faces in the levels of industrial sites – communication (group C) the following content: 15 mg Cd, 600 mg Pb, 1000 mg Zn, 600 mg Cu, 1000 mg Cr kg^{-1}.

Figure 8 shows the heavy metal contents of plants from vicinity of Zaklady Górniczo-Hutnicze "Boleslaw" in Bukowno.

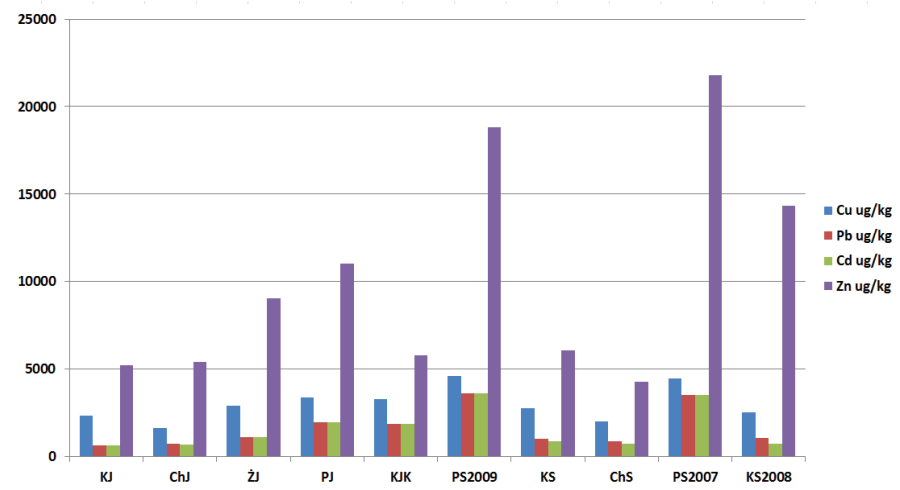

Fig. 8. Heavy metal contents of plants from vicinity of Zaklady Górniczo-Hutnicze "Boleslaw" in Bukowno

All species *Diphasiastrum tristachyum* collected on the sites contain significantly larger quantities of heavy metals than *Lycopodium annotinum.*

The lead content in the test area was in the range of 627,25 to 3625,69 μg Pb kg^{-1}. The highest levels of metal found in the case *Diphasiastrum tristachyum in Pomorzany* (PS) and the smallest in the case *Lycopodium annotinum in Kolbark* (KJ).

The zinc content in the studied areas was in a wide range of 5,40 to 21,82 mg Zn kg^{-1}. The highest values, as in the case of Zn were found in *Diphasiastrum tristachyum in Pomorzany* (PS) and lowest *Diphasiastrum tristachyum in Chrzastkowice* (ChS). In the case of Decree of the Minister for the Environment (2002) and the content of Zn in the analysis proposed above-mentioned land to the border of the soils given by Kabata-Pendias et al. (1995) the contents of Zn in the land of all the analyzed service station does not exceed the limit values.

In the case of Cu was observed content of this metal within the range from 1,65 for *Lycopodium annotinum in Chrzastkowice* (ChJ) to 4.50 mg Cu kg-1 for *Diphasiastrum tristachyum in Pomorzany* (PS). The contents of the copper content of the samples did not exceed specified by Kabata-Pendias et al. (1995) and in the Ministry of Environment [2002].

The cadmium content in the studied areas was in a wide range of 0.63 to 3.63 mg Cd kg^{-1}. The highest values, as in the case of Cd were found in *Diphasiastrum tristachyum in Pomorzany* (PS) and lowest *Lycopodium annotinum in Kolbark* (KJ). In the case of Decree of the Minister for the Environment (2002) and the content of Cd in the analysis proposed above-mentioned land to the border of the soils given by Kabata-Pendias et al. (1995) the contents of Cd in the analyzed service station exceed the limit values was observed for ZJ, PJ, KJK and PS.

In the case ears (KJK) and for green vegetative part (KJ) of *Lycopodium annotinum* the higher concentration of all metals is observed for ears.

For PS collected in 2009 year was observed slightly higher concentration of heavy metals than collected in 2007.

The content of metal ions corresponds with thermal properties for *Lycopodium annotinum* and *Diphasiastrum tristachyum.* The studies show, that the thermal stability of studied species increase with distances from Zaklady Górniczo-Hutnicze “Boleslaw” (Fig. 2 and 3).

Conclusion

For *Diphasiastrum tristachyum* from Pomorzany collected in 2009 year was observed slightly higher concentration of heavy metals than collected in 2007.

The content of metal ions corresponds with thermal properties for *Lycopodium annotinum* and *Diphasiastrum tristachyum.*

Little changes of thermal stability over the time are associated with the processes of oxidation and reduction caused by heavy metal ions.

Lower thermal stability of ears probably inform, that heavy metal ions accumulate mainly in ears.

Lycopodium annotinum and *Diphasiastrum tristachyum* are a good tools for monitoring environmental hazards.

References

[1] Rozporządzenie Ministra Środowiska z dnia 9 lipca 2004 roku w sprawie gatunków dziko występujących roślin objętych ochroną (Dz. U. Nr 168, poz. 1764)

[2] Plan urzadzania lasu sporządzony na lata od 2001 do 2010 dla Nadleśnictwa Olkusz

[3] Wika S., Zagadnienia geobotaniczne środkowej części Wyżyny Krakowsko-Wieluńskiej. Uniw. Śląski, Katowice 1986: 1–156.

[4] Piękoś-Mirkowa H., Mirek Z., Flora Polski. Atlas roślin chronionych Wydawnictwo Mulico, Oficyna Wydawnicza, Warszawa 2003.

[5] Grochowski W., Chrońmy widłaki. PWN Warszawa 1956, s. 95.

[6] Mirek Z., Piękoś-Mirkowa H., Zając A., Zając M., Krytyczna lista roślin naczyniowych Polski, 2007-05-20

[7] http://bobas.ib-pan.krakow.pl/cgi/foxweb.exe/czek/gatdframe?rodz= Lycopodiella

[8] http://bobas.ib-pan.krakow.pl/cgi/foxweb.exe/czek/gatdframe?rodz= Lycopodium

[9] http://bobas.ib-pan.krakow.pl/cgi/foxweb.exe/czek/gatdframe?rodz= Diphasiastrum

[10] Curzydło J., 1995. Skażenie motoryzacyjne wzdłuż dróg i autostrad oraz sposoby przeciwdziałania ujemnym skutkom motoryzacji w środowisku. Zesz. Prob. PNR, 418, 265–270.

[11] Indeka L., Karczun Z., 1999. Kumulacja wybranych metali ciężkich w glebach przy ruchliwych trasach komunikacyjnych. Ekolg. i Techn., 6, 174-180.

[12] Jasiewicz Cz., Buczek J., 2000. Zawartość metali ciężkich w glebie i pszenicy narażonej na wpływ zanieczyszczeń komunikacyjnych. Zesz. Prob. PNR, 472, 341-347.

[13] Skręt I., Szlachta Z., 1996. Możliwości zmniejszania motoryzacyjnego skażenia powietrza w miastach poprzez stosowania do napędu autobusów niskosiarkowego oleju napędowego, [w:] Materiały I Forum Inżynierii Ekologicznej, Wyd. PTIE, Lublin-Nałęczów, 283–288.

[14] Potarzycki J. i in. 1999. Stan geochemiczny gleb i jakość płodów rolnych w strefie oddziaływania tarasy komunikacyjnej Poznań-Świecko. Rocz. AR. Pozn., CCCX, Melior. Inż. Środ. 20, I, 77–85.

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LYCOPODIACEA JAKO NARZĘDZIE DO MONITOROWANIA ZAGROŻEŃ ŚRODOWISKOWYCH

Streszczenie

Przeprowadzono rozkład termiczny dwóch gatunków Lycopodiaceae. Zmierzono ubytki masy (TG) i efekty termiczne (DSC) im towarzyszące. Przeprowadzono także pomiary zawartości jonów metali: Cd2+, Pb2+, Cu2+ I Zn2+ przy użyciu absorpcyjnej spektroskopii atomowej. Badania rozkładu termicznego Lycopodiaceae ujawniły zwiększoną ich stabilność termiczną związaną ze wzrostem odległości od Zakładów Górniczo-Hutniczych „Bolesław" oraz zawartością metali ciężkich w próbkach roślin i gruntów pobranych z miejsc położonych w różnych odległościach od Zakładów Górniczo-Hutniczych „Bolesław".

Słowa kluczowe: Lycopodiaceae, jony metali ciężkich, gleba, rozkład termiczny