



## THE CONTENT OF HEAVY METALS IN THE SOIL AND LITTERFALL IN A BEECH-PINE-SPRUCE STAND IN NORTHERN POLAND

JERZY JONCZAK<sup>1\*</sup>, AGNIESZKA PARZYCH<sup>2</sup>

<sup>1</sup>Department of Geocology and Geoinformation, Institute of Geography  
and Regional Studies, Pomeranian Academy,  
Partyzantów 27, 76-200 Słupsk, Poland

<sup>2</sup>Environmental Chemistry Research Unit,  
Institute of Biology and Environmental Protection, Pomeranian Academy,  
Arciszewskiego 22b, 76-200 Słupsk, Poland

\*Corresponding author's email: jerzy.jonczak@gmail.com

**Keywords:** Mixed forests, litterfall chemistry, environment pollution.

**Abstract:** The concentrations of Cu, Mn, Ni and Zn in the soil and litterfall, as well as influx of the elements to the soils with litterfall were studied in a mixed beech-pine-spruce stand in northern Poland during the years 2007–2009. Annual influx of litterfall to the soil amounted from 3.234 to 4.871 t/ha. Beech, pine and spruce litterfall contributed in total litterfall in 50.8–70.1%, 11.4–11.9% and 1.6–24.0% respectively. The following average annual concentrations of heavy metals in total litterfall during the 3-year study period were noticed: 2469.3–3469.2 mg Mn/kg, 153.6–160.8 mg/kg Zn, 8.0–14.3 mg Ni/kg and 5.0–6.8 mg Cu/kg. In general, the concentrations of Mn and Cu were higher in beech litterfall in comparison to pine and spruce. The contents of Zn and Ni in beech, pine and spruce litterfall were comparable. Annual influx of metals to the soil with litterfall was: 10341.6–14422.4 g/ha Mn, 460.3–748.1 g/ha Zn, 37.4–66.6 g/ha Ni and 20.2–31.8 g/ha Cu. The fluxes were higher for Mn, Zn and Ni, and comparable for Cu in relation to those observed in other beech, pine, spruce and mixed stands in northern Europe.

### INTRODUCTION

It is well known that litterfall, throughfall and stemflow, as important sources of elements for soil, play an important role in the functioning of forest ecosystems. Chemical composition of litterfall and annual influx of elements to the soil depends on several factors, such as species composition of forest stand [2, 3, 6, 15, 16, 18, 23], tree age [1, 24], stand density [12], site [1, 7, 26] and climate conditions [6]. Extreme phenomena, such as droughts or pest gradations sometimes play an important role too [9, 17]. Permanent input to the soil of litterfall and waters having specific chemical composition can cause changes in chemical and microbiological composition of the soil, and initiate or intensify some processes [3, 22]. Litterfall, as one of the primary links between producers and

decomposers [10], can be considered as a good indicator of the ecological state of forest ecosystems [3, 25].

The studies of plant litterfall usually focus on concentrations and fluxes of macroelements such as N, P, K, Ca, Mg, Fe, Al and rarely on trace elements. Meanwhile, the content of trace elements in litterfall and soil in too high concentrations can strongly impact the functioning of forest ecosystems due to their toxicity to organisms [14], and have impact on the intensity of biological processes in soils [29]. Elevated concentrations of some heavy metals can reduce the rate of litter decomposition resulting in its accumulation in forest floors [4, 8, 20, 27]. Heavy metals can form relatively stable complexes with soil organic matter and accumulate in ectohumus and humic horizons. Especially high accumulation of metals in these horizons is observed near sources of air pollution [5, 11].

In the paper, we present results of the studies on concentrations of Mn, Zn, Ni and Cu in the soil and litterfall in mixed, beech-pine-spruce stand located in the environment of low air pollution in northern Poland.

## MATERIAL AND METHODS

### *Site description*

The studies have been conducted in Forest Division Leśny Dwór, Forestry Łysomice (northern Poland), where average annual sum of precipitation is about 770 mm with maximum in July and average annual temperature is about 7.6°C. Research area was located in forest division number 147a, in mixed beech-pine-spruce stand. The stand comprised 66% of 70–110 year-old beech (European beech), 19% of about 120 year-old pine (Scots pine), and 15% of about 70 year-old spruce (Norway spruce). Tree species were distributed irregularly in the stand. Height of the trees was 21–27 m for beech, 27 m for pine and 22–28 m for spruce. Beech was the II and III yield class, pine and spruce II class. Year 2009 was seed year for beech. In 2008 spruce was attacked by bark beetle and cut at the end of the year. Within a few dozen kilometers from the study area there are no significant sources of the emission of the investigated metals.

### *Soil sampling and analysis*

Three soil profiles located under beech, beech-pine and beech-spruce canopies were described, and soil was sampled and analyzed. The following properties were analyzed: textural group on the basis of particle size distribution analysis with sieve and pipette methods (textural fractions were divided after the classification of the Polish Soil Science Society 2008), pH was determined potentiometrically in water and 1M KCl solution, total organic carbon (TOC) using Tiurin (for mineral samples) and Alten (for organic samples) methods and total nitrogen (TN) with Kjeldahl's method using distilling unit VELP UDK 127. The content of Mn, Zn, Cu and Ni in mineral samples was analyzed in solution after digestion in aqua regia and in organic samples after digestion in a mixture of 65% HNO<sub>3</sub> and 30% H<sub>2</sub>O<sub>2</sub>. The content of elements in solutions was analyzed by microwave plasma atomic emission spectrometry method (Agilent 4100 MP-AES).

### *Litterfall sampling and analysis*

The studies of litterfall were conducted in the years 2007–2009. Sixteen circular litter traps with 0.2 m<sup>2</sup> openings were set in a regular grid in a plot of 40×40 m. Litterfall was collected

every month, dried at 65°C until the constant weight, divided into fractions (beech leaves from spring, summer and autumn, beech branches, beech flowers, beech seeds, beech seed coats, pine needles from winter, spring, summer and autumn, pine branches, pine cones, spruce needles from winter, spring, summer and autumn, spruce branches, spruce cones, other components from winter, spring, summer and autumn – bark and other difficult to identify fragments), and weighted. The content of Mn, Zn, Ni and Cu in litterfall was analyzed in a solution after digestion in mixture of 65% HNO<sub>3</sub> and 30% H<sub>2</sub>O<sub>2</sub> by microwave plasma atomic emission spectrometry method (Agilent 4100 MP-AES).

### ***Statistical analysis***

Based on the data, annual weighted mean concentrations of Mn, Zn, Ni and Cu were calculated in beech, pine and spruce litterfall, as well as in total litterfall during the years 2007, 2008 and 2009. Statistical significance of differences between beech, pine and spruce litterfall in the content of analyzed metals was analyzed with T-test Student. Annual influx of elements to the soil was calculated as a function of their concentration and mass of litterfall components.

## RESULTS

### ***Soil characteristics***

Dystric Arenosols with moder (in beech patches) or mor (in beech-pine and beech-spruce patches) type of humus were noticed in the stand. Reaction of the soils was strongly acid – pH<sub>H<sub>2</sub>O</sub> ranged from 3.62–5.05 for organic horizons and 3.62–3.90 for humic horizons. Slightly higher values of pH were observed in other horizons (3.82–5.75) (Table 1). The content of TOC was 52.84–54.93% in OI horizons; 37.66–50.35% in Ofh, Of and Oh horizons; 2.05–2.83% in AEs horizons and 0.17–1.78% in B-horizons. The soils were poor in nitrogen, the content of which was: 0.686–0.990% in OI horizons; 1.167–1.361% in Ofh, Of and Oh horizons; 0.090–0.159% in AEs horizons and 0.017–0.092% in B-horizons. TOC:TN ratios ranged from 29:1–80:1 in ectohumus and 10:1–23:1 in mineral horizons.

The highest content of Mn was noticed in ectohumus (255.3–3551.9 mg/kg) and the lowest in AEs horizons (27.2–47.4 mg/kg). A higher content of Mn was observed in soil profile under beech in relation to profiles located under beech-pine and beech-spruce canopies. The content of Zn was 37.7–55.3 mg/kg in OI horizons, 37.7–62.7 mg/kg in Of, Ofh and Oh horizons, 15.0–17.8 mg/kg in AEs horizons, 12.6–24.9 mg/kg in B-horizons and 12.2–33.6 mg/kg in parent material. For Ni it was respectively: 4.9–7.3 mg/kg; 5.4–10.4 mg/kg; 0.9–1.6 mg/kg; 0.8–4.1 mg/kg; 1.7–6.7 mg/kg, and for Cu: 7.7–9.8 mg/kg; 9.1–12.7 mg/kg; 2.6–3.2 mg/kg; 1.6–2.7 mg/kg (Table 2).

### ***Plant litterfall characteristics***

Annual influx of litterfall to the soil during the study period amounted from 3.234 to 4.871 t/ha (Table 3). Beech, pine and spruce contributed in total litterfall mass in 50.8–70.1%, 11.4–11.9% and 1.6–24.0% respectively. Beech leaves were the major component of litterfall (39.6–52.4% of its total mass). In the seed year for beech (2009), seed coats and beech seeds had also a significant contribution in total mass of litterfall. The bark beetle outbreak, which occurred during the study period, influenced the dynamics

Table 1. Selected properties of the soils

	horizon	depth [cm]	textural group	pH		TOC [%]	TN [%]	TOC:TN
				H <sub>2</sub> O	KCl			
beech patches	Ol	4–2	–	5.05	4.36	54.19	0.990	55
	Ofh	2–0	–	4.52	3.83	47.68	1.361	35
	AEs	0–5	sand	3.70	2.94	2.61	0.126	21
	Bhs	5–9	sand	3.97	3.18	1.24	0.057	22
	BhsBv	9–25	sand	4.62	4.21	0.49	0.037	13
	Bv	25–50	sand	4.61	4.27	0.17	0.017	10
	C	50–140	sand	5.75	4.32	–	–	–
beech-pine patches	Ol	6–4	–	4.33	3.66	54.93	0.686	80
	Of	4–2	–	4.36	3.68	50.35	1.263	40
	Oh	2–0	–	3.62	2.62	37.66	1.167	32
	AEs	0–5	sand	3.72	2.80	2.05	0.090	23
	Bhs	5–13	sand	4.17	3.30	0.94	0.043	22
	BhsBv	13–27	sand	4.66	3.92	0.56	0.035	16
	BvC	27–49	sand	4.93	4.25	0.24	0.018	13
	Ab	49–75	sand	4.94	4.11	0.29	0.019	15
	Bvb	75–88	sand	4.51	4.12	0.16	0.014	12
C	88–138	sand	4.65	4.23	–	–	–	
beech-spruce patches	Ol	7–5	–	4.30	3.43	52.84	0.695	76
	Of	5–3	–	4.31	3.63	49.73	1.209	41
	Oh	3–0	–	3.90	3.07	38.51	1.310	29
	AEs	0–5	sand	3.62	2.81	2.83	0.159	18
	Bhs	5–11	sand	3.82	3.13	1.78	0.092	19
	BhsBv	11–30	sand	4.53	3.91	0.76	0.042	18
	Bv	30–64	sand	4.85	4.17	0.34	0.023	15
	C1	64–75	sand	5.13	4.22	–	–	–
	C2	75–86	sand	4.87	4.06	–	–	–
C3	86–140	sand	5.47	4.28	–	–	–	

of spruce needle fall. In the outbreak year (2008), a several fold increase in the mass of needle fall, mainly green needles, from spruce trees was observed [15]. Spruce was removed from a study plot at the end of 2008.

### ***The content of heavy metals in litterfall***

Very high differences between the tree-species and litterfall components were observed in the content of Mn, whose minimum concentration was in pine cones (73.4–86.1 mg/kg during subsequent years), and maximum in beech leaves collected during the autumn (4399.9–5599.0 mg/kg) (Table 4). Average annual content of Mn was 2928.7–4711.1 mg/kg in beech litterfall, 460.8–1378.2 mg/kg in pine litterfall, 1907.7–2180.4 mg/kg in spruce litterfall and 1135.9–1502.8 mg/kg in ‘others’ (Table 5). The observed differences in Mn content between beech and coniferous species were statistically significant (Table 7).

Weighted mean annual concentrations of Zn in total litterfall ranged from 153.6 mg/kg to 160.8 mg/kg (Table 5). The content of the element in beech litterfall was 110.9–132.2 mg/kg, in pine litterfall 112.6–135.9 mg/kg, in spruce litterfall

Table 2. Content of heavy metals in the soils

	horizon	depth [cm]	Mn mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg
beech patches	Ol	4–2	3551.9	37.7	7.3	9.8
	Ofh	2–0	3231.2	37.2	10.4	12.7
	AEs	0–5	47.4	15.0	1.6	3.2
	Bhs	5–9	416.6	14.7	1.0	1.7
	BhsBv	9–25	663.2	23.3	2.8	1.7
	Bv	25–50	454.1	21.4	4.1	2.3
	C	50–140	115.6	12.2	3.0	1.7
beech-pine patches	Ol	6–4	1071.6	39.8	7.1	7.7
	Of	4–2	2114.3	53.7	7.0	9.2
	Oh	2–0	255.3	46.4	7.9	9.1
	AEs	0–5	27.2	16.6	1.2	2.6
	Bhs	5–13	85.9	12.6	1.0	1.6
	BhsBv	13–27	200.7	15.5	1.6	1.9
	BvC	27–49	219.2	19.0	3.0	2.2
	Ab	49–75	418.1	18.1	1.7	2.0
	Bvb	75–88	264.9	20.6	2.4	1.6
	C	88–138	60.5	18.4	2.3	1.6
beech-spruce patches	Ol	7–5	758.1	55.3	4.9	7.8
	Of	5–3	1944.6	62.7	7.2	9.6
	Oh	3–0	949.7	47.7	5.4	9.1
	AEs	0–5	41.5	17.8	0.9	2.8
	Bhs	5–11	56.4	17.7	0.8	2.7
	BhsBv	11–30	172.1	23.9	1.6	2.7
	Bv	30–64	212.4	24.9	2.2	2.2
	C1	64–75	166.3	25.1	4.9	2.9
	C2	75–86	429.2	33.6	6.7	4.8
	C3	86–140	183.6	20.7	1.7	3.4

Table 3. Litterfall mass in the studied stand during 2007–2009

Year	Litterfall mass [t/ha]				SUM
	beech	pine	spruce	other components	
2007	1.879	0.386	0.205	0.764	3.234
2008	2.419	0.566	1.143	0.632	4.760
2009	3.416	0.555	0.079	0.821	4.871
mean	2.571	0.502	0.476	0.739	4.288

115.9–143.3 mg/kg and in other components 320.1–408.0 mg/kg. Minimum concentration was observed in pine cones (58.2–99.1 mg/kg), whereas maximum in ‘others’ (261.3–605.8 mg/kg) (Table 4).

The concentration of Ni and Cu in litterfall was much lower in relation to other studied elements. The average annual content of Ni in total litterfall ranged from 8.0 to

Table 4. Content of metals in litterfall during 2007–2009

	litterfall component	Mn mg/kg	Zn mg/kg	Ni mg/kg	Cu mg/kg
2007	beech leaves – spring	2750.9	162.2	14.8	12.3
	beech leaves – summer	2814.1	144.7	9.5	9.2
	beech leaves – autumn	5599.0	91.8	9.9	6.3
	beech branches	1532.8	189.9	11.9	8.9
	pine needles – spring	1390.6	127.9	14.7	6.0
	pine needles – summer	1434.5	115.9	10.8	4.0
	pine needles – autumn	1970.8	134.3	22.0	3.7
	spruce needles – spring	2180.4	143.3	16.7	5.2
	pine cones	85.7	58.2	14.9	2.9
	others – spring	1127.4	356.7	17.1	9.0
others – summer	1179.9	395.5	17.6	8.8	
2008	beech leaves – spring	2340.4	144.7	17.0	9.6
	beech leaves – summer	3073.2	168.0	13.1	8.0
	beech leaves – autumn	4827.2	121.0	15.6	5.8
	beech branches	1239.0	125.3	14.8	5.6
	pine needles – summer	1728.3	169.0	15.3	3.4
	pine needles – autumn	2062.7	138.7	13.3	2.1
	spruce needles – spring	2346.1	110.6	15.2	2.5
	spruce needles – summer	2147.3	120.4	12.5	2.8
	spruce branches	753.3	242.6	17.1	7.3
	pine cones	73.4	99.1	12.8	1.8
	spruce cones	107.5	101.1	14.1	4.3
	others – winter	1404.0	605.8	9.8	7.0
	others – spring	1563.0	368.9	9.7	7.4
	others – summer	1196.2	419.0	10.7	6.8
others – autumn	1750.5	261.3	13.5	8.1	
2009	beech leaves – summer	3881.4	147.9	10.1	6.9
	beech leaves – autumn	4399.9	132.2	7.7	5.5
	beech branches	1397.3	142.4	9.6	5.7
	beech flowers	1553.8	236.9	4.1	11.6
	beech seed coats	760.3	97.0	8.6	4.5
	beech seeds	1970.4	125.2	10.0	15.7
	pine needles – spring	1458.1	209.2	11.2	4.1
	pine needles – summer	1109.6	135.2	5.7	1.8
	pine needles – autumn	422.3	156.3	8.6	4.0
	pine branches	357.3	132.3	7.2	3.4
	pine cones	86.1	91.8	5.7	1.9
	others – spring	1382.6	304.1	7.3	7.1
	others – summer	1302.5	413.8	5.1	7.6
	others – autumn	1806.0	295.4	4.6	9.3

Table 5. Weighted mean concentrations (mg/kg) of metals in beech, pine, spruce and total litterfall during 2007–2009

	litterfall component	Mn	Zn	Ni	Cu
		mg/kg			
2007	beech	4711.1	110.9	10.1	7.1
	pine	1378.2	112.6	17.1	3.8
	spruce	2180.4	143.3	16.7	5.2
	others	1135.9	363.0	17.2	9.0
	<b>total</b>	<b>3469.2</b>	<b>154.4</b>	<b>12.7</b>	<b>6.8</b>
2008	beech	4450.7	123.5	15.4	5.9
	pine	1257.3	126.1	13.3	2.1
	spruce	1907.7	115.9	14.8	3.0
	others	1502.8	408.0	10.1	7.3
	<b>total</b>	<b>3099.6</b>	<b>160.8</b>	<b>14.3</b>	<b>5.0</b>
2009	beech	2928.7	132.2	8.2	7.2
	pine	460.8	135.9	7.4	3.1
	spruce	–	–	–	–
	others	1406.7	320.1	6.7	7.4
	<b>total</b>	<b>2469.3</b>	<b>153.6</b>	<b>8.0</b>	<b>6.8</b>

14.3 mg/kg. In beech litterfall the observed values were 8.2–15.4 mg/kg, in pine litterfall 7.4–17.1 mg/kg, in spruce litterfall 14.8–16.7 mg/kg and in ‘others’ 6.7–17.2 mg/kg. The lowest content of Ni was observed in beech flowers (4.1 mg/kg), other components in 2009 (4.6–7.3 mg/kg), as well as in pine needles collected during the summer of 2009 (5.7 mg/kg), and pine cones from the same year (5.7 mg/kg). The highest content of Ni was noticed in pine needles from the autumn of 2007 (22.0 mg/kg).

Table 6. Metals influx to the soil with litterfall (g/ha) during 2007–2009

	litterfall component	Mn	Zn	Ni	Cu
2007	beech	8856.0	208.4	18.9	13.3
	pine	680.4	55.6	8.4	1.9
	spruce	240.3	15.8	1.8	0.6
	others	564.9	180.5	8.5	4.5
	<b>Sum</b>	<b>10341.6</b>	<b>460.3</b>	<b>37.8</b>	<b>20.2</b>
2008	beech	10766.1	298.7	37.3	14.3
	pine	675.2	67.7	7.1	1.1
	spruce	2029.8	123.4	15.8	3.2
	others	951.3	258.3	6.4	4.6
	<b>Sum</b>	<b>14422.4</b>	<b>748.1</b>	<b>66.6</b>	<b>23.2</b>
2009	beech	10613.5	479.2	29.8	26.2
	pine	253.9	74.9	4.1	1.7
	spruce	–	–	–	–
	others	738.5	168.0	3.5	3.9
	<b>Sum</b>	<b>11605.9</b>	<b>722.1</b>	<b>37.4</b>	<b>31.8</b>

The average annual concentration of Cu in beech litterfall ranged from 5.9 mg/kg to 7.2 mg/kg, in pine litterfall 2.1–3.8 mg/kg, in spruce litterfall 3.0–5.2 mg/kg and in other components 7.3–9.0 mg/kg (Table 5). The lowest content of Cu was observed in pine needles collected during the summer of 2009 (1.8 mg/kg) and the highest in beech seeds (15.7 mg/kg) (Table 4).

Table 7. Statistically significance of differences in the content of heavy metals between beech, pine and spruce litterfall (– no statistically significant differences; + differences statistically significant at  $p < 0,05$ )

	Mn	Zn	Ni	Cu
2007 – beech vs pine	+	–	+	–
2007 – beech vs spruce	+	–	+	–
2007 – pine vs spruce	–	–	–	–
2008 – beech vs pine	+	–	–	+
2008 – beech vs spruce	+	–	–	–
2008 – pine vs spruce	–	–	–	–
2009 – beech vs pine	+	–	–	–

### ***Influx of heavy metals to the soil with litterfall***

Annual influx to the soil of the analyzed heavy metals with litterfall during the years 2007–2009 was: 10341.6–14422.4 g/ha for Mn, 460.3–748.1 g/ha for Zn, 37.4–66.6 g/ha for Ni and 20.2–31.8 g/ha for Cu (table 6). Beech litterfall, as the main component of total litterfall in the studied tree-stand, was the most important source of the analyzed elements for soil.

## DISCUSSION

Anthropogenic pollution of environment is usually the reason of elevated concentrations of heavy metals in forest soils [19, 29, 31]. Litterfall represents secondary, internal source of heavy metals in forest ecosystems. Falling on soil surface metals as components of dust, rainwater, or litterfall are included to biological turnover by plant roots and microorganisms, bounded by mineral and organic components of the soil, or leaching. Vertical distribution of heavy metals in soil profiles is a result of their influx to the soil, as well as the intensity of biological turnover, weathering and leaching. Physical and chemical properties of soil, especially sorption and acidity, which determine mobility and bioavailability of elements, play a very important role.

Large variability in the content of Mn in litterfall components was observed in the studied stand (73.4–5599.0 mg/kg). Especially rich in Mn was beech litterfall. The observed values were higher in comparison to the data of other authors [e.g. 23], who observed 990–2430 mg/kg. Extremely low concentrations of Mn were noticed in beech leaf litterfall by Małek et al. [21] in Ojców National Park – 80.7–178 mg/kg, and slightly higher in Forest Experimental Station in Krynica – 515.2–772.8 mg/kg. The content of Mn in pine and spruce litterfall was lower and ranged from 460.8 to 1378.2 mg/kg for pine and 1907.7–2180.4 mg/kg for spruce. Fyles et al. [10] noticed average annual concentrations of Mn in pine litterfall 660 mg/kg, and in spruce litterfall



900 mg/kg, whereas Ukonmaanaho et al (2008) 630–1430 mg/kg in pine needles and 550–1980 mg/kg in the needles of spruce. Annual influx of Mn to the soil with litterfall exceeds 10 kg per hectare every year (Table 6). Our data were slightly higher in relation to the data of Nordén [23], who noticed fluxes of Mn up to 7.41 kg·ha<sup>-1</sup> in beech stands, and much higher in relation to Małek et al. [21].

The concentrations of Zn in biomass over 300 mg/kg can limit the rate of its decomposition [29]. In the studied stand we observed 58.2–605.8 mg/kg of Zn in litterfall components, but the content over 300 mg/kg was noticed only in 'others', which was not a significant amount in total litterfall. Differences between the components of litterfall in the content of Zn were large (Table 4), but weighted mean annual concentrations of the element in beech, pine and spruce litterfall were comparable within the range from 110.9 mg/kg to 143.3 mg/kg. The observed values were higher than observed by Ukonmaanaho et al [30] in Scots pine (average 60 mg/kg) and Norway spruce (average 70 mg/kg) stands, by Huang et al [13] in the stand dominated by Norway spruce (18–35 mg/kg), as well as by Fyles et al [10] in pine (average 50 mg/kg) and spruce (average 90 mg/kg) stands in Norway. The concentrations of Zn in beech leaves collected during autumn (91.8–132.2 mg/kg) referred to Małek et al [21] who observed 60.9–112.0 mg/kg of Zn in Ojców National Park.

The content of Ni in beech, as well as in pine and spruce litterfall was in general higher than observed by other authors. We observed 7.7–15.6 mg/kg of Ni in beech brown leaves, whereas Małek et al. [21] in Ojców National Park noticed 0.3–2.1 mg/kg and in Forest Experimental Station in Krynica 1.1–3.4 mg/kg. Huang et al. [13] in a Norway spruce stand noticed 1.36–4.62 mg/kg of Ni, whereas we noticed weighted mean annual concentrations of Ni in spruce litterfall in a range of 14.8–16.7 mg/kg. However, we should bear in mind that in the investigated stand a gradation of bark beetle had an impact on chemical composition of litterfall. The content of Ni in litterfall was lower during the year 2009 (mast year for beech) in relation to 2007 and 2008.

Copper can reduce microbiological activity of soil microorganisms, when it is in concentration over 20 mg/kg [29]. We observed average annual concentrations of the element in total litterfall between 5.0 and 6.8 mg/kg (Table 5). The richest in Cu, except the fraction 'others', was beech litterfall with average annual concentrations of 5.9–7.2 mg/kg. The content of Cu in brown beech leaves (5.5–6.3 mg/kg) was similar to the data of Małek et al. [21], who observed 6.4–8.7 mg/kg. The content of Cu in spruce litterfall (average 3.0–5.2) also refers to other data – e.g. Huang et al [13], who noticed 3.10–5.83 mg/kg. Annual influx of Cu to the soil with litterfall was low in relation to other studied elements, and amounted from 20.2 to 31.8 g/ha.

## CONCLUSIONS

A mixed beech-pine-spruce stand is a source of litterfall components characterized with different content of heavy metals. In general, the concentrations of Mn and Cu trended to be higher in beech litterfall in relation to pine and spruce. Differences in concentration of these elements in beech, pine and spruce litterfall were reflected in spatial variability of their concentration in organic horizons of the soils. Zn and Ni amounted in beech, pine and spruce litterfall in comparable concentrations. In comparison to other investigations, the observed concentrations of elements were higher for Mn and Ni in beech litterfall

and Zn and Ni for pine and spruce litterfall. The observed in total litterfall weighted mean annual concentrations of Zn (153.6–160.0 mg/kg) and Cu (5.0–6.8 mg/kg) were below the limits, which can reduce biological activity of the soil – 300 mg/kg for Zn and 20 mg/kg for Cu. The influx of the elements to the soil with total litterfall was higher for Mn, Zn and Ni and comparable for Cu in relation to those observed in other beech, pine, spruce and mixed stands in northern Europe.

## REFERENCES

- [1] Albrektson, A. (1988). Needle litterfall in stands of *Pinus sylvestris* L. in Sweden, in relation to site quality-stand age and latitude, *Scandinavian Journal of Forest Research*, 3, 333–342.
- [2] Astel, A., Parzych, A. & Trojanowski, J. (2009). Comparison of litterfall and nutrient return in a *Vaccinio uliginosi*-*Betuletum pubescentis* and a *Empetro nigri*-*Pinetum* forest stands in northern Poland, *Forest Ecology and Management*, 257, 2331–2341.
- [3] Augusto, L., Ranger, J., Binkley, D. & Rothe, A. (2002). Impact of several common tree species of European temperate forests on soil fertility, *Annales of Forest Science*, 59, 233–253.
- [4] Berg, B., Ekbohm, G., Söderström, B. & Staaf, H. (1991). Reduction of decomposition rates of Scots pine needle litter due to heavy metal pollution, *Water, Air & Soil Pollution*, 59, 165–177.
- [5] Bergbäck, B. & Carlsson, M. (1995). Heritage of cadmium and lead. A case study of a Swedish accumulator factory, *Forest Ecology and Management*, 166, 35–42.
- [6] Bray, J.R. & Gorham, E. (1964). Litter production in forests of the world, *Advances in Ecological Research*, 2, 100–157.
- [7] Christensen, O. (1975). Wood litter fall in relation to abscission, environmental factors and the decomposition cycle in a Danish oak forest, *Oikos*, 26, 187–195.
- [8] Cotrufo, M.F., De Santo, A.V., Alfani, A., Bartoli, G. & De Cristofaro, A. (1995). Effects of urban heavy metal pollution on organic matter decomposition in *Quercus ilex* L. woods, *Environmental Pollution*, 89, 81–87.
- [9] Dziadowiec, H. & Plichta, W. (1985). The effect of nun moth (*Lymantria monacha* L.) outbreak on characteristics of litter fall in the pine forest, *Ekologia Polska*, 33, 715–728.
- [10] Fyles, J.W., Laroi, G.H. & Ellis, R.A. (1986). Litter production in *Pinus banksiana* dominated stands in northern Alberta, *Canadian Journal of Forest Research*, 16, 772–777.
- [11] Greszta, J. & Malek, S. (2001). Tentative results of studies on the dynamics of selected chemical properties of the soils in beech stands on the example of experimental plots located in Ojców National Park and Experimental Forest Station in Krynica in the period 1997–1998, Monitoring of processes occurring in beech stands in the changing environmental conditions on the example of the Ojców National Park and the Forest Experimental Station in Krynica, 113–129.
- [12] Hennessey, T.C., Dougherty, P.M., Cregg, B.M. & Wittwer, R.F. (1992). Annual variation in needle fall of a loblolly pine stand in relation to climate and stand density, *Forest Ecology and Management*, 51, 329–338.
- [13] Huang, J.H., Ilgen, G. & Matzner, E. (2011). Fluxes and budgets of Cd, Zn, Cu, Cr and Ni in a remote forested catchment in Germany, *Biogeochemistry*, 103, 59–70.
- [14] Hue, N.V., Craddock, G.R. & Adams, F. (1986): Effect of organic acids on aluminum toxicity in subsoils, *Soil Science Society of America Journal*, 50, 28–34.
- [15] Jonczak, J. (2011). Structure, dynamics and properties of litterfall in a 110-year-old beech stand with admixture of pine and spruce, *Sylvan*, 155, 760–768.
- [16] Jonczak, J. (2013). Dynamics, structure and properties of plant litterfall in a 120-year old beech stand in Middle Pomerania between 2007–2010, *Soil Science Annual*, 64, 1, 9–14.
- [17] Jonczak, J. & Czarnecki, A. (2008). Risk assessment for biomass plantations planning on marginal soils as an effect of increasing frequency of weather extreme events, *Ecological Questions*, 9, 113–118.
- [18] Jonczak, J., Dziadowiec, H., Kacprowicz, K. & Czarnecki, A. (2010). An assessment of the influence of poplar clones Hybrid275 and Robusta on soil cover based on the characteristics of their plant litterfall, *Polish Journal of Soil Science*, 42, 2, 9–19.
- [19] Kabała, C. & Singh, S.S. (2001). Fractionation and mobility of copper, lead, and zinc in soil profiles in the vicinity of a copper smelter, *Journal of Environmental Quality*, 30, 485–492.

- [20] Lomander, A. & Johansson, M-B. (2001). Changes in concentrations of Cd, Zn, Mn, Cu and Pb in spruce (*Picea abies*) needle litter during decomposition, *Water, Air, and Soil Pollution*, 132, 165–184.
- [21] Małek, S., Wężyk, P. & Nowak, W. (2001). A quantitative and qualitative analysis of litterfall in beech stands on monitoring plots in the Ojców National Park and the Forest Experimental Station in Krynica in the years 1996–1998. Monitoring of processes occurring in beech stands in the changing environmental conditions on the example of the Ojców National Park and the Forest Experimental Station in Krynica, 93–113.
- [22] Nilsson, M.Ch., Wardle, D.A. & Dahlberg, A. (1999). Effects of plant litter species composition and diversity on the boreal forest plant-soil system, *Oikos*, 86, 16–26.
- [23] Nordén, U. (1994). Leaf litterfall concentrations and fluxes of elements in deciduous tree species, *Scandinavian Journal of Forest Research*, 9, 9–16.
- [24] Ovington, J.D. (1959). The circulation of minerals in plantations of *Pinus silvestris* L., *An. Bot. N.S.*, 90, 71–80.
- [25] Pedersen, L.B. & Bille-Hansen, J. (1999). A comparison of litterfall and element fluxes in even aged Norway spruce, sitka spruce and beech stands in Denmark, *Forest Ecology and Management*, 114, 55–70.
- [26] Prescott, C.E., Kabzems, R. & Ząbek, L.M. (1999). Effects of fertilization on decomposition rate of *Populus tremuloides* foliar litter in a boreal forest, *Canadian Journal of Forest Research*, 29, 393–397.
- [27] Scheid, S., Gu Nthardt-Georg, M.S., Schulin, R. & Nowacki, B. (2009). Accumulation and solubility of metals during leaf litter decomposition in non-polluted and polluted soil, *European Journal of Soil Science*, 60, 613–621.
- [28] Starr, M., Lindroos, A.J., Ukonmaanaho, L., Tarvainen, T. & Tanskanen, H. (2003). Weathering release of heavy metals from soil in comparison to deposition, litterfall and leaching fluxes in a remote, boreal coniferous forest, *Applied Geochemistry*, 18, 607–613.
- [29] Tyler, G. (1992). Critical concentrations of heavy metals in the mor horizon of Swedish forests, Swedish Environmental Protection Agency, Report 4078, (pp. 38), Solna
- [30] Ukonmaanaho, L., Merilä, P., Nöjd, P. & Nieminen, T.M. (2008). Litterfall production and nutrient return to the forest floor in Scots pine and Norway spruce stands in Finland, *Boreal Environment Research*, 13, 67–91.
- [31] Warfvinge, P. & Svedrup, H. (1992). Calculating critical loads of acid deposition with PROFILE. A steady state soil chemistry model, *Water, Air and Soil Pollution*, 63, 119–143.

#### ZAWARTOŚĆ METALI CIĘŻKICH W GLEBIE I OPADZIE ROŚLINNYM W DRZEWOSTANIE BUKOWO-SOSNOWO-ŚWIERKOWYM NA OBSZARZE POLSKI PÓŁNOCNEJ

W latach 2007–2009, w drzewostanie bukowo-sosnowo-świerkowym zlokalizowanym na obszarze Polski Północnej, prowadzono badania zawartości Cu, Mn, Ni i Zn w glebie i opadzie roślinnym oraz dopływu tych składników do gleby z opadem. Roczna produkcja opadu roślinnego w okresie badań wynosiła od 3.234 do 4.871 t/ha. W całkowitej jego masie udział opadu buka wynosił 50.8–70.1%, sosny 11.4–11.9%, a świerka 1.6–24.0%. Średnie ważone roczne stężenia badanych metali w opadzie roślinnym mieściły się w przedziale: 2469.3–3469.2 mg Mn/kg, 153.6–160.8 mg Zn/kg, 8.0–14.3 mg Ni/kg i 5.0–6.8 mg Cu/kg. Na ogół wyższe stężenia Mn i Cu obserwowano w opadzie buka w porównaniu z opadem sosny i świerka, a zawartość Zn i Ni była porównywalna. Roczny dopływ metali do gleby z opadem roślinnym wynosił: 10341.6–14422.4 g Mn/ha, 460.3–748.1 g Zn/ha, 37.4–66.6 g Ni/ha i 20.2–31.8 g Cu/ha. Na tle danych uzyskanych przez innych autorów w drzewostanach bukowych, sosnowych, świerkowych i mieszanych występujących w Europie Północnej, odnotowany w badanym drzewostanie dopływ Mn, Zn i Ni był większy, a Cu porównywalny.