Transport of heavy metals from soil to *Pinus sylvestris* L. and *Betula pendula* trees

Donatas Butkus, Edita Baltrėnaitė

Department of Environmental Protection, Vilnius Gediminas Technical University, Saulėtekio al. 11, LT-10223 Vilnius, Lithuania
E-mail: butkus@ap.vtu.lt, edita@ap.vtu.lt

Rapid urbanization, unregulated industrialization, growing transport intensity and agricultural activities have created a problem of heavy metal (HM) contamination worldwide. HMs are long-term contaminants with the ability to accumulate in soil and plants and have no natural way to be removed. Forests near local contamination sources have been subjected to HMs concentration measurements. Trees are HMs bioindicators capable to record HM concentrations in the environment in the past. In this paper, concentrations of HMs determined in wood trees were compared with phytotoxic, excessive, deficiency and naturally found HM concentrations in plants.

Results of our investigation showed that HM concentrations in trees that grew in potentially contaminated areas did not exceed phytotoxic and excessive values of HMs found in plants. Concentrations of HMs in wood of pines varied: Ni – 0.1–3.50 mg·kg⁻¹; Cr – 0.1–1.50 mg·kg⁻¹; Cu – 0.25–3.00 mg·kg⁻¹; Mn – 10–160 mg·kg⁻¹; Zn – 2–75 mg·kg⁻¹; Pb – 0.05–2.80 mg·kg⁻¹ and those for birch ranged: Ni – 0.90–3.20 mg·kg⁻¹; Cr – 0.90–2.50 mg·kg⁻¹; Mn – 40–130 mg·kg⁻¹; Pb – 1.0–3.50 mg·kg⁻¹. The higher transfer of HMs to wood was associated with higher concentrations of HMs in tree environment (soil and nearby water bodies) and the function of some HMs as elements necessary for tree physiological processes. The values of HM transfer factors for trees were: Ni – 0.001–0.55; Cu – 0.04–0.45; Zn – 0.03–0.6; Mn – 0.001–0.75; Pb – 0.002–0.085; Cr – 0.005–0.11.

Key words: annual rings, birch, heavy metals, military grounds, pine

INTRODUCTION

Rapid urbanization, unregulated industrialization, growing transport intensity and agricultural activities have created a problem of heavy metal (HM) contamination worldwide. According to the Korte index which expresses hazard to environmental quality, HMs are among such major problems as contamination with pesticides, acid rain, oil spills, chemical fertilizers and noise (Stravinskienė, 2005). HMs are long-term contaminants with the ability to accumulate in soil and plants and have no natural way to be removed (White, LeTard, 2002). Most hazardous are toxic HMs: lead (Pb), manganese (Mn), chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), and their soluble compounds (Mažvila, 2001; Navas, Lindholter, 2005).

Forests near local contamination sources have been subjected to HM concentration measurements. Particularly in coniferous stands with a higher filtering strength, depositions can be much higher. Trees grown in middle climate latitudes with seasonal alterations have a property to form annual increment layers – annual rings – which are extremely sharp in coniferous and leafy woods. Being a long-term plants, within their vegetation period trees can record information about past natural and anthropogenic conditions (Karpavičius, 2004; Puksiene, Bitvinskas, 2001). Tree rings have proven to be a reliable climate archive for short and long-term scales (Битвинскас, 1974; Stravinskienė, 2002) as well as HM bio-indicators capable of recording HM concentrations in the environment. This allows determining the trends of the environmental contamination with HMs and local contamination sources (Ozolincius, 2004; White, LeTard, 2002; DeWalle et al., 1995). High correlations between the concentration of HMs in the soil and recently produced xylem rings have been reported (Larsson, Helmisaar, 1998). The increased Pb concentration in the annual rings of trees is attributed to atmospheric Pb deposition of automobile exhaust (Rolfe, 1974; Kardell, Larsson, 1978; Guyette et al., 1991; Latimer et al., 1996). The natural levels of Mn in scots pine stem are high in old
annual rings and decrease towards the bark (Butkus et al., 2002; Baltrenaite, Butkus, 2004). Ni is detectable in the most polluted areas. Cu and Zn are among the elements that are emitted from smelters, and they are observed to be antagonistic. Zn concentration increased towards the bark in all trees studied (Larsson, Helmisaari, 1998).

The aim of the present research was to determine the uptake trends of Pb, Ni, Cu, Zn, Cr and Mn by pine and birch, taking into account their habitats and local sources of pollution.

MATERIALS AND METHODS

For investigation, five trees (four pine trees Pinus Sylvestris L. and one birch tree Betula pendula) from different growth places were chosen. Two pines (1P and 2P) grew in the Rukla–Gažilainiai Military Ground (Jonna District, Lithuania). The first pine (1P) grew at a distance of 10 m from a water body used for military training, especially in 1940–1990. The second pine (2P) grew near the wetland at a distance of 6 m from a military transport road. The third pine (3P) was cut in the Kairiai Military Ground (Klaipeda District, Lithuania) in the shooting-range at a distance of 1 m from the shooting target. The fourth pine (4P) and the birch (B) grew in South Lithuania, 10 km from the town of Alytus with an intensive industry of machine, textile and refrigerator production. Pines 1P, 2P and 3P were cut down in autumn 2002, pine 4P and birch in winter 2001. Autumn and winter times were selected for a low biological activity in trees. Soil samples were taken from four soil layers (0–10 cm, 10–20 cm, 20–30 cm and 30–40 cm) at four main directions (North, South, East, West) at the growth place of the trees. Selected characteristics of the trees and soil are shown in Table 1.

The trees were cut down and wood rolls 5 cm long were cut away straight from each tree stem at three different heights: 1 m above ground, in the middle of the tree stem and at 3/4 of the stem height. The bark was scraped from the rolls and each roll was split into slivers containing three annual rings each in the direction of the tangent around the tree rings (Baltrėnaitė, 1998).

The total concentration of HMs in soil and wood samples was determined by flame atomic absorption spectrophotometry (FAAS). A graphite furnace was employed to determine metal concentrations when they were too low to be detected accurately by FAAS. Detection limits of both FAAS and GFAAS are given in Table 2. The concentrations of HMs determined at a different height of the same annual rings were averaged. Transfer of HMs from a particular soil layer to the tree annual rings was expressed in the non-dimensional factor (TF) and calculated using the following equation:

\[ TF_i = \frac{W \cdot C_i}{S_i \cdot 100}, \]

where \( W \) is the concentration of HM in the last annual ring, mg·kg\(^{-1}\) dry mass; \( S_i \) is the concentration of HM at i-soil depth, mg·kg\(^{-1}\) dry mass (Table 3); \( C_i \) is the proportion of tree roots at i-soil depth, % of total root mass. Pines and birches 20 to 60 years old have the largest density of roots at a soil depth of 0–30 cm. The 0–10 cm soil layer contains 15% and 40%, soil layer 10–20 cm – 50% and 40% and 20–30 cm soil depth – 30% and 15% of pine and birch roots respectively (Danusevicius, 1994; Beinaravičius, 2005).

<table>
<thead>
<tr>
<th>Tree</th>
<th>Tree characteristics</th>
<th>Soil characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Height, m</td>
<td>Age, years</td>
</tr>
<tr>
<td>1P</td>
<td>16</td>
<td>44</td>
</tr>
<tr>
<td>2P</td>
<td>15</td>
<td>31</td>
</tr>
<tr>
<td>3P</td>
<td>15</td>
<td>32</td>
</tr>
<tr>
<td>4P</td>
<td>30</td>
<td>55</td>
</tr>
<tr>
<td>B</td>
<td>28</td>
<td>51</td>
</tr>
</tbody>
</table>
RESULTS

Figure 1 shows Cr, Cu, Ni, Mn, Zn and Pb concentrations in annual rings of the four pines (1P, 2P, 3P, 4P) and in the birch (B) tree during the period 1978–2001. HM concentrations in all trees did not exceed either the phytotoxic level or the excessive values of HMs determined in plants (Table 4). Cr, Ni, Mn and Zn concentrations were close to naturally found concentrations, while the concentration of Pb (<3.5 mg·kg⁻¹) was found to be lower than the naturally detected level and that of Cu (<3.0 mg·kg⁻¹) was close to the deficiency value (Table 4). Lower than natural and deficient values for both Cu and Pb were found in pines which grew on military training grounds. A little higher concentration of Pb was found in both pine and birch trees near an industrial town (Alytus), however, not exceeding the values of Pb determined in naturally growing trees (Table 4). Cu concentrations were very similar in all the study areas in the period 1978–1998. Elevated Ni concentrations were found in 1978–2001 wood rings of a pine near a wetland (Rukla–Gažiūnai military training area), and from 1990 the concentration of Ni increased in a pine near the shooting range (Kairiai military training area). Two periods, 1981–1986 and 1996–2001, were found to show elevated Cr, Ni, Mn and Pb levels. There were no significant changes in Cu and Zn concentrations in tree rings along 1978–2001. A distinct increase of Cr, Pb concentrations in pines was observed in the further period starting with 1981.

The levels of Cr, Mn and Pb were more elevated in mature than in young trees. According to the age, the order of the test trees was as follows: 4P > B > 1P > 3P > 2P. A similar order was detected for the mean HMs concentrations: for Mn: 4P (84.22 mg·kg⁻¹) > B (77.28 mg·kg⁻¹) > 1P (38.19 mg·kg⁻¹) > 2P (16.69 mg·kg⁻¹) > 3P (16.61 mg·kg⁻¹); for Cr – B (1.433 mg·kg⁻¹) > 4P (0.717 mg·kg⁻¹) > 2P (0.359 mg·kg⁻¹) > 1P (0.289 mg·kg⁻¹) > 3P (0.707 mg·kg⁻¹), and for Pb – B (2.239 mg·kg⁻¹) > 4P (1.138 mg·kg⁻¹) > 3P (0.319 mg·kg⁻¹) > 1P (0.125 mg·kg⁻¹) > 2P (0.070 mg·kg⁻¹). Higher concentrations of Cr (about fourfold), Ni (about twofold), Mn (about twofold) and Pb (about fivefold) were observed in the birch tree wood as compared to the pine trees (Fig. 1). Furthermore, the highest mean values of Cr, Ni, Zn and Mn concentrations in pines from military grounds were found in annual rings representing the most intensive growth years and highest increment, i.e. pine age of 15–30 years (Stravinskienė, 2002) (Table 5). However, no such trends in pine and birch wood were detected in Alytus.

Figure 2 shows the transfer factors (TFs) representing HMs transport from the habitat soil to the latest annual ring and calculated by equation (1). TFs were estimated for four different soil layers taking into account differences of root density at the soil layers. The HM transfer factors ranged within 0.001–0.55 for Ni, 0.04–0.45 for Cu, 0.03–0.6 for Zn, 0.001–0.75 for Mn, 0.002–0.085 for Pb and 0.001–0.55 for Zn, 0.001–0.75 for Mn, 0.002–0.085 for Pb.
Fig. 1. Concentrations of heavy metals in pine and birch trees in 1978–2001 (mean ± standard error of three replicates)

Table 5. Annual rings which contain the highest concentration of HMs. Shaded years represent the most intensive period of tree growth

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>1P</th>
<th>2P</th>
<th>3P</th>
<th>4P</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>81–83</td>
<td>84–86</td>
<td>90–92</td>
<td>96–98</td>
<td>84–86</td>
</tr>
<tr>
<td>Cu</td>
<td>99–01</td>
<td>99–01</td>
<td>99–01</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mn</td>
<td>78–80</td>
<td>78–80</td>
<td>87–89</td>
<td>84–86</td>
<td>96–98</td>
</tr>
<tr>
<td>Zn</td>
<td>78–80</td>
<td>78–80</td>
<td>81–83</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 6. Sequence of trees according to magnitude of HM transfer factors

<table>
<thead>
<tr>
<th>Heavy metals</th>
<th>Order of trees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>1P, B &gt; 2P &gt; 4P &gt; 3P</td>
</tr>
<tr>
<td>Cu</td>
<td>1P &gt; 2P, 3P</td>
</tr>
<tr>
<td>Zn</td>
<td>3P &gt; 2P, 1P</td>
</tr>
<tr>
<td>Mn</td>
<td>B &gt; 4P &gt; 3P, 2P &gt; 1P</td>
</tr>
<tr>
<td>Cr</td>
<td>B &gt; 4P &gt; 2P &gt; 1P &gt; 3P</td>
</tr>
<tr>
<td>Pb</td>
<td>B, 4P &gt; 3P &gt; 1P, 2P</td>
</tr>
</tbody>
</table>
Fig. 2. Factors of heavy metal transfer (TFs) from different soil layers to the latest annual ring of pines (1P, 2P, 3P, 4P) and birch trees (B) for year 2001.
Table 7. Depth of soil (cm) where the calculated values of transfer factors were the highest

<table>
<thead>
<tr>
<th>Trees</th>
<th>Heavy metals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>2P</td>
<td>20–30</td>
</tr>
<tr>
<td>4P</td>
<td>0–10</td>
</tr>
<tr>
<td>B</td>
<td>0–10</td>
</tr>
</tbody>
</table>

n. d. not detected.

and 0.005–0.11 for Cr, however, there were no TFs exceeding 1.0.

Table 6 shows the highest TF determined for Mn, Cr and Pb in the pine and the birch from the Alytus site, and higher TFs for Ni, Cu and Zn were found in pines grown on military training grounds. The results demonstrated the highest transfer for Zn to pine 3P (about 7 times higher than to 1P and about 6 times higher compared to 2P). Higher values of TF for Ni were determined in pine 1P (1.5 times more than for pine 2P, about seven times more than for pine 3P, about three times more than to pine 4P and about 1.4 times more than to the birch). A similar trend was detected for Cu in pine 1P: about four times higher than in pines 2P and 3P. Compared with HM uptake by the pines, the birch accumulated higher amounts of Mn, Cr and Pb (Tables 6, 7).

Table 7 presents soil layers where the values of HM transfer were the highest. The shaded results show that HMs were more actively transported from the soil layer of 20–30 cm. Higher TFs from the 20–30 cm soil layer were found for Pb and Mn. The same soil layer showed the highest TFs for pines in military training areas.

DISCUSSION

Concentrations of HMs in annual rings of the trees were different and varied not only between the tree species but also among the pines. These differences can be influenced by complex natural processes in reciprocity with biotic and abiotic stresses and trees. Results showing no highly elevated HMs concentrations suggest that HM transport to a tree in potentially contaminated territories is not very active. Comparatively small Pb and Cu concentrations in wood reflect a slow transport from soil to trees and might be explained by the facts that Pb has no known function as a nutrient and Cu transport to above-ground parts might be limited because of Cu storage in roots (Khan, 2001; Marschner, 1995) (Fig. 1).

Our results indicated the trend that 1987–1996 annual rings of pines grown in military grounds had about half as low concentrations of Cr, Mn, Pb and Ni. Ni, Pb and Cr are typical in internal-combustion engine emissions to the environment (Kaduñas, 1998) and the observed difference might be due to a decline of military activities, especially in 1990 when Lithuania gained independence and the mass of Russian troops were pulled out. From the year 1986 till 1995 the climate favoured stable pine stand increment (Stravinskenė, 2002), thus the lower concentrations of metals might be explained by the fact that the congenial climate consolidated the defence functions of trees against a higher retention of HMs (Stravinskenė, 2002). The concentrations of Cr, Mn and Pb in wood of trees grown near Alytus were higher (around 4.4, 3.4 and 9.9 times respectively) as compared with wood of trees grown in military grounds. This might be associated with the distant transport of emissions from former industries in Alytus, such as factories of textile, refrigerators, building materials and others (Fig. 1).

Mn, Cr and Pb concentrations were higher in mature than in young trees and suggest the potential of mature trees to accumulate higher levels of Mn, Pb and Cr during the same time period. Increase of Mn concentration in foliage with age was determined by Ulrich (1968) and Kavvadias (1999). Mn is probably the element that is most readily leached from tree foliage by rain, thus increasing its concentration in soil. Cr, Zn, Ni and Mn are nutrients highly demanded by trees (Lassat, 2002; Schutzendubel, Polle, 2002) and thus were identified to accumulate in pine wood during the most intensive growth period (Table 5).

Birches have been identified as more sensitive to air pollution (Rieplas, 1981) and the wax layer coating the leaves of leafy trees retain two times more Cu and Zn and about 1.5 times more Ni (Kaduñas, 1998). Furthermore, the birch has 1.7–4 times more fine roots which play a fundamental role in nutrient uptake, and 2.2 times more large roots than pine (Đanusysvičius, 1994). These facts suggest more favourable conditions for HM transport to birch than to pine.

TFs help to evaluate the ability of trees to take up HMs from soil. Results of our investigation showed a three-fold less TF for Zn comparing with values found in naturally grown trees (1–2) (Korentejar, 1991). For Pb and Cu, TF was slightly higher than the naturally observed factors (0.01–0.05). None of the trees had TF higher than 1.0, showing no higher transfer of HMs to mature trees. On the other side, Scots pine appeared to be closer to accumulator than to excluder plants. The same finding was reported by Baker (1987) and Nieminen (2005). Higher TFs of Ni, Cu and Zn for trees grown on military training grounds might be associated with their higher concentrations in the environment. Pine 3P grew...
at a distance of 1 m from the shooting range targets and bullet falling point where Zn concentration in soil was 2.8 times higher than the average and reached 4.54 mg·kg\(^{-1}\) (Baltrėnas et al., 2005). Zn is known as the main constituent of bullets used in Lithuanian military activities (Greičiūtė, Vasarevičius, 2003). The higher TF values of Ni and Cu for pine 1P might be attributed to the elevated concentrations of Ni and Cu in the nearby water body. Earlier investigations showed Cu concentration to exceed the background level (<5 µg l\(^{-1}\)) 19 times, and the concentration of Ni exceeded the maximum permissible limit for drinking water 22 times (Baltrėnas et al., 2005).

The transfer of Mn and Cr was 14 and 10 times respectively higher for birch than that for pine (4P) grown in the same place, possibly because of a more intensive metabolism conditioned by about twice larger amount of roots in birch than in pine. The highest transport of HMs in the soil layer of 20–30 cm is associated with the higher density of pine horizontal roots at this depth (Laitakarai, 1927; Данисвянчюс, 1994). This soil layer is notable for a high abundance of tree fine roots playing an important role in nutrients transfer to a tree (Table 7).

CONCLUSIONS

Results of our investigation showed that the concentrations of HMs in trees that grew in potentially contaminated areas did not exceed the phytotoxic and excessive values found in plants. HM concentrations in the wood of pines grown in the study areas varied for Ni within 0.1–3.50 mg·kg\(^{-1}\), Cr 0.1–1.50 mg·kg\(^{-1}\), Cu 0.25–3.00 mg·kg\(^{-1}\), Mn 10–160 mg·kg\(^{-1}\), Zn 2–75 mg·kg\(^{-1}\), Pb 0.05–2.80 mg·kg\(^{-1}\); for birch: Ni 0.90–3.20 mg·kg\(^{-1}\), Cr 0.90–2.50 mg·kg\(^{-1}\), Mn 40–130 mg·kg\(^{-1}\), Pb 1.0–3.50 mg·kg\(^{-1}\). The higher transfer of HMs to wood was associated with higher HM concentrations in the environment (soil and nearby water bodies) and the function of some of HMs as necessary elements for physiological processes in trees. The values of HM transfer factors for the study trees were: for Ni 0.001–0.55, Cu 0.04–0.45, Zn 0.03–0.6, Mn 0.001–0.75, Pb 0.002–0.085, Cr 0.005–0.11.

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SUNKIEJI METALAI PUŠIES IR BERŽO METINĖSE RIEVĖSE

Santrauka