

## HEAVY METALS IN THE LEAVES OF TREE SPECIES *PAULOWNIA ELONGATA* S.Y.HU IN THE REGION OF THE CITY OF BELGRADE

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### ABSTRACT

Based on the analysis of the heavy metal content (Zn, Fe, Pb, Cu, Ni, Cr, Mn, Cd, As, Hg) in leaves of the trees growing in the urban part of the city of Belgrade, wider city area and rural area it may be noted that the content of Fe, Pb, Ni, Cr and Cd increases going from rural to urban area. The obtained results may be related to the increased air pollution in urban and suburban areas where some of these heavy metals appear as a direct consequence of fuel combustion.

The level of tolerance of the species *Paulownia elongata* S.Y.HU towards air pollution represents the basis for its development and survival in urban conditions as well as setting up of tree alleys and forming wind protection zones along main traffic lines.

**Keywords:** *Paulownia elongata* S.Y.HU, urban conditions, leaf, heavy metals

### Introduction

With reference to plants air pollution may have double impact: direct and indirect. Irrespective of which of the two mentioned impacts has greater influence in a certain region the result is the same when the critical threshold of a pollutant in the air has been crossed. In the beginning there is a reduction of plant immunity which later results in drying up and decay of plants (4).

*Paulownia elongata* S.Y.HU is a deciduous tree species originating from China which was purposefully introduced in the territory of Serbia in 1993 when an experimental field was made in the vicinity of Bela Crkva. Some of those plants as well as their descendants of the species *Paulownia elongata* S.Y.HU still grow successfully in the region of the city of Belgrade. Owing to the large surface of their leaves and the fact that their bottom side is densely overgrown with hairs, these species may absorb significant quantities of sulfur dioxide from the air and combine it with particles of dust. The paper analyzes the content of heavy metals (Zn, Fe, Pb, Cu, Ni, Cr, Mn, Cd, As, Hg) in the leaves of *Paulownia* trees growing in the urban environmental conditions. The level of tolerance of this species towards air pollution represents the basis for its development and survival in urban conditions as well as setting up of tree alleys and forming wind protection zones along main traffic lines.

### Materials and Methods

For the purpose of determining heavy metal concentrations in the leaves of the species *Paulownia elongata* S.Y.HU growing in urban conditions, samples were collected (leaves) from three

locations shown in **Table 1**. Plant samples from all locations were taken at the end of their vegetation period.

The plantation in Bela Crkva which is positioned far away from the urban environmental conditions was chosen as control location. Leaves were collected from two different sampling points on the tree (the top and the bottom of the tree crown) and an average sample was produced. On the other locations the samples were taken from the middle of the tree crown.

On average 2 kg of fresh leaves were taken from each tree. The average age of the sampling trees was 10 years. From the field the samples were transported in polyethylene bags and on the same day they were placed to dry in room temperature. Airy dry leaves were then processed in dry kiln at 105°C.

The concentrations of heavy metals were determined after dry burning at 450°C under treatment with HCl. The analysis of heavy metal content by means of atomic absorption spectrometry method (with three repetitions) was performed on the master solutions obtained in the described way.

The obtained data were processed by the computer applications „Statistika“ and “Statgraf“ whereby there were determined:

- the values of the concentration of ten heavy metals (Zn, Fe, Pb, Cu, Ni, Cr, Mn, Cd, As, Hg) in the leaves of the analyzed trees (0, 1, 2, 3, 4);
- statistically significant differences between the average values applying t-test;
- interdependence between concentrations of certain heavy metals and experimental trees, applying regression analysis;
- homogenous groups of elements applying cluster analysis.

**TABLE 1**

Marks of trees with description of their location

Tree mark	Location	Distance from the centre of Belgrade [km]	Description of location
0	Bela Crkva	250	Control tree growing in the experimental field in the rural area
1	Mali Mokri Lug	15	Tree growing in the wide urban area, 10 m away from the main traffic line
2		20	Tree growing in the wide urban area, 1 m away from the main traffic line
3	Bulevar Kralja Aleksandra	3	Tree growing in the urban city centre, on the edge of the sidewalk, along the main traffic line
4		3	Trees in urban city centre in the green zone between two lanes of the main traffic line

**Results and Discussion**

Heavy metals are accumulated in plants constantly during the vegetation period and all year round reaching a peak as a rule at the end of the vegetation period. (7, 8, 15).

The variability of heavy metal content (Zn, Fe, Pb, Cu, Ni, Cr, Mn, Cd, As, Hg) in the leaves of the analyzed trees (0, 1, 2, 3, 4) is shown on **Fig. 1**. Literature references suggest influence of heavy metals on morphological, anatomical and physiological characteristics among other wooden species, such as poplars, willows (13) and *Pseudotsuga menziensis* (Mirb.) (20). On the basis of the obtained data the following was noted.

Concentrations of **zinc (Zn)** in plants were relatively low and range from 20-50 mg.kg<sup>-1</sup>. Values less than 20 mg.kg<sup>-1</sup> in dry matter are critical for most of the plant species (3). The marginal value of deficit may be considered at concentrations from 20-25 mg.kg<sup>-1</sup>, and toxicity at the concentration of around 400 mg.kg<sup>-1</sup>. According to Balsberg and Pahlsson (1) zinc may be considered less toxic for plants. Similarly to other metals zinc participates in the operation of enzymes, most important of which being carbonic anhydrase (14). In our research the range of variation on all analyzed locations was from 23.2 (tree 1) to 91.8 mg.kg<sup>-1</sup> (control tree).

Concentration of **iron (Fe)** in dry matter of plants was in a wide range from 50 to 1000 µg/g. Some plants are able to accumulate iron in significantly greater quantities so that the leaves of spinach contain up to 3000 µg Fe g<sup>-1</sup> of dry matter. In

this research the greatest values were recorded in trees 3 and 4 growing in the urban centre of the city, along one of the most busy streets of Belgrade. The range of variation on all locations was from 105.4 mg.kg<sup>-1</sup> (control tree) to 361.6 mg.kg<sup>-1</sup> (tree 4).

Concentration of **lead (Pb)** on all analyzed locations ranged from 0.9 mg.kg<sup>-1</sup> (tree 3) to 3.2 mg.kg<sup>-1</sup> (tree 4). It was noted that lead inhibits plant’s growth (11, 12), sprout growth (9), elongation of cells (10), synthesis of chloroplast pigment (5) and photosynthesis (2). According to the research of Stankovic D. (15, 16), with reference to concentrations of Pb, all plant species show larger value of accumulation i.e. from 50 to 100% at the end in comparison to the beginning of the vegetation period.

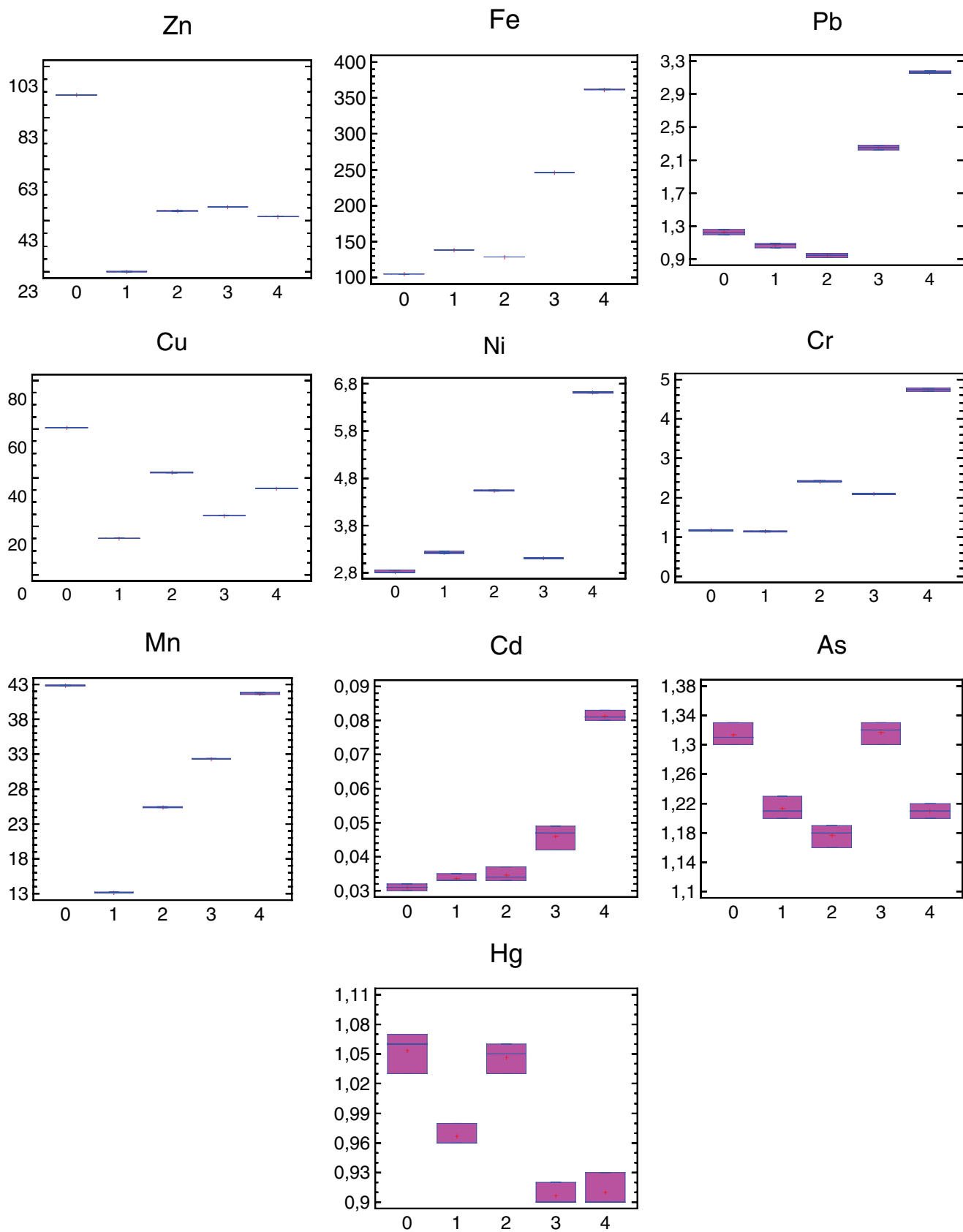
Concentration of **copper (Cu)** in all trees from the analyzed locations significantly exceeded the average values in accordance with ECCE\* (2-20 mg.kg<sup>-1</sup>) exception being the tree 1 with the content of 15.1 mg.kg<sup>-1</sup>. The other trees showed concentrations in wide range from 24.4 mg.kg<sup>-1</sup> (tree 3) to 60.5 mg.kg<sup>-1</sup> (control tree).

Concentration of **nickel (Ni)** ranged from 2.8 mg.kg<sup>-1</sup> (control tree) to 6.6 mg.kg<sup>-1</sup> (tree 4). The symptoms of toxicity include chlorosis, stoppage of root system growth and sometimes interneural necrosis (19).

Concentration of **chromium (Cr)** in this research was larger than the average according to ECCE (6)\* (0.2-1 mg.kg<sup>-1</sup>) and ranged from 1.15 (tree 1) to 4.7 mg.kg<sup>-1</sup> (tree 4). It is not an indispensable element for plants although it has a stimulative effect on the growth and development of some plants. It is considered that plants which are characterized by accumulation of iron also accumulate chromium. The most frequent symptom of surplus of chromium is chlorosis and growth lagging.

Concentration of **manganese (Mn)** ranged within the average values in accordance with ECCE (6)\* (1 to 700 mg.kg<sup>-1</sup>) and in our research was found between 25.4 mg.kg<sup>-1</sup> (tree 2) and 42.8 mg.kg<sup>-1</sup> (control tree). The fact that manganese is one of the heavy metals that traffic does not affect directly (8) was confirmed by this research and it is also shown by the highest average concentrations of manganese in the control tree (0) (38.5 mg.kg<sup>-1</sup>) and the lowest concentration in the tree 1 with an average value of 13.2 mg.kg<sup>-1</sup>. According to research in the area of the National Park “Fruska gora”, the concentrations of manganese were determined in the leaves of 17 plant species differentiated depending on the sampling locations as well as on the plant type. Namely, the highest average concentrations of manganese were found in Hornbeam (*Carpinus betulus*) 720 mg.kg<sup>-1</sup> and Sessile Oak (*Quercus petraea*) 540 mg.kg<sup>-1</sup>. (16, 17, 18).

The highest level of concentration of **cadmium (Cd)** was noted in the leaves of tree 4 (0.08 mg.kg<sup>-1</sup>) while the lowest concentration was recorded in the control tree – 0.03 mg.kg<sup>-1</sup>. Higher cadmium concentrations in plants totally inhibit metabolism, cause chlorosis and thus reduce the intensity of photosynthesis.

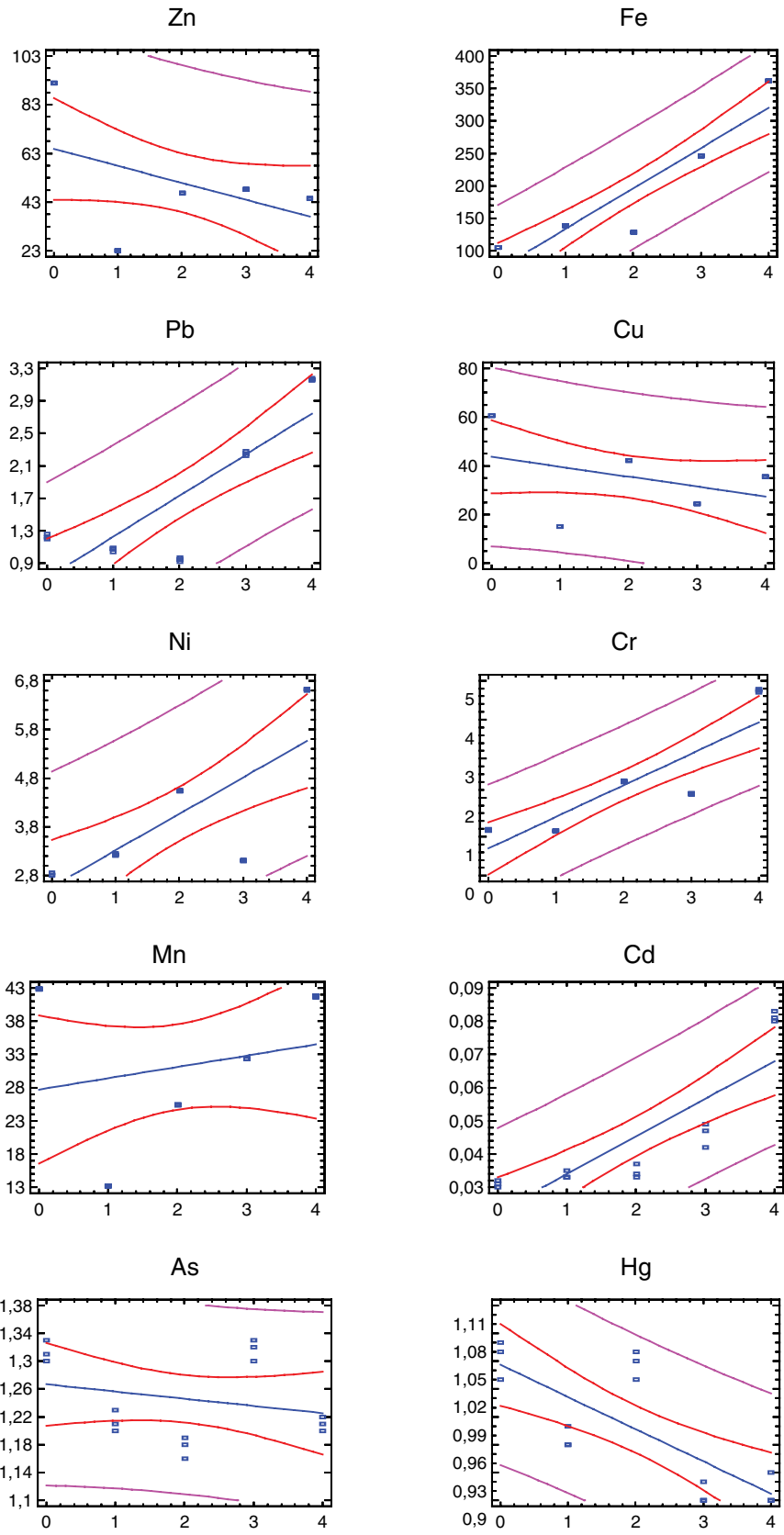


**Fig. 1.** Concentration variability (mg·kg<sup>-1</sup>) of heavy metals (Zn, Fe, Pb, Cu, Ni, Cr, Mn, Cd, As, Hg) in the leaves of analyzed trees (0, 1, 2, 3, 4) *Paulownia elongata* S.Y.Hu in the region of Belgrade

TABLE 2

Average concentrations of heavy metals (Zn, Fe, Pb, Cu, Ni, Cr, Mn, Cd, As, Hg) in the leaves of experimental trees (0, 1, 2, 3, 4) of *Paulownia elongata* S.Y.Hu with a display of t-values

Tree mark	Average value mg.kg <sup>-1</sup>	Standard deviation	t-value				
			K	1	2	3	4
<i>Zinc (Zn)</i>							
K	<b>91.84</b>	0.04	-	-	-	-	-
1	23.15	0.01	2092.43*	-	-	-	-
2	46.72	0.04	1552.92*	-863.74*	-	-	-
3	<b>48.33</b>	0.04	1865.00*	-944.12*	-278.86*	-	-
4	44.65	0.05	1170.37*	-890.02*	44.26*	81.07*	-
Average values ECCE* 15-150 mg.kg <sup>-1</sup>							
<i>Iron (Fe)</i>							
K	105.35	0.13	-	-	-	-	-
1	138.48	0.18	-184.1*	-	-	-	-
2	128.46	0.07	-195.3*	162.3*	-	-	-
3	<b>246.24</b>	0.11	-11723.3*	-640.1*	-1102.6*	-	-
4	<b>361.63</b>	0.13	-1711.1*	-4348.5*	-5333.6*	-828.2*	-
Average values ECCE* 5-200 mg.kg <sup>-1</sup>							
<i>Lead (Pb)</i>							
K	1.22	0.03	-	-	-	-	-
1	1.07	0.03	17.76*	-	-	-	-
2	0.95	0.03	8.71*	4.24	-	-	-
3	2.25	0.03	-307.00*	-204.38*	-40.98*	-	-
4	<b>3.16</b>	0.02	-104.35*	-174.17*	-119.43*	-54.80*	-
Average values ECCE* 0.1-5 mg.kg <sup>-1</sup>							
<i>Copper (Cu)</i>							
K	<b>60.52</b>	0.03	-	-	-	-	-
1	15.10	0.02	1946.71*	-	-	-	-
2	<b>42.09</b>	0.03	579.81*	-3060.0*	-	-	-
3	24.43	0.03	1547.0*	-399.71*	667.49*	-	-
4	35.53	0.04	777.40*	-1532.5*	451.03*	-302.91*	-
Average values ECCE* 2-20 mg.kg <sup>-1</sup>							
<i>Nickel (Ni)</i>							
K	2.83	0.03	-	-	-	-	-
1	3.23	0.02	-17.42*	-	-	-	-
2	<b>4.54</b>	0.01	-118.15*	-62.93*	-	-	-
3	3.11	0.02	-14.14*	20.78*	93.62*	-	-
4	<b>6.62</b>	0.02	-142.25*	-203.20*	-142.92*	-291.77*	-
Average values ECCE* 0.4-4 mg.kg <sup>-1</sup>							
<i>Chromium (Cr)</i>							
K	1.17	0.02	-	-	-	-	-
1	1.15	0.02	3.5	-	-	-	-
2	<b>2.41</b>	0.02	-373.0*	-134.63*	-	-	-
3	2.10	0.02	-278.0*	-164.55*	95.00*	-	-
4	<b>4.74</b>	0.04	-111.06*	-113.0*	-65.96*	-75.96*	-
Average values ECCE* 0.2-1 mg.kg <sup>-1</sup>							
<i>Manganese (Mn)</i>							
K	<b>42.82</b>	0.07	-	-	-	-	-
1	13.18	0.04	461.03*	-	-	-	-
2	25.42	0.07	5219.0*	-200.08*	-	-	-
3	32.33	0.04	232.63*	-439.33*	-157.99*	-	-
4	<b>41.72</b>	0.08	-461.03*	-376.92*	-149.95*	-144.32*	-
Average values ECCE* 1-700 mg.kg <sup>-1</sup>							
<i>Cadmium (Cd)</i>							
K	0.031	0.001	-	-	-	-	-
1	0.034	0.001	-2.22	-	-	-	-
2	0.035	0.002	-2.52	-0.66	-	-	-
3	<b>0.046</b>	0.003	-7.50*	-6.08*	-3.45	-	-
4	<b>0.081</b>	0.001	-151.0*	-32.8*	-26.46*	-19.04*	-
<i>Arsenic (As)</i>							
K	<b>1.31</b>	0.02	-	-	-	-	-
1	1.21	0.02	17.32*	-	-	-	-
2	1.17	0.02	10.25*	4.15	-	-	-
3	<b>1.32</b>	0.02	-0.37	-7.75*	-8.08*	-	-
4	1.21	0.01	7.11*	0.25	-3.78	8.00*	-
K	<b>1.05</b>	0.03	-	-	-	-	-
<i>Mercury (Hg)</i>							
1	0.97	0.01	9.82*	-	-	-	-
2	1.04	0.02	0.37	-5.23*	-	-	-
3	<b>0.91</b>	0.01	16.63*	17.00*	10.25*	-	-
4	0.91	0.02	16.25*	17.00*	7.36*	-0.00	-



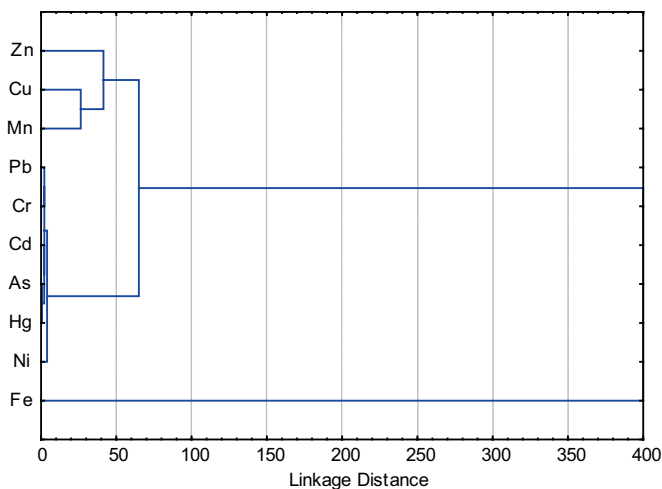
**Fig. 2.** Interdependence of concentrations ( $\text{mg.kg}^{-1}$ ) of heavy metals (Zn, Fe, Pb, Cu, Ni, Cr, Mn, Cd, As, Hg) and analyzed trees (0, 1, 2, 3, 4) of *Paulownia elongata* S.Y.Hu

**Arsenic (As)** is an element naturally present in the water, food and air. It is known as poison and the recorded average concentrations of arsenic (**As**) in this research ranged from 1.2 (tree 2) to 1.3 mg.kg<sup>-1</sup> (control tree). It is important to emphasize that it falls among carcinogenic elements so even its lowest concentration may be considered alarming.

Similarly to nonmetals and opposite to most other metals **mercury (Hg)** forms organic compounds that are stable in the environment. All forms of mercury are potentially toxic yet with different level of toxicity. Plants have the ability of absorption and accumulation of mercury from the environment. Similarly to lead and cadmium it also inhibits germination which results in inhibition of development and elongation of plant roots. The concentrations of mercury (**Hg**) ranged in a relatively narrow range from 0.9 (tree 3 and 4) to 1.1 mg.kg<sup>-1</sup> (control tree).

According to the difference between the average concentrations values of the analyzed heavy metals in the leaves of *Paulownia elongata* S.Y.Hu, from the point of view of statistical significance, it may be noted that the obtained differences in almost all cases are significant which is also shown by t-values (**Table 2**).

The interdependence of the contents of heavy metals (Zn, Fe, Pb, Cu, Ni, Cr, Mn, Cd, As, Hg) and the analyzed trees (0, 1, 2, 3, 4) of *Paulownia elongata* S.Y.Hu is shown in Fig. 2. On the basis of the obtained results of the regression analysis it may be noted that the contents of Fe, Pb, Ni, Cr and Cd increase from the control tree towards tree 4. The increase of the concentration of these elements may be attributed to the presence of polluting substances originating from the exhaust automobile gasses which are the least in rural area, a bit higher in wider urban area and highest in the centre of the city.

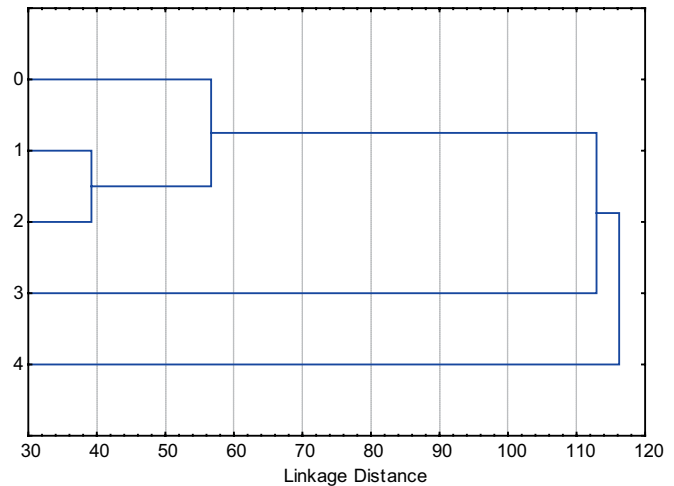


**Fig. 3.** Dendrogram of cluster analysis for the analyzed heavy metals (Zn, Fe, Pb, Cu, Ni, Cr, Mn, Cd, As, Hg) in the leaves of the trees of *Paulownia elongata* S.Y.Hu

The content of Zn, Cu and As decreases from the control tree to tree 4, which may be explained by the fact that these heavy metals are not direct products of fuel combustion. Similar results are shown in the dendrogram of the cluster analysis (**Fig. 3**) on the basis of which we can see that Zn,

Pu and Mn form one and Pb, Cr, Cd, As, Hg and Ni - another homogenous group while Fe stands as a separate element making a group with other elements on a large distance.

There is a clear differentiation among the analyzed experimental trees and the contents of heavy metals in the leaves (**Fig. 4**) which shows that one homogenous group is composed of trees 1 and 2 which form a group with the control tree and also group with trees 3 and 4 on a large distance. This clearly indicates that the content of heavy metals in the leaves of experimental trees of *Paulownia elongata* S.Y.Hu may be correlated with the locations they are growing at.



**Fig. 4.** Dendrogram of cluster analysis for the analyzed experimental trees (0, 1, 2, 3 and 4) *Paulownia elongata* S.Y.Hu

## Conclusions

Owing to its fast growth and extraordinary decorative nature, especially its blossom, *Paulownia elongata* S.Y.Hu is more and more present in the green areas in urban environment. On the basis of comparative analysis of heavy metal content (Zn, Fe, Pb, Cu, Ni, Cr, Mn, Cd, As, Hg) in the leaves of the trees growing in the centre of the city, wider urban area and rural area it may be noted that Fe, Pb, Ni, Cr and Cd content increases starting from the control tree towards the trees 3 and 4.

Values above the average are recorded for Fe and Ni in trees 3 and 4, and Cu and Cr in all analyzed trees. Still those concentrations cannot be labeled as toxic. The conducted research clearly shows that *Paulownia elongata* S.Y.Hu is a tolerant species, which endures urban environmental conditions well and also that it can be recommended for growing in tree alleys and wind protection zones along urban and regional traffic lines.

Bearing in mind that the presented results are based on a limited sample this initial research has to be followed by a more extensive research which would involve greater number of trees and longer period of observation in order to purport these and obtain more reliable data which would be beneficial in scientific as well as practical sense.

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