

CONTENT OF HEAVY METALS IN NEEDLES
OF SCOTS PINE (*Pinus sylvestris* L.) IN SELECTED PINE FORESTS
IN SŁOWIŃSKI NATIONAL PARK

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Keywords: Needles of *pinus sylvestris*, Zn, Cu, Mn, Fe, unpolluted area, reserved area.

Abstract: The paper presents the results of study on heavy metals in needles of *Pinus sylvestris* in selected pine forests in Słowiński National Park. It was evidenced that heavy metal contents (Zn, Cu, Mn and Fe) in needles of *Pinus sylvestris* varied depending on the metal, the age of the needles and the humidity of a forest complex. Variation coefficients of such metals remained at the level of: 13–30% (Zn), 3–6% (Cu), 13–34% (Mn) and 12–30% (Fe) depending on the age of the needles. In the case of Zn, Mn and Fe higher concentrations of researched metal were found in the 2-year-old needles than in 1 year old needles, and in the case of Cu in 1 year old needles than in 2-year-old needles. The increase of zinc concentration found in 1-year-old needles after rainfall sums was (Bw, $r = 0.67$, $p < 0.05$, $n = 24$) and (Bśw, $r = 0.39$, $p < 0.05$, $n = 24$) in 2-year-old needles. The content of the above mentioned metals in needles of dry coniferous forests (Bs), fresh coniferous forests (Bśw) and humid coniferous forests (Bw) of the ground cover constitute the following decreasing series: Mn(323.8) > Fe(103.4) > Zn(65.5) > Cu(5.9).

INTRODUCTION

Heavy metals are natural components of the natural environment and are constituents of minerals and rocks from which they can be gradually released by means of weathering. Their natural content in lithosphere, which constitutes the so-called geothermic background, varies spatially and depends on the geological processes in the past. Emission of heavy metals from anthropogenic sources has been vital in recent centuries. It has led to increase of concentration of such substances in various ecosystems [33]. Heavy metals as components of dusts (PM₁₀ and PM_{2.5}) and aerosols can be transported in atmosphere over substantial distances leading to contamination of ecosystems situated far away from the sources of their emission [1, 29, 32]. Heavy metals constitute the most persistent soil contaminants with a very limited migration [14], thanks to which, the vertical diversity of their concentration in young fluvial deposits and slope deposits in relation to the local

geochemical background can constitute a basis for reconstruction of the character and level of intensity of anthropopression during historical and contemporary periods [37].

Heavy metals, as natural constituents of ecosystems, are vital for correct functioning of plants [35], however, their excessive concentration in environment is harmful. Their specific concentration can disturb the functioning of ecosystems, being hazardous to plants, animals and the man [6, 8, 19]. Heavy metals undergo bioaccumulation in plant and animal tissues so the threat of being poisoned by them increases at subsequent links of the trophic chain – with the man at its end. Particular plant species react to increased concentration of heavy metals in the environment in different ways. The most sensitive ones are used in biomonitoring. *Pinus sylvestris* is a species which is little sensitive to influence of most heavy metals, however their concentration in needles of the species represents close correlations to the concentration of heavy metals in the air [2, 12, 13, 15, 18, 28, 37]. Analysis of heavy metals content in needles of *Pinus sylvestris* can constitute a basis for the evaluation of air pollution with heavy metals.

The aim of the research was: (i) evaluation of the content of selected heavy metals (Zn, Cu, Mn, Fe) in needles of *Pinus sylvestris* depending on the age of the needles, (ii) consideration of the influence of humidity of subsoil on accumulation of heavy metals in needles of *Pinus sylvestris*, (iii) reference of heavy metals content in needles of *Pinus sylvestris* to the volume of emitted dust in Poland, (iv) comparison of accumulation of heavy metals in needles of *Pinus sylvestris* in Słowiński National Park with other national parks in Poland.

MATERIAL AND METHODS

Study Area

Three pine coniferous forest systems (the area of 0.5 ha) which differ in the level of the moistening of the solum at the territory of Słowiński National Park (SNP), in Smołdziński Forest Protection Districts were selected. The first one comprises a 110 years' old cup moss coniferous forest (*Empetro nigri-Pinetum cladonietosum*, dry coniferous forests – Bs) covering loose regsol: O, AC, C, situated at the level of about 10 m a.s.l. outside the reach of underground water. The second research area comprises a 120 years' old crowberry coniferous forest (*Empetro nigri-Pinetum*, fresh coniferous forest – Bśw) at about 4 m a.s.l. which covers proper podzolic soil gleyed from the bottom (O, A, Eesgg, Bfegg, Cgg). A 125 years' old sea coast heath coniferous forest is found over the third research area (*Empetro nigri-Pinetum ericetosum*, wet coniferous forests – Bw), situated at the level of about 2.5 m a.s.l., which covers proper podzolic soil gleyed from the bottom: O, A, Eesgg, Bfegg, Cgg. The soils of the tested forest complexes (Bs, Bśw and Bw) originated from deep dune sands. The average depth of dipping ground water is about 45 cm. The tree stand of the examined pine coniferous forest is characteristic of the uniform productivity index, in spite of difference in height (from 6 to 13 m) and average breast height of the examined tree stands (from 11 to 27 cm), (Tab. 1).

Needles analyses

The needles of *Pinus sylvestris* were collected for testing during growing season from March to October 2010 (once a month) in Bs, Bśw and Bw. The samples of the needles were taken from a dozen trees from each pine forest. Next they were put together

Table 1. Characteristic pine stands in Bs, Bśw and Bw.

Forest association	Age [years]	Growing stock	Average diameter at breast height [cm]	Average height [m]	Site index
Bs	110	0.8	11	6	V
Bśw	120	0.7	17	9	V
Bw	125	0.7	27	13	V

making the mixed samples of 1- and 2-year-old pine needles. After their transport to the laboratory, the plants were washed in the deionized water, dried to the constant mass at the temperature of 65°C, then they were homogenized in a grind. Selected metals: Zn, Cu, Mn and Fe were determined in needles samples after digestion in the mixture of concentrated HNO₃ and 30% H₂O₂ by means of atomic absorption spectrometry method (Aanalyst 300, Perkin Elmer) according to Ostrowska *et al.* [23]. The tests were carried out following the original standards (Merck KGaA, 1g/1000 ml).

Other variables (environmental and soil-related)

Rainfall, air humidity and air temperature were recorded in the Gać meteorological station located inside the boundaries of SNP. Month average values of major climatic conditions for the study period are shown in Fig. 1. In general, marine climate is characterized by mild winters (−1.6°C–1.0°C), not so warm summers (14.2°C–16.2°C) and high air humidity (83%) [27]. In order to assess a possible relation between soil properties in Bs, Bśw and Bw the contents of heavy metals in needles were investigated as well as heavy metals in the soil (Tab. 2).

Statistical Analysis

In order to characterize and compare concentrations of selected heavy metals in the tested needles, mean values, standard deviations, enrichment factors (*EF*) as well as Spearman's correlations were calculated. *Statistica* (7.1) software was used for calculations.

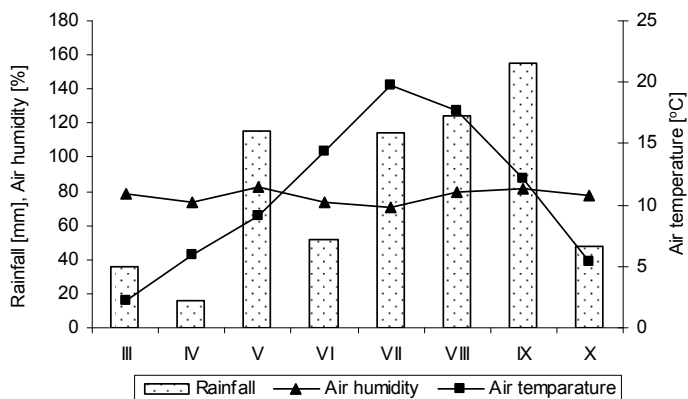


Fig. 1. Atmospheric conditions in growing seasons in 2010 year

Table 2. Characteristics of soil properties under Bs, Bśw and Bw

Forest association	Soil genetic horizon	pH		C [%]	Zn	Cu	Mn	Fe
		H ₂ O	KCl					
Bs	Ol	4.2	3.9	54.0	65.6(±0.03)	4.3(±0.001)	486(±0.09)	2040(±0.01)
	Ofh	3.8	2.9	32.4	32.0(±0.01)	4.5(±0.001)	101(±0.03)	696(±0.01)
	AC	4.1	3.5	0.3	21.6(±0.01)	0.67(±0.001)	10.8(±0.01)	740(±0.19)
	C1	4.2	3.9	0.2	14.0(±0.01)	0.55(±0.000)	6.3(±0.02)	659(±0.14)
	C2	4.4	4.1	0.2	15.2(±0.02)	0.53(±0.000)	6.1(±0.03)	655(±0.02)
	C3	4.2	4.3	0.1	15.6(±0.02)	0.53(±0.001)	6.0(±0.03)	654(±0.02)
Bśw	Ol	4.9	4.4	50.4	70.6(±0.02)	4.9(±0.001)	471.2(± 0.07)	1050(±0.01)
	Ofh	3.8	2.9	37.2	37.7(±0.03)	5.5(±0.002)	29.5(±0.01)	1450(±0.02)
	A	3.9	3.2	1.4	12.1(±0.01)	1.1(±0.002)	4.7(±0.01)	401(±0.07)
	Eesgg	3.9	3.4	0.4	12.9(±0.01)	0.6(±0.001)	5.6(±0.01)	523(±0.12)
	Bfegg	4.1	4.1	0.1	49.7(±0.02)	0.6(±0.001)	5.8(±0.01)	525(±0.12)
	Cgg	4.2	4.3	0.1	45.6(±0.02)	0.61(±0.002)	5.9(±0.02)	524(±0.15)
Bw	Ol	4.2	3.8	55.2	52.0(±0.05)	5.6(±0.002)	182.3(±0.01)	1370(±0.01)
	Ofh	3.5	2.6	43.0	36.7(±0.02)	6.1(±0.002)	52.6(±0.02)	2403(±0.04)
	A	3.9	3.6	0.4	12.5(±0.02)	0.7(±0.00)	7.2(±0.02)	205 (±0.08)
	Eesgg	3.8	3.8	0.2	9.8(±0.01)	0.6(±0.002)	5.2(±0.01)	303(±0.01)
	Bfegg	4.1	4.1	0.1	15.4(±0.01)	0.6(±0.002)	5.6(±0.01)	363(±0.11)
	Cgg	4.2	4.1	0.1	14.4(±0.02)	0.5(±0.002)	5.5(±0.02)	360(±0.08)

RESULTS AND DISCUSSION

The heavy metals contents in the needles of *Pinus sylvestris* varied depending on the metal, the age and humidity of the forest complex (Tab. 3, Fig. 2). The concentration of zinc remained at the level from 53.9 to 63.6 mg·kg⁻¹d.m. in 1-year-old needles and from 64.9 to 83.0 mg·kg⁻¹d.m. in 2-year-old needles. The highest differences in the content of zinc between the 1-year-old and 2-year-old needles were discovered in Bs (27%), slightly lower in Bśw Bśw (20%), and the lowest in Bw (9%).

The zinc content in the needles of *Pinus sylvestris* was changeable within the examined vegetative season (Fig. 2). The highest variability from March to October was found in the case of zinc in 1-year-old needles of Bs (CV = 30%), and the lowest in the needles of 2-year-old needles of Bw (CV = 13%), (Tab. 3). Statistically vital positive correlations were found between the Zn content in 1-year-old needles of *Pinus sylvestris* and the content of Cu-1 (Bs, Bśw and Bw), Cu-2 (Bs and Bw), Mn-1 (Bs and Bw) and Mn-2 (Bs). In addition, a vital negative correlation was found between Zn-1 and Fe-2 in Bs and Bw (Tab. 4). The zinc content in the needles of *Pinus sylvestris* also reflected

Table 3. The average (n=24) content of heavy metals in needles of *Pinus sylvestris* in the growing seasons in Bs, Bśw and Bw of SNP

Forest associaton	Age of needles	Zn	Cu	Mn	Fe
		mg·kg ⁻¹ d.m.			
Bs	1-year	53.9 (30%)	6.0 (6%)	301.4 (22%)	91.5 (30%)
	2-years	68.2 (16%)	5.9 (4%)	426.7 (13%)	132.1 (16%)
Bśw	1-year	63.6 (17%)	6.1 (6%)	368.7 (30%)	97.9 (16%)
	2-years	83.0 (24%)	5.9 (4%)	449.8 (34%)	107.1 (16%)
Bw	1-year	59.4 (26%)	6.0 (5%)	185.1 (32%)	82.4 (12%)
	2-years	64.9 (13%)	5.9 (3%)	211.1 (27%)	109.7 (16%)

Note: (%) – coefficient of variation (CV)

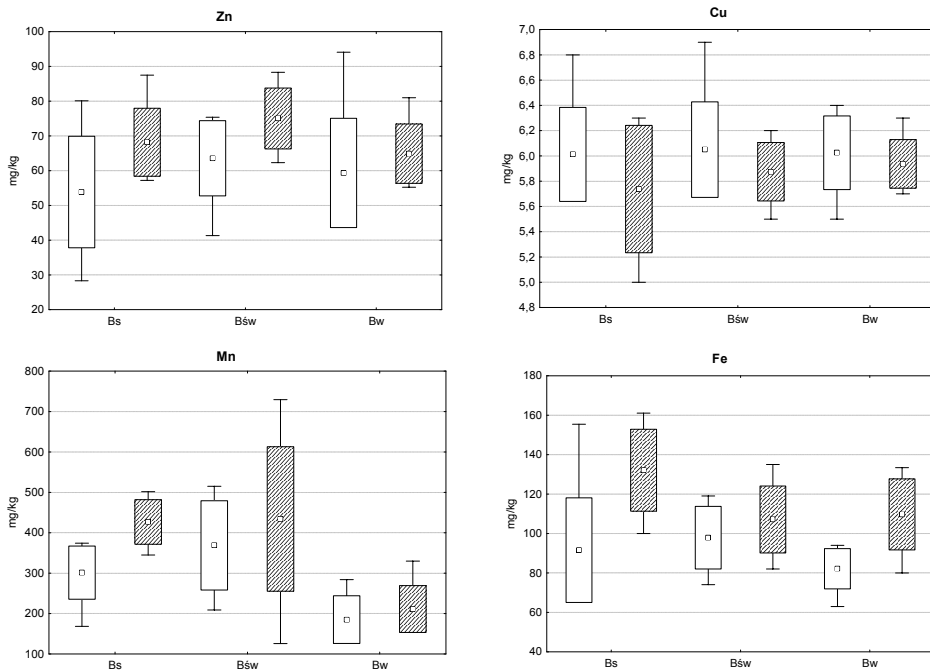


Fig. 2. Comparison of the heavy metals in needles of *Pinus sylvestris* in growing seasons in Bs, Bśw and Bw

Note: colourless rectangle – 1 years of needles, design rectangle – 2 years of needles, point (mean), rectangle (standard deviation), whiskers (minimum-maximum)

relations to rainfall. The increase of zinc concentration along with the increase of rainfall months sums was found in 1-year-old needles of (Bw, $r = 0.67$, $p < 0.05$, $n = 24$) and 2 year old needles of (Bśw, $r = 0.39$, $p < 0.05$, $n = 24$). In the ecosystem of Bs, it was discovered that the rainfall had vital impact on the lowering of zinc concentration in 2-year-old needles of ($r = -0.79$, $p < 0.05$, $n = 24$). The phenomenon of washing out of

ions of Zn^{2+} from the foliage was described in research work done by Stachurski and Zimka [30].

The average zinc content in overground parts of the plants which were not affected by contamination, remains at the level of 10–70 $mg \cdot kg^{-1}$. To cover physiological demand of most plants, the sufficient concentration in the foliage is within the range of 15–30 $mg \cdot kg^{-1}$ [9]. The low concentration of Zn in examined needles of *Pinus sylvestris* reflects a small content of that element in podzols of SPN, produced on the basis of deficient dune sand (Tab. 2). Similar volumes of zinc were found in the needles of *Ps* in Poland: from 35 to 72 $mg \cdot kg^{-1}$ (1-year-old needles) and from 41 to 99 $mg \cdot kg^{-1}$ (2-year-old needles) in Świętokrzyski National Park [17], from 31 to 61 $mg \cdot kg^{-1}$ (1-year-old needles) and from 45 to 99 $mg \cdot kg^{-1}$ (2-year-old needles) in Stalowa Wola [28], from 40.9 to 173.7 $mg \cdot kg^{-1}$ in Białowieża Primeval Forest, [3] and 35–74 $mg \cdot kg^{-1}$ in various low land habitats in Poland [24].

From among the examined metals, copper revealed the smallest content in *Ps* needles, being almost at the constant level during the whole growing season, which confirms the small mobility of that element in plants [9]. In 1-year-old needles, the Cu concentration was maintained at the level from 5.7 to 6.9 $mg \cdot kg^{-1} \cdot d.m.$, with little standard deviation (from 0.3 in Bw to 0.4 in Bs and Bśw). In 2-year-old needles, the Cu content was also maintained at the level from 5.5 to 6.3 $mg \cdot kg^{-1} \cdot d.m.$, with a standard deviation of (0.2 in Bs, Bśw and Bw). Copper revealed the highest variability in 1-year-old needles of Bś and Bśw (CV = 6%), and the lowest in 2-year-old needles of Bw (CV = 3%), (Tab. 3).

Most plants need a small quantity of Cu at the level $> 2 mg \cdot kg^{-1}$ to fulfill their physiological needs. The copper content in plants is maintained usually below 4–5 $mg \cdot kg^{-1}$ and varies a lot depending on the part of the plant, its developmental stage, sub-species and species. Its average content in overground parts of plants is from 5 to 20 $mg \cdot kg^{-1}$ [9]. The concentration of Cu was maintained in Świętokrzyski National Park (ŚNP), at the level of 5–9 $mg \cdot kg^{-1} \cdot d.m$ in 1-year-old needles and 3–4 $mg \cdot kg^{-1} \cdot d.m$ in 2-year-old needles [17], within the area of Stalowa Wola from 5.0 to 8.6 $mg \cdot kg^{-1}$ (1-years-old needles) and from 4.7 to 7.8 $mg \cdot kg^{-1}$ (2-year-old needles), [28], and in Białowieża Primeval Forest from 2.92 to 3.85 $mg \cdot kg^{-1}$ [3].

In the coniferous forest of SNP, as in ŚNP and Stalowa Wola, a small predominance of the copper content in 1-year-old needles in comparison with 2-year-old needles (Tab. 3, 4, Fig. 2) was discovered. In addition, a vital statistic correlation between Cu-1 and Mn-1 content in Bw was found, as well as negative correlation between Cu-1 and Fe-2 in Bw. More vital statistic relationships were found in 2-year-old needles. A positive correlation was found between the concentration of Cu-2 and Mn-1 in Bs and Bw, as well as between Cu-2 and Fe-1 in Bśw. Along with the increase of the copper content in 2-year-old needles, the iron content in 1- and 2-year-old needles in Bw decreased ($r = -0.38$ and -0.69 and $r = -0.59$, $p < 0.05$, $n = 24$). It was also found that the rainfall had a vital statistic impact on the lowering of copper concentration in 1-year-old needles of Bs and Bśw ($r = -0.34$ and $r = -0.49$, $p < 0.05$, $n = 24$), (Tab. 4).

Such relationship was not observed in the case of 1-year-old needles which can suggest that the level of humidity of the solum has vital impact on Cu content in needles of *Pinus sylvestris*. The low Cu content in the needles of *Ps*: Bs, Bśw and Bw does not constitute any threat to them, and quite contrary, it is only sufficient to cover physiological needs.

Table 4. Spearman's correlation coefficients between of heavy metals concentrations in 1-year and 2-year old needles of *Pinus sylvestris* in the growing seasons (n = 24, p < 0.05, R_{crit.} = 0.343)^a.

Forest association		Zn-1	Zn-2	Cu-1	Cu-2	Mn-1	Mn-2	Fe-1	Fe-2
Bs	Zn-1	-							
	Zn-2	-0.10	-						
	Cu-1	0.47	0.41	-					
	Cu-2	0.44	-0.23	0.16	-				
	Mn-1	0.72	-0.05	0.00	0.60	-			
	Mn-2	-0.37	0.83	0.00	-0.13	-0.23	-		
	Fe-1	-0.28	0.86	0.17	-0.38	-0.19	0.64	-	
	Fe-2	-0.41	0.60	-0.06	-0.69	-0.33	0.64	0.59	-
	rainfall	0.04	-0.79	-0.34	0.30	-0.04	-0.77	-0.45	-0.65
Bśw	Zn-1	-							
	Zn-2	0.16	-						
	Cu-1	0.41	-0.11	-					
	Cu-2	0.32	0.08	0.10	-				
	Mn-1	0.02	0.44	0.04	0.25	-			
	Mn-2	0.26	0.69	0.11	0.23	0.01	-		
	Fe-1	0.26	0.38	-0.01	0.38	-0.44	0.44	-	
	Fe-2	0.85	0.20	0.05	0.30	-0.22	0.28	0.48	-
	rainfall	-0.29	0.39	-0.49	0.21	0.65	0.61	-0.13	0.39
Bw	Zn-1	-							
	Zn-2	0.27	-						
	Cu-1	0.57	-0.15	-					
	Cu-2	0.71	0.61	0.08	-				
	Mn-1	0.94	0.18	0.47	0.68	-			
	Mn-2	-0.24	-0.30	-0.31	-0.02	-0.07	-		
	Fe-1	0.06	-0.59	-0.06	-0.26	0.10	0.48	-	
	Fe-2	-0.69	-0.09	-0.40	-0.59	-0.48	0.10	-0.27	-
	rainfall	0.67	-0.07	0.44	0.04	0.67	-0.22	0.39	-0.24

Note: 1 – one year old needles, 2 – two years old needles, a – critical values of Spearman's coefficient [36]

The manganese content in the needles of *Pinus sylvestris* at SNP was maintained at the level from 185.1 to 368.7 mg·kg⁻¹ in 1-year-old needles and from 211.1 to 449.8 mg·kg⁻¹ in 2-year-old needles (Tab. 3, Fig. 2). It was discovered that 2-year-old needles cumulate more quantity of Mn than 1-year-old needles. The lowest Mn content was found in the

needles of *Pinus sylvestris* at Bw, and the highest in the needles of Bśw. Similarly, the plants of ground cover indicated a higher manganese content in Bśw than in Bs and Bw at SNP [25]. Accumulation of manganese in needles of *Pinus sylvestris* varied within the examined growing season (Fig. 2). The highest variability was found from March to October in the concentration of Mn in 2-year-old needles of Bśw (34%), and the lowest in 2-years-old needles of Bs (13%). According to various authors, the concentration of Mn in plants at the area outside the influence of contamination is usually: 340–1339 mg·kg⁻¹ [16], 1540–3952 mg·kg⁻¹ [11], 122–837 mg·kg⁻¹ [4], 180–300 mg·kg⁻¹ [5, 7] and from 75 to 1849 mg·kg⁻¹ [25]. Statistical analyses of the research results indicated identical tendency between the content of Mn-2 and Fe-1 (a strong positive correlation) both in Bs, Bśw and Bw, independent of the level of humidity of the forest ecosystem. Rainfall had vital impact on the lowering of manganese concentration in 2-year-old needles only in the case of Bs (Tab. 4).

The iron content in the needles of *Pinus sylvestris* varied within one growing season. 2-year-old needles in *Ps* were characteristic of the highest abundance, in which the iron concentration was maintained at the level from 107.1 mg·kg⁻¹ in Bw to 132.1 mg·kg⁻¹ in Bs and represented variability from March to October at the level of 16%, (Tab. 3). 1-year-old needles revealed slightly lower accumulation of Fe from 82.4 mg·kg⁻¹ in Bw to 97.9 mg·kg⁻¹ in Bśw, at CV = 12–30%. Fe is a mobile element. Its content in the needles of *Pinus sylvestris* was strongly connected with rainfall. In Bs, along with the increase of rainfall, the Fe content decreased in 1-year-old needles ($r = -0.45$) and 2-year-old needles ($r = -0.65$, $p < 0.05$, $n = 24$), (Tab. 4). The highest standard deviation occurred in the case of Fe content in 1-year-old needles (Fig. 2). The iron content measured in the needles of *Ps* (SNP – Bs, Bśw and Bw) is slightly lower form that obtained by Samecka-Cymerman *et al.*, [28]: 64–169 mg·kg⁻¹ (in 1-year-old needles) and 77–270 mg·kg⁻¹ (in 2-year-old needles), and Ostrowska *et al.*, [24]: from 183 to 294 mg·kg⁻¹ in 1-year-old needles and from 247 to 430 mg·kg⁻¹ in 2-year-old needles and close to the results obtained by Staszewskiego *et al.*, [31] at Kampinoski National Park.

Little content of Zn, Cu, Mn and Fe in needles of *Pinus sylvestris* (SNP) results, among others, from little content of such metals in the soil (Tab. 2.), small tourist activity [26] and relatively clean air. It is mainly due to the location of the park far away from the largest sources of dust emission. It was confirmed by the results of the tests of the suspended particulate matter PM₁₀ (a potential source of heavy metals) preformed in 2010 within the area of Słowiński National Park SNP (17 µg·m⁻³), [1]. In 1995 (529 t), emission of suspended particulate matter substantially decreased in comparison to the year 1990 (1165 t), [20, 21]. According to some tests of moss and other plant bio-indicators within the SNP, that area was recognized as one of the cleanest areas in Poland in the 1970s [5, 6, 7, 25], however, with further development of industry and location of new industrial establishments in the north of Poland, even this park can be under the pressure of pollution. At present, the parks situated in vicinity of large industrial areas are most exposed, such as: Ojcowski, Wielkopolski, Karkonoski and Świętokrzyski National Parks [5, 34].

Little content of Zn, Cu, Mn and Fe in the soils and needles of *Pinus sylvestris* of examined Bs, Bśw and Bw of SNP can be translated into a low value of enrichment factors (*EF*), Tab. 5. The lowest enrichment factors were found in the case of iron ($EF < 1.4$), and slightly higher in the case of zinc ($EF < 2.8$), cooper ($EF < 3.2$) and manganese ($EF < 5.1$). These values indicate that manganese represents the highest accumulative

Table 5. Enrichment factors *EF* calculated for the mean concentrations of heavy metals in needles of *Pinus sylvestris* and soil in the growing season

Forest association	Age of needles	Zn	Cu	Mn	Fe
Bs	1-year	1.9	3.2	2.9	1.0
	2-years	2.5	3.2	4.2	1.4
Bśw	1-year	1.7	2.7	4.7	1.3
	2-years	2.0	2.6	5.0	1.4
Bw	1-year	2.5	2.6	5.1	0.9
	2-years	2.8	2.5	4.9	1.3

properties. According to Kłós [10] the values of enrichment factors $EF < 10$ indicate the alluvial soil, as source of metals origin. The obtained values of enrichment factors EF should be treated only for orientation purposes since they were determined on the basis of total concentrations of metals in the soil, where plants accumulate only bio-available form of such contamination.

CONCLUSIONS

The content of Zn, Cu, Mn and Fe in the needles of *Pinus sylvestris* varied within a growing season. The vital impact on the shape of accumulation of heavy metals in the needles of *Pinus sylvestris* had especially: the age of the needles, sums of rainfall and humidity of the solum. Variability coefficients of those metals were maintained at the level of: 13–30% (Zn), 3–6% (Cu), 13–34% (Mn) and 12–30% (Fe) depending on the age of the needles. No accumulation of heavy metals was found in the tested samples of *Ps* needles. In the case of Zn, Mn and Fe higher concentrations were found in 2-year-old needles than in 1-year-old needles, and in the case of Cu in 1-year-old needles than in 2-year-old needles. The concentrations of iron, cooper, zinc and manganese were strictly connected with rainfall which had impact on accumulation of those metals in the needles of *Pinus sylvestris* and shaping of humidity of forest ecosystems.

The examined pine coniferous forests (Bs, Bśw and Bw) due to their location in SNP far away from the sources of contamination, relatively low tourist activity and small content of metals tested in the soil, show no burden of the tested heavy metals, and relations among them are the following: Mn (323.8) > Fe (103.4) > Zn (65.5) > Cu (5.9). The low level of accumulation of the above mentioned metals in the needles of *Pinus sylvestris* is also represented by the values of enrichment coefficients (EF).

Having analyzed the content of the selected heavy metals in the needles of *Pinus sylvestris*, it was discovered that Słowiński National Park was still among the cleanest national parks in Poland.

REFERENCES

- [1] Brożek, A., & Zaremski, A. (2011). Roczna ocena jakości powietrza w województwie pomorskim, Raport za rok 2010, Wojewódzki Inspektorat Ochrony Środowiska, Gdańsk. 2011

- [2] Čeburnis, D., & Steinnes, E. (2000). Conifer needles as biomonitors of atmospheric heavy metal deposition: comparison with mosses and precipitation role of the canopy, *Atmos. Environ.*, 34, 4265–4271.
- [3] Dmuchowski, W., & Bytnerowicz, A. (1995). Monitoring environmental pollution in Poland by chemical analyses of Scots pine (*Pinus sylvestris* L.) needles, *Environ. Pollut.*, 87, 87–104.
- [4] Gałuszka, A. (2006). Biogeochemical background of selected trace elements in mosses *Pleurozium schreberi* (Brid.) Mitt. and *Hylocomium splendens* (Hedw.) B.S.G. from Wigierski National Park, *Pol. J. Environ. Stud.*, 15, 2a: 72–77.
- [5] Grodzińska, K. (1980). Zanieczyszczenie polskich Parków Narodowych metalami ciężkimi, *Ochrona Przyrody*, 43, 9.
- [6] Grodzińska, K., Szarek G., & Godzik B. (1990). Heavy metal deposition in Polish National Parks – changes during ten years. *Water Air Soil Pollut.*, 197–209.
- [7] Grodzińska K., Szarek-Lukaszewska G., & Godzik B. (1999). Survey of heavy deposition in Poland using mosses as indicators, *The Science of the Total Environmental*, 229, 41–51.
- [8] Gruca-Królikowska, S., & Waclawek W. (2006). Metale w środowisku. Cz. II. Wpływ metali ciężkich na rośliny, *Chemia · Dydaktyka · Ekologia · Metrologia*, 11, 1–2: 41–56.
- [9] Kabata-Pendias, A., Pendias, H. (1999). Biogeochemia pierwiastków śladowych, PWN, Warszawa 1999.
- [10] Kłos, A. (2009). Zastosowanie współczynnika wzbogacenia (EF) do interpretacji wyników badań biomonitoringowych, *Chemia-Dydaktyka-Ekologia-Metrologia*, 14, 1–2: 49–55.
- [11] Kozanecka, T., Chojnicki J., & Kwasowski W. (2002). Content of heavy metals in plant from pollution-free regions, *Pol. J. Environ. Stud.*, 11, 4: 395–399.
- [12] Lamppu, J., & Huttunen S. (2002). Relations between Scott pine needle element concentrations and decreased needle longevity along pollution gradients, *Environ. Pollut.*, 122, 119–126.
- [13] Lehndorff, E., & Schwarz, L. (2008). Accumulation histories of major and trace elements on pine needles in the cologne conurbation as function of air quality, *Atmos. Environ.*, 42, 833–845.
- [14] Maciejewska, A. (2003). Problematyka rekultywacji gleb zanieczyszczonych metalami ciężkimi w świetle literatury, [w:] *Obieg pierwiastków w przyrodzie* (Gworek B., Misiak J., red). IOŚ, Warszawa 2003.
- [15] Malzahn E. (2002). Igły sosny zwyczajnej jako bioindykator zagrożeń środowiska leśnego Puszczy Białowieskiej, *Biuletyn Monitoringu Przyrody*, 1 (3).
- [16] Malzahn, E. (2009). Biomonitoring środowiska leśnego Puszczy Białowieskiej, *Ochrona Środowiska i Zasobów Naturalnych*, 40, 439–447.
- [17] Migaszewski, Z.M. (1997). Skład chemiczny igieł sosny zwyczajnej *Pinus sylvestris* L. w Regionie Świętokrzyskim, *Wiad. Bot.*, 42 (3/4), 79–91.
- [18] Mulgrew, A., & Williams, P. (2000): Biomonitoring of air quality using plants. WHO Collaborating Centre for air quality Management and air pollution Control, ISSN 0938–9822, Berlin 2000.
- [19] Nagajyoti, P. C., Lee K.D., & Sreekanth, T.V.M. (2010). Heavy metals, occurrence and toxicity for plants: a review [w:] *Environmental Chemistry Letters*, 8, 199–216.
- [20] Ochrona Środowiska: Materiały i opracowania statystyczne, GUS, Warszawa (1991).
- [21] Ochrona Środowiska: Materiały i opracowania statystyczne, GUS, Warszawa (1995).
- [22] Operat Ochrony Ekosystemów Leśnych na lata 2002–2021. T. 9/1 Opis taksacyjny lasu – Obręb lądowy Oddziały 1–63. Jeleniogórskie Biuro Planowania i Projektowania (2002).
- [23] Ostrowska, A., Gawliński S., & Szczubiałka, Z. (1991). Metody analizy i oceny właściwości gleb i roślin. Katalog, IOŚ, Warszawa.
- [24] Ostrowska, A., Porębska, G., Sienkiewicz, J., & Borzyszkowski, J. (2001). Opracowanie chemiczno-biologicznych wskaźników oceny stanu nizinnych siedlisk leśnych. Opracowanie końcowe-monografia, maszynopis, dyrekcja lasów Państwowych, Warszawa.
- [25] Parzych, A., Sobisz Z., & Trojanowski J. (2012). Content of heavy metals in soil and herbaceous plants in selected of pine forest in the Słowiński National Park, *Arch. Environ. Prot.*, 38 (4).
- [26] Parzych, K. (2001): Ruch turystyczny w Słowińskim Parku Narodowym w latach 1995–1999, Turystyka jako czynnik rozwoju regionów, miast i obszarów wiejskich, Zeszyty Naukowe WPSTiW w Bydgoszczy nr 1, Bydgoszcz 2001.
- [27] Piotrowska, H. (1997). Przyroda Słowińskiego Parku Narodowego, Bogucki Press, Poznań–Gdańsk 1997.
- [28] Samecka-Cymerman, A., Kosior, G., & Kempers, A.J. (2006): Comparison of the moss *Pleurozium schreberi* with needles and bark of *Pinus sylvestris* as biomonitors of pollution by industry in Stalowa Wola (southeast Poland), *Ecotoxicology and Environmental Safety*, 65, 108–117.

- [29] Szarek, G., & Braniewski, S. (1996). Metale ciężkie w opadzie ściółki lasu mieszanego zlewni potoku Ratanica. *Sylwan*, 65, 4, 53–62.
- [30] Stachurski, A., & Zimka, J.R. (2004). Obieg pierwiastków w ekosystemach lądowych. *Kosmos*, 53 (1), 95–105.
- [31] Staszewski, T., Kubiesa P., Łukasik, Uziębło, W., & Wyziębło, K. (2009). Reakcja borów sosnowych na antropopresję w różnych typach siedlisk w Kampinoskim Parku Narodowym. (W:) Andrzejewski, A., Lubański, A. (red.). Trwałość i efektywność ochrony przyrody w Polskich Parkach Narodowych. Wyd. Kampinoski Park Narodowy, Izabelin, 289–298.
- [32] Tainio, M., Kekkonen, J., & Nahorski, Z. (2010). Impact of airborne particulate matter on human health: an assessment framework to estimate exposure and adverse health effect in Poland, *Arch. Environ. Prot.*, 36, 1, 95–115.
- [33] Trojanowski, P., Trojanowski, J., & Parzych, A. (2005). Copper, zinc, manganese, lead and cadmium in plants of Gardno Lake, *Arch. Environ. Prot.*, 31, 4, 45–58.
- [34] Wilgat, T. (1993). Zagrożenia przyrody polskich parków narodowych, *Czasopismo Geograficzne LXIV*, 1, 67–77.
- [35] Wilk, M., & Gworek B. (2009). Metale ciężkie w osadach ściękowych, *Ochrona Środowiska i Zasobów Naturalnych*, 39, 40–59.
- [36] Wolek, J. (2006). Wprowadzenie do statystyki dla biologów, Wyd. Nauk. Akademii Pedagogicznej, Kraków 2006.
- [37] Zgłobicki, W. (2008). Geochemiczny zapis działalności człowieka w osadach stokowych i rzecznych, Wydawnictwo UMCS, Lublin: pp. 240.

ZAWARTOŚĆ METALI CIĘŻKICH W SZPILKACH SOSNY ZWYCZAJNEJ (*Pinus sylvestris* L.)
W WYBRANYCH BORACH SOSNOWYCH SŁOWIŃSKIEGO PARKU NARODOWEGO

Praca przedstawia wyniki badań nad zawartością metali ciężkich w szpilkach *Pinus sylvestris* wybranych borów sosnowych Słowińskiego Parku Narodowego. Wykazano, iż zawartości metali ciężkich (Zn, Cu, Mn i Fe) w igliwii były zróżnicowane w zależności od metalu, wieku igliwia oraz wilgotności ekosystemu leśnego. Współczynniki zmienności tych metali utrzymywały się na poziomie: 13–30% (Zn), 3–6% (Cu), 13–34% (Mn) oraz od 12–30% (Fe) w zależności od wieku igliwia. W przypadku Zn, Mn i Fe stwierdzono większe stężenia badanego metalu w igliwii 2-letnim, niż 1-rocznym, a w przypadku Cu w igliwii 1-rocznym niż 2-letnim. Wykazano między innymi wzrost koncentracji cynku w igliwii 1-rocznym (Bw, $r = 0,67$, $p < 0,05$, $n = 24$) oraz igliwii 2-letnim (Bśw, $r = 0,39$, $p < 0,05$, $n = 24$) wraz ze wzrostem sumy opadów deszczu. Zawartości powyższych metali w igliwii boru suchego (Bs), boru świeżego (Bśw) i boru wilgotnego (Bw) tworzą następujący szereg malejący: Mn(323,8) > Fe(103,4) > Zn(65,5) > Cu(5,9).