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THE TOTAL CONTENT OF NITROGEN IN LEAVES AND WOOD OF TREES GROWING IN THE AREA AFFECTED BY THE GŁOGÓW COPPER SMELTER

Jakub Kostecki, Andrzej Greinert, Michał Drab, Róża Wasylewicz, Mariola Szafraniec, Grzegorz Stodulski, Maciej Wypych

Department of Land Protection and Reclamation
University of Zielona Góra

Abstract

Soils affected by industrial emissions of a copper smelter may contain high amounts of heavy metals. Heavy metal infiltration across the soil is a potential source of groundwater contamination. Simultaneously, many ions, especially Cu^{2+} and Pb^{2+}, can be accumulated by plants growing within the emission range. The aim of this study was to determine the influence of high Cu and Pb soil contamination on the total nitrogen content in leaves and wood of trees growing in an area exposed to copper smelter emissions.

Samples of leaves and wood of *Populus robusta* L. and *Betula pendula* L. as well as soil samples were taken from an area affected by industrial emissions, namely from the former sanitary zone of the Głogów Copper Smelter. The samples were collected in 2010. The particle size distribution, pH, organic carbon, total nitrogen and the total content of Cu and Pb in the soil samples were determined. In the plant samples (foliage and trunks), the total nitrogen was assayed. The results were analysed statistically.

The following conclusions were drawn: the litter horizon of soils affected by industrial emissions contains high level of heavy metals (3450-5400 mg Cu kg^{-1}, 1020-1500 mg Pb kg^{-1}), exceeding threshold values for industrial areas. Also the humic horizon is characterised by an increased Cu and Pb content: 174-1530 mg Cu kg^{-1} and 268-702 mg Pb kg^{-1}. The leaves of the tested species contained more nitrogen than the wood, although the birch wood contained more nitrogen then the poplar. There was no difference in the nitrogen content of the annual tree rings of both species. Despite high levels of copper and lead in the tested soils, there was no effect of this factor on the nitrogen content of the leaves, bark and wood of the studied trees.

Key words: nitrogen, copper, lead, copper smelter, industrial pollution.

Jakub Kostecki, PhD, , Department of Land Protection and Reclamation, Institute of Environmental Engineering, University of Zielona Góra, Prof. Z. Szafrana 15, 65-516 Zielona Góra, Poland, e-mail: J.Kostecki@iis.uz.zgora.pl

INTRODUCTION

The metallurgical industry causes adverse effects on the natural environment. The main factor responsible for environment pollution is the emission of metalliferous dust and gases (MARTLEY et al. 2004). The area around the Głogów Copper Smelter is contaminated with heavy metals, especially with copper and lead (MEDYŃSKA et al. 2009, ROSADA, GRZESIAK 2009, DRZYMAŁA, SPYCHALSKI 2011). The described situation, persisting for decades, in 1990 forced the Governor of Legnica to establish a sanitary zone around the copper smelter. The sanitary zone originally covered 2,840 ha. The land was bought and the local inhabitants resettled. The soil was limed, and then the whole area was planted with trees: poplar (*Populus robusta* L.) and birch (*Betula pendula* L.). The zone has been under continuous environmental pollution monitoring since then.

The impact of heavy metals on the environment is widely described in literature. The vast majority of reports on this subject relates to an increase in soil pollution with heavy metals (ALLOWAY, AYRES 1997, KABATA-PENDIAS, PENDIAS 2001, MOCEK et al. 2006, ROSADA, GRZESIAK 2009). Many studies (PANKOVIČ et al. 2000, KABATA-PENDIAS, PENDIAS, 2001, KABATA-PENDIAS 2004, XIONG et al. 2006, KE et al. 2007, SHAHBAZ et al. 2010) show that the uptake of nutrients can be affected by the presence of other elements, including heavy metals (the phenomenon of antagonism and synergism). Some authors (ANTOSIEWICZ 2005, LOCK et al. 2007, KNAPOWSKI et al. 2012) have reported that certain elements such as nitrogen and potassium, calcium and magnesium can reduce copper and lead retrieval by plants or (depending on plant tissues) increase the content of Cu and Pb (DOMAGAŁA-ŚWIĄTKIEWICZ, GĄSTOŁ 2013).

Nitrogen is one of the biogenic elements. It affects the growth and development of plants, and its deficiency interferes with vital processes (photosynthesis, creation and distribution of assimilates, the synthesis of proteins and chlorophyll). The impact of heavy metals on plant metabolism is a well-recognised topic (GARG and AGGARWAL 2011, SOLANKI and DHANKHAR 2011). NIEBOER and RICHARDSON (1980) described the important mechanism of heavy metal toxicity as a consequence of binding different chemical groups of different compounds, i.e. –SH group. The mechanism of heavy metals forming bonds with enzymes, whose activity is thereby inhibited is a very characteristic development, especially in respect of nitrite and nitrate reductase above a certain threshold (VAN ASSCHE, CLIJSTERS 1986, 1990, ARORA et al. 2010, SOLANKI, DHANKHAR 2011). KUCHARSKI et al. (2011) noted the significant decrease in the activity of many soil enzymes (dehydrogenase, urease, acid phosphatase, α-glucosidase and arylsulphatase) due to zinc pollution. According to observations made by ALLOWAY and AYRES (1997) and KABATA-PENDIAS and PENDIAS (2001), copper may affect the metabolism of nitrogen compounds in plants by raising the level of proteins. Nevertheless, literature references do not exhaust the question of significant correlations between the uptake of respective elements. The influence of heavy metals on the uptake of nitrogen by plants has been discussed in few publications (Hernández et al. 1997, Quariti et al. 1997, Lim et al. 2003, Ke et al. 2007, Shahbaz et al. 2010).

Most scientific papers have focused on microorganisms, herbaceous plants and the behaviour of mosses, whilst there is a shortage research on trees species. The aim of this study was to determine possible changes of the total nitrogen content in leaves and wood of trees growing in an area exposed to industrial emissions, especially on dust high in copper and lead.

MATERIAL AND METHODS

The study took place in the former sanitary zone of the Głogów Copper Smelter (Lower Silesia Province, the western part of Poland). Żukowice I, II and Bogomice are located within the sanitary zone. Żukowice I is about 0.1 km to the SW of the smelter, Żukowice II is about 0.3 km E, and Bogomice is about 1 km NE from the smelter (Figure 1). The control site was located at some distance from the smelter, – in Stypułów, about 15 km NW from the smelter (N: 51°41′44.30″ W: 15°36′13.70″).

Soil samples were taken in June 2010, from all genetic horizons of the soil profile. Each sample was collected as a mixed one, representing material from the whole depth of the horizon. Soil material was air-dried and sieved

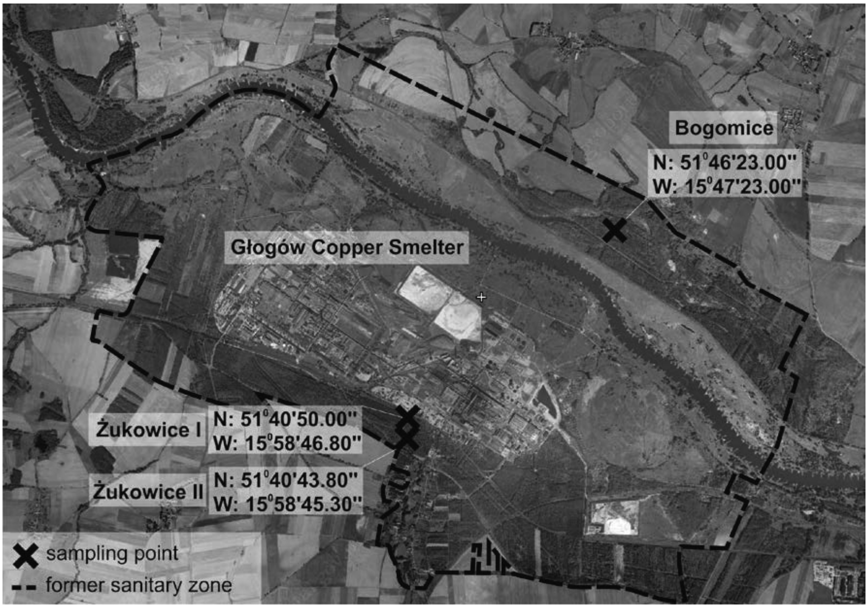

Fig. 1. Location of the site on the Geoportal map (2013)

through a sieve with a mesh diameter of 2.0 mm. Having prepared the material prepared as explained above, the following analyses were made:

- particle size distribution – using the areometric method (Mocek et al. 2006);
- pH – in H_2O and 1M KCl suspension (potentiometrically), soil:liquid 1:2.5 (Mocek et al. 2006);
- organic carbon – using the Tiurin's method (Mocek et al. 2006);
- total nitrogen – using the Kjeldahl method;
- Cu and Pb total content – using atomic absorption spectrometry, after mineralisation in *aqua regia* (PN-ISO 11466:2002).

All the soil analyses were performed in triplicate.

Averaged samples of unwashed leaves of *Populus robusta* L. and *Betula pendula* L. were collected in the autumn of 2010. After drying, the leaves were ground in a mill. After mineralization of the samples in concentrated H_2SO_4, the nitrogen was determined using the Kjeldahl method. The analyses were performed in triplicate. Averaged samples of wood were taken from saw-cut discs at a height of 1.3 m from 3 selected trees at each site. Each disc was divided mechanically into 5-year tree rings. After drying and grinding, the tree samples were mineralized in concentrated H_2SO_4. Nitrogen in the solution was determined with the Kjeldahl method. The analyses were performed in triplicate.

The results were statistically analysed using the Statsoft Statistica 10 procedures.

RESULTS AND DISCUSSION

The results of this study showed a wide variation in soil properties in the area surrounding the Copper Smelter. This is due to fluvial activity (the Odra River Valley), land relief, lithogenesis (mosaic of the sand, loam and organic materials), pedogenesis (Albic Luvisols, Haplic Gleysols, Mollic Fluvisols, Fluvic Cambisols, Fluvic Endogleyic Cambisols, Sapric Histosols, Gleyic Phaeozems, Brunic Arenosols) and also anthropogenic pressure (agriculture, industry, reclamation). The physical and chemical properties of the soils are shown in Table 1. The particle size distribution of the soils covering the sanitary zone is mostly that of sandy loam and loamy sand. The pH of the tested soils varies from acid (Żukowice I, Bogomice), neutral (Stypułów) to alkaline reactions (Żukowice II). This variation is a typical effect of liming as a reclamation technique (Żukowice, Bogomice) and of agricultural activities (Stypułów). In some literature references, information dust emmision increasing thesoil pH can be found (Medyńska-Juraszek, Kabała 2012). Next to the total concentration of heavy metals, the soil reaction is one of the most frequently cites factors implicating bioavailability of heavy metals..

Table 1

Selected properties of soil

Site	Depth	Sand	Silt	Clay	pH		C_{org}	$N_{tot.}$	C:N	$Cu_{tot.}$	$Pb_{tot.}$
		2.0-0.05 (mm)	0.05-0.002 (mm)	< 0.002 (mm)							
	(cm)	(%)			H_2O	1M KCl	(%)			(Mg kg^{-1})	
Żukowice I	3-0	-	-	-	5.9	5.5	-	1.58	-	5400	1320
	0-23	69	31	0	6.2	6	1.33	0.07	19	1530	416
	23-44	63	34	3	5.3	4.9	0.57	0.05	11.4	52	304
	44-59	58	33	9	5.5	5.4	0.54	0.04	13.5	45	79
	59-79	83	11	6	5.9	4.4	0.3	0.03	10	45	76
	>79	82	18	0	6.4	5.9	0.13	0.01	13	38	109
Żukowice II	2-0	85	15	0	6.9	6.6	3.14	0.34	9.2	3450	1020
	0-27	79	21	0	7.8	7	2.13	0.16	13.3	958	268
	27-40	78	22	0	7.8	7.1	1.61	0.14	11.5	41	60
	>40	87	13	0	7.9	7.2	1.26	0.12	10.5	100	75
Bogomice	3-0	-	-	-	6.3	5.9	-	2.1	-	4110	1510
	0-20	65	34	1	5.1	3.8	1.48	0.13	11.4	174	702
	20-37	61	37	2	5.2	3.8	1.35	0.12	11.3	99	114
	37-67	65	34	1	5.7	4.3	1.23	0.1	12.3	85	108
	>67	80	19	1	5.6	4.3	1.26	0.1	12.6	60	106
Stypułów	0-30	90	10	0	7.7	7.2	0.92	0.07	13.1	7	10
	30-70	97	3	0	7.4	6.5	0.14	0.02	7	6	9
	70-90	98	2	0	7.4	6.6	0.17	0.03	5.7	6	9
	>90	79	12	9	6.7	5.2	0.3	0.03	10	7	9

The content of both organic carbon and total nitrogen in the surface and subsurface horizons was significantly higher than in samples from deeper layers. This regularity recurred at all sites. The highest average content of organic carbon was found in the soil profiles from Żukowice II and Bogomice, and the lowest – from Stypułów. The highest average content of total nitrogen was found in Bogomice and Żukowice I, and the lowest – again in Stypułów. Differences in the content of these elements are an effect of genetic variation. One possible reason is the dominance of different plant species, e.g.the dominant species in the former sanitary zone is the poplar (*Populus robusta* L.), and the admixed species is the birch (*Betula pendula* L.). The control site was dominated by the oak. The difference in the carbon and nitrogen content can be habitat-dependent, as was shown by ENOKI, KAWAGUCHI (2000). Statistical analysis showed a highly significant ($P < 0.01$) effect of the sampling depth and the total nitrogen content.

The C: N ratio of the tested soils varied. In most of the samples from the former sanitary zone, it amounted to 12 : 1. A slightly higher C:N ratio was observed in samples taken from the control site, but even in this profile a low C:N index was found. The average ratio in the profiles ranged from 9.2 to 19.0 in the areas affected by industrial emissions and from 5.7 to 13.1 in the control area. The differences are connected with the pedogenesis and land use (including covering with trees) rather than with the industrial influence. The impact of heavy metals on the organic matter mineralisation cannot be confirmed unambiguously. The mineralisation processes may be limited by the diversity, activity and abundance of soil microorganisms (NEILL, GIGNOUX 2006).

The highest concentration of heavy metals was found in the humus and subsurface horizons of the tested soil profiles. This is particularly marked in the site located in the former sanitary zone, where the metal content exceeds the limits for industrial areas in Poland – limits for Cu and Pb: 600 mg kg^{-1} (*Regulation* … 2002). The horizons located lower in the soil profiles contain copper and lead at levels typical for uncontaminated areas. What is very characteristic for the described area of the sanitary zone is the presence of extremely big differences in the heavy metal content in different places, even the ones located in close proximity. A clear manifestation was the outcome of a comparison with other data from this area – 855-13143 mg Cu kg^{-1} and 585-9181 mg Pb kg^{-1} in the 0 horizon and 200-2875 mg Cu kg^{-1} and 92-723 mg Pb kg^{-1} in the Ap horizon (MEDYŃSKA-JURASZEK, KABAŁA 2012). A much lower heavy metal content was found in the control samples.

The high content of heavy metals in soils covering areas exposed to industrial impact is a well-known fact (KABATA-PENDIAS, PENDIAS 2001, MEDYŃSKA-JURASZEK, KABAŁA 2012). In addition to the main source of pollution in the analyzed former sanitary zone (metal containing dusts), secondary pollution occurs as a result of litter decomposition and dust washed off the leaves into the soil. It is worth mentioning that, according to literature reports, most of the described pollution factors have only exerted a superficial impact (MEDYŃSKA-JURASZEK, KABAŁA 2012). Thus, soil sorption comes to the foreground as a process realised both by clay minerals and organic soil matter. It prevents the heavy metals from penetrating to the deeper soil horizons *via* ground and surface waters. The high content of organic matter in the litter and humus horizons effectively influences the Pb and Cu sorption capability. Statistical analysis showed a significant positive correlation between the content of copper and lead and organic matter in the soil ($r_{\text{Pb-C}} = 0.75$, $r_{\text{Cu-C}} = 0.76$).

Many studies show differences in the nitrogen content in plant tissues. In our analyses performed on the chosen tree species, a significantly higher nitrogen content was found in the bark than in the wood (Figure 2). More nitrogen was found in the poplar bark than in the birch bark. Annual tree-rings showed small differences in the content of this element, although a higher content of nitrogen was found in the birch wood than in the poplar wood. The total nitrogen content in the leaves varied within a wide range (Figure 3). The birch leaves had a higher content of nitrogen than the poplar

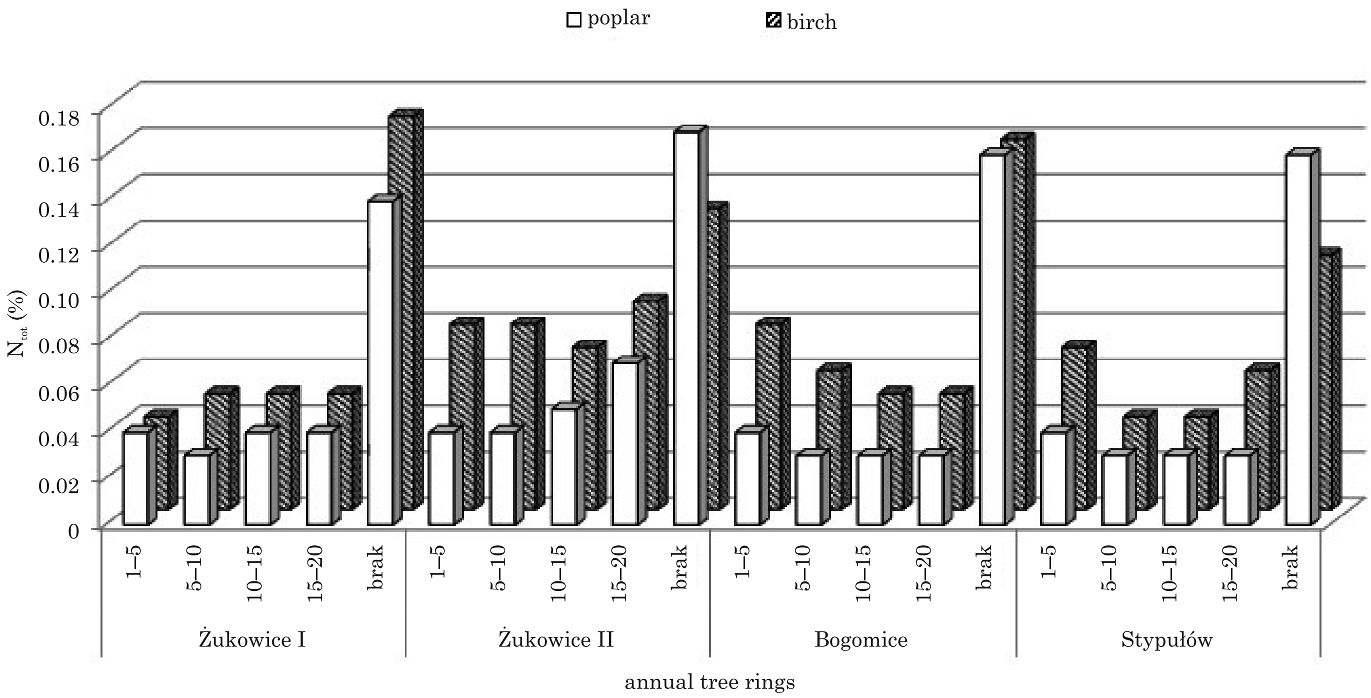

Fig. 2. The nitrogen content in the annual tree-rings of poplar and birch

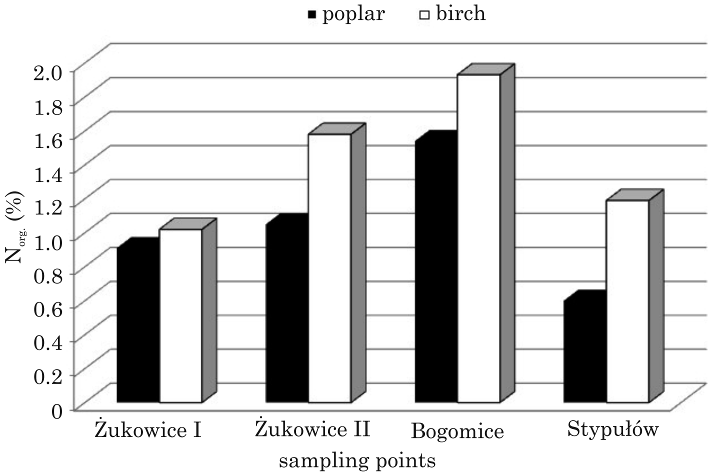

Fig. 3. The nitrogen content of the poplar and birch leaves

ones – differences from 2 to 98% were observed. A higher content was found in young tissues (leaves and bark) than in the wood of the birch and poplar.

The results of the nitrogen content were lower than those found in the literature or both the birch (Saramäki, Hytönen 2004) and the poplar (Fortier et al. 2010). Several authors have indicated that the nitrogen content in plant tissues may be affected by many factors, such as the plant age, season of the year, exposure and nutrient content of the soil (Coll et al. 2010, Fortier et al. 2010).

The statistical analysis showed no relationship between the content of heavy metals and nitrogen in plant samples taken from the areas exposed to the direct impact of the industrial plant (Table 2). A positive correlation was found between the content of nitrogen in the poplar stem and the lead content of the soil (r = 0.99) and also between the content of nitrogen in the birch stem and the copper content of the soil (r = 0.96). In the control area, a correlation between the C content of the soil and the N content of the poplar stem (r = 0.98) and another one between the N content of the soil and the N content of the the poplar stem (r = 0.98) were found. Analysing the behaviour of trees growing in the sanitary zone, a positive relation between the C:N ratio of the soil and the nitrogen content of the stem of birch (r = 0.98) was noted.

The decomposition of organic matter is possible only with the participation of micro-organisms. Their biodiversity and abundance turns into the efficiency and quality of the matter decomposed. Many authors emphasize the reduced activity of the soil micro flora in areas highly contaminated with heavy metals (Alloway, Ayres 1997, Kabata-Pendias, Pendias 2001, Wang et al. 2007). Fertilisation of soils contaminated with heavy metals with nutrients available for microorganisms can be beneficial to the growth and colony size (Peltola et al. 2006, Odlare, Pell 2009). Lime applied in the 1990s

Table 2

Correlation matrices for chosen soil properties and nitrogen content in plant organs

Variable	Correlation coefficient, $p < 0.05$					
	Populus robusta L.			*Betula pendula* L.		
	N_{leafs} (%)	N_{stem} (%)	N_{bark} (%)	N_{leafs} (%)	N_{stem} (%)	N_{bark} (%)
Samples from the former sanitary zone of Głogów Copper Smelter						
pH H_2O	-0.37	0.69*	0.11	0.00	0.67*	-0.79*
pH 1M KCl	-0.55	0.71*	-0.05	-0.23	0.59	-0.65
$C_{org.}$ (%)	0.11	0.19	-0.14	-0.05	-0.07	0.32
$N_{tot.}$ (%)	0.21	0.21	-0.01	0.08	0.09	0.23
C:N	0.09	0.16	-0.19	-0.08	-0.10	0.34
$Cu_{tot.}$ (mg kg^{-1})	-0.16	0.16	-0.07	-0.20	0.04	0.05
Pb_{tot} (mg kg^{-1})	0.13	0.03	0.00	0.04	0.14	0.11
Samples from control site						
pH H_2O	0.00	0.63	0.00	-0.49	0.00	0.00
pH 1M KCl	0.05	0.65	-0.05	-0.44	0.03	0.05
$C_{org.}$ (%)	0.03	0.98*	-0.03	-0.05	0.88	0.03
$N_{tot.}$ (%)	0.18	0.98*	-0.18	0.04	0.83	0.18
C:N	-0.16	0.84	0.16	-0.03	0.98*	-0.16
$Cu_{tot.}$ (mg kg^{-1})	0.00	0.58	0.00	0.30	0.96*	0.00
Pb_{tot} (mg·kg^{-1})	0.00	0.99*	0.00	-0.17	0.78	0.00

* statistically significant

(especially in the first years) might have accelerated the rate of the mineralisation of organic matter and increased the abundance of nitrogen. The soil nitrogen unavailable for microorganisms could have been translocated deeper into the soil profile (in the form of nitrates), released into the atmosphere (in the form of ammonia) or lost in the process of denitrification.

The study on the afforested areas in the vicinity of the Głogów Copper Smelter shows satisfactory condition of the trees. Despite the high heavy metal content in the top horizons of soil, the nitrogen content in the leaves, wood and bark of the tested plants is comparable to the one in the samples taken from the control site. Such an effect, dependent on the biological barriers to the heavy metal uptake by plants has been stated by many authors (MEDYŃSKA et al. 2009). Comparing to the results of other studies, a lower content of nitrogen in tree tissue has been noted (FORTIER et al. 2010, PEARSON et al. 2010, PALVIAINEN, FINÉR 2011).

CONCLUSIONS

1. The topsoil contained more nitrogen, copper and lead than the deeper layers – as the sampling depth increased, the content of the analysed elements decreased.

2. The total nitrogen content in leaves and bark was much higher than in the wood of the tested tree species at all research sites. The birch wood contained more nitrogen than the poplar wood. Annual tree rings did not show differences in the nitrogen content during the growth of the poplars and birches.

3. The influence of the high content of heavy metals in soils affected by industrial emissions on the nitrogen content in the plant tissues was unobserved.

4. Samples taken from the control site with well-balanced soil chemical composition, showed a significant correlation between the content of copper in the soil, and the nitrogen in the leaves of the birch and poplar and the bark of birch. No significant correlations were found between the lead content of the soil of the control area and the nitrogen content of the plant tissues.

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