

CASE STUDY ON METAL(LOID)S DISTRIBUTION IN LINDEN TREE PARTS, IN AREAS WITH HIGH ENVIRONMENTAL POLLUTION

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ABSTRACT – The investigation focuses on the distribution of Al, Fe, Cu, Zn, Pb, As, and Cd, in the roots, branches and leaves of linden tree, a very common plant species used in traditional medicine, sampled in the area affected by pollution from the mining-metallurgical facilities for copper production, and one unpolluted zone. Plant samples were collected and processed following the established scientific methods, while concentrations of metal(loid)s were determined using the ICP-AES. Distinct patterns in the metal(loid)s distribution in the linden parts were revealed, which varied depending on the environmental pollution levels, highlighting obvious differences between the polluted and unpolluted zones.

Keywords: Linden, Medicinal Plants, Environmental Pollution, Copper, Lead, Arsenic.

INTRODUCTION

Tilia sp. is highly adaptable to a wide range of environmental conditions, making it a vital species for urban greening due to its capacity to improve air quality. The flowers, leaves, and bark of *Tilia* sp. have edible values, with its flowers particularly appreciated for making herbal tea known to alleviate anxiety and promote better sleep [1]. The safety of the use of medicinal plants is an important public health concern in the polluted areas, due to the potential risk of their contamination with metal(loid)s [2]. Medicinal plants can readily absorb both organic and inorganic compounds from all environmental compartments (water, soil and air), which can ultimately be transferred to humans via teas, other drinks, cosmetics, etc. [3,4]. In the Review article about contamination of herbal medicinal products, by Opuni et al. [2], it was stated that metals were indicated as one of the predominant group of contaminants with 56.0%, in comparison with microbial, mycotoxins, pesticides, and residual solvents. Elements such as Cu, Zn, Mn, Fe, B, Mo and Cl, represent the essential micronutrients for all plants, required in small amounts, but their excessive contents can also adversely affect plant growth and metabolism. Aluminum is a common constituent of all plants, but its physiological function is not clear, although there is some evidence that low levels of Al can have a

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beneficial effects on the plant growth [5]. Arsenic, lead and cadmium are considered as non-essential and toxic for plants, significantly impacting a wide range of physiological responses [6-8]. This investigation aims to give insights about the distribution of metal(loid)s among parts of linden trees sampled in a polluted and unpolluted environment, which is in accordance with the pressing issue about contamination of medicinal plant species.

EXPERIMENTAL

Linden trees are a very common plant species in the study area that the local population has used in traditional medicine since the ancient times. Roots, branches and leaves of three to five healthy linden trees, were sampled from 10 sampling sites, located in 7 zones: UI (urban-industrial zone/sampling site), U (urban zone/sampling site), SU (suburban zone/sampling site), I1 and I2 sampling sites (industrial zone, I), T1 (Brestovac spa) and T2 (Bor lake) (tourist zone, T), R1 and R2 sampling sites (rural zone, R), B (background zone/sampling site, unpolluted area). Almost all sampling sites, except the site B, were under the influence of polluting substances emitted from the mining and metallurgical facilities, as well as from the flotation tailing ponds, and overburden dumps. The UI zone has been highly endangered for decades due to extreme air pollution with sulfur dioxide (SO₂) and metal(loid)s primarily emitted from the copper smelter [9]. The R zone was particularly emphasized due to its large area of agricultural land intended for food production, which was under the pollution from the copper smelter, flotation tailing ponds and acid mine drainage. Plant material was sampled in autumn, under the stable weather conditions. Leaves and branches (about 2 cm thick) were sampled at the high of 1.5 to 2 m, from the several sides of the canopy. One half of the composite leaf sample was remained unwashed, while the other half was washed in distilled water. Branches remained unwashed. Roots (up to 4 cm thick) were sampled at a depth of 10–20 cm, with several sides of the canopy. The composite samples of roots were repeatedly washed in distilled water with brushing. Plant samples were air dried at the room temperature and then milled. Microwave digestion of the plant material was performed according to the US EPA method [10]. The concentrations of Al, Fe, Cu, Zn, Pb, As, and Cd in the plant parts were determined at the Mining and Metallurgy Institute Bor, on the atomic emission coupled plasma–induced spectrometer, with radial and axial plasma observations, (ICP–AES). In order to compare the element concentrations in different linden parts, a paired Wilcoxon Signed Rank test was performed, since the statistical distribution of most variables determined by chemical analyses did not exhibit a normal distribution with the Shapiro–Wilk test. All significant differences were at P<0.05 level. The statistical significance of the difference between As and Cd in linden parts was not calculated because the contents of these elements were below the limits of determination in some samples.

RESULTS AND DISCUSSION

Linden roots contained higher Al concentrations than the branches and leaves, which can be presented by following order: branches<washed leaves<unwashed leaves<roots,

except at the sampling sites R1 and I1, where unwashed leaves had the highest Al contents (Figure 1a).

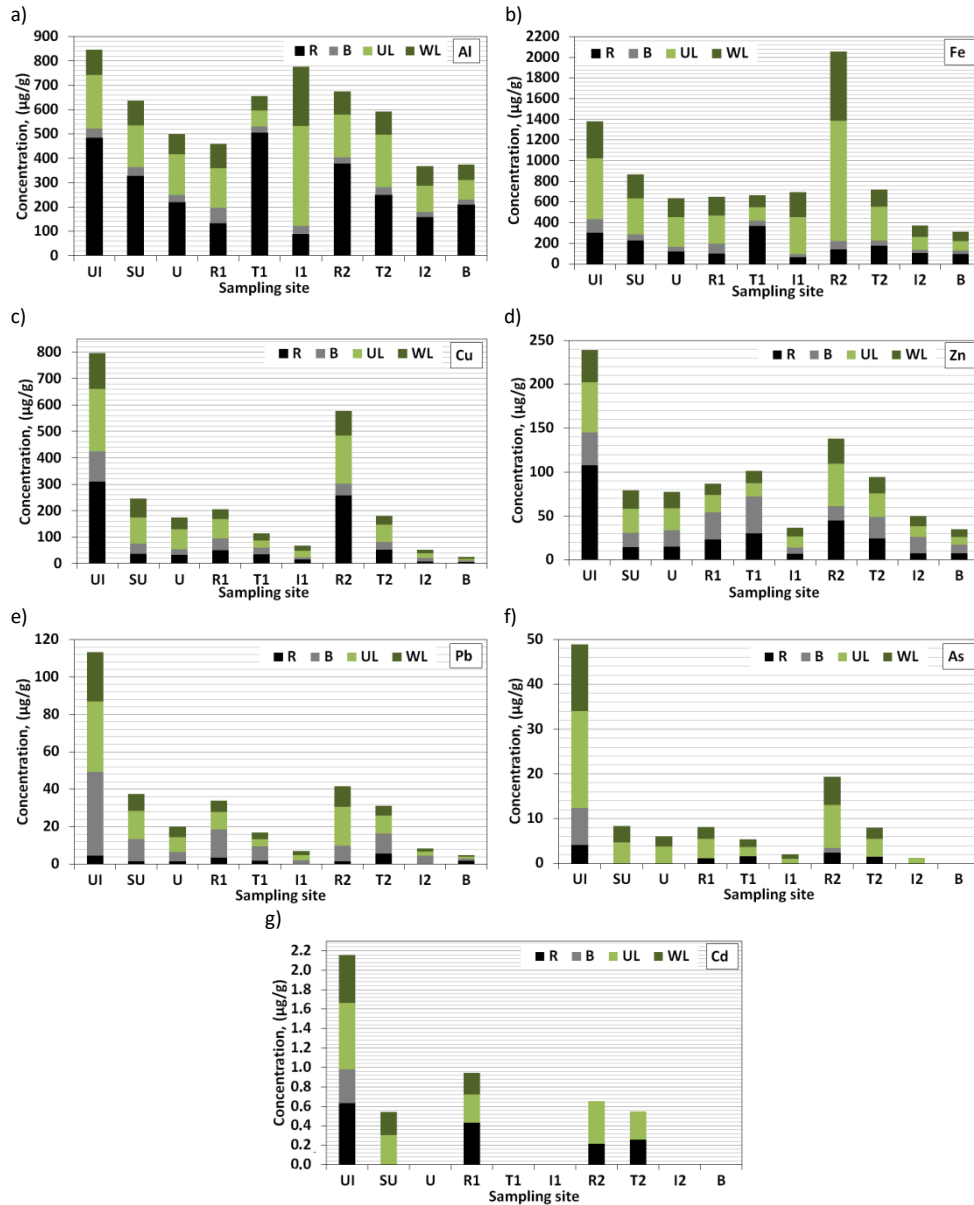


Figure 1 Distribution of a) Al, b) Fe, c) Cu, d) Zn, e) Pb, f) As, and g) Cd in the linden tree (R-roots; B-branches; UL-unwashed leaves; WL-washed leaves)

Such pattern could be influenced by the atmospheric particles rich in Al, deposited on the surfaces of leaves. From the obtained results it can be assumed that linden has naturally developed ability to retain the highest proportion of Al in its roots, which was in accordance with the distribution of Al within the linden tree from the B sampling site. Only difference between Al contents in the unwashed leaves and roots was not statistically significant (Table 1).

Table 1 Statistical significance of differences between concentrations of examined elements in linden parts (Wilcoxon Signed Rank test)

Linden parts	Al	Fe	Cu	Zn	Pb
UL-R	_*	_*	_*	_*	✓ **
UL-B	✓ **	✓ **	✓ **	_*	_*
WL-R	✓ **	_*	_*	_*	✓ **
WL-B	✓ **	✓ **	✓ **	_*	_*
R-B	✓ **	✓ **	✓ **	_*	✓ **
UL-WL	✓ **	✓ **	✓ **	✓ **	✓ **

UL – unwashed leaves; WL –washed leaves; R-roots; B-branches; *_ Not statistically significant difference; **Statistically significant difference at P<0.05 level.

The highest share of Fe was determined in the linden unwashed leaves, except at the T1 and B sampling sites, where roots contained the highest Fe levels (Figure 1b). At the B sampling site, roots contained slightly higher Fe content, compared to the leaves, which indicated that in the unpolluted environments, Fe is almost equally distributed between roots and leaves of linden, which is in accordance with the results by Ancuceanu et al. [11]. The lowest Fe concentrations were determined in the linden branches at all the sampling sites. Obtained results indicated that linden leaves have higher efficiency to trap atmospheric particles rich in Fe compared to branches. The differences were not statistically significant only between the Fe concentrations in the unwashed leaves and roots, as well as in the washed leaves and roots (Table 1).

Linden unwashed leaves contained higher Cu levels than the other parts, except at the sampling sites UI, T1, and R2, where roots were the plant parts with the highest Cu contents (Figure 1c). Such observation was in the accordance with the statement of Kabata-Pendias and Pendias [5], emphasizing that the roots of plants have a strong capability to hold Cu against the transport to aerial parts under the conditions of Cu excess, which was the case at the UI sampling site with the highest Cu soil content, about 5000 mg/kg [3]. At the B sampling site, where Cu concentrations in soil were the lowest [3], this metal was almost equally distributed in the roots, branches and leaves. The lowest Cu concentrations were predominantly determined in the linden branches, as in the case of Fe, suggesting that linden leaves have higher efficiency to trap atmospheric particles compared to branches. The differences were not statistically significant only between the Cu concentrations in unwashed leaves and roots, as well in the washed leaves and roots, as in the case for Fe (Table 1).

The highest share of Zn was found in the linden aboveground parts, unwashed leaves (at the sites SU, U, I1, R2, T2), and branches (at the sites R1, T1, I2, B), except at the UI sampling site, where linden roots had the highest Zn contents (Figure 1d). This is in

agreement with the findings of Kabata-Pendias and Pendias [5] that roots predominantly contained much more Zn than above-ground plant parts, in Zn-rich soils, which was the case for the UI zone [3]. At the B sampling site, Zn was almost equally distributed among the linden parts. Differences between Zn concentrations in the analysed linden parts were not statistically significant, except for the Zn contents in the unwashed and washed leaves (Table 1).

The lowest contents of Pb were determined in the linden roots, except at the sampling sites T2 and B (Figure 1e). At the sampling site B, the Pb concentrations in the roots were the highest indicating the opposite pattern compared to the UI sampling site. At the rest of the sampling sites, the highest Pb concentrations were determined in the linden branches (sampling sites UI, RI, T1, T2, I2) and unwashed leaves (sampling sites SU, U, I1, R2). According to Kabata-Pendias and Pendias [5], most of the Pb in soil is unavailable to plant roots, and the translocation of Pb from roots to aboveground plant parts is greatly limited, whereby only 3% of the Pb in the roots could be translocated to the aerial parts. However, there is evidence that airborne Pb, is also readily taken up by plants through foliage, which could be the case in this study. This was the indication of different ways of accumulation and translocation of this element in the linden tree, depending on the environmental pollution level. Differences were not statistically significant only for the pairs: unwashed leaves–branches, and washed leaves–branches (Table 1).

The linden unwashed, as well as washed leaves had the highest As contents at all the sampling sites where As concentrations were above the limit of determination. This suggests that linden leaves are more efficient in trapping the atmospheric particles rich in As, than linden branches (Figure 1f).

From the available data, it could be concluded that the highest Cd concentrations were detected in the unwashed leaves, and only at the sampling site R1 the highest Cd content was determined in the linden roots (Figure 1g). According to Kabata-Pendias and Pendias [5], when the amount of Cd is increased in the growth medium, the concentration of this metal in roots exceeds its content in the aboveground parts of plants by about 100 times, but this was not the case in this study for the UI sampling site. The possible reason for such behavior could be the certain quantity of Cd in the atmospheric particulates, which were absorbed by the linden leaves. Linden leaves are more efficient in trapping the atmospheric particles rich in Cd, than linden branches.

CONCLUSION

The obtained results showed that linden tree has naturally developed mechanisms to retain the highest proportion of Al in its roots. In the urban-industrial zone, the most polluted area, the highest share of Cu and Zn was observed in linden roots; the highest share of Fe, As and Cd was detected in linden unwashed leaves, and the highest share of Pb was observed in linden branches. In contrast to that, in the unpolluted zone (B), the highest contents of Fe and Pb were determined in the linden roots and of Cu in the unwashed leaves. The As and Cd concentrations in the linden parts from the B sampling site were under the limit of quantification. The linden leaves had higher efficiency to trap atmospheric particles compared to branches, according to the Fe, Cu, As and Cd

distribution among linden parts, probably because larger surface area of leaves and smooth bark of the linden branches. It could be concluded that the share of studied metal(loid)s among linden parts was distinct among the unpolluted zone and in the zones under the influence of polluting substances from the mining and metallurgical facilities. Considering the obtained results, it is necessary to develop sustainable practices of raising public awareness about the risk of collecting and consuming the medicinal plants from the polluted areas. Ensuring the quality and safety of medicinal herbs is essential for their effective use, underscoring the necessity for continuous scientific research on the metal(loid)s uptake, distribution at the soil/water-plant interface, translocation from under-to-above plant parts and vice versa.

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