HEAVY METALS IN SOILS OF SECONDARY SPRUCE FORESTS IN THE SLOVENSKÉ RUDOHORIE MOUNTAINS, AND THEIR ACCUMULATION BY SOME TREES

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Abstract

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The contribution presents the results on the accumulation of heavy metals by leaves and wooden parts of 9 years old seedlings of some trees (*Tilia cordata, Acer pseudoplatanus*). The seedlings were planted in permanent experimental plots being established in 1996 on clearings after died secondary spruce forests in district of the village of Nálepkovo (Slovenské rudohorie Mts). The results from year 2004 are compared with those observed in 1998, which were collected from the same trees and the same localities. Lime tree (*Tilia cordata*) appeared again as an important hyper-accumulator that accumulates heavy metals in its wooden tissues and not leaves, contrary to *Acer pseudoplatanus*.

Key words: heavy metals, accumulation by trees

Actual state of dealt problem

Ecological-sanitation measures being applied in stands and soils of calamity-destroyed secondary spruce forests have been observed during years 1995–2004 in the vicinity of the village of Nálepkovo. The study area is located in the Volovské vrchy Mts (Slovenské rudohorie Mts), in altitudes between 600 and 1200 m, where total annual rainfall reaches 790 mm and average temperature varies at about 6 °C. Geological ground is built by *gemerid* rocks (porphyroids, phylite and quartzite), from which Cambic Podzols have developed

(Juráni, 1997). Soil reaction varies between 3.3 and 3.9 (measured in KCl) in whole profile (Dlapa et al., 1997a). The development of such soils was affected by secondary spruce forests as they had been artificially as well as naturally regenerated for at least two generations. The health was getting worse by the end of 70s, and in the year 2000, secondary spruce stands totally crashed. Doubtlessly the impact of industrial imissions from long-distance transmissions and local sources, which occurred in 60s and 70s of the past century, can be added to various causes of massive dying of secondary spruce forests (synergic effect of numerous factors). After recession of metal industry in this region, heavy metals remained in soil of forest ecosystems as pollutants (Dlapa et al., 1997b). Besides lead, copper and nickel, especially high contents of mercury (Hg) and arsenic (As) can be observed in upper soil horizons. Moreover, such damage occurs in soils within aluminium buffer range that is critical for development of forest ecosystems (deficiency of macro-nutrients such as Ca^{2+}, Mg^{2+}, K^{+}, toxic effect of aluminium, inhibition of organic matter mineralization – Dlapa et al., 1997a).

The team of the Department of Soil Science, Faculty of Natural Sciences at the Comenius University in Bratislava, together with experts from the District forests of Nálepkovo, has studied the processes. Two permanent experimental plots were established on emerged calamity clearings, where target trees of future forests (*Fagus, Abies*) together with accumulation trees were planted. Especially *Tilia cordata* and *Acer pseudoplatanus* are considered as accumulators by this research. A special attention was paid to *Tilia cordata*, which has been already before planting assumed to accumulate heavy metals to its wooden and phloem tissues, not leaves; and that is most wanted effect as for biodegradation of heavy metals. This effect has been partially proven already three years after planting the *T. cordata* seedlings, i.e. in 1998 by Šomšák et al. (2000). We decided to repeat the measurement using the same seedlings 9-years after planting, i.e. 6 years after previous experiment, because the results of the initial experiment can be considered as informative only as seedling were adapting to new environment.

Methods

The samples were taken from those sites of the experimental plot, where sanitation measures, such as liming and fertilizing by phosphate fertilizers, have been applied; and non-limed sites certainly. Terminal branches were taken from 20 individuals of each tree species (*Tilia cordata, Acer pseudoplatanus*), from which the average samples were prepared. Leaves together with peduncles were considered as a leaf part. Wooden samples were taken from 1–3 years old branches after defoliation. Also in this case an average sample was prepared.

The results come from two separate experimental plots. The first plot – Surovec – occurs in altitude 800–870 m with east exposition and 50% slope. The height of lime-tree individuals varies between 170 and 370 cm, maple tree between 90 and 210 cm. Plot No. 2 – Záhajnica – occurs in altitude 630–690 m, exposed to the north-west, with 30% slope. The height of study individuals is: *Tilia cordata* 70–130 cm, *Acer pseudoplatanus* 60–370 cm.

Chemical analyses were provided by the Forest Research Institute in Zvolen. Total contents of arsenic (As), cadmium (Cd), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) were analysed in dry matter. Following methods were used: AAS.ETA for As, Cd, Cu, Ni and P, the method AES-ICP for Zn. Mercury (Hg) was analysed in solid samples (AMA 254).

The results are summarised in three tables. Table 1 presents data obtained in 2004 from leaves and wooden tissues in two experimental plots, both from limed and non-limed sites separately for *Tilia* and *Acer*. Table 2 compares in details over-mentioned results with those gathered in 1998 by Šomšák et al. (2000). Table 3 informs on decreasing trend in accumulation following individual elements.

The accumulation rates are given as total contents of a heavy metal in $mg.kg^{-1}$ of dry matter.

Results and discussion

First experiments with accumulation of heavy metals by "amelioration trees", such as *Tilia cordata* and *Acer pseudoplatanus*, showed that *Tilia cordata* is better accumulator. It is especially because *T. cordata* accumulates prevailing part of taken heavy metals to its woody tissues, not leaves (Juráni et al., 1993). Accumulation of heavy metals to leaves does not improve soil properties, even opposite, falling-down leaves would return heavy metals back to upper soil horizons. The first stage of sampling the leaves and woods from 3 years old seedlings of lime tree and maple being realised in 1998 in experimental plots of Nálepkovo (Šomšák et al., 2000) proved this assumption, however, only in the case of *T. cordata*. Higher rates of accumulation by wooden tissues were observed for cadmium (Cd) as wood accumulated nearly the 100% more of Cd compared to leaves. Similarly the 75% increase of copper (Cu) was observed in wood compared to leaves, the 50% increase of zinc (Zn) and 10% of nickel (Ni) in non-limed, and 120% in limed experimental plot.

Repeated experiment from year 2004, being realised in the same experimental plots and the same tree individuals though 9 years older, are summarised by Table 1. Also repeated sampling has proven this trend, however only in the plot No. 2 (Záhajnica), and limed sites actually.

Acer pseudoplatanus appeared as bad accumulation tree. Prevailing part of accumulated heavy metals occurred in leaves as given by the experiment realised in 1998 (three years old seedlings – Šomšák et al., 2000) as well as in 2004. A less significant exception is seen in a higher accumulation of cadmium by wooden parts of maple tree.

The results of accumulated metals gathered from years 1998 and 2004 are in details presented by Table 2. Based on comparison we are allowed to conclude following conclusions:

T a b l e 1. The accumulation of heavy metals in leaves and woody tissues of *Tilia cordata* and *Acer pseudoplatanus* observed in 2004 in semi practice experimental plots (Nálepkovo).

Element		As		Cd		Cu		Hg		Ni		Pb		Zn	
Locality, tree		n	l	n	l	n	l	n	l	n	l	n	l	n	l
Plot No.1 Surovec	leaves	< 1.00	< 1.00	0.126	1.46	4.91	4.1	0.0266	0.0282	3.651	1.681	3.202	0.959	31.8	30.0
Tilia cordata	wood	< 1.00	< 1.00	0.19	0.097	4.38	4.12	0.0062	0.0062	2.072	0.491	1.506	1.055	56.3	56.4
Plot No.2 Záhajnica	leaves	< 1.00	< 1.00	0.14	0.185	5.64	4.12	0.0269	0.0264	3.622	2.21	1.117	1.075	28.1	34.7
Tilia cordata	wood	< 1.00	< 1.00	0.25	0.114	5.09	6.59	0.0066	0.065	1.601	< 1.00	0.492	1.914	57.9	64.0
Plot No.1 Surovec	leaves	< 1.00	< 1.00	0.195	0.22	4.33	5.0	0.0286	0.0265	1.378	1.326	1.225	1.209	40.1	46.9
Acer pseudoplatanus	wood	< 1.00	< 1.00	0.254	0.183	2.48	2.87	0.0057	0.0042	0.544	0.431	1.071	0.804	26.4	25.5
Plot No.2 Záhajnica	leaves	< 1.00	< 1.00	0.213	0.197	4.95	3.56	0.0264	0.0343	1.994	0.698	0.658	1.04	49.6	46.6
Acer pseudoplatanus	wood	< 1.00	< 1.00	0.269	0.274	2.02	2.59	0.0046	0.0045	1.365	1.225	0.42	0.815	31.2	33.3

Notes: n – not limed, l - limed

T a b l e 2. Measured accumulations of metals in *Tilia cordata* and *Acer pseudoplatanus* in two experimental plots (years 1998 and 2004) in limed and non-limed sites – in mg DM kg^{-1}.

Element	Tree	Vegetative organ	Experimental plot	1998		2004	
				not limed	limed	not limed	limed
As	*Tilia cordata*	leaves	Surovec	0.100	0.100	< 1.000	< 1.000
			Záhajnica	0.100	0.100	< 1.000	< 1.000
		wood	Surovec	0.100	0.100	< 1.000	< 1.000
			Záhajnica	0.100	0.100	< 1.000	< 1.000
	Acer pseudoplatanus	leaves	Surovec	0.100	0.212	< 1.000	< 1.000
			Záhajnica	0.100	0.100	< 1.000	< 1.000
		wood	Surovec	0.100	1.100	< 1.000	< 1.000
			Záhajnica	0.624	0.287	< 1.000	< 1.000
Cd	*Tilia cordata*	leaves	Surovec	0.232	0.233	0.126	0.146
			Záhajnica	0.298	0.270	0.14	0.185
		wood	Surovec	0.348	0.472	0.19	0.097
			Záhajnica	0.635	0.572	0.25	0.114
	Acer pseudoplatanus	leaves	Surovec	0.482	0.452	0.195	0.220
			Záhajnica	0.486	0.543	0.213	0.197
		wood	Surovec	0.517	0.514	0.254	0.183
			Záhajnica	0.364	0.46	0.269	0.274
Cu	*Tilia cordata*	leaves	Surovec	8.880	10.990	4.91	4.10
			Záhajnica	9.930	9.670	5.64	4.12
		wood	Surovec	15.920	15.190	4.38	4.12
			Záhajnica	19.390	22.730	5.09	6.59
	Acer pseudoplatanus	leaves	Surovec	8.110	4.83	4.33	5.00
			Záhajnica	6.830	4.550	4.95	3.56
		wood	Surovec	11.920	5.080	2.48	2.87
			Záhajnica	6.51	7.47	2.02	2.59
Hg	*Tilia cordata*	leaves	Surovec	0.0754	0.0621	0.0266	0.0282
			Záhajnica	0.0592	0.0483	0.0269	0.0264
		wood	Surovec	0.0221	0.0238	0.0062	0.0062
			Záhajnica	0.0208	0.0247	0.0066	0.0065
	Acer pseudoplatanus	leaves	Surovec	0.0574	0.0574	0.0286	0.0265
			Záhajnica	0.0454	0.0137	0.0264	0.0343
		wood	Surovec	0.0526	0.0322	0.0057	0.0042
			Záhajnica	0.0322	0.0163	0.0660	0.0065

T a b l e 2. (Continued)

Element	Tree	Vegetative organ	Experimental plot	1998 not limed	1998 limed	2004 not limed	2004 limed
Ni	*Tilia cordata*	leaves	Surovec	2.378	5.084	3.651	1.681
			Záhajnica	4.127	3.955	3.622	2.21
		wood	Surovec	5.263	2.466	2.072	0.491
			Záhajnica	3.862	12.493	1.601	< 1.00
	Acer pseudoplatanus	leaves	Surovec	1.620	1.61	1.378	1.326
			Záhajnica	10.110	2.260	1.994	0.698
		wood	Surovec	2.390	0.990	0.544	0.431
			Záhajnica	5.10	1.88	1.365	1.225
Pb	*Tilia cordata*	leaves	Surovec	2.60	6.75	3.202	0.959
			Záhajnica	2.23	2.37	1.117	1.075
		wood	Surovec	2.02	2.43	1.506	1.055
			Záhajnica	2.38	2.29	0.492	1.914
	Acer pseudoplatanus	leaves	Surovec	3.97	2.53	1.225	1.209
			Záhajnica	4.66	2.50	0.658	1.04
		wood	Surovec	2.41	2.68	1.071	0.804
			Záhajnica	2.76	3.81	0.42	0.815
Zn	*Tilia cordata*	leaves	Surovec	37.66	24.340	31.8	30.0
			Záhajnica	18.72	26.270	28.1	34.7
		wood	Surovec	88.03	80.210	56.3	56.4
			Záhajnica	93.50	79.530	57.9	64.0
	Acer pseudoplatanus	leaves	Surovec	58.84	47.82	40.1	46.9
			Záhajnica	53.59	24.250	49.6	46.6
		wood	Surovec	35.620	22.720	26.4	25.5
			Záhajnica	41.73	41.8	31.2	33.3

Tilia cordata

- cadmium (Cd), copper (Cu), nickel (Ni), zinc (Zn) and partially lead (Pb) are preferentially accumulated by wood compared to leaves,
- site-specific differences were revealed in accumulation of observed heavy metals after comparing two experimental plots, and it is true nearly for all dealt elements, and for first as well as second sampling period (1998 and 2004),
- the effect of liming on accumulation of heavy metals by vegetative organs of *Tilia cordata* appeared as very variable, however, some elements were accumulated in lower rates when sites had been treated by liming (Cd, Hg).

T a b l e 3. Average weight of accumulated elements in decreasing order in two permanent experimental plots (Surovec, Záhajnica) in mg DM.kg^{-1} .

Element	Tree	Vegetative organ	1998 Not limed	1998 limed	2004 Not limed	2004 Limed
Zn	*Tilia cordata*	leaves	28.19	25.30	29.95	32.35
		wood	90.76	79.87	57.10	60.20
	Acer pseudoplatanus	leaves	56.21	36.03	44.73	46.25
		wood	38.67	32.26	28.80	29.90
Cu	*Tilia cordata*	leaves	9.36	10.33	5.27	29.4
		wood	17.65	19.46	4.73	5.35
	Acer pseudoplatanus	leaves	7.47	4.69	4.64	4.28
		wood	9.21	6.27	2.25	2.73
Ni	*Tilia cordata*	leaves	3.152	4.519	3.636	1.945
		wood	4.562	7.479	1.836	0.295
	Acer pseudoplatanus	leaves	5.860	1.930	1.686	1.012
		wood	3.740	1.430	0.954	1.078
Pb	*Tilia cordata*	leaves	2.410	4.560	2.159	1.012
		wood	2.190	2.310	0.999	1.484
	Acer pseudoplatanus	leaves	4.315	2.015	0.441	1.124
		wood	2.585	3.245	0.245	0.165
Cd	*Tilia cordata*	leaves	0.260	0.251	0.132	0.165
		wood	0.491	0.522	0.220	0.105
	Acer pseudoplatanus	leaves	0.484	0.477	0.204	0.203
		wood	0.440	0.487	0.261	0.228
Hg	*Tilia cordata*	leaves	0.0673	0.0552	0.0277	0.0273
		wood	0.0214	0.0242	0.0064	0.0063
	Acer pseudoplatanus	leaves	0.0514	0.0355	0.0275	0.0304
		wood	0.0424	0.0242	0.0358	0.0053
As	*Tilia cordata*	leaves	< 1.00	< 1.00	< 1.00	< 1.00
		wood	< 1.00	< 1.00	< 1.00	< 1.00
	Acer pseudoplatanus	leaves	< 1.00	< 1.00	< 1.00	< 1.00
		wood	< 1.00	< 1.00	< 1.00	< 1.00

Acer pseudoplatanus

- both experiments (1998, 2004) clearly show that maple tree accumulates significantly more of taken pollutants in its leaves as in wood. The conclusion is valid for both experimental plots (Surovec, Záhajnica), and similarly for limed and non-limed sites.

The total amount of accumulated pollutants is another important effect of sanitation trees, such as *Tilia cordata* and *Acer pseudoplatanus* in this case. Table 3 is organised by descending contents of individual accumulated elements. The table shows decreasing contents of dealt elements being accumulated by vegetative parts of observed tree species. Zinc (Zn) occurs on the top of the list of accumulation. It is important to highlight the accumulation of Zn by *Tilia cordata*, by its wooden tissues actually. There is to notice 40% more of Zn in woods compared to leaves in control site (non-limed), and even 100% more in limed segments of the experimental plots. The second experiment (2004) revealed generally lower contents of accumulated Zn, but the tendency to accumulate this element mostly by wood is proven as well. The gathering effect for zinc by *Acer pseudoplatanus* is high as well, however not effective for biodegradation issues.

The second place is attributed to copper (Cu). The results from the experiment in 1998 prove the accumulation in wooden tissues rather than in leaves in the case of *Tilia cordata* with nearly a 100% increase. Relatively surprising results were collected in 2004, when leaves accumulated more copper than wood. Moreover the total content of copper was much lower in year 2004 (200% less in wood and 95% less in leaves).

Nickel (Ni) is the next one element following the descending order given by Table 3. The results obtained in 1998 show again a higher accumulation effect of wooden organs in case of *Tilia cordata*. The values from year 2004 confirm a significant decrease of accumulated Ni in wood as well as in leaves.

Next element in the order of accumulation by trees, the fourth one actually, is lead (Pb). In this case however, the prevailing effect of accumulation by wood was not proved for maple tree. Even oppositely, leaves have accumulated higher contents of Pb in both years 1998 and 2004, excluding limed sites of the experimental plot in year 2004. *Acer pseudoplatanus* again shows higher accumulation by leaves then wood.

The fifth place is occupied by cadmium (Cd). The dominant role of wood in its accumulation was observed again, especially in year 1998. An interesting state is a higher accumulation by wood also for *A. pseudoplatanus*.

Mercury (Hg) occurs in the lowest contents in leaves and wooden organs. However, a final comparison shows that this element has accumulated in higher rates in leaves in both study trees.

There is no way to conclude the accumulation of arsenic (As) as the method used does not allow differentiating the values lower than 1.0.

Conclusion

The study of heavy metals that were absorbed in wooden and leaf organs of *Tilia cordata* and *Acer pseudoplatanus* (realised in 1998 and 2004) proved an important position of *Tilia cordata.* Accumulated elements concentrate in wood more than in leaves in lime tree. This is an important fact for biodegradation of heavy metals in soil environment because the pollutants would be taken away from the locality with timber in the future. Additional interesting and encouraging findings are published by Maňkovská (2003) from the same area. She analysed the accumulation of heavy metals in differently old wood of lime tree (10 years sequences), being sampled by the Pressler's auger, and compared them with values obtained from Norway spruce (*Picea abies*). Higher concentrations in wood of lime tree compared to those in spruce are reported for As, Cd, Ni; for Zn the difference occurs only in older wooden tissues (70–80 years old). Maňkovská (2003) measured high accumulation rates by wood of lime tree compared to spruce also for other elements that have not been included to our study. For example, Mn is accumulated 200% more in lime then in spruce, Ba about 90% and Br 80%.

Based on achieved results we are allowed to conclude that *Tilia cordata* is a tree that is very suitable for biodegradation of heavy metals in studied diseased soils.

Some information on accumulation of Pb, Hg and Mg by needles of *Picea abies* form Podzols and Andosols of selected mountain regions (Martinské hole, Nízke Tatry, Kremnické vrchy and Vysoké Tatry) are published by Čemanová (2004). Despite these results are not compared with lime tree, they are similar to contents given by Maňkovská (2003) for spruce.

Acer pseudoplatanus is less attractive tree for biodegradation issues due to it accumulates studied elements mostly in leaves. The defoliation causes that leaves return back to soil again – to the topsoil horizons (rhizosphere) actually.

The effect of liming on total amounts of accumulated elements by vegetative organs of *Tilia cordata* and *Acer pseudoplatanus* was not clearly proved. It is probably due to different site conditions of two experimental plots. Plot No. 1 (Surovec) has the slope about 50% whereas plot No. 2 (Záhajnica) about 20–30%. The slope is closely related to the kinetics of rainwater outlet. Dusty dolomite is dissolved more intensively where water stagnates for longer time, and the accumulation processes are more affected. The assumption is supported for example by higher accumulation of Ni in limed side of the experimental plot No. 2, less evidently also by Zn.

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