ECOLOGICAL CHEMISTRY AND ENGINEERING A

Vol. 16, No. 9 2009

Marta KANDZIORA[1], Ryszard CIEPAŁ
and Aleksandra NADGÓRSKA-SOCHA

EVALUATION OF HEAVY METAL LOAD IN SELECTED NATURE RESERVES OF SOUTHERN POLAND

OCENA STOPNIA ZAGROŻENIA METALAMI CIĘŻKIMI WYBRANYCH REZERWATÓW POŁUDNIOWEJ POLSKI

Abstract: In this study we investigated heavy metals (Cd, Pb, Zn, Cu and Fe) accumulation in upper layer of soils (from three levels: 0–10 cm, 10–20 cm, 20–30 cm) and in the leaves of *Pinus sylvestris* L., *Picea abies* [L.] Karst., *Maianthemum bifolium* [L.] F.W. Schmidt and *Hedera helix* L. collected from nature reserves: Bukowa Kepa, Ostreznik, Zielona Gora, and Slotwina situated south of Poland. The investigations were carried out in 2004–2007. In soil samples from reserves Ostreznik and Slotwina higher concentrations of Cd was noted than "normal" level for protected area (1 mg/kg). Elevated Pb content in upper layer of soil were estimated in reserves of Bukowa Kepa (84.9 mg/kg) and Ostreznik (68.9 mg/kg). The level of Pb and Zn in plants leaves was below the values considered as toxic. However the concentration of Cd in leaves of *Hedera helix* L. collected in nature reserves Bukowa Kepa, Ostreznik and Zielona Gora was higher than the level considered as toxic (5–10 mg/kg d.m.). Relatively low Cu concentration in the leaves of investigated plants indicated poor plant nutrition.

Keywords: heavy metals, nature reserves of southern Poland, *Pinus sylvestris* L., *Picea abies* [L.] Karst., *Maianthemum bifolium* [L.] F. W. Schmidt and *Hedera helix* L.

Nature reserves are one of area forms of nature protection enabling a protection of ecosystems valuable from a natural point of view [1]. Protection of nature in a form of nature reserves enables maintenance of those reserves durability, their biodiversity as well as ecological processes proceeding there [2].

Forest ecosystems, including protected reserves, are a subject to different dangers which scale increases all the time. Results of those hazards can be seen, among other things, in increase of number of forest fires, damages of forest stands as a result of weather anomalies, shortening of periods between gradations of pests and increasing acreage of their mass occurrence, dying out of trees and forest stands as a result of emission as well as without any found reason [3]. Rare species of plants disappear, other appear, synanthropic, brought by a man. Plant associations are a subject of

[1] Department of Ecology, Silesian University, ul. Bankowa 9, 40–007 Katowice, Poland, email: marta.kandziora@yahoo.pl

adverse changes and degradation. Very adverse and dangerous for reserves are changes in site conditions resulting from anthropogenic impact [4]. The most important ingredient contaminating and degrading natural environment are chemical elements emitted in accordance with different processes of human activity. Introduced into ecosystems, they cause a disturbances in homeostasis [5–7]. The most durable and onerous for environment of those elements are heavy metals whose concentration, despite a falling tendency, are still hazardous for environment and living organisms [5, 8, 9]. Plants, particularly chemical content of their assimilation apparatus, are susceptible indicator of biophysical and chemical changes of environment [5, 10–12].

In threatened areas, that is where environment contamination by toxic metals and gases repeatedly exceeds standards for protected areas, there occur 3/4 of Polish national parks and 2/3 reserves [13].

The objective of this piece of research was to determine a load factor of chosen heavy metals (Zn, Cu, Pb, Fe and Cd) in the Slotwina Reserve, Bukowa Kepa Reserve, Ostreznik Reserve and Zielona Gora Reserve on the basis of a chemical analysis of soil as well as assimilation apparatus of chosen plant species.

Material and methods

The investigation was carried out in the soil and leaves and needles of *Picea abies* [L.] H. Karst., *Pinus sylvestris* L., *Maianthemum bifolium* [L.] F.W. Schmidt, *Hedera helix* L. Karst in the Slotwina Reserve, Bukowa Kepa Reserve, Ostreznik Reserve and Zielona Gora Reserve. Samples of soil (from the level 0–10 cm) and leaves and needles *Picea abies* [L.] H. Karst., *Pinus sylvestris* L., *Maianthemum bifolium* [L.] F.W. Schmidt, *Hedera helix* L. Karst abies were collected in the vegetation season of 2003–2004 (Slotwina Reserve) and 2006–2007 (the rest of reserve). In order to determine the heavy metals concentration, plants material dried in 105 ^{o}C to a constant weight, ground to a powder, then mineralized and dissolved in 10 % HNO_3. After filtration Cd, Pb, Zn, Cu and Fe content were measured using 10 % HNO_3. The measurements were carried out using the conventional Atomic Absorption Spectrometry (AAS) [14]. The quality of analytical procedures was controlled by using the reference material (Certified Reference Material CTA – OTL – 1 Oriental Tabacco Leavs).

Results and discussion

Contents of heavy metals in examined samples were presented in Tables 1 and 2.

Natural content of cadmium in soil significantly depends on an occurrence of this element in country rocks. Amount of imission has a significant influence on a noted current concentration of this element.

Average content of cadmium in soils of Poland amounts to 0.2 μg/g [15].

Concentrations of this element in a top layer of a soil, in case of the Bukowa Kepa Reserve and the Zielona Gora Reserve were beyond a limit of determination so they were lower than 0.1 μg/g. In the Ostreznik Reserve and the Slotwina Reserve, content of cadmium varied from 0.98 μg/g to 3.42 μg/g and exceeded permissible concentrations of that element in soil in protected area. In both cases, a decrease of cadmium content was observed together with a depth of collected samples.

Table 1

Content of zinc, copper, lead, iron and cadmium [μg/g d.m.] in leaves and needles of chosen plant species

Nature reserve	Species	Zn	Cu	Pb	Fe	Cd
Slotwina	*Picea bies* L.	18.84	2.04	1.64	17.5	nd
	Pinus sylvestris L.	42.95	3.59	2.88	22.27	nd
	Maianthemum bifolium L.	44.54	3.69	1.66	53.87	nd
	Hedera helix L.	66.82	4.99	2.14	48.88	nd
Bukowa Kepa	*Picea abies* L.	28.3	0.94	1.32	33.3	0.37
	Pinus sylvestris L.	25.4	0.87	2.03	39.1	0.49
	Maianthemum bifolium L.	28.0	2.42	8.61	72.3	3.07
	Hedera helix L.	247.1	2.56	6.70	53.5	5.40
Ostreznik	*Picea abies* L.	21.2	0.38	1.57	24.6	0.11
	Pinus sylvestris L.	23.2	0.73	2.32	21.8	0.5
	Maianthemum bifolium L.	23.9	1.86	4.42	78.1	2.57
	Hedera helix L.	213.0	2.07	4.42	65.1	4.75
Zielona Gora	*Picea abies* L.	nd	nd	nd	nd	nd
	Pinus sylvestris L.	27.3	0.94	1.24	56.4	0.53
	Maianthemum bifolium L.	28.5	2.14	4.42	69.4	1.81
	Hedera helix L.	223.0	3.51	9.75	72.3	4.18

Table 2

Content of zinc, copper, lead, iron and cadmium [μg/g] in the upper layer of the soil

Elements	Layer [cm]	Nature reserve			
		Slotwina	Bukowa Kepa	Ostreznik	Zielona Gora
Cd	0–10	3.42	nd	2.04	nd
	10–20	2.03	nd	1.77	nd
	20–30	1.3	nd	0.98	nd
Pb	0–10	4.97	84.9	68.9	41.7
	10–20	2.46	23.5	22.3	15.0
	20–30	2.46	9.3	12.3	7.9
Zn	0–10	22.42	33.1	42.6	18.4
	10–20	20.68	11.8	32.1	4.6
	20–30	13.44	7.3	23.1	3.0
Cu	0–10	3.61	1.98	1.98	1.67
	10–20	3.21	1.14	1.46	1.03
	20–30	1.22	0.82	1.03	0.72
Fe	0–10	344.0	1301.0	613.0	643.0
	10–20	258.5	1066.0	408.0	419.0
	20–30	125.0	818.0	289.0	326.0

Soil analysis results in this elaboration, regarding content of cadmium, are comparable with results received for other protected areas. Ciepal et al [16] determined an average concentration of Cd in a top layer of soil within a range 0.5–0.9 μg/g on Mt Babia Gora, and on Mt Pilsko 1.9–3.1 μg/g of air-dry soil. Kimsa et al [17] determined 2.7–3.4 μg/g of Cd in a top layer of soil of the Swietokrzyski National Park. Ciepal et al [18] noted 2.0 μg/g of Cd in a top layer of soil in the Bukowica Reserve, whereas in the Lipowiec Reserve it was 4.0 μg/g of Cd. Ciepal and Lipka [19] give out a cadmium content in a top layers of soil in the Smolen Reserve at the level of 17.0 μg/g and for Gora Chelm 16 μg/g. Lukasik [20] noticed in soil of the Parkowe Reserve 1.5 μg/g of Cd.

In case of plants, cadmium is an element not necessary for their growth but still easily absorbed both by root system and leaves, usually proportionally to a concentration in environment [15].

Sawicka-Kapusta [21] gives out a range of cadmium occurrence in plants from not contaminated areas: 0.12–0.5 μg/g d.m., whereas Kabata-Pendias and Pendias [15] state that in such areas content of cadmium does not exceed 1 μg/g d.m. Content of cadmium at the level of 5–10 μg/g d.m. for susceptible plants and 10–30 μg/g d.m. for resistant plants is considered as phytotoxic [22].

Szarek et al [23] discovered average amount of cadmium 2.6 μg/g d.m. in plants of ground cover in beech forest in the area of the Ojcowski National Park. Ciepal et al [18] found a cadmium content of 2.4–6.0 μg/g d.m. in the Bukowica Reserve and 4.5–7.0 μg/g in the Lipowiec Reserve, depending on species. Ciepal and Lipka [19] gives out a content of cadmium in plants of ground cover at the level of 0.5–16.0 μg/g d.m. in the Smolen Reserve and 0.7–18 μg/g d.m. in the Gora Chelm Reserve and in both cases the highest concentration regarded *Hedera helix* L. Ciepal [24] gives out a cadmium content in needles of *Pinus sylvestris* L. originating from the Bukowica Reserve and it amounts to 0.5–6.0 μg/g d.m., from the Smolen Reserve 4.0–10.0 μg/g d.m. and from the Gora Chelm Reserve 7.0–14.0 μg/g d.m. Ciepal and Rycman [25] in an analogical material originating from Roztoczanski National Park noted a cadmium content within a range from 0.6 to 1.05 μg/g d.m. For spruce needles, Ciepal [24] gives out following contents of cadmium: 2.0–7.0 μg/g d.m. in the Bukowica Reserve, 12.0–21.0 μg/g d.m. in the Smolen Reserve and 14.0–21.0 μg/g d.m. in the Gora Chelm Reserve. Received results indicate relatively high content of cadmium in plants of a ground cover of examined reserves. Whereas content of cadmium in needles of *Pinus sylvestris* [L.] Karst and *Picea abies* L. does not exceed a level characterizing plants from non-polluted areas. In comparison with discussed protected areas, results received for coniferous trees in examined reserves present that these areas are clean, not threatened by cadmium contamination.

Similarly to cadmium case, content of lead in soil is closely connected with a mineralogical and granulometric content as well as origin of soil bed-rocks but simultaneously, occurrence of this element in a top layer of soil is mostly connected with all anthropogenic factors.

Kabata-Pendias and Pendias [15] give out an average content of lead for soils of Poland not exceeding 20 μg/g. Permissible concentration of Pb in soils in areas protected on the basis of law regulations regarding protection of nature amounts to 50 μg/g.

Kimsa et al [17] determined in the surface layer of soil in the Swietokrzyski National Park a lead concentration amounting to 18.0–19.0 μg/g. Ciepal et al [18] determined in the surface layer of soil in the Bukowica Reserve a lead concentration amounting to 60.0 μg/g and in the Lipowiec Reserve 80.0 μg/g. In the area of the Jurajskie Landscape Parks – a part located in the former Czestochowskie province, Slezanski [26] gives out lead concentrations within a range from 19.90 to 323.0 μg/g.

Received results concerning lead content in a surface layer of soils in examined reserves are between 4.97–84.9 μg/g. Only in two reserves (the Slotwina Reserve and Zielona Gora Reserve) of four taken into consideration the permissible lead contents were not exceeded.

Regular (physiological) content of lead in plants varies from 5 to 14 μg/g d.m., and amount of 30 μg Pb/g d.m. is considered as toxic [15].

Ciepal [24] found contents of lead, depending on a research season, amounting to 0.5–4.0 μg/g d.m. for *Hedera helix* L. in the Bukowica Reserve and 24.0–26.0 μg/g d.m. for *Maianthemum bifolium* [L.] F.W. Schmidt in the Gora Chelm Reserve.

Czarnowska and Stasiak [27] give out a content of lead in needles of *Pinus sylvestris* L. from non-polluted areas and it amounts to 0.5–14 μg/g d.m. In mountain pine communities on Mt Babia Gora and Mt Pilsko the determined lead content was correspondingly 5.9 μg/g d.m. and 8.5 μg/g d.m. Needles of *Picea abies* [L.] Karst contained amounts of this metal within a range 15–21.5 μg/g d.m. regarding Mt Babia Góra and 21–35 μg/g d.m. regarding Mt Pilsko [16].

Received results concerning lead content in assimilation apparatus of chosen plants from examined reserves indicate insignificant threat by this metal. The highest contents found in *Hedera helix* L. or *Maianthemum bifolium* [L.] F.W. Schmidt are far from values considered as toxic.

Average zinc concentration in soils of different countries is within limits of 30–120 μg/g. Average zinc content for non-polluted soils in Poland is 40 μg/g [15]. Permissible content of zinc in soils of protected areas amounts to 100 mg/kg.

Ciepal and Lipka [19] found 350 ěg Zn/g in a surface layer of soil in the Gora Chelm Reserve and in the Smolen Reserve it was 200 μg Zn/g. Lukasik [20] at the upper level of soil in the Parkowe Reserve found that an average concentration of zinc equals 85 μg/g. On Mt Babia Gora a content of zinc was from 105.0 to 215 μg/g and on Mt Pilsko 185.0–325.0 μg/g [16].

In this elaboration, received results were within a range of 18.4–42.6 μg Zn/g. In each examined protected area the permissible concentrations of this metal were not exceeded.

In case of plants, zinc is a necessary for proper growth. To cover physiological requirements of plants, a concentration in leaves at the level of 15–30 μg/g d.m. is sufficient and in aboveground parts of a plant, staying away from pollution influences, is around 10–70 μg/g [15].

Zinc concentrations in examined samples presents predispositions of *Hedera helix* L. to an accumulation of this element. In case of this species, concentration of zinc exceeded a level considered as physiological. Contents found in leaves of other plants of a ground cover and in needles of *Picea abies* [L.] Karst and *Pinus sylvestris* L. did not exceed permissible standards.

Content of copper and iron in examined soils in any case did not exceeded permissible values. Ranges of concentrations were within 1.67–3.61 μg Cu/g and 344–1301 μg Fe/g.

Copper and iron, similarly to zinc, belong to the biogenic group of elements, used by plants in many metabolic traces [15].

Content of iron in plants changes significantly during vegetation period, in a different degree for particular plant, the most often within limits 10–400 μg/g d.m. [15].

Content of iron in plants changes significantly during vegetation period, in a different degree for particular plant, the most often within limits 10–400 μg/g d.m. [15].

Considering copper, Kabata-Pendias and Pendias [15] give out a physiological content of copper in leaves of different species at the level of 5–30 μg/g d.m.

In examined plant material, concentrations of this element varies from 0.38 to 4.99 μg/g d.m. and do not exceed permissible values and present even a deficiency of copper in an assimilation apparatus of chosen plant species.

Conclusions

Conducted research results present that there is no excessive heavy metals load in the Slotwina Reserve, Bukowa Kepa Reserve, Ostreznik Reserve and Zielona Gora Reserve. Content of heavy metals in soil, leaves and needles of chosen plant species growing in the areas of the Slotwina Reserve, Bukowa Kepa Reserve, Ostreznik Reserve and Zielona Gora Reserve in most cases were several times lower than average contents mentioned in literature and values characteristic for other protected areas. Therefore, chosen reserves may become a good control point for research on heavy metals content in a plant material and soil of areas influenced by a strong anthropogenic impact.

References

[1] Medwecka-Kornaś A.: *Ocena rezerwatowa*, [in:] *Ochrona przyrody i jej zasobów*. Wyd. Zakł. Ochr. Przyr. PAN, Kraków 1965.
[2] Wika S.: *Lasy województwa śląskiego*. Wyd. Kubajak, Krzeszowice 1999.
[3] Szujecki A.: *Współczesne zagrożenia lasów polskich i ich prognoza długoterminowa*, [in:] *Reakcje biologiczne drzew na zanieczyszczenia przemysłowe.* Mat. Symp., Sorus, Poznań 1996, 17–27.
[4] Czubiński Z., Gawłowska J. and Zabierowski K.: *Rezerwaty w Polsce*. PWN, Warszawa 1977.
[5] Łukasik I., Palowski B., Ciepał R. and Dobosiewicz J.: *Wybrane metale ciężkie w glebie i aparacie asymilacyjnym drzew i krzewów rosnących na obszarze zurbanizowanym*. IV Krajowe Sympozjum "Reakcje biologiczne drzew na zanieczyszczenia przemysłowe", Poznań–Kórnik 2002, 813–818.
[6] Przybylski T.: *Zagrożenie środowiska przyrodniczego w województwie katowickim*. Biblioteka Fundacji Ekologicznej "Silesia", Katowice 1991.
[7] Boubel R.W., Fox D.L., Turner D.B. and Stern A.C.: *Fundamentals of air pollution*. Academic Press, Oxford 1994.
[8] Krochmal D.: *Ocena sytuacji monitoringu zanieczyszczeń powietrza w aglomeracji katowickiej*. Chem. Inż. Ekol. 1997, **4**(1), 49–63.
[9] Hławiczka S.: *Ocena emisji metali ciężkich do powietrza z obszaru Polski. Cz. II. Emisje w latach 1980–1995*. Arch. Ochr. Środow. 1998, **24**(4), 91–108.
[10] Chambers J.C. and Siddle R.C.: *Fate of heavy metals in abandoned lead zinc tailing ponds: I Vegetation*. J. Environ. Qual. 1991, **20**, 745–750.

[11] Grodzińska K. and Szarek G.: *Skażenie środowiska Polski na tle Europy*. Wiad. Bot. 1995, **39**(1/2), 31–38.
[12] Anderson S., Chappelka A.H., Flynn K., and Odom J.W.: *Lead accumulation in Quercus nigra and Q. velutina near smelting faciliting in Alabama, USA*. Water, Air Soil Pollut. 2000, **118**, 1–11.
[13] Bandoła-Ciołczyk E.: Czy *rezerwaty są bardziej odporne na zanieczyszczenia?* Chrońmy Przyrodę Ojczystą 1992, **3**, 54–61.
[14] Ostrowska A., Gawliński S. and Szczubiałka Z.: *Metody analizy i oceny właściwości gleb i roślin*. Wyd. IOŚ, Warszawa 1991.
[15] Kabata-Pendias A. and Pendias H.: *Biogeochemia pierwiastków śladowych*. PWN, Warszawa 1993.
[16] Ciepał R., Kimsa T., Palowski B. and Łukasik I.: *Concentration of heavy metals and sulphur in plants and soil of different plant communities of Babia Góra and Pilsko*, [in:] Proc. of 2nd Int. Conf. "Trace elements effects on organism and environment", Cieszyn 1998, 33–37.
[17] Kimsa T., Palowski B., Łukasik I. and Ciepał R.: *Concentration of heavy metals and sulphur in plants species of different layers of mixed forest in Świętokrzyski National Park*, [in:] Proc. of 2nd Int. Conf. "Trace elements effects on organism and environment". Cieszyn 1998, 39–42.
[18] Ciepał R., Kimsa T., Palowski B., Kudyba B. and Łukasik I.: *Ocena stopnia obciążenia metalami ciężkimi i siarką rezerwatów przyrody Bukowica i Lipowiec*. Acta Biol. Siles., Katowice 2000, **34**(51), 31–47.
[19] Ciepał R. and Lipka C.: *Ocena stopnia zagrożenia rezerwatów przyrody Góra Chełm i Smoleń metalami ciężkimi i siarką*. Acta Biol. Siles., Katowice 1995, **26**(43), 19–27.
[20] Łukasik I.: *Degradacja starodrzewów bukowych Luzulo pilosae-Fagetum w warunkach zróżnicowanej antropopresji na Wyżynie Śląsko-Krakowskiej*. Wyd. UŚl., Katowice 2006, 1–145.
[21] Sawicka-Kapusta K.: *Reakcja roślin na dwutlenek siarki i metale ciężkie w środowisku – bioindykacja*. Wiad. Ekol. 1990, **XXXVI**(3), 94–109.
[22] Kabata-Pendias A.: *Biogeochemia kadmu*. [in:] Kadm w środowisku – problemy ekologiczne i metodyczne, Zesz. Nauk. Komit. "Człowiek i Środowisko" PAN, 1998, **26**, 9–17.
[23] Szarek E., Chrzanowska E. and Godzik B.: *Zawartość metali ciężkich i mikropierwiastków w roślinności runa w Ojcowskim Parku Narodowym*. Prac. Muzeum im. Szafera, Prądnik 1998, (7–8), 159–160.
[24] Ciepał R.: Kumulacja metali ciężkich i siarki w roślinach wybranych gatunków oraz glebie jako wskaźnik stanu skażenia środowiska terenów chronionych województwa śląskiego i małopolskiego. Wyd. UŚl., Katowice 1999.
[25] Ciepał R. and Rycman E.: *Ocena zagrożenia metalami ciężkimi i siarką Roztoczańskiego Parku Narodowego na podstawie analizy chemicznej liści i szpilek wybranych gatunków roślin.* Acta Biol. Siles., Katowice 1996, **28**(45), 26–35.
[26] Ślęzański M.: *Zawartość wybranych metali ciężkich w glebach ZJPK w granicach województwa częstochowskiego*, [in:] Stan środowiska przyrodniczego woj. częstochowskiego, Częstochowa 1995, 75–82.
[27] Czarnowska K. and Stasiak J.*: Zawartość składników mineralnych w igłach, drewnie i korze sosny zwyczajnej (P. sylvestris) w zależności od wieku drzew*, [in:] Reakcje biologiczne drzew na zanieczyszczenia przemysłowe. II Krajowe sympozjum Kórnik, Wyd. UAM, Poznań 1987, 183–189.

OCENA STOPNIA ZAGROŻENIA METALAMI CIĘŻKIMI WYBRANYCH REZERWATÓW POŁUDNIOWEJ POLSKI

Katedra Ekologii, Wydział Biologii i Ochrony Środowiska
Uniwersytet Śląski w Katowicach

Abstrakt: Badano akumulację metali ciężkich (Cd, Pb, Zn, Cu i Fe) w glebie (z głębokości 0–10 cm, 10–20 cm, 20–30 cm) oraz w szpilkach *Pinus sylvestris* L., *Picea abies* [L.] Karst., i liściach *Maianthemum bifolium* [L.] F.W. Schmidt i *Hedera helix* L. rosnących na terenach wybranych rezerwatów przyrody południowej Polski (Bukowa Kępa, Ostrężnik, Zielona Góra i Słotwina).

Materiał do analiz zbierano w okresie wegetacyjnym 2003–2004 (rezerwat Słotwina) oraz 2006–2007 (pozostałe rezerwaty). W próbkach gleby z rezerwatów Ostrężnik i Słotwina odnotowano przekroczenie normy zawartości Cd dla gleb obszarów chronionych (1 mg/kg), a z kolei ponadnormatywną zawartość Pb odnotowano w wierzchniej warstwie gleby z rezerwatu Bukowa Kępa (84,9 μg/g) i Ostrężnik (68,9 μg/g). W żadnym z badanych rezerwatów nie stwierdzono przekroczenia fitotoksycznych wartości progowych Pb i Zn. W przypadku Cd w liściach *Hedera helix* L. z rezerwatów Bukowa Kępa, Ostrężnik i Zielona Góra stwierdzono stężenia mieszczące się w dolnym zakresie wartości uznawanych za fitotoksyczne (5–10 μg/g). Odnotowane w roslinach badanych terenów chronionych stężenia Cu wskazują na niedobór tego pierwiastka i zły stan odżywienia roślin.

Słowa kluczowe: metale ciężkie, rezerwaty południowej Polski, *Pinus sylvestris* L., *Picea abies* [L.] Karst., *Maianthemum bifolium* [L.] F.W. Schmidt and *Hedera helix* L.