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ORYGINAL ARTICLE

Dynamics of Cu, Mn, Ni, Sr and Zn release during decomposition of four types of litter in headwater riparian forests in northern Poland

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Abstract. The aim of the study was to compare the dynamics of Cu, Mn, Ni, Sr and Zn release during decomposition of leaves of Black alder (native material), Norway maple, Red oak and European beech (exogenous material) in the area of headwater riparian forests along the upper course of the Kamienna Creek (Northern Poland). Litter bag method was used in the experiment. Initial materials differed in terms of their chemical composition. Cu, Mn, Ni, Sr and Zn contents were low in general, and in fact, even a few times lower than limit values for decomposition rate. Different trends in the dynamics of the leaf metal content during decomposition were observed in particular tree species despite the fact, that every materials were exposed in the same site. Release dynamics was strongly affected by the content of metals in initial materials and in topsoil. Accumulation of Cu, Mn and Zn was observed during decomposition of poorest in the elements maple leaves, as well as Ni in alder leaves and Sr in the leaves of maple, alder and oak. In beech leaves we observed intensive leaching of Ni, whereas downward trends in the Cu concentration of beech leaves, as well as Mn and Zn in beech and oak leaves, were related to weight loss of the leaves. In some cases, the dynamics of metal release displayed a more complicated two- or three-stage character (release of Ni from maple and oak leaves; Cu from maple leaves; Sr from alder, maple and oak leaves; and Zn from alder and maple leaves).

Key words: leaf litter decomposition, headwater areas, heavy metals, strontium

1. Introduction

Decomposition of litter as a mechanism of nutrient release is a key process in the functioning of natural and some modified ecosystems (Berg and Cortina 1995; Dziadowiec 1990; Jonczak 2013; Nordén 1994). Different types of litter decompose with varied intensity determined by the chemical composition of initial material (Berg and Staaf 1980; Bosatta and Staaf 1982; Jonczak 2009; Preston et al. 2009; Tablot et al. 2012), site conditions such as properties of soil, especially its pH, content of nitrogen and biological activity, as well as local climate conditions (Adams and Angradi 1996; Cortez 1998; Drewnik 2006; Herlitzius 1983; Lorenz et al. 2004; Prescott 1996), tree species composition and herb layer in a forest stand (Albers et al. 2004; Dziadowiec 1987) and sometimes different forms of human activity (Berg et al. 1987; Berg et al. 1991; Cotrufo et al. 1995; Emmaerling and Eisenbeis 1998; Gill and Lavender 1983; Gunapala et al. 1998; Li et al. 2009; Prescott et al. 1999; Ritter 2005; Smith et al. 2009). Fast decomposition of litter is especially important in the functioning of forest ecosystems associated with nutrient-poor soils. Macro-elements such as N, P, K, Ca and Mg play the most important role in functioning of forest ecosystems, and so quantitative and qualitative studies of litter and its decomposition are usually focused on these elements. Meanwhile, litter is also a stage in the cycle of heavy metals. Terrestrial and aquatic plants accumulate heavy metals during the

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growth with different intensities and immobilise them in cellular structures (Parzych and Jonczak 2013; Smith et al. 2009). As a result of litter decomposition, stable, organic forms of metals are converted into labile forms – the potential source of environment contamination. Therefore, understanding the mechanism of release of elements from a decaying litter can help us to control their turnover and reduce toxic effect on organisms.

The aim of this study was the evaluation of the dynamics of Cu, Mn, Ni, Sr and Zn release during decomposition of Black alder leaves (native material), Norway maple, Red oak and European beech leaves (exogenic material) in headwater riparian forest in northern Poland.

2. Materials and methods

Stand characteristics

The study was carried out from October 2011 to October 2012 in a riparian forest located in the area of peatland in the upper course of the Kamienna Creek – the left bank tributary of the Słupia River (54°19'N; 17°10'E). Tree layer in the stand is dominated by 40–86-year-old Black alder (*Alnus glutinosa*). Norway maple (*Acer platanoides* L.), Red oak (*Quercus rubra* L.) and European beech (*Fagus sylvatica* L.) occur in the vicinity of the peatland, and their litter also supplies the peat bog. The herb layer of the stand is very rich in plant species – 106 species of vascular plants, 17 species of mosses and 8 species of liverworts were observed in 2012. The average annual temperature for the region is 7.6°C, and the sum of precipitation is 770 mm. The average temperature for the study period measured in a study plot 1 cm above the ground level in 1-hour intervals was 7.7°C, with a maximum of 32°C in July and a minimum of -13.5°C in February.

Litter bag study

Litter bag method (20×20 cm litter bags made from 1×1 mm nylon mesh) was used in this study. Initial material (leaves of alder, maple, oak and beech) was collected during the maximal fall of leaves in October 2011 and then dried in a temperature of 65°C. Litter bags were filled with 10 g of leaves and then exposed on the soil surface in three locations (spaced approximately 30 m) in a study plot. Samples of decaying leaves were collected every two months. After removing roots, fresh parts of plants and other foreign particles, samples were dried at 65°C until a constant weight, then weighted and homogenised.

Soil sampling

Soil samples were taken from each litter bag locations up to a depth of mineral bed in 10 cm intervals. After removing roots and parts of wood larger than 1 cm, samples were dried in 40°C and homogenised. In this article, only the results for topsoil (0–10 cm) layer are presented because this part of the soil directly affects the process of decomposition of leaves.

Chemical analysis of litter and soils

The content of Cu, Mn, Ni, Sr and Zn in leaves and soils was analysed with microwave plasma atomic emission spectrometry method (Agilent 4100 MP-AES) in a solution after digestion of leaf samples in a mixture of 65% HNO_3 and 30% H_2O_2 and soil samples in 65% HNO_3, 60% $HClO_4$ and 95% H_2SO_4 in a proportion 20:5:1 by volume. The content of soil organic matter in soils and leaves was analysed as a loss on ignition in 550°C (combustion time 3 hours) and pH was measured potentiometrically in water suspension (in a proportion 1:10). Lignin content in initial material was analysed with the Klason method.

Statistical analyses

Mean values of Cu, Mn, Ni, Sr and Zn concentrations were calculated for each tree species and represented three replications for each sampling term. Spearman's linear correlation coefficients were calculated between the contents of particular metals.

3. Results

Up to 90 cm thick Histosols formed from alder and alder-sedge peat occurred in the investigated stand. The soil was slightly acidic and contained 72.50–81.08% of soil organic matter in 0–10 cm topsoil layer in the litter bag locations (Table 1). The content of the investigated metals was: 9.99–10.44 mg Cu/kg, 474.78–1053.76 mg Mn/kg, 7.47–7.97 mg Ni/kg, 82.86–100.80 mg Sr/kg and 34.50–66.76 mg Zn/kg.

The leaf litter initial material used in the experiment differed in terms of the content of ash, lignin and pH and decomposed at different rates (Table 2). The fastest decomposition was observed in the case of alder (k = 2.77), slower in maple (k = 1.02) and the slowest in oak and beech (k = 0.49) leaves.

The content of Cu in initial material ranged from 2.9 mg/kg in maple leaves to 7.9 mg/kg in the leaves of beech. Relatively constant concentration of the above-mentioned element during decomposition was observed in alder and oak leaves, whereas in maple leaves a strong upward trend (from 2.9 to 7.6 mg/kg) was observed. In

Table 1. pH, and content of soil organic matter SOM and metals in topsoil (0–10cm) in litter bag locations

Location	pH_{H2O}	SOM	Ash	Cu	Mn	Ni	Sr	Zn
		%		mg/kg				
1	6.1	72.5	27.50	10.27	1053.76	7.62	85.41	34.50
2	6.5	81.08	18.92	9.99	474.78	7.97	100.80	65.03
3	5.9	80.52	19.48	10.44	850.72	7.47	82.86	66.76

Table 2. pH, content of ash and lignin in initial materials and rates of decomposition *k* of litters

	Alder	Maple	Oak	Beech
pH	4.30	4.27	4.19	4.90
Ash (g/kg)	59.61	106.11	53.11	74.35
Lignin (g/kg)	305.60	327.40	343.34	419.97
k (year^{-1})	2.77	1.02	0.49	0.49

Table 3. Mean concentrations of Cu, Mn, Ni, Sr and Zn during leaves decomposition ±SD (n = 3)

Months of decomposition	Cu	Mn	Ni	Sr	Zn
	mg/kg				
	Alder				
0	4.9±0.0	427.8±0.0	15.4±0.0	34.4±0.0	23.1±0.0
2	4.4±1.4	369.7±81.9	15.0±0.8	39.6±5.1	23.6±6.7
4	4.3±0.2	358.0±18.4	18.4±0.7	32.9±2.3	22.9±0.6
6	4.7±0.6	359.0±32.9	20.5±1.9	37.7±5.2	22.7±1.3
8	4.3±0.3	366.7±37.7	18.2±0.4	35.4±0.7	29.0±3.6
10	4.2±0.0	327.0±0.0	25.4±0.0	41.6±0.0	17.5±0.0
12	-	-	-	-	-
	Maple				
0	2.9±0.0	251.1±0.0	15.2±0.0	81.7±0.0	9.8±0.0
2	3.4±0.2	210.7±13.0	11.5±2.8	75.1±3.3	11.9±2.7
4	2.9±0.5	213.7±6.6	10.1±1.5	79.3±2.9	12.1±3.4
6	5.8±1.7	207.8±13.1	6.6±0.9	88.9±11.5	25.0±6.4
8	7.4±0.5	358.7±108.2	8.8±1.1	92.2±9.8	30.8±6.9
10	7.6±0.3	358.9±0.1	11.3±0.2	84.3±6.1	33.8±0.1
12	7.3±1.0	447.0±0.0	15.5±2.5	54.6±3.4	28.5±3.4
	Oak				
0	5.0±0.0	1120.8±0.0	20.7±0.0	18.0±0.0	18.6±0.0
2	4.8±0.3	998.5±36.4	30.2±1.6	15.2±1.3	16.3±2.0
4	4.6±0.3	902.5±33.0	30.0±2.6	19.3±3.8	12.9±4.7
6	5.2±0.1	863.5±65.0	31.1±6.1	18.9±2.2	15.9±2.3
8	5.2±0.3	874.8±199.0	31.6±2.7	29.2±7.4	15.2±1.4
10	5.2±0.8	843.5±78.8	31.2±2.0	23.7±6.1	7.9±0.7
12	5.0±0.1	945.1±120.7	18.3±2.1	25.4±1.6	13.3±0.6
	Beech				
0	7.9±0.0	2749.5±0.0	49.5±0.0	32.8±0.0	22.8±0.0
2	5.4±0.5	2253.2±390.6	36.0±1.8	32.3±4.4	19.5±0.2
4	4.5±0.7	2498.4±3.6	30.5±2.8	33.5±6.0	17.3±1.7
6	6.4±0.0	2308.8±23.5	20.3±3.3	34.0±3.5	20.4±0.3
8	5.7±0.6	2063.7±354.4	16.2±2.0	39.8±6.8	17.9±2.6
10	3.9±0.1	2437.2±106.9	19.9±0.1	35.5±0.2	15.2±0.1
12	4.0±1.3	2264.0±212.7	12.1±0.2	39.0±6.3	13.9±9.8

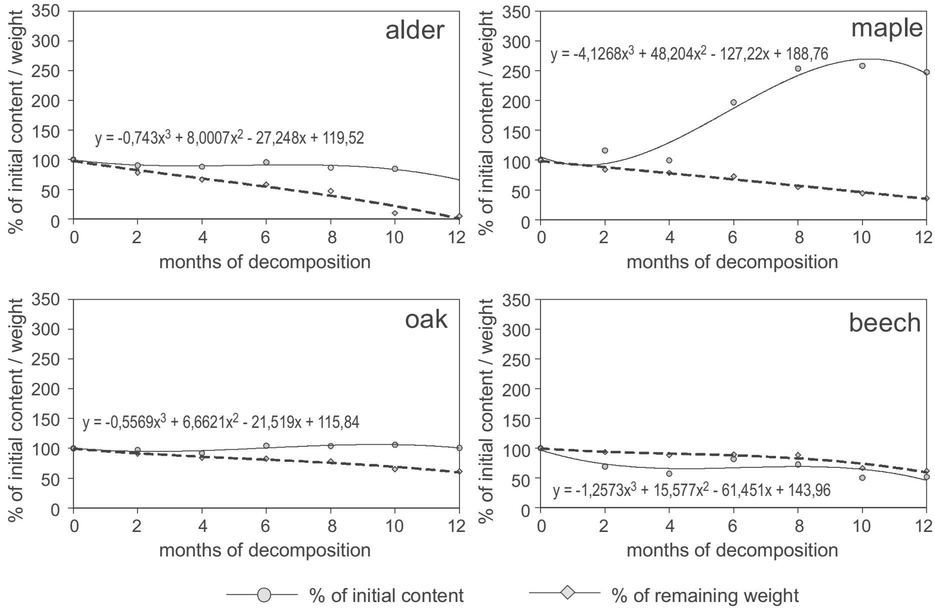

Figure 1. Changes in the content of Cu and weight loss during decomposition (based on mean values

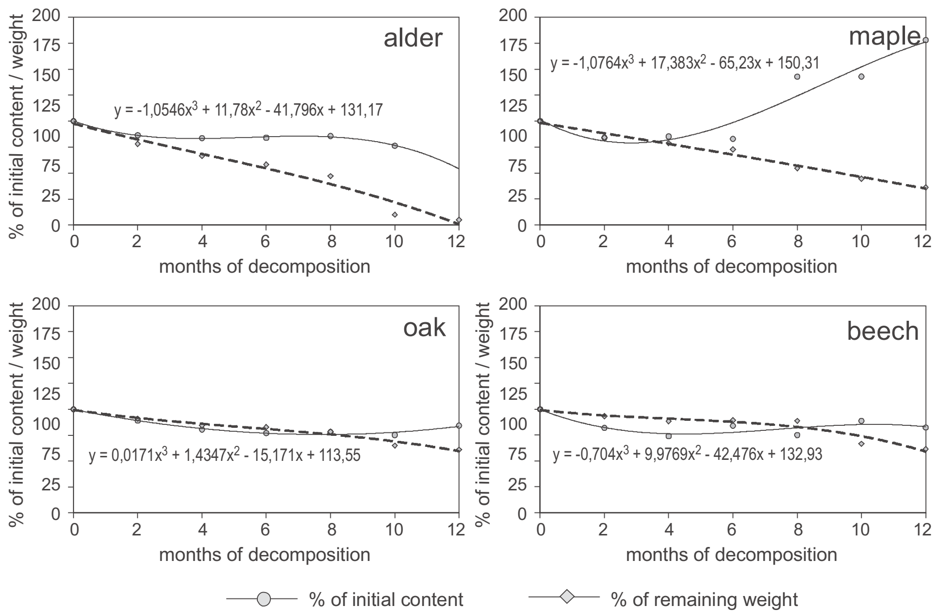

Figure 2. Changes in the content of Mn and weight loss during decomposition (based on mean values)

beech leaves, trend lines for the content of Cu and weight loss were in general comparable (Table 3, Fig. 1).

More than tenfold differences were stated between initial materials in the content of Mn. The lowest concentration of Mn was noticed in maple (251.1 mg/kg), higher in alder (427.8 mg/kg) and oak (1120.8 mg/kg) whereas the highest was recorded in beech leaves (2749.5 mg/kg). During decomposition of poor in Mn maple and alder leaves, accumulation of this element was observed, whereas in oak and beech leaves the dynamics of concentrations was comparable with weight loss (Table 3, Fig. 2).

Release of Ni was in different patterns for each of the investigated materials. In alder leaves, an increase in content of the element from 15.4 mg/kg to 25.4 mg/kg was noticed as a result of biological or chemical accumulation. An intensive accumulation of Ni was also observed during the first half of the year in oak leaves, and then a downward trend was reported. Leaching of Ni was observed in rich in the element beech leaves – a

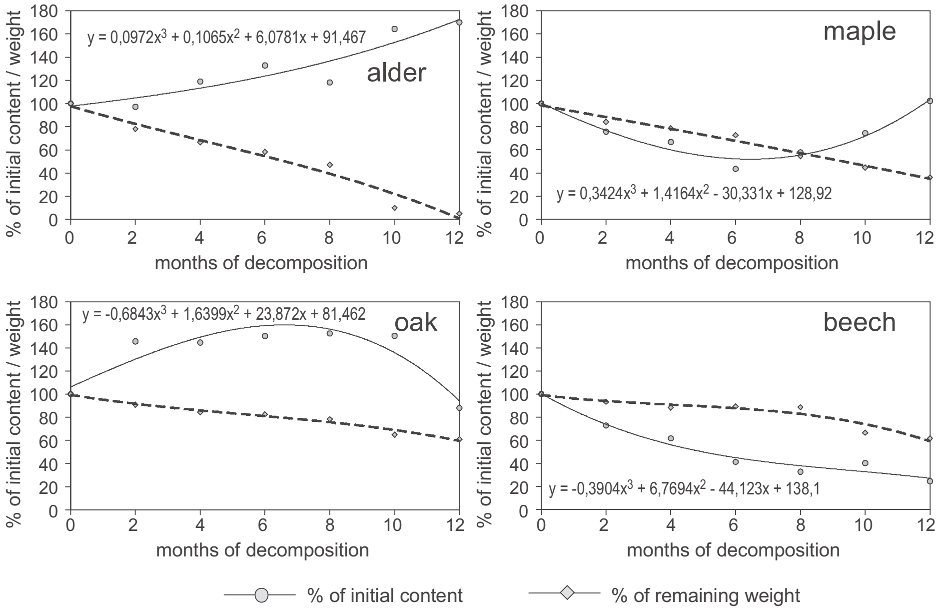

Figure 3. Changes in the content of Ni and weight loss during decomposition (based on mean values)

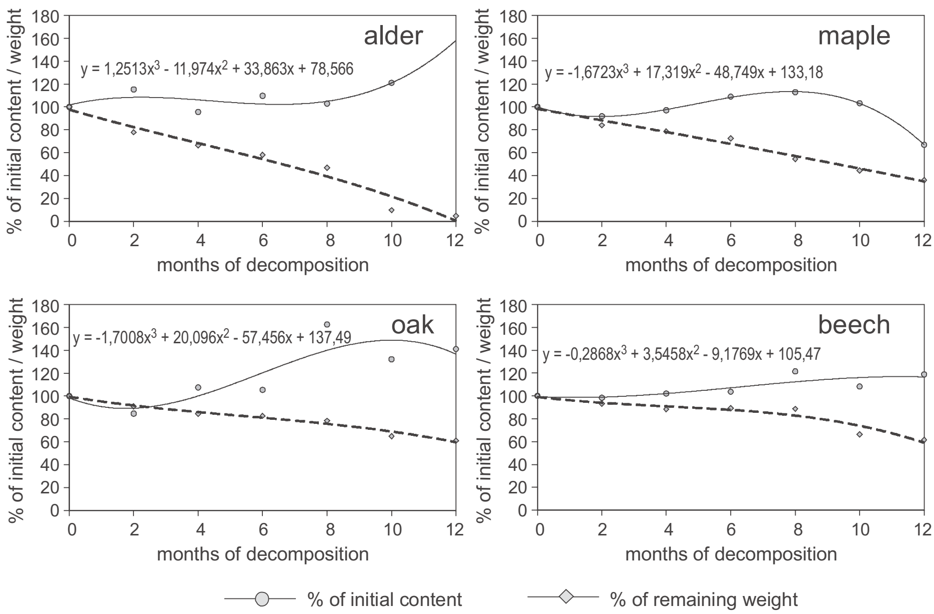

Figure 4. Changes in the content of Sr and weight loss during decomposition (based on mean values)

decrease of the content from 49.5 to 12.1 mg/kg. In maple leaves during the first half of the year, leaching and decrease of the content from 15.2 mg/kg to 6.6 mg/kg was observed and then accumulation and increase up to 15.5 mg/kg (Table 3, Fig. 3).

The accumulation of Sr was observed in every type of litter. The highest intensity of the process was noticed in alder (changes in content from 34.4 to 41.6 mg/kg) and oak (from 18.0 to 25.4 mg/kg) and smaller in beech (from 32.8 to 39.8 mg/kg) and maple (from 81.7 to 92.2 mg/kg) leaves (Table 3, Fig. 4).

Comparable content of Zn was noticed in alder, oak and beech initial material – 23.1, 18.6 and 22.8 mg/kg, respectively, and lower one in maple – 9.8 mg/kg (Table 3). In oak and beech leaves, the content of the element changed along with weight loss, whereas in alder and especially in oak leaves accumulation was observed (Fig. 5).

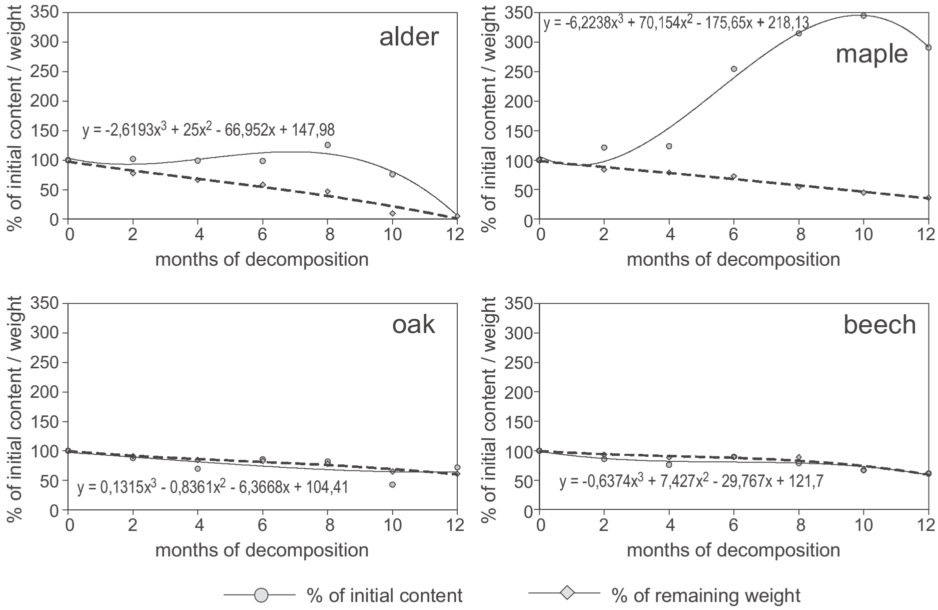

Figure 5. Changes in the content of Zn and weight loss during decomposition (based on mean values)

4. Discussion

Litter decomposition, as a result of mineralisation and humification, is a multi-stage, biochemical process controlled by a complex of slightly different key factors in each of the stages. The rate of decomposition in initial phase is strongly affected by chemical composition of the initial material and site conditions (Berg and Staaf 1980; Berg et al. 1987; Prescott 1996; Cortez 1998; Limpens and Berendse 2003; Jonczak 2009; Preston et al. 2009). The bioavailability of nutrients, especially nitrogen as well as water presence determines the intensity of litter colonisation by microorganisms. In poor in nutrients litter, the process of colonisation can be accelerated by influx of nutrients from external sources, like soil or admixtures of rich in the components litter (Taylor et al. 1989; Dziadowiec 1990; Prescott 1996; Salamanca et al. 1998; Robinson et al. 1999). The content and chemistry of resistance to decomposition lignins are important factors controlling the decomposition rate in its second phase (Gill and Lavender 1983; Berg et al. 1984; Tablot et al. 2012).

Intensity of decay can be inhibited by excessive concentrations of different organic and inorganic contaminants, including heavy metals (Berg et al. 1991; Cotrufo et al. 1995). However, limit values for heavy metals are relatively high – for example, 300 mg/kg for Zn and 20 mg/kg for Cu (Tyler 1992) – and are exceeded only in the vicinity of emission sources. In stands located over the range of the objects, the content of heavy metals in litter is usually small (Małek et al. 2001; Jonczak 2013). The initial concentrations of Cu, Mn, Ni, Sr and Zn in the investigated types of litter varied, but in general were low or medium and did not exceed limit values (Table 3).

The release of the elements during decomposition can run according to different patterns. Some of the elements are always released in a similar way, despite the kind of litter. For example potassium, which is present in plants only as an ionic form, is strongly leached just in the initial phase of decomposition. In turn, aluminium and iron are usually accumulated, which is a result of bonding of their ionic forms by newly formed humic acids (Dziadowiec 1990). However, most of the elements can be released in different patterns depending on their content in initial material, bioavailability in site, needs of living organisms, time-varying weather conditions and other factors. Our study shows that in the same site conditions, including temperature, humidity and a complex of soil properties, release patterns of Cu, Mn, Ni, Sr and Zn are strongly affected by chemical composition of initial material. In general, increasing/upward trends in the content of analysed elements, affected by biological or chemical accumulation, were observed in poorest in the elements materials. The source of Cu, Mn, Sr and Zn influx to litter was probably soil where, in general, higher concentrations of the metals were observed in comparison with initial material. In rich in elements types of material, more or less intensive leaching was observed. Much lower concentrations of Ni in soil than in initial material and the accumulation of this element in alder and oak leaves suggest an impact of other external factors. Lomander

Table 4. Correlation coefficients between the contents of metals in leaves during decomposition (in bold correlations statistically significant at p.05)

Correlated metals	Alder	Maple	Oak	Beech
Cu vs Mn	**0.823**	**0.797**	-0.357	0.552
Cu vs Ni	-0.523	-0.145	0.117	0.655
Cu vs Sr	-0.343	-0.014	0.499	-0.382
Cu vs Zn	0.073	**0.989**	-0.229	**0.946**
Mn vs Ni	-0.777	0.432	-0.644	0.571
Mn vs Sr	-0.556	-0.452	-0.503	-0.389
Mn vs Zn	0.375	0.731	0.692	0.465
Ni vs Sr	0.522	-0.724	-0.020	**-0.787**
Ni vr Zn	-0.608	-0.237	-0.282	**0.768**
Sr vs Zn	-0.522	0.075	-0.403	-0.621

and Johansson (2001) suggest that in litter bag experiments, newly fallen litter can be the source of some elements. Our study was conducted only for one year, so we have to exclude the influence of tree leaf litter but we cannot exclude the influence of litter from herb layer. In medium rich in metal materials, the concentrations changed usually in a way close to the weight loss. Two- or three-stage character of the release of the elements observed in a few cases can be an effect of indirect or direct impact of the succession of seasons, and gradual decomposition of organic compounds of different resistance to decomposition (usually associated with specific cellular structures). Only in a few cases statistically significant differences between the contents of metals were stated (Table 4), which suggests different patterns of release of each of them.

5. Conclusions

The results of our study indicate that the dynamics of Cu, Mn, Ni, Sr and Zn release from different materials decaying in the same site conditions can vary. It seems that differentiated chemistry of initial materials including the content of investigated metals and the ratio of the metals content in leaves to the content in soil were the main factors determining the dynamics of the release. The recorded concentrations of metals in initial materials used in the experiment were various but in general low and did not exceed limit values for decomposition rate. In poor in metal leaves, where their concentrations were usually lower in comparison with soil, upward trends affected by microbiological or chemical accumulation were observed. Especially, the high accumulation was noticed for Cu, Mn and Zn in maple; Ni in alder; and Sr in alder, maple and oak leaves. Faster decrease of Ni concentration than the weight loss was observed in beech leaves. Changes in the contents of Cu in beech, Mn in oak and beech, and Zn in oak and beech leaves were related to weight loss. Sometimes two- or three-stage process of release was reported, which can be a result of seasonal dynamics of leaching, soil biological activity, uptake intensity and processes of microbiological and chemical accumulation. The contents of Cu, Mn, Ni, Sr and Zn changed according to various patterns, which is confirmed by very small quantity of statistically significant correlations between the contents of the elements during the decomposition.

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Contributions

J.J. designed the study, conducted field study and chemical analysis of leaves and soils, analysed the data and wrote most of the manuscript. A.P. conducted some chemical analysis of leaves, analysed the data and wrote a part of the manuscript. Z.S. described plant communities in a study plot and wrote a part of the manuscript.

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ORIGINAL RESEARCH ARTICLE

Dynamics of Cu, Mn, Ni, Sr and Zn release during decomposition of four types of litter in headwater riparian forests in northern Poland

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Abstract. The aim of the study was to compare the dynamics of Cu, Mn, Ni, Sr and Zn release during decomposition of leaves of Black alder (native material), Norway maple, Red oak and European beech (exogenous material) in the area of headwater riparian forests along the upper course of the Kamienna Creek (Northern Poland). Litter bag method was used in the experiment. Initial materials differed in terms of their chemical composition. Cu, Mn, Ni, Sr and Zn contents were low in general, and in fact, even a few times lower than limit values for decomposition rate. Different trends in the dynamics of the leaf metal content during decomposition were observed in particular tree species despite the fact, that every materials were exposed in the same site. Release dynamics was strongly affected by the content of metals in initial materials and in topsoil. Accumulation of Cu, Mn and Zn was observed during decomposition of poorest in the elements maple leaves, as well as Ni in alder leaves and Sr in the leaves of maple, alder and oak. In beech leaves we observed intensive leaching of Ni, whereas downward trends in the Cu concentration of beech leaves, as well as Mn and Zn in beech and oak leaves, were related to weight loss of the leaves. In some cases, the dynamics of metal release displayed a more complicated two- or three-stage character (release of Ni from maple and oak leaves; Cu from maple leaves; Sr from alder, maple and oak leaves; and Zn from alder and maple leaves).

Key words: leaf litter decomposition, headwater areas, heavy metals, strontium

1. Introduction

Decomposition of litter as a mechanism of nutrient release is a key process in the functioning of natural and some modified ecosystems (Berg and Cortina 1995; Dziadowiec 1990; Jonczak 2013; Nordén 1994). Different types of litter decompose with varied intensity determined by the chemical composition of initial material (Berg and Staaf 1980; Bosatta and Staaf 1982; Jonczak 2009; Preston et al. 2009; Tablot et al. 2012), site conditions such as properties of soil, especially its pH, content of nitrogen and biological activity, as well as local climate conditions (Adams and Angradi 1996; Cortez 1998; Drewnik 2006; Herlitzius 1983; Lorenz et al. 2004; Prescott 1996), tree species composition and herb layer in a forest stand (Albers et al. 2004; Dziadowiec 1987) and sometimes different forms of human activity (Berg et al. 1987; Berg et al. 1991; Cotrufo et al. 1995; Emmaerling and Eisenbeis 1998; Gill and Lavender 1983; Gunapala et al. 1998; Li et al. 2009; Prescott et al. 1999; Ritter 2005; Smith et al. 2009). Fast decomposition of litter is especially important in the functioning of forest ecosystems associated with nutrient-poor soils. Macro-elements such as N, P, K, Ca and Mg play the most important role in functioning of forest ecosystems, and so quantitative and qualitative studies of litter and its decomposition are usually focused on these elements. Meanwhile, litter is also a stage in the cycle of heavy metals. Terrestrial and aquatic plants accumulate heavy metals during the

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growth with different intensities and immobilise them in cellular structures (Parzych and Jonczak 2013; Smith et al. 2009). As a result of litter decomposition, stable, organic forms of metals are converted into labile forms – the potential source of environment contamination. Therefore, understanding the mechanism of release of elements from a decaying litter can help us to control their turnover and reduce toxic effect on organisms.

The aim of this study was the evaluation of the dynamics of Cu, Mn, Ni, Sr and Zn release during decomposition of Black alder leaves (native material), Norway maple, Red oak and European beech leaves (exogenic material) in headwater riparian forest in northern Poland.

2. Materials and methods

Stand characteristics

The study was carried out from October 2011 to October 2012 in a riparian forest located in the area of peatland in the upper course of the Kamienna Creek – the left bank tributary of the Słupia River (54°19'N; 17°10'E). Tree layer in the stand is dominated by 40–86-year-old Black alder (*Alnus glutinosa*). Norway maple (*Acer platanoides* L.), Red oak (*Quercus rubra* L.) and European beech (*Fagus sylvatica* L.) occur in the vicinity of the peatland, and their litter also supplies the peat bog. The herb layer of the stand is very rich in plant species – 106 species of vascular plants, 17 species of mosses and 8 species of liverworts were observed in 2012. The average annual temperature for the region is 7.6°C, and the sum of precipitation is 770 mm. The average temperature for the study period measured in a study plot 1 cm above the ground level in 1-hour intervals was 7.7°C, with a maximum of 32°C in July and a minimum of -13.5°C in February.

Litter bag study

Litter bag method (20×20 cm litter bags made from 1×1 mm nylon mesh) was used in this study. Initial material (leaves of alder, maple, oak and beech) was collected during the maximal fall of leaves in October 2011 and then dried in a temperature of 65°C. Litter bags were filled with 10 g of leaves and then exposed on the soil surface in three locations (spaced approximately 30 m) in a study plot. Samples of decaying leaves were collected every two months. After removing roots, fresh parts of plants and other foreign particles, samples were dried at 65°C until a constant weight, then weighted and homogenised.

Soil sampling

Soil samples were taken from each litter bag locations up to a depth of mineral bed in 10 cm intervals. After removing roots and parts of wood larger than 1 cm, samples were dried in 40°C and homogenised. In this article, only the results for topsoil (0–10 cm) layer are presented because this part of the soil directly affects the process of decomposition of leaves.

Chemical analysis of litter and soils

The content of Cu, Mn, Ni, Sr and Zn in leaves and soils was analysed with microwave plasma atomic emission spectrometry method (Agilent 4100 MP-AES) in a solution after digestion of leaf samples in a mixture of 65% HNO_3 and 30% H_2O_2 and soil samples in 65% HNO_3, 60% $HClO_4$ and 95% H_2SO_4 in a proportion 20:5:1 by volume. The content of soil organic matter in soils and leaves was analysed as a loss on ignition in 550°C (combustion time 3 hours) and pH was measured potentiometrically in water suspension (in a proportion 1:10). Lignin content in initial material was analysed with the Klason method.

Statistical analyses

Mean values of Cu, Mn, Ni, Sr and Zn concentrations were calculated for each tree species and represented three replications for each sampling term. Spearman's linear correlation coefficients were calculated between the contents of particular metals.

3. Results

Up to 90 cm thick Histosols formed from alder and alder-sedge peat occurred in the investigated stand. The soil was slightly acidic and contained 72.50–81.08% of soil organic matter in 0–10 cm topsoil layer in the litter bag locations (Table 1). The content of the investigated metals was: 9.99–10.44 mg Cu/kg, 474.78–1053.76 mg Mn/kg, 7.47–7.97 mg Ni/kg, 82.86–100.80 mg Sr/kg and 34.50–66.76 mg Zn/kg.

The leaf litter initial material used in the experiment differed in terms of the content of ash, lignin and pH and decomposed at different rates (Table 2). The fastest decomposition was observed in the case of alder (k = 2.77), slower in maple (k = 1.02) and the slowest in oak and beech (k = 0.49) leaves.

The content of Cu in initial material ranged from 2.9 mg/kg in maple leaves to 7.9 mg/kg in the leaves of beech. Relatively constant concentration of the above-mentioned element during decomposition was observed in alder and oak leaves, whereas in maple leaves a strong upward trend (from 2.9 to 7.6 mg/kg) was observed. In

Table 1. pH, and content of soil organic matter SOM and metals in topsoil (0–10cm) in litter bag locations

Location	pH_{H2O}	SOM	Ash	Cu	Mn	Ni	Sr	Zn
		%		mg/kg				
1	6.1	72.5	27.50	10.27	1053.76	7.62	85.41	34.50
2	6.5	81.08	18.92	9.99	474.78	7.97	100.80	65.03
3	5.9	80.52	19.48	10.44	850.72	7.47	82.86	66.76

Table 2. pH, content of ash and lignin in initial materials and rates of decomposition *k* of litters

	Alder	Maple	Oak	Beech
pH	4.30	4.27	4.19	4.90
Ash (g/kg)	59.61	106.11	53.11	74.35
Lignin (g/kg)	305.60	327.40	343.34	419.97
k (year^{-1})	2.77	1.02	0.49	0.49

Table 3. Mean concentrations of Cu, Mn, Ni, Sr and Zn during leaves decomposition ±SD (n = 3)

Months of decomposition	Cu	Mn	Ni	Sr	Zn
	mg/kg				
	Alder				
0	4.9±0.0	427.8±0.0	15.4±0.0	34.4±0.0	23.1±0.0
2	4.4±1.4	369.7±81.9	15.0±0.8	39.6±5.1	23.6±6.7
4	4.3±0.2	358.0±18.4	18.4±0.7	32.9±2.3	22.9±0.6
6	4.7±0.6	359.0±32.9	20.5±1.9	37.7±5.2	22.7±1.3
8	4.3±0.3	366.7±37.7	18.2±0.4	35.4±0.7	29.0±3.6
10	4.2±0.0	327.0±0.0	25.4±0.0	41.6±0.0	17.5±0.0
12	-	-	-	-	-
	Maple				
0	2.9±0.0	251.1±0.0	15.2±0.0	81.7±0.0	9.8±0.0
2	3.4±0.2	210.7±13.0	11.5±2.8	75.1±3.3	11.9±2.7
4	2.9±0.5	213.7±6.6	10.1±1.5	79.3±2.9	12.1±3.4
6	5.8±1.7	207.8±13.1	6.6±0.9	88.9±11.5	25.0±6.4
8	7.4±0.5	358.7±108.2	8.8±1.1	92.2±9.8	30.8±6.9
10	7.6±0.3	358.9±0.1	11.3±0.2	84.3±6.1	33.8±0.1
12	7.3±1.0	447.0±0.0	15.5±2.5	54.6±3.4	28.5±3.4
	Oak				
0	5.0±0.0	1120.8±0.0	20.7±0.0	18.0±0.0	18.6±0.0
2	4.8±0.3	998.5±36.4	30.2±1.6	15.2±1.3	16.3±2.0
4	4.6±0.3	902.5±33.0	30.0±2.6	19.3±3.8	12.9±4.7
6	5.2±0.1	863.5±65.0	31.1±6.1	18.9±2.2	15.9±2.3
8	5.2±0.3	874.8±199.0	31.6±2.7	29.2±7.4	15.2±1.4
10	5.2±0.8	843.5±78.8	31.2±2.0	23.7±6.1	7.9±0.7
12	5.0±0.1	945.1±120.7	18.3±2.1	25.4±1.6	13.3±0.6
	Beech				
0	7.9±0.0	2749.5±0.0	49.5±0.0	32.8±0.0	22.8±0.0
2	5.4±0.5	2253.2±390.6	36.0±1.8	32.3±4.4	19.5±0.2
4	4.5±0.7	2498.4±3.6	30.5±2.8	33.5±6.0	17.3±1.7
6	6.4±0.0	2308.8±23.5	20.3±3.3	34.0±3.5	20.4±0.3
8	5.7±0.6	2063.7±354.4	16.2±2.0	39.8±6.8	17.9±2.6
10	3.9±0.1	2437.2±106.9	19.9±0.1	35.5±0.2	15.2±0.1
12	4.0±1.3	2264.0±212.7	12.1±0.2	39.0±6.3	13.9±9.8

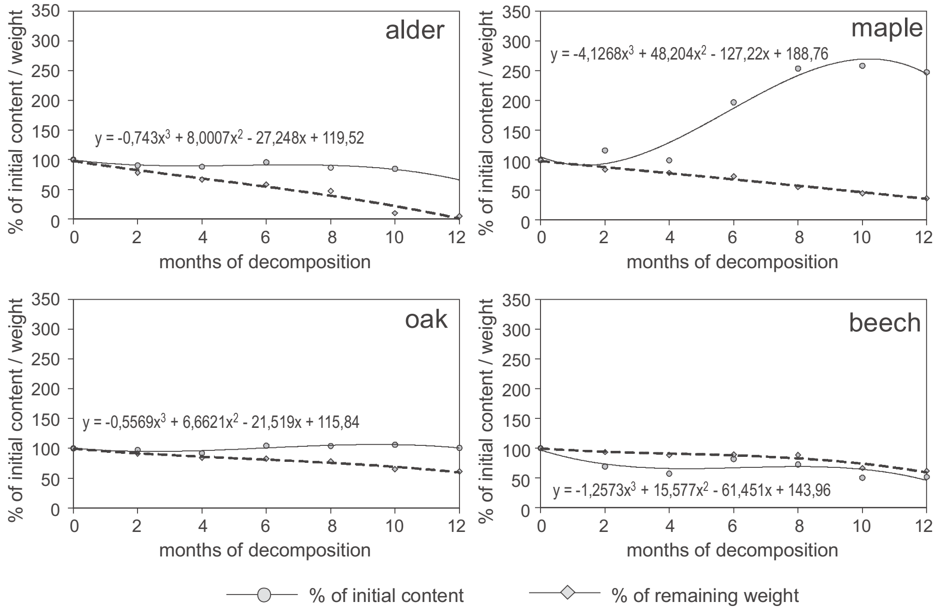

Figure 1. Changes in the content of Cu and weight loss during decomposition (based on mean values

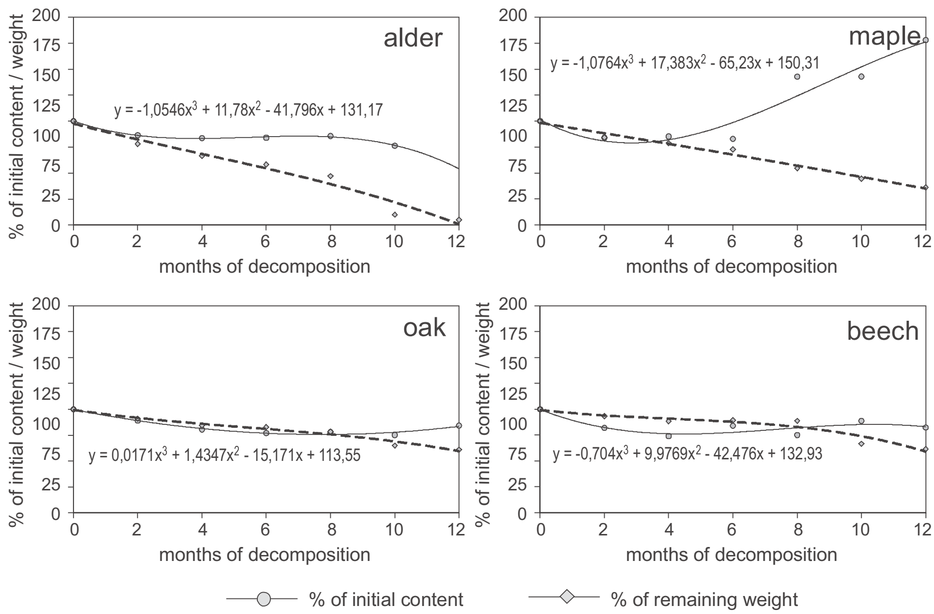

Figure 2. Changes in the content of Mn and weight loss during decomposition (based on mean values)

beech leaves, trend lines for the content of Cu and weight loss were in general comparable (Table 3, Fig. 1).

More than tenfold differences were stated between initial materials in the content of Mn. The lowest concentration of Mn was noticed in maple (251.1 mg/kg), higher in alder (427.8 mg/kg) and oak (1120.8 mg/kg) whereas the highest was recorded in beech leaves (2749.5 mg/kg). During decomposition of poor in Mn maple and alder leaves, accumulation of this element was observed, whereas in oak and beech leaves the dynamics of concentrations was comparable with weight loss (Table 3, Fig. 2).

Release of Ni was in different patterns for each of the investigated materials. In alder leaves, an increase in content of the element from 15.4 mg/kg to 25.4 mg/kg was noticed as a result of biological or chemical accumulation. An intensive accumulation of Ni was also observed during the first half of the year in oak leaves, and then a downward trend was reported. Leaching of Ni was observed in rich in the element beech leaves – a

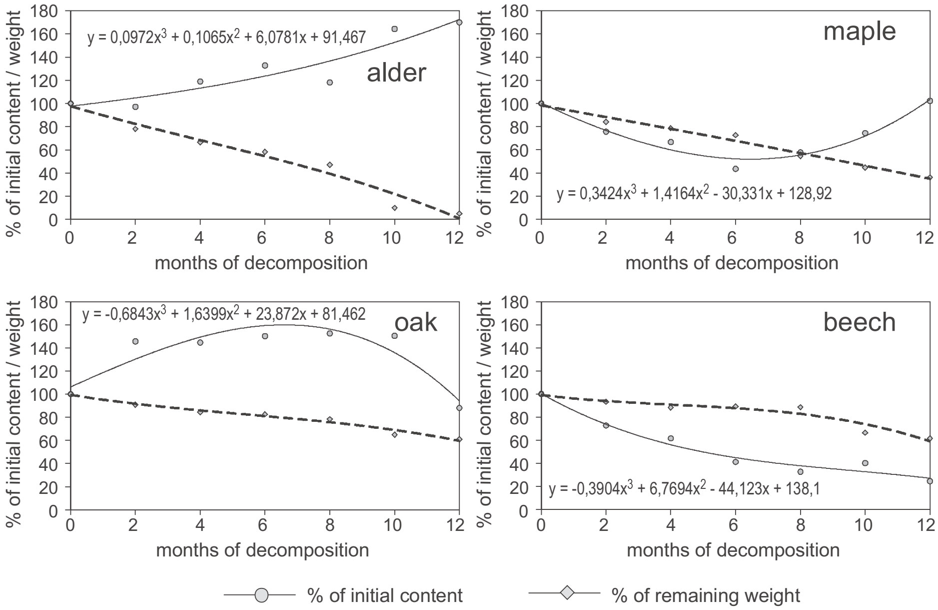

Figure 3. Changes in the content of Ni and weight loss during decomposition (based on mean values)

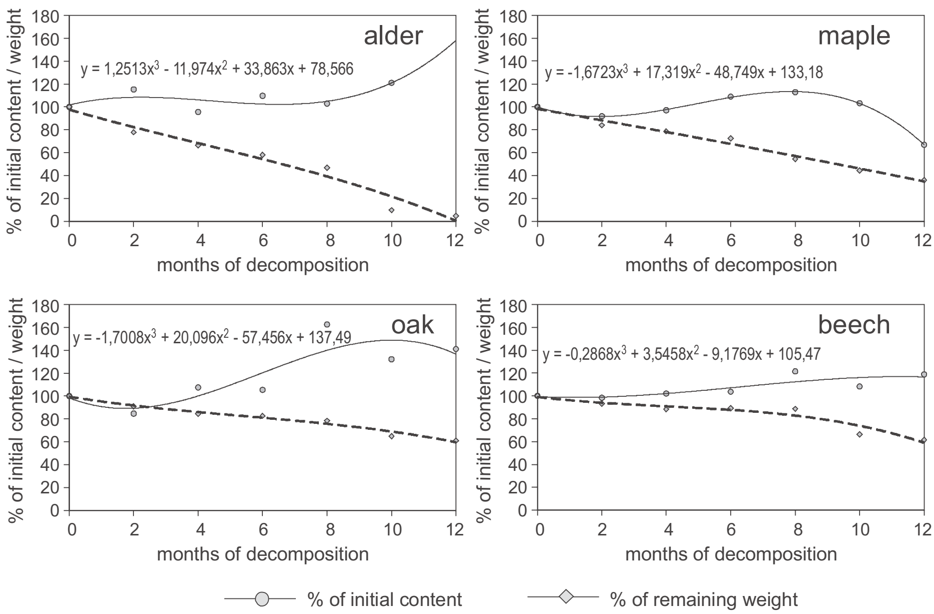

Figure 4. Changes in the content of Sr and weight loss during decomposition (based on mean values)

decrease of the content from 49.5 to 12.1 mg/kg. In maple leaves during the first half of the year, leaching and decrease of the content from 15.2 mg/kg to 6.6 mg/kg was observed and then accumulation and increase up to 15.5 mg/kg (Table 3, Fig. 3).

The accumulation of Sr was observed in every type of litter. The highest intensity of the process was noticed in alder (changes in content from 34.4 to 41.6 mg/kg) and oak (from 18.0 to 25.4 mg/kg) and smaller in beech (from 32.8 to 39.8 mg/kg) and maple (from 81.7 to 92.2 mg/kg) leaves (Table 3, Fig. 4).

Comparable content of Zn was noticed in alder, oak and beech initial material – 23.1, 18.6 and 22.8 mg/kg, respectively, and lower one in maple – 9.8 mg/kg (Table 3). In oak and beech leaves, the content of the element changed along with weight loss, whereas in alder and especially in oak leaves accumulation was observed (Fig. 5).

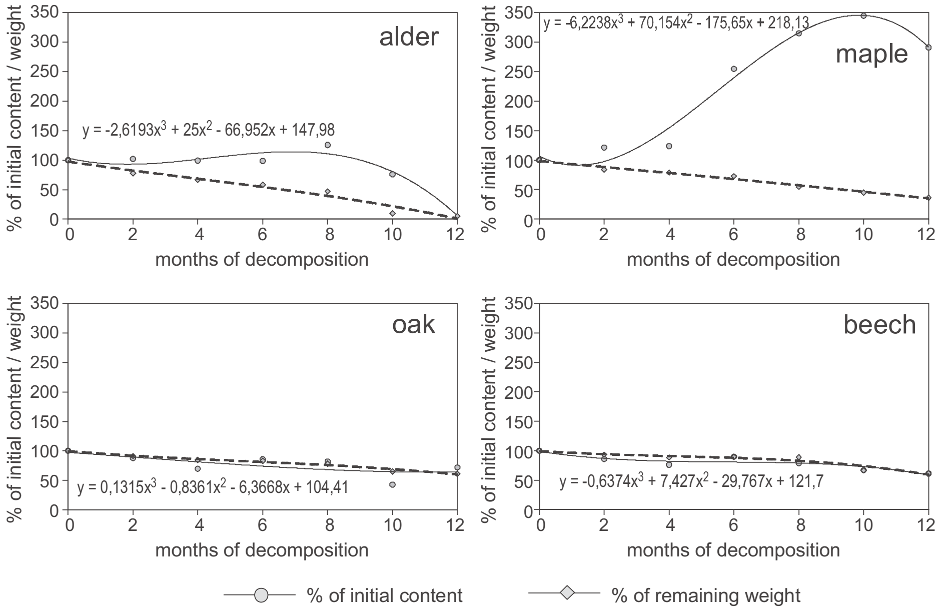

Figure 5. Changes in the content of Zn and weight loss during decomposition (based on mean values)

4. Discussion

Litter decomposition, as a result of mineralisation and humification, is a multi-stage, biochemical process controlled by a complex of slightly different key factors in each of the stages. The rate of decomposition in initial phase is strongly affected by chemical composition of the initial material and site conditions (Berg and Staaf 1980; Berg et al. 1987; Prescott 1996; Cortez 1998; Limpens and Berendse 2003; Jonczak 2009; Preston et al. 2009). The bioavailability of nutrients, especially nitrogen as well as water presence determines the intensity of litter colonisation by microorganisms. In poor in nutrients litter, the process of colonisation can be accelerated by influx of nutrients from external sources, like soil or admixtures of rich in the components litter (Taylor et al. 1989; Dziadowiec 1990; Prescott 1996; Salamanca et al. 1998; Robinson et al. 1999). The content and chemistry of resistance to decomposition lignins are important factors controlling the decomposition rate in its second phase (Gill and Lavender 1983; Berg et al. 1984; Tablot et al. 2012).

Intensity of decay can be inhibited by excessive concentrations of different organic and inorganic contaminants, including heavy metals (Berg et al. 1991; Cotrufo et al. 1995). However, limit values for heavy metals are relatively high – for example, 300 mg/kg for Zn and 20 mg/kg for Cu (Tyler 1992) – and are exceeded only in the vicinity of emission sources. In stands located over the range of the objects, the content of heavy metals in litter is usually small (Małek et al. 2001; Jonczak 2013). The initial concentrations of Cu, Mn, Ni, Sr and Zn in the investigated types of litter varied, but in general were low or medium and did not exceed limit values (Table 3).

The release of the elements during decomposition can run according to different patterns. Some of the elements are always released in a similar way, despite the kind of litter. For example potassium, which is present in plants only as an ionic form, is strongly leached just in the initial phase of decomposition. In turn, aluminium and iron are usually accumulated, which is a result of bonding of their ionic forms by newly formed humic acids (Dziadowiec 1990). However, most of the elements can be released in different patterns depending on their content in initial material, bioavailability in site, needs of living organisms, time-varying weather conditions and other factors. Our study shows that in the same site conditions, including temperature, humidity and a complex of soil properties, release patterns of Cu, Mn, Ni, Sr and Zn are strongly affected by chemical composition of initial material. In general, increasing/upward trends in the content of analysed elements, affected by biological or chemical accumulation, were observed in poorest in the elements materials. The source of Cu, Mn, Sr and Zn influx to litter was probably soil where, in general, higher concentrations of the metals were observed in comparison with initial material. In rich in elements types of material, more or less intensive leaching was observed. Much lower concentrations of Ni in soil than in initial material and the accumulation of this element in alder and oak leaves suggest an impact of other external factors. Lomander

Table 4. Correlation coefficients between the contents of metals in leaves during decomposition (in bold correlations statistically significant at p.05)

Correlated metals	Alder	Maple	Oak	Beech
Cu vs Mn	**0.823**	**0.797**	-0.357	0.552
Cu vs Ni	-0.523	-0.145	0.117	0.655
Cu vs Sr	-0.343	-0.014	0.499	-0.382
Cu vs Zn	0.073	**0.989**	-0.229	**0.946**
Mn vs Ni	-0.777	0.432	-0.644	0.571
Mn vs Sr	-0.556	-0.452	-0.503	-0.389
Mn vs Zn	0.375	0.731	0.692	0.465
Ni vs Sr	0.522	-0.724	-0.020	**-0.787**
Ni vr Zn	-0.608	-0.237	-0.282	**0.768**
Sr vs Zn	-0.522	0.075	-0.403	-0.621

and Johansson (2001) suggest that in litter bag experiments, newly fallen litter can be the source of some elements. Our study was conducted only for one year, so we have to exclude the influence of tree leaf litter but we cannot exclude the influence of litter from herb layer. In medium rich in metal materials, the concentrations changed usually in a way close to the weight loss. Two- or three-stage character of the release of the elements observed in a few cases can be an effect of indirect or direct impact of the succession of seasons, and gradual decomposition of organic compounds of different resistance to decomposition (usually associated with specific cellular structures). Only in a few cases statistically significant differences between the contents of metals were stated (Table 4), which suggests different patterns of release of each of them.

5. Conclusions

The results of our study indicate that the dynamics of Cu, Mn, Ni, Sr and Zn release from different materials decaying in the same site conditions can vary. It seems that differentiated chemistry of initial materials including the content of investigated metals and the ratio of the metals content in leaves to the content in soil were the main factors determining the dynamics of the release. The recorded concentrations of metals in initial materials used in the experiment were various but in general low and did not exceed limit values for decomposition rate. In poor in metal leaves, where their concentrations were usually lower in comparison with soil, upward trends affected by microbiological or chemical accumulation were observed. Especially, the high accumulation was noticed for Cu, Mn and Zn in maple; Ni in alder; and Sr in alder, maple and oak leaves. Faster decrease of Ni concentration than the weight loss was observed in beech leaves. Changes in the contents of Cu in beech, Mn in oak and beech, and Zn in oak and beech leaves were related to weight loss. Sometimes two- or three-stage process of release was reported, which can be a result of seasonal dynamics of leaching, soil biological activity, uptake intensity and processes of microbiological and chemical accumulation. The contents of Cu, Mn, Ni, Sr and Zn changed according to various patterns, which is confirmed by very small quantity of statistically significant correlations between the contents of the elements during the decomposition.

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Contributions

J.J. designed the study, conducted field study and chemical analysis of leaves and soils, analysed the data and wrote most of the manuscript. A.P. conducted some chemical analysis of leaves, analysed the data and wrote a part of the manuscript. Z.S. described plant communities in a study plot and wrote a part of the manuscript.