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Content and distribution of some chemical elements in the poplar leaves (*Populus laurifolia*) in Ulaanbaatar

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Abstract: In the last more than two decades, technogenic environmental pollution of Ulaanbaatar (Mongolia) has become a critical issue due to the rapid growth of the city's population and environmental objects such as soil, plant and water in Ulaanbaatar territory have been heavily contaminated through air. The objectives of this study were (1) to determine the toxic and biophilic elements in the leaves of laurel poplar (*Populus laurifolia*) in Ulaanbaatar (Mongolia) and to study the behaviour and interdependence of its distribution, (2) and to assess the ecological state of laurel poplar (*Populus laurifolia*). In the leaves of laurel poplar (*Populus laurifolia*) on the territory of Ulaanbaatar, the distribution of most of the studied toxic and biophilic elements is even, but only Mg, Ca, and Mn are not evenly distributed. The biogeochemical feature of laurel poplar (*Populus laurifolia*) on the territory of Ulaanbaatar was studied by comparing it with the value of the world clarke and with the average content of elements in plant ash according to Alekseenko and with the background value. Our study revealed the accumulation of Zn, Ni, Cd, Pb and the scattering of Fe, Mn, Co, Cu in the leaves of laurel poplar (*Populus laurifolia*) in Ulaanbaatar. In *Populus laurifolia* leaves in Ulaanbaatar area the median value of Fe/Mn ratio is 4.2-2.7 times, and the median value of Pb/Mn ratio is 6.7 times higher the normal and Cu/Zn ratio is at an equilibrium. The highest Fe/Mn ratios are found along the main highway (10.45) and in the city centre (11.09).

Keywords: toxic and biophilic elements; poplar leave; soil; Ulaanbaatar;

INTRODUCTION

In the last more than two decades, technogenic environmental pollution of Ulaanbaatar (Mongolia) has become a critical issue due to the rapid growth of its population

and environmental objects such as soil, plant and water in Ulaanbaatar territory have been heavily contaminated through air.

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Therefore, investigation of soil and plant contamination with heavy metals and biophilic elements could be a good indicator of the gravity and seriousness of environmental pollution in the city.

In an urban environment, trees, as long-lived organisms, reflect the cumulative effects of environmental pollution from the soil and the atmosphere, and they also act as an important barrier to the spread of heavy metals into the environment. Their assimilation organs, that is, leaves that have a widely developed exchange surface with the surrounding air, absorb and precipitate the largest amount of atmospheric impurities [1] from the air, but at the same time, they themselves are much more damaged than other organs.

In many countries, a number of authors have shown that poplar leaves accumulate specific elements, the pollution sources of which are emissions from enterprises using fuel and energy, petrochemical, metallurgical,

machine-building, mining and other industries [2-8]. Djingova et al [8] first proposed biomonitoring of atmospheric air in industrial areas using black poplar leaves. Poplar differs from other woody plants by its rapid growth and more frequent use for landscaping urban areas.

Poplar laurel (*Populus laurifolia*) is most widespread on the territory of Ulaanbaatar and it makes up for almost 75% of the tree plantations.

Earlier, in order to determine the elements in the leaves of laurel poplar (*Populus laurifolia*), first the background content was determined and the ecological state of laurel poplar (*Populus laurifolia*) on the Ulaanbaatar territory [2, 5] was studied.

The objective of the present study are (1) to determine the toxic and biophilic elements in the leaves of laurel poplar (*Populus laurifolia*) in Ulaanbaatar (Mongolia) study the behaviour and interdependence of its distribution, (2) and to assess the ecological state of the laurel poplar (*Populus laurifolia*).

MATERIALS AND METHODS

The object of our study were poplars leaves (*Populus laurifolia*) and the soil, where the sampled poplars leaves were growing. The key sampling sites are the main highway from

“Tavan Shar” in the west of Ulaanbaatar to “the Palace of Army Officers” in the east, and others. A total of 20 samples (Fig.1) were collected for the study.

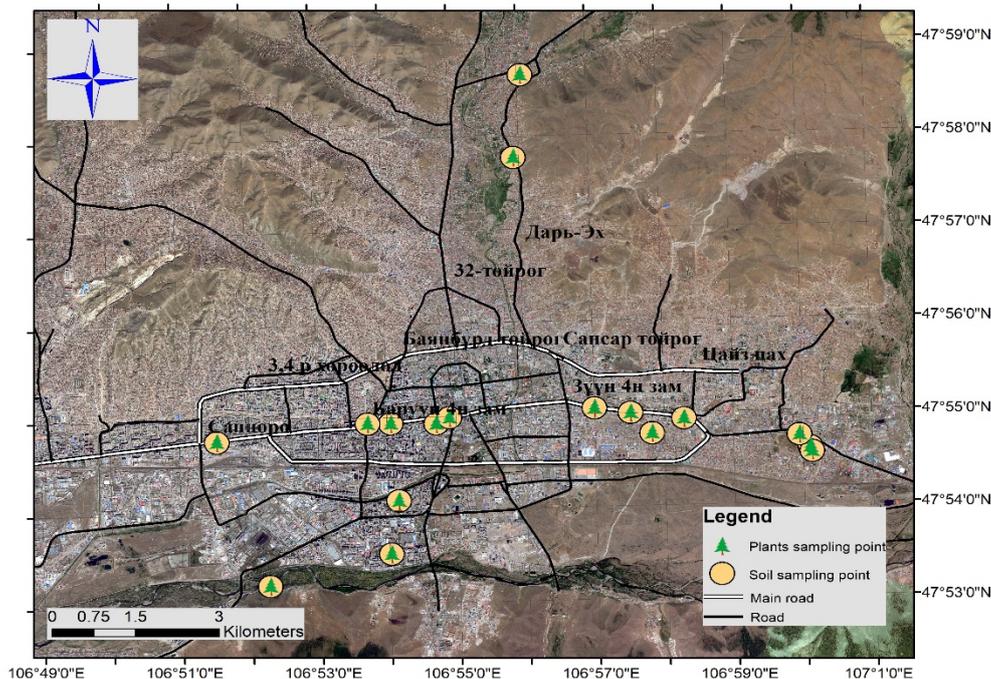


Figure 1. Sample collection scheme

Sampling of poplars leaves (*Populus laurifolia*) on the territory of Ulaanbaatar was carried in accordance with accepted methods, in dry weather using the method of average sample at a height of 1.5–2.0 m from the ground surface and during the full development of the leaf blade (June-July). Samples were not pre-treated chemically, which eliminated inaccuracy at the expense of introduction and removal of elements together with the reagents. Sample preparation for analysis included the following operations: drying at room temperature, grinding, weighing, and ashing at 550°C for 5 hours by dry mineralization, according to GOST 26929–94 [9] standard. The plant ash was dissolved in 1% HCl solution and the content of Fe, Ca, Mg, Cd, Cu, Fe, Mn, Pb, Cr, Co, Zn, and Ni was determined using an AA-6300 C atomic absorption spectrometer (Shimadzu, Japan) with flame atomization. The accuracy of the analysis was verified using certified reference materials, created at IGC, Russia: birch leaf (LB-1) - 8923-2007 and grass mixture (Tr-1) - 8922-2007. The root-mean-square error in determining the content of elements is no more than 25-30%.

To identify biogeochemical anomalies of poplars leaves (*Populus laurifolia*) on the territory of Ulaanbaatar, the concentration coefficients of the elements were calculated by the following equation.

$$K_c = \frac{C}{C_{BG}} \quad (1)$$

where, C and CBG are the metal content in the studied plant and the regional background, respectively, mg/kg of dry matter. The data obtained by Russian scientists in previous works [2, 5] were used as regional background values of elements.

The ecological state of *Populus laurifolia* on the Ulaanbaatar territory was assessed by the following parameters - Fe/Mn, Pb/Mn and Cu/Zn, which represent the ratio of some toxic and biophilic elements. The Fe/Mn ratio is one of the most informative parameters of photosynthetic processes; the Pb/Mn ratio characterizes the relationship between technogenic and biophilic elements, and the Cu/Zn ratio determines the proportionality of the contribution of these biogenic metals to enzyme synthesis [2, 5].

Statistical analyses were performed with STATISTICA-13 for Windows.

RESULTS AND DISCUSSIONS

Content and distribution of some elements in the leaves of *Populus laurifolia*

The content and distribution of some studied toxic and biophilic elements in the

leaves of the *Populus laurifolia* in the Ulaanbaatar territory are summarized in Table 1.

Table 1. Statistical parameter of the distribution of elements in the ash of *Populus laurifolia* leaves on the Ulaanbaatar territory.

Element	Statistics of set of obtained concentration					Statistics of of data spread		Coefficients, describing data		
	μ	M	C_{GM}	C_{min}	C_{max}	σ	V	S	K	$W_p > 0.05$
Fe	189.21	179.56	185.19	125.66	266.68	40.27	21	0.33	-0.82	0.73
Mg	51.55	49.38	51.38	47.62	61.34	4.44	9	1.19	-0.22	0.00
Ca	768.45	742.85	764.72	649.41	947.45	80.09	10	1.06	0.30	0.01
Mn	32.32	30.52	29.68	17.84	69.36	14.49	45	1.18	1.07	0.02
Pb	1.17	1.23	1.16	0.85	1.41	0.17	15	-0.77	-0.38	0.05
Zn	41.36	40.51	41.23	36.37	50.84	3.50	8	1.03	1.61	0.17
Cu	6.51	6.33	6.39	4.50	8.82	1.33	20	0.30	-0.92	0.44
Co	1.49	1.50	1.45	0.74	2.03	0.34	23	-0.35	0.00	0.72
Ni	2.59	2.54	2.51	1.40	4.23	0.64	25	0.66	1.30	0.69
Cd	0.68	0.69	0.67	0.38	0.92	0.13	20	-0.23	0.69	0.55
Cr	2.63	2.79	2.17	0.54	5.13	1.46	56	0.16	-1.19	0.37

According to our results, the distribution of studied toxic and biophilic elements in the leaves of the *Populus laurifolia* on the territory of Ulaanbaatar is even and only Mg, Ca, and Mn are not evenly distributed. The median, arithmetic and geometric mean values of the

content distribution are characterized by comparability and insignificant data spread. The Shapiro-Wilkes test ($p > 0.05$) confirms that only Mg, Ca and Mn are not distributed evenly. The behaviour and distribution of the studied elements are shown in Figure 2.

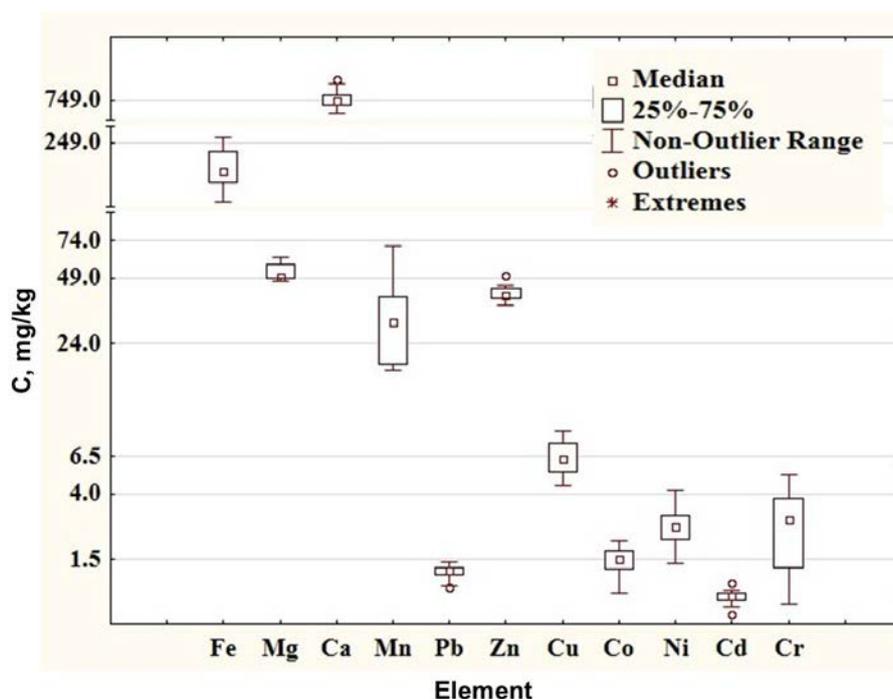


Figure 2. Average and minimum-maximum concentrations (mg/kg) of chemical elements in the leaves of *Populus laurifolia* on the Ulaanbaatar territory

A number of studies [2, 5] on the elemental composition in the leaves of *Populus laurifolia* on the territory of Ulaanbaatar were carried out. The average abundance of elements found in this work are shown in Table 2, comparing with the result of the earlier studies. Also, given in Table 2 is the background content of elements in the leaves of *Populus laurifolia* [2, 5], the world Clarke of elements in the plants [8], the average content of elements in the plant ash [10] and average value of concentration of certain elements in plants [11].

Ca, Fe, Co, Zn, Cu, Mn and Mg are essential elements or are vital for living organisms, their exclusive function in ensuring the vital activity of organisms [12-15] have been determined. Iron and trace elements, such as Cu, Mn and Zn are essential for plant nutrition, and they are required for the activity

of various types of enzymes [12-15]. Pollution from motor traffic can lead to significant accumulation of certain heavy metals, such as Pb, Cd, Zn and Cu in both roadside soils and plants, primarily resulting from vehicle emissions, mechanical abrasion and normal wear and tear [16, 17].

According to our results, the distribution of Fe, Co, Cu and Zn in the leaves of *Populus laurifolia* on the territory of Ulaanbaatar is close to normal and the distribution of Ca, Mn, Mg is close to log-normal. The contents of essential elements, except cobalt, is much higher, because the minimum value of Zn and Cu is measured in dozens, and highs of Ca, Mn, Mg and Fe, and have tens and hundreds of mg/kg.

The average content of Ca, Mg, Fe, Mn, Zn, Cu and Co in the leaves *Populus laurifolia* on the Ulaanbaatar territory is 742.85, 49.38,

179.56, 30.52, 40.51, 6.33 and 1.5 mg/kg, respectively. The average content of Cu and Co in the leaves of *Populus laurifolia* on the Ulaanbaatar territory is higher than the Clarke, according to [8], the average content of all studied essential elements is less than the average content in plant ash, according to Alekseenko [10]. When compared with average values of concentrations of some elements in plants (mg/kg) the average content of Mn, Zn and Cu falls within the sufficient range or

normal concentrations, the concentration level of Co was higher than sufficient or normal concentrations, but less than the range of excessive or toxic concentrations [12]. In the leaves of the poplar (*Populus laurifolia*) on the territory of Ulaanbaatar, when compared with the results of previous studies [2, 5], the average content of Co had increased, while the average content of Zn had decreased, and the average content of Cu had not changed and had remained the same.

Table 2. The World Clark, the average content of elements in plant ash, the average values of concentrations of certain elements in plants (mg/kg), the background content of elements and the content of elements in the leaves *Populus laurifolia* on the Ulaanbaatar territory, obtained by various researchers.

Element	World Clark [8]	Average content of elements in plant ash [10]	Average value of concentration of certain elements in plants (mg/kg) [11]		Background content [2, 5]	Populus laurifolia on the Ulaanbaatar territory		
			Normal	excess		Kosheleva et al. [2]	Kasimov et al. [5]	In this study
Ca	-	30000	-	-	-	-	-	742.85
Mg	-	70000	-	-	-	-	-	49.38
Fe	-	10000	-	-	400	-	-	179.56
Mn	-	750	30-300	40-10000	85	-	-	30.52
Pb	1.25	1	5-10	30-300	0.37	0.77	0.78	1.23
Zn	-	900	27-150	100-400	22.5	70	70.7	40.51
Cu	5.05	20	5-30	20-100	5.1	6.6	6.6	6.33
Co	0.7	15	0.02-1	15-50	1.65	0.71	0.69	1.50
Ni	1.78	5	0.1-5	10-100	1.25	1.1	1.14	2.54
Cd	0.2	0.01	0.05-0.2	5-30	0.08	0.25	0.25	0.69
Cr	0.4	250	0.1-0.5	5-30	2.2	1.8	1.2	2.79

Cr and Ni are conditionally essential (or conditionally vital) elements, the vital necessity of which was not established for all studied organisms [12, 15]. The increasing concentration of heavy metals in soil increased plant uptake. Anthropogenic activities further release Ni and Cr into the soil through various sources, such as smelting, burning of fossil fuel, vehicle emissions, disposal of household debris, municipal and industrial wastes, metal mining, fertilizer application, and organic, alloys, chrome plating, dyes and pigments, textiles, leather tanning, and wood preserving [18].

According to our results, the average content of Cr and Ni in the leaves of laurel poplar (*Populus laurifolia*) on the territory of Ulaanbaatar is 2.79 and 2.54 mg/kg, respectively, and it is higher than the Clarke values (Djingova et al. 1995) and lower than the values of the average content of elements in plant ash according to Alekseenko [10]. The average Ni content in the leaves of poplar laurel (*Populus laurifolia*) in Ulaanbaatar is within the normal concentration of the average concentration values, and the average Cr content is greater than the normal concentration values of the average concentration values and within the toxic concentration of the average

concentrations of some elements in plants (mg/kg) [11].

Also, the average content of Cr and Ni in the leaves of laurel poplar (*Populus laurifolia*) in Ulaanbaatar has increased in comparison with the results of previous studies [2, 5]. While comparing the background values, it was found that the average Ni content in the leaves of poplar laurel (*Populus laurifolia*) on the territory of Ulaanbaatar was several times higher than in the previous studies, indicating biogeochemical anomaly or a change in the composition of Ni in poplar laurel (*Populus laurifolia*) under the influence of urbanization in Ulaanbaatar, while the average Cr content is identical.

Trace elements, such as Cd and Pb, do not have any known physiological function in plants, and can be toxic [12, 15]. Pb is available to plants from soil and aerosol sources. In Urban areas automobile exhaust contributes substantially to atmospheric pollution. Pb compounds are major pollutants emitted by automobiles. Plants growing near highways are usually exposed to pollutants, more than in other localities [16].

The average content of Pb and Cd in the leaves of poplar *laurifolia* (*Populus laurifolia*) on the territory of Ulaanbaatar is 1.23 and 0.65 mg/kg, respectively, and the average Cd content is higher than the Clarke value [8] and the values of average content of elements in plant ash according to Alekseenko [10], and the average Pb content is almost identical to these

data. In comparison with the average values of the concentrations of some elements in plants (mg/kg) [11], the average Cd content is greater than the normal concentration limit and less than the normal concentration, the average Pb content is less than normal concentration. Also, the average content of Pb and Cd in the leaves of laurel poplar (*Populus laurifolia*) on the Ulaanbaatar territory this time had increased as compared to the results of previous studies [2, 5]. In comparison with the background values, the average Pb and Cd content in the leaves of poplar *laurifolia* (*Populus laurifolia*) on the territory of Ulaanbaatar was several times higher - Pb (3.32) and Cd (8.63) respectively, indicating biogeochemical anomaly or a change in the composition of Pb and Cd in poplar laurel (*Populus laurifolia*) under the influence of urbanization in the city. When compared with the average content of elements in plant ash, according to Alekseenko, the average content of Ca, Mg, Fe, Mn, Zn, Co, Cr and Ni in the leaves of poplar *laurifolia* (*Populus laurifolia*) on the Ulaanbaatar territory is lower, the average content of Cd is higher and on the contrary, the average Pb content is also identical.

The correlation between the elements reflects their same biogeochemical characteristics in absorption and dispersion in leaves and sources of plant pollution. The results of the correlation analysis of elements in the leaves of *Populus laurifolia* are summarized in Table 3.

Table 3. Correlation matrix of elements in the leaves of *Populus laurifolia* (P=95%)

	Fe	Mg	Ca	Mn	Pb	Zn	Cu	Co	Ni	Cd	Cr
Fe	1.00										
Mg	-0.44	1.00									
Ca	-0.23	0.91	1.00								
Mn	0.37	0.18	0.39	1.00							
Pb	0.49	-0.03	0.14	0.45	1.00						
Zn	-0.15	0.45	0.46	0.18	0.30	1.00					
Cu	0.54	-0.44	-0.38	0.20	0.29	0.07	1.00				
Co	0.79	-0.44	-0.24	0.54	0.64	-0.09	0.59	1.00			
Ni	0.40	-0.49	-0.40	0.21	0.29	-0.25	0.29	0.70	1.00		
Cd	0.48	-0.33	0.03	0.23	0.24	-0.12	-0.05	0.35	0.25	1.00	
Cr	0.52	-0.78	-0.67	-0.15	-0.13	-0.50	0.30	0.44	0.54	0.45	1.00

Our result revealed that Pb shows significant positive bonds with Fe, Mn and Co;

Zn with Mg, Ca and Cr; Cu and Fe, Co, Cr and Ni; Co with Fe, Mn, Pb, Cu, Ni and Cr; Ni with

Fe, Co and Cr; Cd with Fe and Cr; Cr with Fe, Co, Ni, Cd, Mg, Ca and Zn respectively.

The ecological state of *Populus laurifolia* on the Ulaanbaatar territory

Statistical parameters of the distribution of ecological indicators of *Populus laurifolia* on the Ulaanbaatar territory are presented in Table 4 and shown in Figure 3.

Table 4. Statistical parameters of the distribution of ecological indicators of *Populus laurifolia* on the Ulaanbaatar territory

The ecological indicators	Statistical estimates of contents found in samples					Statistics of data spread		Coefficients, describing data		
	μ	Me	C_{GM}	C_{min}	C_{max}	σ	V	S	K	$W, p > 0.05$
	Fe/Mn	6.66	6.64	6.24	2.77	11.09	2.37	36	0.25	-0.71
Cu/Zn	0.16	0.16	0.15	0.10	0.22	0.03	21	0.30	-0.82	0.53
Pb/Mn	0.04	0.04	0.04	0.02	0.08	0.02	37	0.61	-0.27	0.44

Iron is an important nutrient for plants and plays an important role in the electron transport chains associated with photosynthesis and respiration. However, iron is toxic when it accumulates in large quantities. High concentration of iron can also cause iron-induced deficiencies in essential nutrients (such as Mn, P, K, Ca, and Mg) in plants [15]. Manganese is an important trace element for most organisms. In plants, it is involved in the structure of photosynthetic proteins and enzymes. Mn deficiency is dangerous for chloroplasts, because it affects the water-soluble system of the plant photosystem, which provides the necessary electrons for photosynthesis [12-15]. The Fe/Mn in the range of 1.5-2.5 is considered optimal for normal plant development [11].

According to our results, the Fe/Mn ratio in *Populus laurifolia* leaves in Ulaanbaatar, according to the median value is 6.64, and is 4.2-2.7 times higher than the optimal Fe/Mn ratio for normal plant development. The highest Fe/Mn ratios are found along the main highway

(10.45) and in the city centre (11.09). The Pb/Mn ratio for non-polluted land plants is 0.006 [2]. According to our study, the Pb/Mn ratio in *Populus laurifolia* leaves on the Ulaanbaatar territory varies from 0.02 to 0.08 and averages at 0.04, which is 6.7 times higher than in non-polluted plants, and this result almost coincides with the data [2]. The optimal Cu/Zn ratio for non-polluted terrestrial plants is 0.27 [2]. For poplar leaves, the decisive role in the accumulation of pollutants is played by atmospheric transport and absorption of heavy metals from atmospheric deposition. The main enrichment reason of Ulaanbaatar soils with potentially toxic elements are dust-aerosols from coal combustion by fuel and energy complexes (B, Bi, Ca, Mo, S and Sr) and vehicle emissions (Cu, Pb, Sn and Zn) [19]. Traffic pollution can cause significant accumulation of certain heavy metals, such as Pb, Cd, Zn and Cu in both roadside soils and plants, primarily resulting from vehicle emissions, and mechanical abrasion and normal wear and tear [16-18].

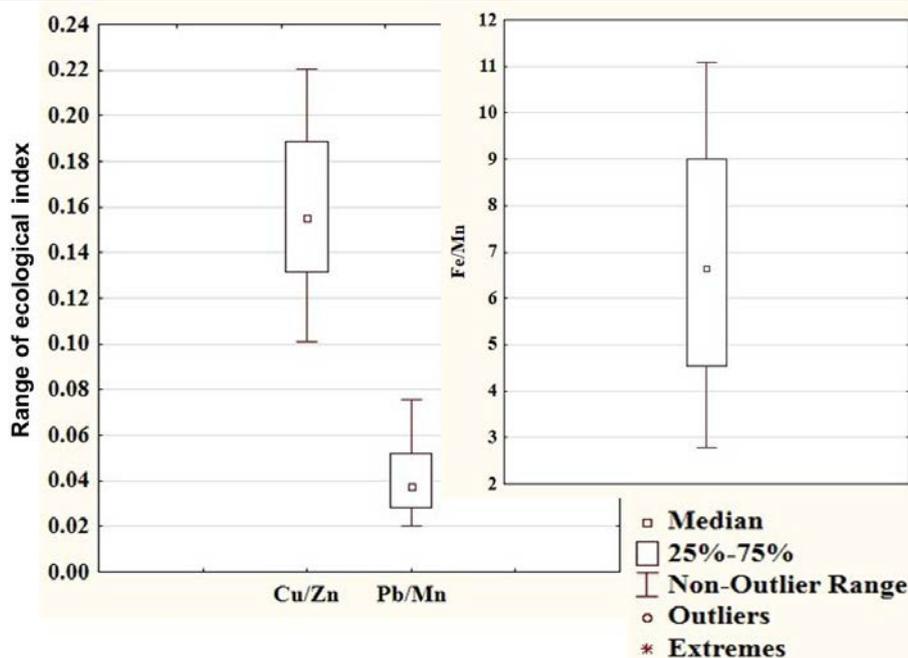


Figure 3. Average value and spread of minimum- maximum value of ecological indices of *Populus laurifolia* leaves on the territory of Ulaanbaatar

The Cu/Zn ratio in *Populus laurifolia* leaves on the Ulaanbaatar territory varies from 0.10 to 0.22 and averages at 0.16, which

indicates the balancing of the provision of enzyme synthesis in *Populus laurifolia* leaves on the Ulaanbaatar territory

CONCLUSIONS

- In the leaves of laurel poplar (*Populus laurifolia*) on the territory of Ulaanbaatar, the distribution of most of the studied toxic and biophilic elements is even and only Mg, Ca, and Mn are not evenly distributed.
- In the leaves of poplar laurel (*Populus laurifolia*) on the Ulaanbaatar territory, the average content of studied biophilic and toxic elements is 742.85 (Ca), 49.38 (Mg), 179.56 (Fe), 30.52 (Mn), 40.51 (Zn), 6.33 (Cu) and 1.5 (Co), 2.79 (Cr) and 2.54 (Ni), 1.23 (Pb) and 0.65 (Cd) mg/kg respectively.
- The biogeochemical feature of laurel poplar (*Populus laurifolia*) on the Ulaanbaatar territory was studied by comparing it with the value of the world clark and with the average content of elements in plant ash according to Alekseenko and with the

background value. Our study revealed the accumulation of Zn, Ni, Cd, Pb and the scattering of Fe, Mn, Co, Cu in the leaves of laurel poplar (*Populus laurifolia*) on the territory of Ulaanbaatar and the scattering of Fe, Mn, Co, Cu.

- In *Populus laurifolia* leaves in Ulaanbaatar area, the median value of Fe/Mn ratio is 4.2-2.7 times higher, the median value of Pb/Mn ratio is 6.7 times higher and Cu/Zn ratio is balanced.

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