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HEAVY METALS AND MACRONUTRIENTS TRANSFER FROM SOIL TO *PINUS SYLVESTRIS* L.

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Abstract. Forest soil near pollution sources receives large amounts of heavy metals because of rapid urbanization and industrialization. Heavy metals from soils are easily accumulated on trees. The transfer factors of heavy metals of lead (Pb), cadmium (Cd), copper (Cu) and zinc (Zn) and macronutrients potassium (K) and magnesium (Mg) were determined from soil to tree (*Pinus sylvestris* L.) in contaminated and control sites. The differences among transfer factors for both sites were discussed. The higher transfer value of heavy metals and macroelements to wood was associated with higher element concentration in the soil and the uptake of an element by a tree which is primarily dependent on the tree species, its inherent controls, and the soil quality.

Keywords: Transfer factors, *Pinus sylvestris* L., heavy metals, soil contamination, macronutrients.

1. Introduction

Metals are considered to be among the most dangerous environmental pollutants, because they do not disintegrate with physical processes and therefore remain for longtime period (Kasassi *et al.* 2008). An increased input of metals and synthetic chemicals in the terrestrial environment due to rapid industrialization coupled with inadequate environmental management in Europe has led to large-scale pollution of the environment. These chemicals in the terrestrial environment clearly pose a significant risk to the quality of soils, plants, natural waters and human health (Gowd *et al.* 2010). In numerous kinds of soil pollutions, heavy metals contaminations have become an important environmental issue because of their nonbiodegradable nature and long biological half–live for elimination from the body (Wu and Zhang 2009).

Heavy metals are easily accumulated in trees (Alloway 1995; Adriano *et al.* 2001; Prasad *et al*. 2006; Butkus and Baltrėnaite 2007). In trees, some metals are accumulated in roots (especially Pb), probably due to physiological barriers against metal transport to the aerial parts, while others are easily transported into trees, for example Cd (Boruvka *et al.* 1997; Kabata-Pendias and Pendias 2000). Therefore, the uptake of heavy metals by *Pinus sylvestris* L. is a complex process and its efficiency depends on the soil pH, redox potential, soil texture, soil organic matter content, soil metal content and metal availability (Seregin and Ivanov 2000; Baltrėnaitė and Butkus 2007). To evaluate tree response to heavy metals transfer factor (TF) are often estimated. Moreover, it is a convenient way of quantifying the relative differences in bioavailability of metals to plants (Alloway and Ayres 1997). TF is based on root uptake, however plants can accumulate metals by absorption of atmospheric deposits on tree needles or bark (Alloway and Ayres 1997).

Due to heavy metals such as Pb, Cd, Cu and Zn cumulative nature they are the most important components of anthropogenic pollution. In this study, the TFs of Pb, Cd, Cu and Zn and macronutrients Mg and K were determined and the transfer of these metals from soil to tree (*Pinus sylvestris L.*) was evaluated in contaminated and control sites.

2. Materials and methods

2.1. Site description and sampling

The sampling site is located in Lithuania (Eastern Europe) in Panevėžys (55°44"0' N, 24°21"0' E), city near the former factory (Fig 1). For more than 40 years, this factory had been manufacturing glass components, colour TV tubes and electron gun systems. It was the main manufacturer of TV tubes in the Baltic States ("Ekranas" Company's… 2004). Intensive heavy metal contamination was formed from the manufacturer aerosol emission significantly influencing the total soil geosanitary state. Heavy metals migrated into the deeper soil horizons (Kadūnas and Radzevičius 2001). Moreover, the maximum allowable concentration of Pb in surface layer is exceeded in factory sanitary protection zone. Here particularly dangerous for biota mobile forms of Pb and other metals are contaminated soil to a depth of 0.6 meters (Strategic environmental… 2007).

The control site had similar soil type and species and is placed near Kaunas (experimental forest of Dubrava Institute (Fig 1) out of the influence of any nearby pollution source.

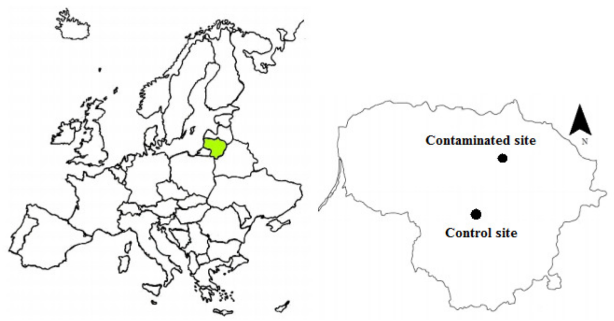

Fig 1. Location of the sampling sites in Lithuania

Sampling was carried out in early May 2009, during vegetation period when plants are most physiologically active. Southwest winds are reported to be dominant (Panevėžys city municipality 2005). Sampled trees were at least 10 m away from each other. Tree (*Pinus sylvestris* L.) cores were taken at breast height (1.5 m) from the north – facing aspects (facing the industry) (Watmough and Hutchinson 1996). Ten trees (*Pinus sylvestris* L.) in control and contaminated sites, respectively was taken using acid washed 10 mm stainless steel increment borer. Samples were immediately sealed in dry plastic straws and were stored for further analysis.

Soil samples were collected and stored in plastic bags, near the selected trees from depths 0–20 cm in contaminated site and 0–20 in control site.

Table 1. Selected soil parameters (Pundyte *et al.* 2011) and soil background and limit values of heavy metals (Hygiene standard of Lithuania HN 60:2004)

	Control site		Contaminated site	
pH	5.29±0.09		6.59±0.06	
TOC	2.47±0.48		4.22±0.34	
Predominant soil	sand, sandy loam		sand, sandy loam	
Soil				
Metal	Pb	Cd	Cu	Zn
Limit values mg·kg^{-1}	100	3	100	300
Background values, mg·kg^{-1}	15	0.15	8.1	26

Values of soil pH, TOC, type of soil and background and limit values are presented in Table 1. Methodology of chemical analysis for wood samples, soil samples, soil pH and TOC is presented in paper Pundyte *et al.* (2011).

Values of TOC and pH at contaminated site were higher than in control. The soil type was similar in both sites and the predominant soil was sand and sandy loam.

TF for metals Pb, Cd, Zn, Cu, Mg and K was determined using the Equation 1 (Alloway 1995; Adriano *et al.* 2001; Butkus and Baltrėnaitė 2007):

$$TF = \frac{C_{pinewood}}{C_{soil}}; \qquad (1)$$

where $C_{pinewood}$ – average metal concentration in pinewood, mg·kg^{-1} DW; C_{soil} – average total metal concentration at soil depth of 0–20 cm mg^{-1} DW.

2.2. Statistical analysis of the data

Some descriptive statistics of control and contaminated TFs were carried, namely mean (m), minimum (min), maximum (max), median (M) and standard deviation (SE). Previously to comparison between treatments, we tested data normality with the Shapiro-wilk test (Shapiro and Wilk 1965) considered normal at a $p<0.05$. Since the majority of the distributions did not respect the Gaussian distribution we applied a neperian logarithm (ln) to normalize it. After this transformation all the distributions followed the normality. After that we compared TFs differences between areas with a ONE WAY ANOVA test, considered significant at a $p<0.05$. Graphics are represented with non-transformed data and comparisons with normalized data. All calculations were performed using the statistical package Statistica 6.0 (Statsoft.Inc).

3. Results and discussion

3.1. Transfer factor (TF) of macronutrients

TFs of macronutrients values were estimated in contaminated and control site (Figs 2–3).

K is characterized by high mobility in trees, however, K uptake by trees is highly selective and closely coupled with metabolic activity (Jokela *et al.* 1996). K in soil can be in three forms: unavailable, slowly available or fixed, readily available or exchangeable (Rehm *et al.* 2002). During K uptake trees also greatly reduce the K concentration in the immediate vicinity of the roots ant this can induce release of K from minerals. K released by minerals into the soil solution can then be taken up directly by trees roots or be adsorbed by soil colloids (Mengel *et al.* 2001).

K showed higher mean value of TF in contaminated site comparing with control (Fig 2). The mean value of TF in contaminated site was 0.038 and in control 0.029. TF of K did not show any significant difference in the contaminated site in comparison to control.

Within the tree, Mg is moderately mobile, with the average concentration between 0.1 and 0.5 % on a dry weight basis, in pine trees 0.09–0.50 % (Barker *et al.* 2006). Mg is the second of the most important cation after K. If K supply is limited, Mg concentration may rise (Jeffrey 1987).

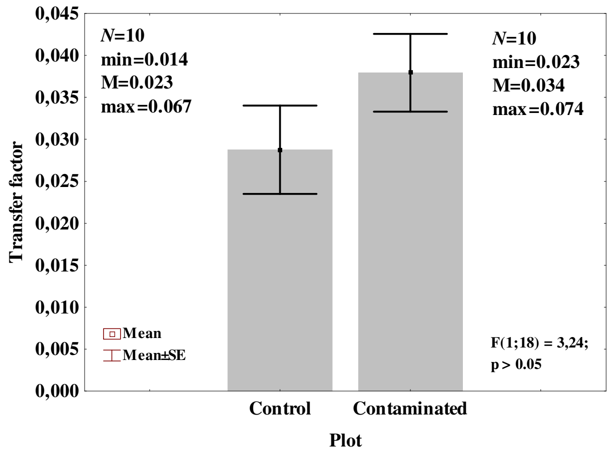

Fig 2. Descriptive statistics and summary of ONE WAY ANOVA results of K transfer factor. Significant differences are considered at a $p<0.05$

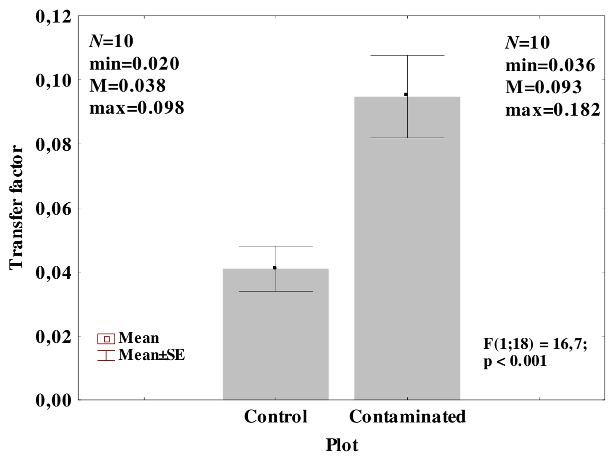

Fig 3. Descriptive statistics and summary of ONE WAY ANOVA results of Mg transfer factor. Significant differences are considered at a $p<0.05$

Mg presented higher TF value comparing with K. Mg showed higher transfer factor value in the contaminated site than in control (Fig 3). The mean value in the contaminated site was 0.094 and in control it was 0.041. TF of Mg in contaminated site was significantly ($p<0.001$) higher than in contaminated.

3.2. Transfer factor (TF) of Cd, Cu, Pb and Zn

Cd uptake by plants is a function of forms of Cd in soils. Soil properties influencing Cd uptake in plants are: pH, soil organic matter, redox potential, temperature, total Cd content, and the presence of other soluble compounds or ions (Hossain *et al.* 2007). The uptake of Cd ions seems to be in competition for the same transmembrane carrier with nutrients, such as K, Ca, Mg, Fe, Mn, Cu, Zn, Ni. The cell membrane plays a role in metal hemeostasis, preventing or reducing entry into the cell. Cd is one of the most dangerous metals due to its high mobility and the small concentration at which its effects on trees begin to appear (Benavides *et al.* 2005).

According to Alloway (1997) the TF for Cd varies from 1 to 10. According to Chojnacka *et al.* (2005) TF values of Cd were 31.02 in the Rudna mine area, Poland.

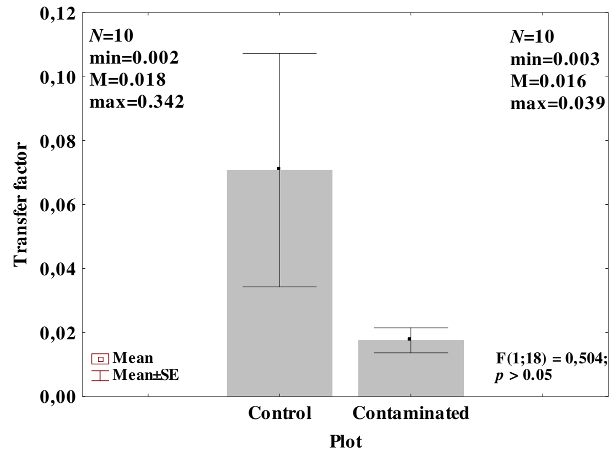

Fig 4. Descriptive statistics and summary of ONE WAY ANOVA results of Cd transfer factor. Significant differences are considered at a $p<0.05$

Cd showed higher TF value in the control site than in contaminated (Fig 4). The mean value of TF in contaminated site was 0.018 in control 0.071. Cd did not show any significant difference of TF at the control site in comparison to contaminated. The major factor was that total amount of Cd was higher in control site. Soil pH was one of the factors determining the higher availability of Cd into the pinewood.

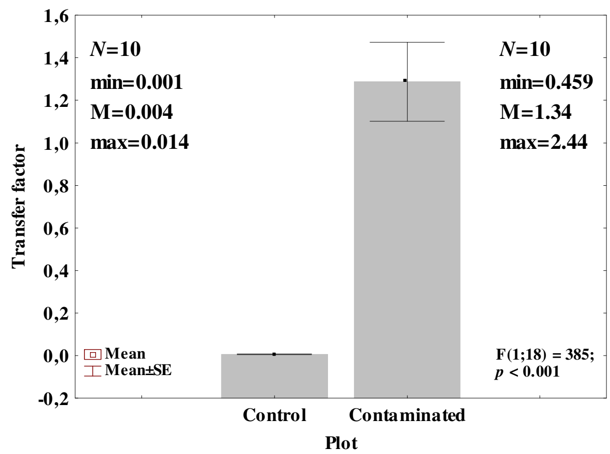

Fig 5. Descriptive statistics and summary of ONE WAY ANOVA results of Pb transfer factor. Significant differences are considered at a $p<0.05$

Values of Pb transfer factors for *Pinus sylvestris* L. varied from 0.002 to 0.085 (Butkus and Baltrėnaitė 2007). According to Alloway (1997) TF varied from 0.01 to 0.1 for Pb. Moreover, according to Chojnacka *et al.* TF value of Pb reached 32.99 in the Rudna mine area, Poland.

Pb in the contaminated site demonstrated the higher TF value comparing with control site (Fig 5). The mean value of TF in the contaminated site was 1.29 and in the control site only 0.006. Transfer factor of Pb in contaminated site was significantly (p<0.001) higher than in contaminated one.

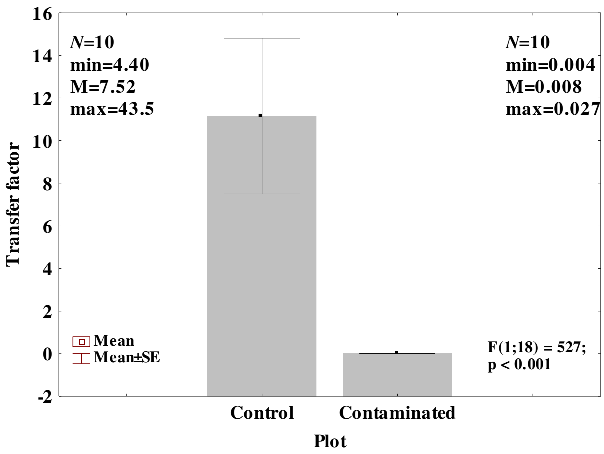

Fig 6. Descriptive statistics and summary of ONE WAY ANOVA results of Cu transfer factor. Significant differences are considered at a p<0.05

Cu concentrations in trees normally do not build up to high levels when toxicity occurs. Even under conditions of Cu toxicity, most of the excess Cu accumulates in the roots, very little is transported to the aerial portion of the trees (Singh 2005).

The values of Cu TF for pine tree were 0.04–0.45 (Butkus and Baltrėnaitė 2007), from 0.1 to 10 (Alloway 1995). According to Chojnacka *et al.* (2005) TF value for Cu reached 118.6 in the Rudna mine area, Poland. TF of Cu was higher in control site than in contaminated one (Fig 6), however, variation among control site data was considerable. The mean value in the contaminated site was 0.013 and in control it was 11.2. TF of Cu in the contaminated site was significantly (p<0.001) higher than in the contaminated.

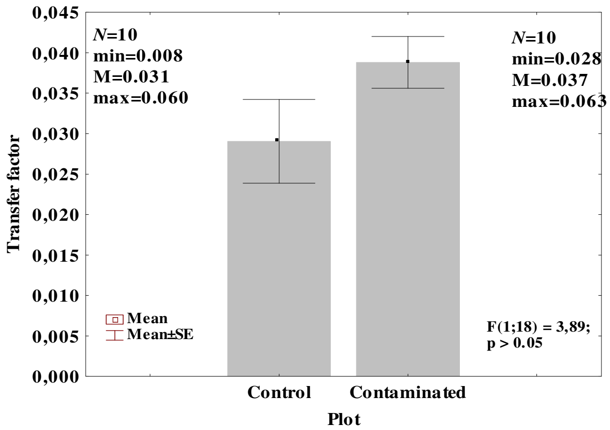

Fig 7. Descriptive statistics and summary of ONE WAY ANOVA results of Zn transfer factor. Significant differences are considered at a p<0.05

Higher plants predominantly absorbe Zn as a divalent cation (Zn^{2+}). Availability of Zn to the trees depends on the total Zn content in soil, pH, organic matter (Alloway 1995). Availability of Zn decreases at increasing pH values due to its lower solubility of Zn minerals and increasing adsorption of Zn by negatively charged colloidal soil particles. Interaction with other nutrients mainly Zn-Fe antagonism and Zn-Cu, Zn-Ni and Zn-Ca interactions may also decrease Zn availability, (Maiti and Jaiswal 2008).

TF values of Zn in the mine area, Poland was 4005. According to Alloway (1997) the TF for Zn varies from 1 to 10. According to Butkus and Baltrėnaite (2007) TF values of Zn were 0.03–0.6.

TF of Zn showed higher mean value in the contaminated site comparing with the control site (Fig 7). The mean value in contaminated site was 0.039 and in the control it was 0.029. Zn did not show any significant difference in concentration at the contaminated site in comparison to control site. Zn in both sites demonstrated relatively high transfer factor from soil to *Pinus sylvestris* L. and confirmed that trees can tolerate high Zn levels. Our study showed that heavy metals such as Zn, Cd are readily translocated to the top of tree, Cu is intermediate and Pb is translocated to the least extent.

4. Conclusions

1. The higher transfer value of heavy metals and macro-elements to wood was associated with higher element concentration in the soil and the uptake of an element by a tree which is primarily dependent on the tree species, its inherent controls, and the soil quality.
2. Values of element transfer factors in the contaminated site were: for Pb 0.459–2.44, Cd 0.003–0.039, Cu 0.004–0.027, Zn 0.028–0.063 for macronutrients K 0.023–0.074, Mg 0.036–0.182. In control site TF were: for Pb 0.001–0.014, Cd 0.002–0.342, Cu 4.40–43.5, Zn 0.008–0.060, K 0.014–0.067, Mg 0.020–0.098.
3. Results showed that Pb and Mg are most readily taken and translocated of all the elements considered at contaminated site. In contrast, at control site Cu and Cd showed higher metal transfer from soil to pine. Cu in the control site demonstrated the highest transfer factor value among the studied metals (11.2).
4. A sequence of decreasing transfer values: Pb>Zn>Cd>Cu were in the contaminated site. Opposite results, Cu>Cd>Zn>Pb were obtained in the control site. This might have been influenced by differences between sites, soil pH and TOC.

Acknowledgement

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