

## The macro- and microelemental content of *Pinus sylvestris* L. and *Pinus nigra* J.F. Arn. needles in *Cladonio-Pinetum* habitat of the Słowiński National Park

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**Abstract.** The study of pine needles was carried out in 2005 within the confines of the Słowiński National Park (SNP). In soil from *Cladonio-Pinetum* habitat, most macro- and microelements accumulate in the organic sub-horizons (O1 and Ofh), however the nutrient content of the mineral horizons was very low. Needles of *Pinus sylvestris* (Ps) were characterised by higher content of N, P, K, Ca, and Fe in comparison to needles of *Pinus nigra* (Pn); whereas needles of Pn were higher in content of Mg, Zn, Cu and Mn than those of Ps. Two-year-old needles contained on average more Ca, Mn, Cu, Fe than one-year-old needles for both species. A Mann Whitney test confirmed statistically-significant differences in the dynamics of P, K, Mg, Zn and Mn concentrations both in 1-year-old and 2-year-old needles examined in *Cladonio-Pinetum*. The greatest differences between research forests stands of *Pinus sylvestris* and *Pinus nigra* were in the sum contents of elements accumulated in the needles. In the needles of *Pinus nigra* there was notably higher accumulation of P, K, Ca, Mg and Mn than in the needles of *Pinus sylvestris*.

**Key words:** *Pinus sylvestris*, *Pinus nigra*, needles, accumulation of elements.

### 1. Introduction

Functioning of forest ecosystems is expressed mainly by the quality of stands which decide the habitat's fertility, degradation degree and also the influence of various stress types: climate, nutritional or anthropogenic (Ostrowska et al. 2006). Scots pine, like Black pine, absorbs a range of chemical ingredients from soil and air that are essential for maintenance of life functions (Migaszewski 1997).

Absorption of the majority of elements by flora is a process regulated metabolically (Pugnaire, Chapin 1993), and their accumulation can be related with development and ageing process occurring in it (Malzahn 2002; Ostrowska, Porębska 2002) and with availability in soil of given elements. Chemical composition of pine's needles is determined by changeability, resulting

from the natural habitat's fertility factors conditioning absorbing soil elements and their transport (Ostrowska et al. 2006). The concentration of nutrients in trees' assimilation apparatus indicates their nutritional status (De Vries, Heij 1991; Schachtman et al. 1998), and shortages observed especially on coniferous habitats are a reflection of their insufficient amount in soil (Prescott et al. 1992; Wang, Klinka 1997).

For normal functioning of plants, basic macroelements – N, P, K, Ca and Mg – are essential and also microelements in small amounts – Fe, Zn, Cu and Mn – which constitute the natural ecosystem component (Wilk, Gworek 2009). However, concentration of excessive nutrients in environment is harmful and with sufficiently high concentration they interfere with functioning of ecosystems, creating a threat for plants, animals and people (Gruca-Królikowska, Waclawek 2006;

Malzahn 2009; Nagajyoti et al. 2010). Heavy metals undergo a bioaccumulation process in plants and animal tissues, as a result of which the threat of poisoning increases in following trophic chain links, on the top of which is the human. Individual plant species in various ways react on increased concentration of heavy metals. In case of substantial environment contamination, flora may absorb many chemical components in amounts exceeding its demand (Roo-Zielińska 2004; Ostrowska et al. 2006). *Pinus nigra* (*Pn*) in comparison with other coniferous trees species indicates a high tolerance for soil's pH changes (Arsova 1999).

Both Scots pine and Black pine are used for bioindication research. In Poland and in many countries of Europe, they are used for air contamination level evaluation, and besides 1-year-old and 2-year-old needles of these species, their bark is also used (Molski et al. 1983; Pavlova et al. 1991; Dmuchowski, Bytnerowicz 1995; Migaszewski, Gałuszka 1997; Ceburnis, Stennes 2000; Sawidis et al. 2001; Lamppu, Huttunen 2002; Yilmaz, Zengin 2003; Aboal et al. 2004; Piccardo et al. 2005; Świercz 2003, 2006; Lehndorff, Schwarz 2008).

*Pinus nigra* is a foreign species for The Słowiński National Park (SNP) flora and is present here only because of planting. Mass Scots pine and Black pine plantings on mobile dunes of Miejrzeja Łebska (Łebska Spit) took place in the years 1920–1938; their present age and area occupied by individual species are: Scots pine (230 ha) and Black pine (64 ha) (Schechtel 1984; Piotrowska 1997; Kluczyński, Kreft 2003).

The aim of this research undertaken was the comparison of biogens and accumulation ability of chosen heavy metals by Scots pine's needles (*Pinus sylvestris* L.) (*Ps*) and Black pine's needles (*Pinus nigra* J.F.Arn.) growing on dry coniferous forest habitat (Bs), beyond ground water reach, on the area of the SNP. The content of macro- and microelements in needles was analysed considering each element separately in an integrated way by comparing nutrient demand. In this research, the age of needles and soil's abundance in chemical components were included.

## 2. Materials and research methods

### Research area

The research was conducted in 2005 in the SNP. SNP is situated in northern part of Poland on an area under the direct influence of Baltic Sea, relatively free from industrial air pollution. Average annual air tem-

perature on the park's area is 7.3°C, and average annual rainfall 700 mm (Matuszkiewicz 2002). For this research, dry coniferous forest located in central part of the Park (17°15'E, 54°45'N) was selected. The stand of examined *Cladonio-Pinetum* unit included 105-year-old Scots pine and 105-year-old Black pine. *Cladonio-Pinetum* occupying the area on hill around 14 m n.p.m, beyond ground water reach, overgrew embryonic loose soil: O, AC and C were formed from deep dune sands.

The examined trees species were characterised with equal average height (10 m) and nearing diameter at breast height size, which results from production ability factor's value (quality classification – V) (Table 1). Despite equal growth condition, the Scots pine's stand had twice the bigger wood stock than Black pine's stand.

**Table 1.** Characteristics of examined stands

Specification	<i>Pinus sylvestris</i> L.	<i>Pinus nigra</i> J.F. Arn.
Age [years]	105	105
Average height [m]	10	10
Average dbh [cm]	19	18
Stand density index	0.7	–
Growing stock per ha [m <sup>3</sup> /ha]	65	30
Site index (stand quality)	V	V

Source: Operat Ochrony Ekosystemów Leśnych, 2002.

### Research methodology

On 0.5 ha of research area performed were three soil pits from which a structure of soil trench was characterised. The soil taxonomy was described on the basis of Polish Soil Taxonomy PTG (1989). Designation of soil's basic physical and chemical features was made in May 2005 by collecting samples with the use of drill from all genetic horizons to a depth of 75 cm due to trees main root mass. Plant material originated from several randomly chosen *Pinus sylvestris* and *Pinus nigra* trees. Needles for research were collected from March to October 2005, from 7<sup>th</sup> whorl. From plant material obtained collective samples of weight from 10 to 20 g were prepared, including species diversity and needles' age (1-year-old needles and 2-year-old needles separately) according to recommendations of ICP Manual Forest (Rautio et al. 2010). After delivering to laboratory, the needles were carefully washed in deion-

ised water, then dried in temperature of 65°C and homogenised in a mill. The samples after drying were kept in tightly closed polyethylene containers.

In soil samples, specific density – with pycnometer method; pH (H<sub>2</sub>O) and pH (KCl) – with potentiometric method; humidity – with weight method; and organic matter content by definition of calcination loss in muffle stove in temperature of 550°C were marked. Prepared plant material were marked with commonly used methods, total azote (T-N) and total phosphorus (T-P), according to Ostrowska et al. (2001) after earlier digested in mixture of H<sub>2</sub>SO<sub>4</sub> and 30% H<sub>2</sub>O<sub>2</sub>. Chosen metals K, Ca, Mg, Zn, Cu, Mn and Fe in needles and soil samples were marked after mineralisation in mixture of concentrated HNO<sub>3</sub> and 30% H<sub>2</sub>O<sub>2</sub> by atomic absorption spectrometry method (ASA, Aanalyst 300, Perkin Elmer) according to Ostrowska et al. (1991). Designation was made accordingly to original standards (Merck KGaA, 1 g/1000 ml).

### Elaboration of results

In order to characterise the chosen macro- and microelements and to compare their concentration in examined needles and soil, average, minimum and maximum values and standard deviations were calculated. Diversity significance of macro- and microelements content in Scots pine's and Black pine's needles was verified with the use of U Mann–Whitney test. For calculation, program Statistica (7.1) was used. The demand for nutrients in *Ps* and *Pn* was described with the use of *Accumulation Nutrient Elements* method (Ostrowska 1987; Ostrowska et al. 2006). The sum of components (Y) in mmol<sub>c</sub>-kg<sup>-1</sup> was calculated from model:

$$Y = \sum_{i=1}^i \frac{Z}{z}$$

where:

Z – content of element in mg·kg<sup>-1</sup>,  
z – atomic mass/ion valence.

After calculating Y, proportionate share (X) of every element in this sum was calculated:

$$X = \frac{Z \div z \cdot 100}{Y}$$

The content of macro- and microelements in 1-year-old needles and 2-year-old needles was analysed, considering each component separately and in an integrated way – by comparing nutrient demand. Additionally calculated were *Ps* and *Pn* needle enrichment factors (EFs) in heavy metals (Zn, Cu, Fe, Mn):

$$EF_{(Zn)} = C_{z(Zn)} : C_{g(Zn)}$$

where:

EF<sub>Zn</sub> – zinc enrichment factor,  
C<sub>z(Zn)</sub> – zinc content in leaves,  
C<sub>g(Zn)</sub> – zinc content in soil.

### 3. Research results and discussion

*Ps* and *Pn* overgrew embryonic loose soils (Ol, Ofh, AC, C), created from deep dune sands. The smallest specific density had poorly formed humus horizon (AC 2.50 g·cm<sup>-3</sup>). With soil's trench depth the specific density slightly increased, reaching maximum value in host rock horizon (2.53–2.58 g·cm<sup>-3</sup>) (Table 2). Examined soils had strongly acid reaction, which decreased with depth. Organic horizon was characterised by the highest humidity. Humidity of mineral horizons was much

**Table 2.** Physicochemical properties of researched soil (average ± standard deviation)

Soil genetic horizon	Depth	Thickness of soil	Specific density	pH <sub>(H<sub>2</sub>O)</sub>	pH <sub>(KCl)</sub>	Humidity of soil	Organic matter
	cm						
Ol	3–5	2	-	4.3±0.4	3.9±0.2	47.5±7.1	96.1
Ofh	3–0	3	-	3.8±0.6	2.9±0.4	46.4±8.2	52.6
AC	0–11	11	2.50	4.1±0.5	3.5±0.5	6.7±4.1	0.44
C1	11–30	19	2.53	4.2±0.5	3.9±0.4	5.8±4.5	0.24
C2	30–50	20	2.55	4.3±0.5	4.1±0.4	4.5±5.6	0.19
C3	50–75	25	2.58	4.4±0.6	4.2±0.4	4.3±5.8	0.18

smaller, decreased into the trench's depth reaching in individual horizons average value from 6.7 to 4.3%. Such low soil's humidity is related with low groundwater level. The highest amount of organic matter was accumulated in organic sub-horizons: litter (Ol) – 96.1% and fermentation-humus (Ofh) – 52.6%. Mineral hori-

zons contained very small amounts of organic matter (0.18%–0.44%) (Table 2).

Soil under pine's stand created from deep dune sands turned out to be very abundant in nutrients. The highest amount of examined components was collected in organic sub-horizons (Ol and Ofh). In mineral hori-

**Table 3.** Chemical properties of researched soil (average  $\pm$  standard deviation)

Parameter	Soil genetic horizon					
	Ol	Ofh	AC	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>
T-N, %	0.920 $\pm$ 0.15	0.700 $\pm$ 0.09	0.290 $\pm$ 0.06	0.285 $\pm$ 0.02	0.250 $\pm$ 0.01	0.245 $\pm$ 0.01
T-P, %	0.0207 $\pm$ 0.02	0.0131 $\pm$ 0.03	0.0014 $\pm$ 0.001	0.001 $\pm$ 0.0004	0.001 $\pm$ 0.00	0.001 $\pm$ 0.00
Corg, %	53.5 $\pm$ 1.2	36.6 $\pm$ 1.0	0.32 $\pm$ 0.02	0.20 $\pm$ 0.01	0.20 $\pm$ 0.00	0.12 $\pm$ 0.00
K, mg·kg <sup>-1</sup>	609 $\pm$ 47	253.5 $\pm$ 33	45.5 $\pm$ 8	71.7 $\pm$ 9	43.2 $\pm$ 10	42.0 $\pm$ 10
Ca, mg·kg <sup>-1</sup>	2884 $\pm$ 136	719.0 $\pm$ 90	103.1 $\pm$ 8	115.2 $\pm$ 10	128.6 $\pm$ 11	125.1 $\pm$ 9
Mg, mg·kg <sup>-1</sup>	1126.0 $\pm$ 167	471.5 $\pm$ 45	423.0 $\pm$ 40	91.1 $\pm$ 23	113.4 $\pm$ 25	120.2 $\pm$ 26
Zn, mg·kg <sup>-1</sup>	62.8 $\pm$ 0.03	58.1 $\pm$ 0.03	2.11 $\pm$ 0.04	2.76 $\pm$ 0.04	1.97 $\pm$ 0.03	1.88 $\pm$ 0.02
Fe, mg·kg <sup>-1</sup>	81.4 $\pm$ 0.03	101 $\pm$ 0.04	61.0 $\pm$ 0.06	65.0 $\pm$ 0.10	64.9 $\pm$ 0.11	62.0 $\pm$ 0.05
Cu, mg·kg <sup>-1</sup>	7.0 $\pm$ 0.001	7.1 $\pm$ 0.002	0.7 $\pm$ 0.002	0.73 $\pm$ 0.002	0.71 $\pm$ 0.002	0.70 $\pm$ 0.002
Mn, mg·kg <sup>-1</sup>	165.1 $\pm$ 0.04	168 $\pm$ 0.02	5.9 $\pm$ 0.02	6.0 $\pm$ 0.02	6.2 $\pm$ 0.02	6.1 $\pm$ 0.02

**Table 4.** Macro- and microelements contents in needles of *Pinus sylvestris* and *Pinus nigra*

Parameter	<i>Pinus sylvestris</i> L.		<i>Pinus nigra</i> J.F. Arn.	
	1-year	2-year	1-year	2-year
	average $\pm$ standard deviation minimum – maximum			
T-N, %	1.194 $\pm$ 0.16 1.050–1.270	1.061 $\pm$ 0.12 0.910–1.150	0.737 $\pm$ 0.08 0.650–0.800	0.678 $\pm$ 0.07 0.600–0.740
T-P, %	0.0925 $\pm$ 0.01 0.086–0.097	0.0943 $\pm$ 0.01 0.087–0.098	0.087 $\pm$ 0.01 0.075–0.090	0.078 $\pm$ 0.01 0.070–0.085
K, mg·kg <sup>-1</sup>	3289 $\pm$ 0.014 3281–3293	2952 $\pm$ 0.06 2932–2983	3463 $\pm$ 0.167 3375–3542	2151 $\pm$ 0.300 2106–2398
Mg, mg·kg <sup>-1</sup>	1492 $\pm$ 0.017 1484–1506	1169 $\pm$ 0.012 1166–1172	1703 $\pm$ 0.016 1696–1712	1608 $\pm$ 0.033 1591–1623
Ca, mg·kg <sup>-1</sup>	2025 $\pm$ 0.09 1992–2080	2770 $\pm$ 0.02 2681–2876	1734 $\pm$ 0.097 1679–1774	2285 $\pm$ 0.136 2206–2325
Zn, mg·kg <sup>-1</sup>	62.5 $\pm$ 0.02 60.7–64.0	60.3 $\pm$ 0.01 59.0–62.1	58.9 $\pm$ 0.02 56.7–60.7	77.0 $\pm$ 0.024 75.0–78.1
Cu, mg·kg <sup>-1</sup>	6.6 $\pm$ 0.00 6.6–6.6	6.9 $\pm$ 0.002 6.8–7.1	6.6 $\pm$ 0.001 6.6–6.7	7.3 $\pm$ 0.001 7.2–7.4
Mn, mg·kg <sup>-1</sup>	181.3 $\pm$ 0.013 178.0–186.0	264.1 $\pm$ 0.024 261.0–266.0	226.1 $\pm$ 0.05 221.0–232.1	256.9 $\pm$ 0.034 253.0–260.0
Fe, mg·kg <sup>-1</sup>	98.0 $\pm$ 0.004 96.0–102.4	134.0 $\pm$ 0.002 132.1–136.8	82.0 $\pm$ 0.004 77.0–86.0	106.0 $\pm$ 0.003 105.0–111.0

zons, in which the main root's mass was present, content of macro- and microelements was very poor (Table 3).

Needles' abundance in examined components was precisely related with needles' age (Table 4). In Scots pine the highest concentration of azote was stated in 1-year-old needles on average by 11% higher than in 2-year-old needles. In case of Black pine, the azote content was on average 0.737% in 1-year-old needles and 0.678% in 2-year-old needles. Phosphorus content in *Ps* needles was included in the range of 0.086%–0.098% and in case of *Pn* 0.070%–0.0990%. These values are acknowledged by the Coordination Center for assimilation apparatus cases, operating within ICP-Forest (Forest Foliar Condition in Europe 1997), as insufficient. In *Ps* and *Pn* needles a lack of azote (<1.3%) and phosphorus (<0.1%) was stated, manifesting itself inter alia in limited plant growth (Starck 2006), as evidenced by small stand's height, on average around 10 m (Table 1). In case of *Pn* needles, the azote content was <1%, which – according to Gawliński (1991) – should be considered as a substantial shortage of this component. The lower than the national average abundance of Baltic Sea region pine stands in macroelements confirms the research results presented by Małachowska et al. (2006).

In *Ps* needles, on average, higher content of K and Ca than in *Pn* needles was stated adequately by 11% and 19%. Despite this, in none of examined needles the content of those components was on level allowing the defining of pine's supply in these macroelements as optimal, according to Ostrowska and Porębska (2002): 0.54% K and 0.25% Ca. In case of potassium, the research indicated extreme shortage of this element in needles both in *Ps* and *Pn*. Due to comparison standards given by Ostrowska, Porębska (2002); and Malzahn (2002), the needles of examined pines turned out to be abundant enough in magnesium compounds, wherein the content of magnesium was higher in *Pn* needles than in *Ps* needles.

The concentration of zinc maintained on level from 59.0 to 64.0 to  $\text{mg}\cdot\text{kg}^{-1}$  in *Ps* needles and from 56.7 to 78.1  $\text{mg}\cdot\text{kg}^{-1}$  in *Pn* needles (Table 4) and was similar to the one in *Ps* needles in other Poland areas from 35 to 99  $\text{mg}\cdot\text{kg}^{-1}$  in Stalowa Wola (Samecka-Cymerman et al. 2006).

In *Ps* and *Pn* needles among examined metals copper was the least present. Its content maintained on an almost constant level through whole growing season (6.6–7.3  $\text{mg}\cdot\text{kg}^{-1}$ , Table 4), which confirms the small mobility of this element in plants (Kabata-Pendias, Pendias 1999). The small content of Cu in *Ps* and *Pn* needles is sufficient only to cover their physiological needs. In the area of the Świętokrzyski National Park, the con-

densation of Cu in needles of Scots pine was near and maintained on 3–9  $\text{mg}\cdot\text{kg}^{-1}$  (Migaszewski 1997).

Manganese content in *Ps* needles of SPN was 178.0–226.0  $\text{mg}\cdot\text{kg}^{-1}$ , and in case of *Pn* 221.0–260.0  $\text{mg}\cdot\text{kg}^{-1}$  (Table 4). It was noted that 2-year-old needles contain higher amount of Mn than 1-year-old needles. Mn condensation in flora on areas outside the influence of direct pollution according to Malzahn (2009) is most frequently 340–1339  $\text{mg}\cdot\text{kg}^{-1}$ , and according to Grodzińska (1980) 180–300  $\text{mg}\cdot\text{kg}^{-1}$ .

Iron content in Scots pine's and Black pine's needles in 2005 growing season was varied. With the highest Fe content were needles of *Ps*, in which iron condensation maintained on level from 98.0 to 134.0  $\text{mg}\cdot\text{kg}^{-1}$ .

Iron content in *Ps* needles in the SNP was slightly lower than the one stated by Samecka-Cymerman et al. (2006) in the Kampinoski National Park.

Microelements condensation in examined pines needles was relatively low, which is the effect of the small content of those metals in soil (Table 3) and relatively clean environment of the SNP (Grodzińska 1980). *Pn* needles were characterised by higher zinc, copper and manganese content than *Ps* needles. Two-year-old needles showed larger amounts of Ca, Mn, Cu and Fe than 1-year-old needles, both in case of *Ps* and *Pn*, which finds a confirmation in Ostrowska et al. (2006).

The results if non-parametric U Mann–Whitney test showed statistically-significant differences ( $p < 0.05$ ) between *Ps* and *Pn* needles, both 1-year-old and 2-year-old, in terms of phosphorus, potassium, magnesium, zinc and manganese content in 2005 growing season in *Cladonio-Pinetum* on the area of SNP.

Scots pine needles accumulated from 1100.0 to 1193.0  $\text{mmol}\cdot\text{kg}^{-1}$  of all analysed components, wherein the lowest value of components accumulated were in 2-year-old *Ps* needles. Ionic composition of components sum in 1-year-old and 2-year-old *Ps* needles was similar. Azote share was 68.5%–71.5%, phosphorus 2.5%–2.8%, potassium 6.9%–7.1%, magnesium 10.4%–12.6%, calcium 8.5%–8.7% and microelements jointly constituted 1.2%. *Pn* needles accumulated in comparison with Scots pine much smaller amount of analysed components (1-year-old: 813.0  $\text{mmol}\cdot\text{kg}^{-1}$ ; 2-year-old: 872.0  $\text{mmol}\cdot\text{kg}^{-1}$ ). The ionic composition of components sum in 1-year-old and 2-year-old *Pn* needles was similar. Azote share was 59.6%–60.4%, phosphorus 3.1%–3.2%, potassium 6.8%–10.2%, calcium 9.9%–14.0%, magnesium 16.3%–16.5% and microelements jointly constituted 1.7%–2.1% (Table 5). Large manganese and iron share in the sum of measured components showed their excessive absorption

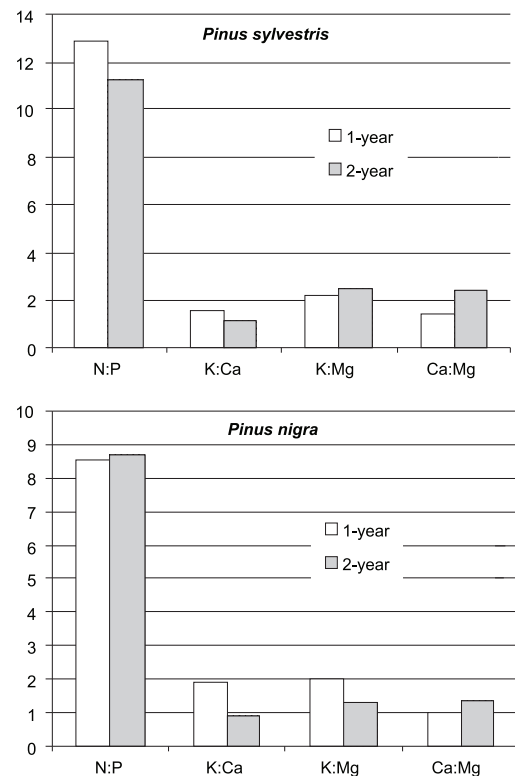
**Table 5.** Average accumulation of elements\* in needles of *Pinus sylvestris* and *Pinus nigra*

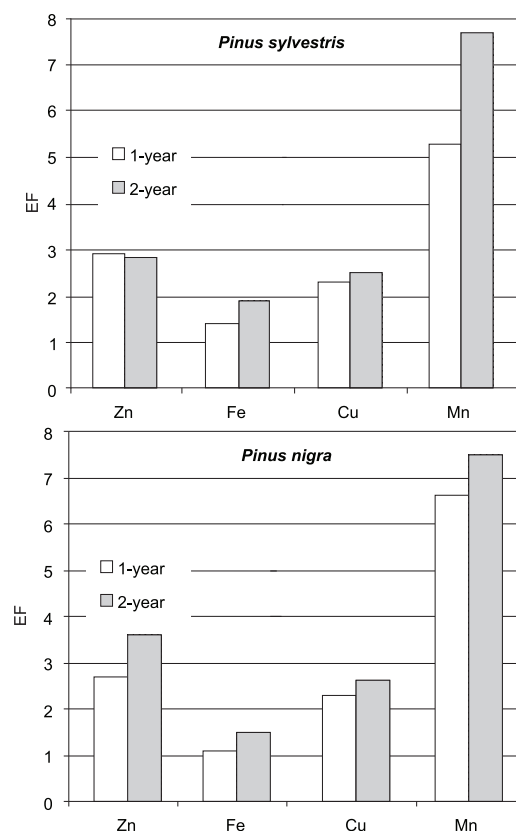
Elements	<i>Pinus sylvestris</i> L.		<i>Pinus nigra</i> J.F. Arn.	
	1-year	2-year	1-year	2-year
$\Sigma$ makro [mmol <sub>c</sub> · kg <sup>-1</sup> ]:	1193.0	1100.0	872.0	813.0
% N	71.5	68.9	60.4	59.6
% P	2.5	2.8	3.2	3.1
% K	7.1	6.9	10.2	6.8
% Ca	8.5	8.8	9.9	14.0
% Mg	10.4	12.6	16.3	16.5
$\Sigma$ mikro [mmol <sub>c</sub> · kg <sup>-1</sup> ]:	14.0	19.0	15.0	17.7
% Zn	13.8	9.9	12.2	13.5
% Cu	1.5	1.3	1.5	1.3
% Mn	47.2	50.6	54.8	52.8
% Fe	37.5	38.2	29.5	32.4

\* Expressed as a form of an amount of these components and their participation in the total.

from soil by examined stands, which facilitates strongly acid soil environment of dry coniferous forest (Table 2). One-year-old needles of examined pines accumulated more azote, phosphorus, potassium and copper, and 2-year-old needles more calcium, magnesium and manganese. Similar results between the amount of measured components in Scots pine needles were shown by Ostrowska et al. (2006).

N:P ratio in *Ps* needles was from 11.2 to 12.9, and in *Pn* needles from 8.5 to 8.7 depending on needles' ages (Fig. 1). According to Guswell and Koerselman (2002), N:P ratio in flora on natural positions maintain most frequently from 12 to 13, and according to Malzahn (2002), optimal trees supply in azote and phosphorus occurs with a ratio of 7:10. According to Zhiguo et al. (2007), maximum plant growth and maximum supply in biogens occurs with N:P close to 9.5. According to Guswell et Koerselman (2002), during growing season, the ratio N:P may take values from 10 to 20, and according to Commission Advice Forest Fertilization (1990) a ratio of N:P >12 in pine needles means critical value, exceeding which may cause a threat to the health condition of the forest. Earlier, Parzych's research (2010) conducted in dry coniferous forests, fresh coniferous forests and moist coniferous forests of SPN indicated that N:P ratio in Scots pine needles maintains usually from 9.3 to 11.1 depending on needles' age and forest's unit abundance.

**Figure 1.** Ratios between macroelements in needles of *Pinus sylvestris* and *Pinus nigra*



**Figure 2.** Enrichment factors  $EF$  calculated for the average concentrations of heavy metals in needles

Average K:Ca ratio in 1-year-old needles was 1.6 (*Ps*) and 1.9 (*Pn*), and with 2-year-old needles 1.1 and 0.9 respectively (Fig. 1). In none of examined needles samples did it exceed the threshold value (K:Ca = 2), meaning according to Commission Advice Forest Fertilization (1990) a danger for forest's health condition. Slightly smaller K:Ca values in Pines needles from Kampinos National Park were obtained by Staszewski et al. (2009): 0.8–1.3 in 1-year-old needles and 0.6 in 2-year-old needles.

K:Mg ratio in *Ps* needles was in the range 2.2–2.5, wherein a higher value was in 2-year-old needles, and in *Pn* needles it was 1.3–2.0 and was higher in the case of 1-year-old needles (Fig. 1). According to Burg (1990), optimal pines supply in potassium and magnesium occurred with K:Mg ratio of 2.2–6.4. Results of needles studies obtained in the SNP indicate a lack of potassium compounds supply in *Pn* needles. Higher K:Mg ratio (3.45–6.02) in pines needles of Kampinos National Park were seen by Staszewski et al. (2009).

In examined needles, a calcium to magnesium ratio in 1-year-old needles was on average 1.4 (*Ps*) and 1.0 (*Pn*) and was lower than in 2-year-old needles, in which it reached 1.4 and 2.4 accordingly. During growing season, the lower limit of optimal values of Ca:Mg ratio, amounting to 2.5 (Burg 1990), were not exceeded.

The small content of Zn, Cu, Mn and Fe in soil and needles of dry coniferous forest – *Ps* and *Pn* – results in an enrichment factor of small value (EF, Enrichment Factor; Fig. 2).

The smallest enrichment factor was noted in case of iron (EF<7.7). Those values indicate that among examined metals the highest accumulation was manganese, which also confirms manganese percentage share in the sum of mineral components (Table 5).

According to Kłos (2009), the value of EF factor indicates an alluvial pollution character or a soil as a source of metal origin. Strong soil acidification favours manganese ion release to soil solution and their absorption by flora. Received EF factors values should however be treated indicatively because they were established on the basis of total metal concentrations in soil, wherein plants accumulate only bio-available forms of these elements.

#### 4. Summary

*Ps* and *Pn* stand being a part of SPN *Cladonio-Pinetum* unit overgrew embryonic loose soil produced from deep dune sands. This soil was characterised by strong acidification, both organic and mineral horizons. Moreover, it was poor in nutrients. The greatest amount of macro- and microelements was accumulated in organic sub-horizons (O1 and Ofh). In mineral horizons, in which main root mass occurs, the content of macro- and microelements was very low.

Scots pines needles were characterised by higher content of azote, phosphorus, potassium, calcium and iron than Black pines needles, and *Pn* needles showed higher content of magnesium, zinc, copper and manganese than *Ps* needles. Two-year-old needles contained on average more Ca, Mn, Cu and Fe than 1-year-old needles, both in *Ps* and *Pn*. U Mann–Whitney test results showed statistically-significant differences ( $p < 0.05$ ) of P, K, Mg, Zn and Mn content both in 1-year-old needles and in 2-years-old needles of examined pines in *Cladonio-Pinetum* within the SNP.

Differences between examined Scots pines and Black pines needles were visible first of all in values of its accumulated components sum. In *Pn* needles much

greater accumulation of P, K, Ca, Mg and Mn was seen than in *Ps* needles, which may indicate that Black pine has a much better biologically-breeding condition and a chance for longer life of this individual species in a situation of unfavourable soil and climatic conditions in Mierzeja Łebska (Łebska Spit). Values of enrichment factors indicate that the highest needle enrichment properties are those for manganese.

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